Towards the formulation of a new multi–determinant electron propagator for open–shell molecular systems

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Abstract

Over the past decades, natural sciences have successfully provided an understanding of macroscopic phenomena that reflect molecular structures and mechanisms. However, the desire for a deeper understanding and manipulation of nature and its processes on an atomistic level has generated an intersection of key concepts from quantum mechanics and chemistry. In many important cases, the accurate description of processes involving electron transfer could give insights for the development of new nanomaterials, biomaterials, catalysts and for the elucidation of complex metabolic processes in living organisms. Accurate determination of ionization energies (IEs) and electron affinities (EAs) is crucial for understanding these processes since they are associated with the ability of a molecule to gain or lose electrons. The employment of theoretical methods for the determination of these quantities provides an inexpensive and advantageous guide for the development of several fundamental and applied research projects, especially when experimental measurements are difficult to obtain.

From a theoretical point of view, two strategies are often practiced to calculate vertical electron binding energies, the direct and indirect approaches. The indirect, or ΔE approach, requires the calculation of the total energy of an ionized species (with $N \pm 1$ electrons) at the geometry of the N-electron parent molecule. The total energies are commonly computed with coupled–cluster (CC) or density-functional theory (DFT) methods [1–4]. The direct approach, the simplest strategy for the calculation of binding energies, is based on the Koopmans–theorem (KT) [5] approximation for the case of wave function methods and its extension by Janak [6] for the case of density functional theory (DFT) methods. This direct approach uses energies of the highest occupied and lowest unoccupied canonical Hartree–Fock or Kohn–Sham orbitals of N–electron species. Direct methods for calculations of IEs and EAs can describe multiple electronic states in a single calculation. Closed–shell, N–electron reference states are less likely to introduce symmetry problems. Therefore, the direct approach is often free from spin–contamination and artificial symmetry breaking whereas these qualities are not always true for the indirect approach. Direct methods are divided into two main families. The first family includes methods which employ an exponential Ansatz

for the molecule and then applies a linear combination of ionization operators to the reference state to obtain final–state wave-functions and energies such as the equation–of–motion, coupled–cluster (EOM–CC) [1] method and the symmetry–adapted–cluster, configuration-interaction (SAC–CI) [7] method. These two methods may only reflect differences in the symmetry–adaptation of excitation or ionization operators, algorithms for the determination of matrix elements between ionization operators, techniques of diagonalization or numerical criteria for the selection of ionization operators [1, 7, 8]. The second family of methods is based on Many-body Green's functions [2, 9–11]. The many-body Green's functions or propagators were introduced by Linderberg and Öhrn [12, 13]; subsequent contributions to the propagator theory and methodology were made by several authors, such as Cederbaum, von Niessen, Schirmer, Yeager, Ortiz and others [14–16]. Electron-propagator (EP) methods are among the most robust *ab-initio* methodologies capable of generating powerful computational tools for the description of the electronic structure of atoms and molecules. One of the most important advantages of the electron propagator methods is the direct calculation of observables without wavefunctions and balanced treatments of initial and final states [2]. Electron propagator methods not only provide means to directly calculate electron binding energies, Dyson orbitals, one-electron properties, and total energies of molecules, but also allow systematic improvements in determining correlation and relaxation effects [10].

The flexibility of the theory and mathematical concepts on which electron propagator methods are based produces propagators that have correct qualitative trends with arithmetic scaling factors as low as $\mathcal{O}(N^3)$ [10, 17, 18], as well as propagators with scaling factors of $\mathcal{O}(N^5)$ capable of produce results of the same acurracy and quality as the ones produced by more computationally intensive *ab-initio* correlated methods [18]. The results obtained by *ab-initio* electron propagator methods may be systematically improved by increasing the flexibility of self–energy approximations and by enlargement of basis sets [3, 10, 11, 18, 19]. Electron propagator methods have successfully predicted electron binding energies of large varieties, sizes, and types of chemical systems, ranging from diatomic molecules to nucleotides, fullerenes, substituted porphyrins, and biologically relevant molecules [3, 19–25]. The predictive capabilities of electron propagator methods have been examined recently[18]. In this study, EP results were compared with extrapolated energies calculated with coupled–cluster singles and doubles plus perturbative triples [26], *i.e.*, CCSD(T), and correlation–consistent double, triple and quadruple ζ basis sets [27–30]. EP calculations are proven to be capable of predicting ionization energies with average errors smaller than 0.15 eV and iterative arithmetic bottlenecks of O^3V^2 where O and V are respectively the numbers of occupied and virtual spin-orbitals [10]. In electron propagator methodology, many

approximate forms of the self–energy matrix, $\mathbf{\Sigma}(E)$, assumes a canonical, Hartree–Fock basis of orbitals in which closed-shell reference determinants have been employed. The extension to unrestricted Hartree–Fock spin orbitals is readily accommodated by the usual formalism. However, when spin contamination becomes strong in unrestricted reference determinants, the assignment of spin quantum numbers to initial and final states becomes problematic. A restricted Hartree–Fock determinant could be advantageous in such circumstances. The efforts of this thesis are focused on extending the capabilities of the current single determinant electron propagator formalism to a formulation in which multiple determinants can be employed, enabling the formulation of a new electron propagator approximation that allows the calculation of ionization energies of open–shell molecules in which spin–contamination represents a challenge in the calculation of correct and accurate ionization energies. This new electron propagator method overcomes the spin–contamination problem by using determinants that are more general than those generated in restricted Hartree–Fock theory. For this new electron propagator formulation, generalized matrix elements of the superoperator Hamiltonian that accommodate non–integer occupation numbers associated with general, orthogonal spin orbitals were obtained for the first time. For the definition of the self–energy matrix of this new propagator, the partitioning scheme for the primary and secondary blocks of the superoperator Hamiltonian was redefined. In this new formulation, the ionization–operator spaces will contain sets of operators that change the quantum number M_s by $\pm 1/2$. These sets include electron removal plus spin–flip processes. This new method not only has the advantage of conserving correct spin quantum number ($\langle S^2 \rangle$) values but also takes advantage of point-group symmetry. It also has an O^2V^3 arithmetic scaling factor, where O and V are, respectively, the numbers of occupied and virtual spin-orbitals.

Acknowledgement

Thanks to everybody especially to Olga and Slava.

Contents

1

The Green's Function

> *Wer ein mathematisches Buch nicht mit Andacht ergreift, und es wie Gottes-Wort liest, der versteht es nicht.*
>
> — **Novalis**
> (Poet from the German Romanticism)

Green's function techniques are in several areas of science and engineering one of the most well known and useful strategies for solving nonhomogeneous linear differential equations with boundary conditions by describing the input function, the function that makes the differential equation nonhomogeneous, as a series of impulses. In physics, Green's functions are powerful mathematical tools not only for solving differential equations but also for the elucidation of the effects associated to non-contact force sources. An illustration of the extraordinary capabilities of the Green's functions is given in the Quantum field theory (QFT), where they are used as the n-point correlation functions [31–34]. Since their introduction by Richard Feynman [35–37], Green's functions have produced some of the most stunningly precise and accurate descriptions of quantum phenomena [31–33].

1.1 Mathematical overview of the Green's function

Consider an nth-order, inhomogeneous, differential equation with the general form

$$\boldsymbol{L}u(x) = f(x) \quad \text{with} \quad a < x < b, \tag{1.1}$$

where $\boldsymbol{L}$ is a partial differential operator involving the independent variable x and $f(x)$ is the input function of the differential equation. Then, the solution $u(x)$ may be found by the inverse operator $\boldsymbol{L}^{-1}$ such that the function $u(x)$ can be written as

$$u(x) = \boldsymbol{L}^{-1}f(x). \tag{1.2}$$

In particular, if the operator $\boldsymbol{L}$ happens to be some Hermitian linear differential operator with boundary conditions on a Lebesgue space [38] L^2, *i.e.* a square integrable function space that forms a Hilbert space, and λ is a real constant that is not in the spectrum of eigenvalues of $\boldsymbol{L}$, then, for a differential equation with the form

$$(\boldsymbol{L} - \lambda)u(x) = f(x), \tag{1.3}$$

the solution is given by the Fredholm integral [39] equation defined as:

$$u(x) = \int \boldsymbol{G}_\lambda(x, y) f(y) dy. \tag{1.4}$$

The kernel of this integral transformation is known as the Green's function [40–42] and can be obtained by solving the δ-source problem given by:

$$(\boldsymbol{L} - \lambda)\boldsymbol{G}_\lambda(x, y) = \delta(x - y). \tag{1.5}$$

The Green's function describes the response or effect on the value of the nonhomogeneous equation at the point x after a perturbation [40, 42] due to a δ-source[1] located at y. Furthermore, for a distributed source (figure 1.1) the solution to the δ-source problem can be found through the superposition of each of the δ-sources [42]. In other words, the input function $f(x)$ in equation (1.3) is a superposition of δ-sources and can be expressed as

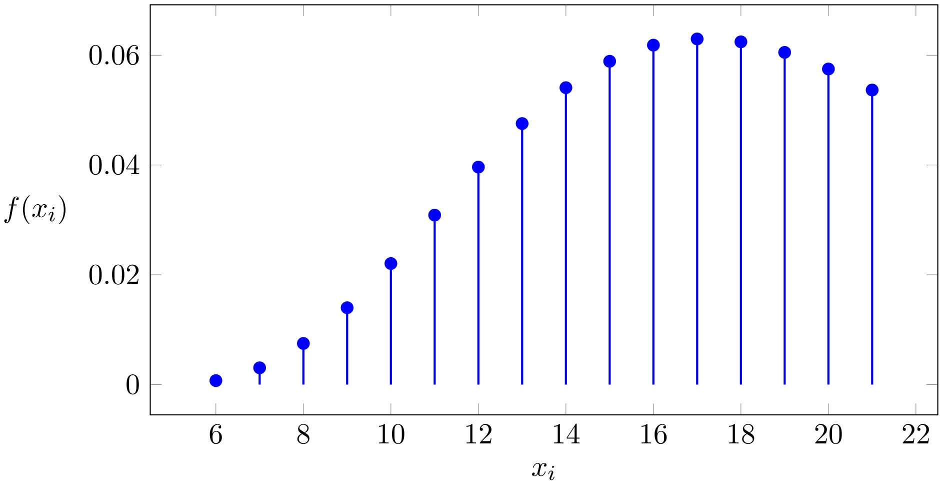

Fig. 1.1.: Distribution of sources and point sources

$$f(x) \approx f(x_1)\delta(x-x_1)+f(x_2)\delta(x-x_2)+\cdots+f(x_n)\delta(x-x_n) \approx \sum_{x_i} f(x_i)\delta(x-x_i). \tag{1.6}$$

---

[1] The input function $f(x)$ in equation 1.3 is commonly referred as a function source or just as a source.

In this context, $f(x)$ is a source function that can be thought of as an integral over δ-source points. In the most cases, $f(x)$ is solved by simply knowing the solution of a point source from the distribution, *i.e* by finding the Green's function, $g(x,x')$, (figure 1.2). Subsequently, the overall solution of the source $f(x)$ is obtained by superposing all the solutions of the individual δ-source points of the distribution (figure 1.3) and adding them up. When the fundamental solution $f(x)$ from Equation (1.3) is assumed to be a distribution, the solution $u(x)$ is obtained by adding up the Green's function for each δ-source located at x_i [39, 42] such that equation 1.4 is rewritten as

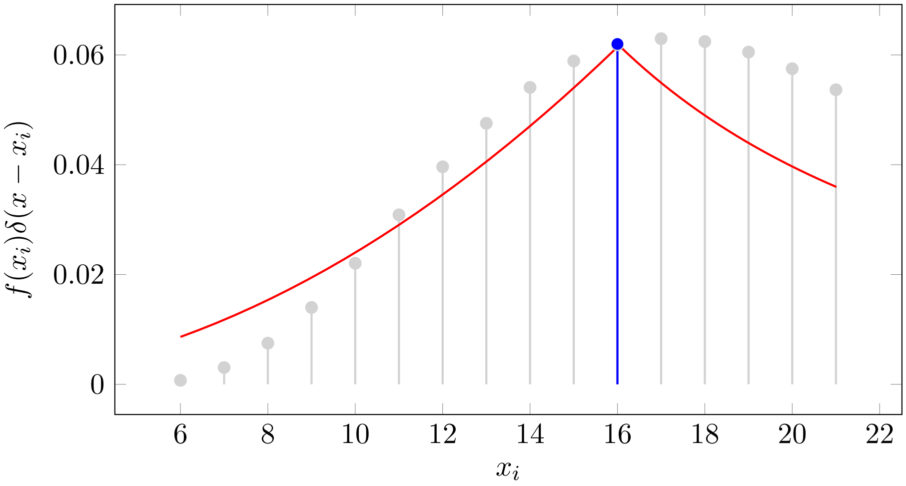

Fig. 1.2.: The solution to a point source is also known as the Green's function

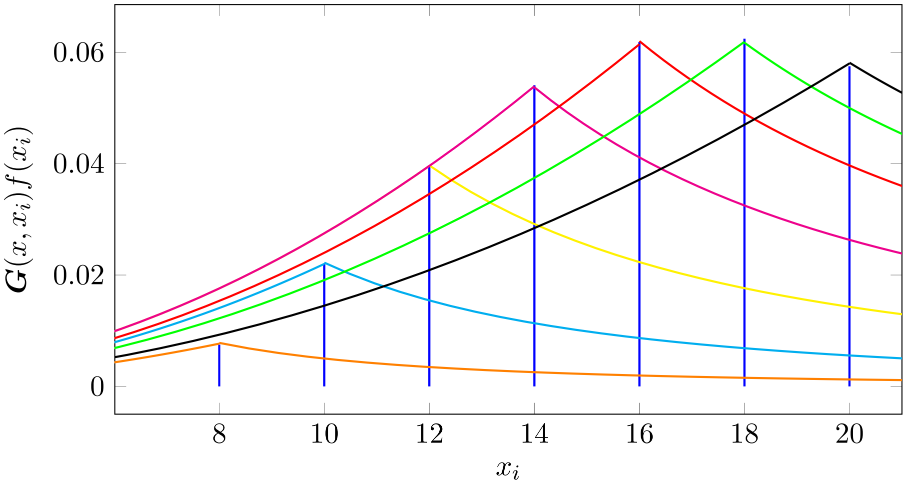

Fig. 1.3.: Green's function for the distributed source

$$u(x) \approx \boldsymbol{G}(x,x_1)f(x_1) + \cdots + \boldsymbol{G}(x,x_n)f(x_n) \approx \sum_{x_i} \boldsymbol{G}(x,x_i)f(x_i). \tag{1.7}$$

Therefore, the solution to $u(x)$ is a superposition of the solution of each of the projections of $f(x_i)$ over $\delta(x - x_i)$ (figure 1.3). An exemplification of the main idea of this

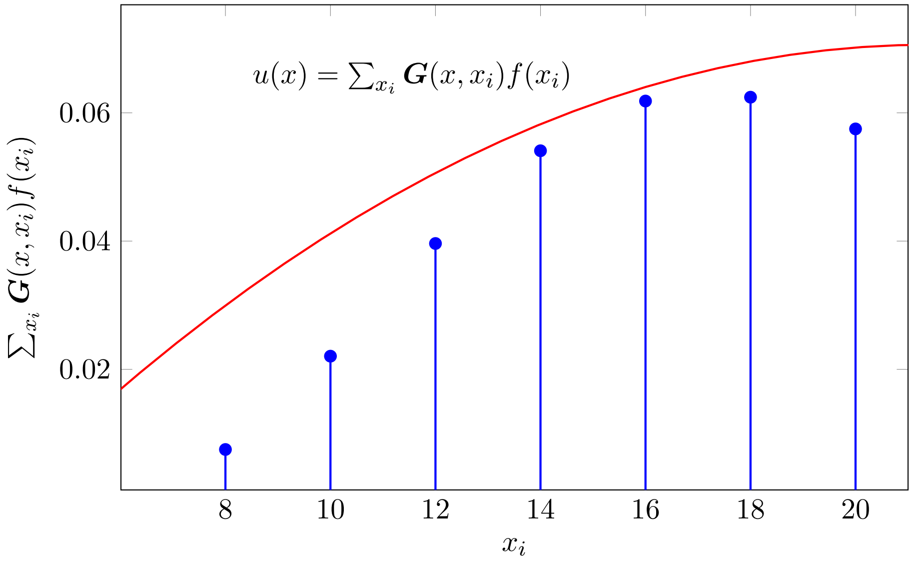

Fig. 1.4.: Green's function for the distributed source

procedure is given in the context of electrostatic fields and the resulting potential from point charges where a point charge may be seen as a δ-source of charge. The potential of any distribution of charges is calculated by adding up the distribution of charges once the solution to a point charge is known.

1.2 Quantum Scattering and the Green's function

Green's functions are widely used for the description of quantum scattering processes [40, 43, 44], in which the δ-source is now seen as a wave source. The Schrödinger equation can be written in the form of Equation (1.3). If the operator $\boldsymbol{L}$ is defined as the kinetic energy operator ($\boldsymbol{\nabla}^2$), the constant λ as the negative of the square of the wavenumber ($-k^2$) and the source $f(x)$ as $\frac{2m}{\hbar^2} V \psi$ the Schrödinger equation may be expressed as

$$(\boldsymbol{\nabla}^2 + k^2)\psi = \frac{2m}{\hbar^2} V \psi. \tag{1.8}$$

Notice that if the input function[2] was zero, Equation (1.8) would have the same form as the Helmholtz equation[3]. Thus, if one could find a function $G(\boldsymbol{r})$ that solves the Helmholtz equation such that the Helmholtz equation may be written as

$$(\nabla^2 + k^2)\boldsymbol{G}(\boldsymbol{r}) = \delta^3(\boldsymbol{r}), \tag{1.9}$$

then, ψ could be expressed as

$$\psi(\boldsymbol{r}) = \int \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}_0) f(\boldsymbol{r}_0) d^3\boldsymbol{r}_0.^4 \tag{1.10}$$

Therefore, the Schrödinger equation in (1.8) satisfies:

$$(\boldsymbol{\nabla}^2 + k^2)\psi(\boldsymbol{r}) = \int [(\boldsymbol{\nabla}^2 + k^2)\boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}_0)] f(\boldsymbol{r}_0) d^3\boldsymbol{r}_0 = \int \delta^2(\boldsymbol{r} - \boldsymbol{r}_0) f(\boldsymbol{r}_0) d^3\boldsymbol{r}_0 = f(\boldsymbol{r}), \tag{1.11}$$

where $G(\boldsymbol{r})$ is the Green's function for the Helmholtz equation. Then, the solution to this last equation can be found by finding the solution $G(\boldsymbol{r})$; this may be accomplished by means of the Fourier transform[5]. If the Green's function $G(\boldsymbol{r})$ is defined as

$$G(\boldsymbol{r}) = \frac{1}{(2\pi)^{3/2}} \int e^{i\boldsymbol{s}\cdot\boldsymbol{r}} g(\boldsymbol{s}) d^3\boldsymbol{s}. \tag{1.12}$$

Then, by applying the Fourier transform to the left and right hand side of the Equation (1.9) one obtains:

$$\frac{1}{(2\pi)^{3/2}} \int (-s^2 + k^2) e^{i\boldsymbol{s}\cdot\boldsymbol{r}} g(\boldsymbol{s}) d^3\boldsymbol{s} = \frac{1}{(2\pi)^3} \int e^{i\boldsymbol{s}\cdot\boldsymbol{r}} d^3\boldsymbol{s}, \tag{1.13}$$

where

$$g(\boldsymbol{s}) = \frac{1}{(2\pi)^{3/2}(k^2 - s^2)}. \tag{1.14}$$

Substituting this expression in Equation (1.12) yields

$$G(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \int \frac{1}{(k^2 - s^2)} e^{i\boldsymbol{s}\cdot\boldsymbol{r}} d^3\boldsymbol{s}, \tag{1.15}$$

which is the solution of equation 1.9 expressed in terms of momentum variables. In order to obtain the Green's function in terms of position variables, the inverse Fourier transform needs to be carried out. The variable r is a fixed variable, therefore, the

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[2] $f(x) = \frac{2m}{\hbar^2} V\psi$ which makes the equation (1.8) inhomogeneous.

[3] The Helmholtz equation with form $(\boldsymbol{\nabla}^2 + k^2)\psi = 0$ arises from the transform of the wave equation into the frequency domain and constitutes a time-independent representation of the wave equation.

[4] $d^3\boldsymbol{r}_0$ or in general $d^3\boldsymbol{x}$ represents a higher order differential using Leibnitz notation [45].

[5] The Fourier transform turns a differential equation into an algebraic equation.

integral in equation 1.15 can be divided into its spherical coordinate components[40, 41, 43], s, θ and φ. Consequently this equation can be rewritten as[6]

$$G(\boldsymbol{r}) = \frac{1}{(2\pi)^2} \int \frac{1}{(k^2 - s^2)} s ds \int e^{isr\cos(\theta)} \sin(\theta) d\theta. \tag{1.16}$$

The integration with respect to the θ coordinate in this equation yields

$$G(\boldsymbol{r}) = \frac{2}{(2\pi)^2 r} \int_0^\infty \frac{s\sin(sr)}{(k^2 - s^2)} ds. \tag{1.17}$$

In this last expression the product of the numerator in the integral is even, therefore, the limits of this integral can be changed and one may rewrite the integral as

$$G(\boldsymbol{r}) = \frac{1}{4\pi^2 r} \int_{-\infty}^\infty \frac{s\sin(sr)}{(k^2 - s^2)} ds. \tag{1.18}$$

Notice that the resulting integral in equation 1.18 blows up at $k = \pm s$, there are two poles on the real axis. Therefore this is not a trivial integrate to evaluate. The easiest way to evaluate this integral is by using the contour integration technique and Cauchy's integral formulation[41]. When taking Cauchy's theorem[7] under consideration, equation (1.18) becomes

$$G(\boldsymbol{r}) = \frac{1}{4\pi^2 r} \int_{-\infty}^\infty \frac{s(e^{isr} - e^{-isr})}{2\pi i(k-s)(k+s)} ds, \tag{1.19}$$

and after the integration of this last equation the Green's function is found to be

$$G(\boldsymbol{r}) = -\frac{e^{-ikr}}{4\pi r}. \tag{1.20}$$

Finally, using this expression for the Green's function one may write the general solution of the Schrödinger equation given by Equation 1.8 as

$$\begin{aligned} \psi(\boldsymbol{r}) &= \psi_0(\boldsymbol{r}) + \frac{2m}{\hbar^2} \int G(\boldsymbol{r}, \boldsymbol{r}_0) V(\boldsymbol{r}_0) \psi(\boldsymbol{r}_0) d^3\boldsymbol{r}_0, \\ &= \psi_0(\boldsymbol{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|\boldsymbol{r}-\boldsymbol{r}_0|}}{|\boldsymbol{r} - \boldsymbol{r}_0|} V(\boldsymbol{r}_0) \psi(\boldsymbol{r}_0) d^3\boldsymbol{r}_0. \end{aligned} \tag{1.21}$$

This solution, Equation 1.21, is known as the integral form of the Schrödinger equation and it is entirely equivalent to its more popular differential form.

---

[6] This new expression for $G(\boldsymbol{r})$ does not have an integral over φ since the value of this integral is just 2π.

[7] Cauchy's theorem demonstrates that when integrating around a closed loop in the complex plane, the integral can be deformed in any way and the result is the sum of the residues which are due to the poles that are inside the curve on the complex plane.

1.2.1 The Born approximation

The integral form of the Schrödinger equation provides a valid expression for the $\psi(\boldsymbol{r})$ function for a given potential V. It is important to point out that this solution, given by equation 1.21, depends on an integral that involves the same solution that one is trying to find. In principle, this can be a problematic defect of this solution to $\psi(\boldsymbol{r})$, however, there are means to overcome this problem. One way may consist in making some considerations about the physical attributes of a process one is trying to describe. For instance, in the case of scattering processes, one may assume that the potential $V(\boldsymbol{r}_0)$ in equation (1.21) is a weak potential that drops to zero outside some delimited region such that $V(\boldsymbol{r}_0)$ is localized at $\boldsymbol{r}_0 = 0$. Therefore, for a much greater region than the region where the potential is nonzero, $\boldsymbol{r} >> \boldsymbol{r}_0$, the wave–function ψ is not substantially altered. One may hypothesize that $\psi \approx \psi_0$ and rewrite equation (1.21) as

$$\psi(\boldsymbol{r}) = \psi_0(\boldsymbol{r}) - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_0}V(\boldsymbol{r}_0)\psi_0(\boldsymbol{r}_0)d^3\boldsymbol{r}_0. \tag{1.22}$$

For the case of plane waves[8] this equation becomes

$$\psi(\boldsymbol{r}) = e^{ikz} - \frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int e^{i(k\hat{z}-\boldsymbol{k})\cdot\boldsymbol{r}_0}V(\boldsymbol{r}_0)d^3\boldsymbol{r}_0, \tag{1.23}$$

and when rearranging the equation as

$$\psi(\boldsymbol{r}) = e^{ikz} + \frac{e^{ikr}}{r}\left(-\frac{m}{2\pi\hbar^2}\int e^{i(k\hat{z}-\boldsymbol{k})\cdot\boldsymbol{r}_0}V(\boldsymbol{r}_0)d^3\boldsymbol{r}_0\right), \tag{1.24}$$

the scattering amplitude may be defined as

$$f(\theta,\phi) = -\frac{m}{2\pi\hbar^2}\int e^{i(k\hat{z}-\boldsymbol{k})\cdot\boldsymbol{r}_0}V(\boldsymbol{r}_0)d^3\boldsymbol{r}_0. \tag{1.25}$$

By using the integral form of the Schrödinger equation given in equation (1.21), the solution to the wave function can be expressed as

$$\psi = \psi_0 + \int gV\psi d^3\boldsymbol{r}. \tag{1.26}$$

where

$$g(\boldsymbol{r}) = -\frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r} \tag{1.27}$$

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[8] $\psi_0(\boldsymbol{r}) = e^{ikz}$

Now, if ψ_0 is the incident wave in the scattering process and V is the scattering potential, then, the outgoing wave after a first interaction with the potential V may be expressed as

$$\psi_1 = \psi_0 + \int gV\psi_0 d^3\boldsymbol{r}. \tag{1.28}$$

This first correction to the wave function is known as the first Born approximation [40, 41, 43]. The correction to the wave function ψ can be extended to more than just this first correction. If the expression for ψ_1 is plugged under the integral sign, the second order corrected wave function is obtained

$$\begin{aligned} \psi_2 &= \psi_0 + \int gV\psi_1 d^3\boldsymbol{r} \\ &= \psi_0 + \int gV(\psi_0 + \int gV\psi_0)d^3\boldsymbol{r} \\ &= \psi_0 + \int gV\psi_0 + \int\int gVgV\psi_0 d^3\boldsymbol{r}. \end{aligned} \tag{1.29}$$

In a similar fashion the third order corrected wave function can be obtained

$$\psi_3 = \psi_0 + \int gV\psi_0 d^3\boldsymbol{r} + \int\int gVgV\psi_0 d^3\boldsymbol{r} + \int\int\int gVgVgV\psi_0 d^3\boldsymbol{r} \tag{1.30}$$

This procedure can be repeated multiple times to generate the formal series for ψ known as the Born series

$$\psi = \psi_0 + \int gV\psi_0 d^3\boldsymbol{r} + \int\int gVgV\psi_0 d^3\boldsymbol{r} + \int\int\int gVgVgV\psi_0 d^3\boldsymbol{r} + \cdots \tag{1.31}$$

In each iteration for the Born series the n-solution of ψ is approximated in terms of high dimensional integrals where the only dependency is on the incident wave function ψ_0. A pictorial explanation of the Born series is thought as follow: Under zero–order conditions, the wave function ψ is unperturbed (untouched) by the potential V, then, in first order it is "kicked out" for the potential once and then, it starts to propagate out in some new direction; in the second order correction the propagated wave from is "kicked" again and propagated to a new direction and then kicked again and propagates again to a new direction and so on. The Green's function describes how the perturbation propagates between one interaction to the next. This is the reason why the Green's function is also called the propagator. Feynman's formulation of relativistic quantum mechanics was inspired by the Born series. Feynman's diagrams [34, 37, 40, 42] are pictorial means to represent the Born series, expressed entirely in terms of the vertex factors (V) and the propagators (g) connected together.

1.3 The Quantum Field theory formalism

The scattering process can also be formulated from the perspective of quantum field theory, in which a quantum system with many identical particles can be described by the quantum field [34, 39, 42, 46]. In this context, the vector space that represents the quantum state space of a quantum system of N identical non-relativistic particles is generated by the union of each of the N particle Hilbert spaces, $\mathcal{H}_N$, of the system [47]. The union of all the $\mathcal{H}_N$ spaces of a given N-particle system is known as the Fock space ($\mathcal{F}$) [39, 41, 47, 48] and is mathematically expressed as:

$$\mathcal{F} = \bigcup_{N=0}^{\infty} \mathcal{H}_N \tag{1.32}$$

where the subspace with N equal to zero is formed by a single state known as the vacuum state. The vacuum state represents the state with no physical particles and therefore, it is the lowest possible energy state; this so called vacuum state[9] is denoted as

$$|00\cdots 0\rangle \equiv |\mathbf{0}\rangle. \tag{1.33}$$

The different $\mathcal{H}_N$ subspaces in $\mathcal{F}$ can be connected through a quantum field operator that creates or annihilates a particle at a specific point in space, such that a ket with a single particle in a particular k momentum state can be denoted in terms of the creator operator associated with that momentum acting on the vacuum state,

$$|k_i\rangle = a^{\dagger}_{k_i}|0\rangle. \tag{1.34}$$

Thus, applying the creator operator $a^{\dagger}_{k_i}$ to the vacuum state assigns a particle i to a particular k state. Following this notation, the ket that represent the case of two particles within the same state k is, then, expressed as

$$|k_i, k_j\rangle = a^{\dagger}_{k_j}a^{\dagger}_{k_i}|0\rangle. \tag{1.35}$$

In general, this notation will be conserved for N particles and n states. Since these field operators are spatial functions, a quantum field may be generated by an N particle quantum system[39, 46].

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[9] Since this so called vacuum state represents an abstract state with no particles, the vacuum state ket is different from the null ket.

1.3.1 The Fock space representation of the Hamiltonian

Imagine a system of N non-relativistic particles in a $\mathbb{R}^3$ dimensional space, with coordinates $\{\boldsymbol{r_1}, \boldsymbol{r_2} \cdots, \boldsymbol{r_N}\}$. The Hamiltonian for this system may be expressed as:

$$H = -\frac{1}{2m}\sum_{i=1}^{N} \boldsymbol{\nabla}_i^2 + V(\boldsymbol{r_1}, \boldsymbol{r_2}, \cdots, \boldsymbol{r_N}), \tag{1.36}$$

where the $\boldsymbol{\nabla}_i^2$ is the Laplacian with respect to $\boldsymbol{r_i}$ and V is a symmetric function. The set of eigenfunctions Ψ_n associated with this Hamiltonian is then found by solving the Schrödinger equation:

$$H\Psi_n(\boldsymbol{r_1}, \boldsymbol{r_2}, \cdots, \boldsymbol{r_N}) = E_n\Psi_n(\boldsymbol{r_1}, \boldsymbol{r_2}, \cdots, \boldsymbol{r_N}). \tag{1.37}$$

These eigenfunctions Ψ_n are, then, the state vectors of the many particle system. When this many particle system is assumed to have only identical particles, Ψ_n will be symmetric under an interchange of any two coordinates $\boldsymbol{r_i}$ and $\boldsymbol{r_j}$ for Bosons, whereas, in the case of Fermions, Ψ_n will be antisymmetric. An analogy to Ψ_n can be defined in the context of the quantum field by defining an operator ψ that acts on a ket vector state, $|n_1 n_2 n_3 \cdots\rangle$, that contains the information about how many particles are in the various single particle wave function type states. If the operator $\psi(\boldsymbol{r})$ is interpreted as an operator that annihilates a particle at the $\boldsymbol{r}$ position, then, its Hermitian conjugate $\psi^\dagger(\boldsymbol{r})$ can be regarded as the operator that creates a particle at the same position $\boldsymbol{r}$. When the identical particles in the system are defined as Bosons, these two operators are defined through the commutation relations,

$$\begin{aligned} \left[\psi(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r'})\right] &= \delta^3(r - r') \\ \left[\psi^\dagger(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r'})\right] &= 0 \\ \left[\psi(\boldsymbol{r}), \psi(\boldsymbol{r'})\right] &= 0, \end{aligned} \tag{1.38}$$

whereas, for Fermions the operators are defined through anticommutator relations[10],

$$\begin{aligned} \{\psi(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r'})\} &= \delta^3(r - r') \\ \{\psi^\dagger(\boldsymbol{r}), \psi^\dagger(\boldsymbol{r'})\} &= 0 \\ \{\psi(\boldsymbol{r}), \psi(\boldsymbol{r'})\} &= 0. \end{aligned} \tag{1.39}$$

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[10] In an associative algebra the commutator is defined as $[a, b] = ab - ba$, whereas the anticommutator is defined as $\{a, b\} = ab + ba$ [49].

When the Hamiltonian that describes the many particle system in the Fock space is defined in terms of the N particle subspaces equation (1.36) may be written as

$$H = \sum_{i} f(\boldsymbol{r_i}) + \sum_{i<j} g(\boldsymbol{r_i}, \boldsymbol{r_j}) + \sum_{i<j<k} h(\boldsymbol{r_i}, \boldsymbol{r_j}, \boldsymbol{r_k}) + \cdots \tag{1.40}$$

where the function $f(\boldsymbol{r_i})$ is interpreted as an one-particle operator, $g(\boldsymbol{r_i}, \boldsymbol{r_j})$ as a two-particle operator and so forth. Therefore, an N-particle operator is defined as a sum of functions that only depends on a set of n coordinates, where the operators that act on more than one particle (g, h, etc.) are symmetric with respect to the coordinates of the particles. Thereby, an N-particle operator in the Fock space can be constructed in terms of creation and annihilation operators,

$$\begin{aligned}
&\sum_{i} f(\boldsymbol{r_i}) \rightarrow \int \psi^{\dagger}(\boldsymbol{r}) f(\boldsymbol{r}) \psi(\boldsymbol{r}) d^3r \\
&\sum_{i<j} g(\boldsymbol{r_i}, \boldsymbol{r_j}) \rightarrow \frac{1}{2} \int \psi^{\dagger}(\boldsymbol{r_1}) \psi^{\dagger}(\boldsymbol{r_2}) g(\boldsymbol{r_1}, \boldsymbol{r_2}) \psi(\boldsymbol{r_1}) \psi(\boldsymbol{r_2}) d^3r_1 d^3r_2 \\
&\sum_{i<j<k} h(\boldsymbol{r_i}, \boldsymbol{r_j}, \boldsymbol{r_k}) \rightarrow \frac{1}{3!} \int \psi^{\dagger}(\boldsymbol{r_1}) \psi^{\dagger}(\boldsymbol{r_2}) \psi^{\dagger}(\boldsymbol{r_3}) h(\boldsymbol{r_1}, \boldsymbol{r_2}, \boldsymbol{r_3}) \psi(\boldsymbol{r_1}) \psi(\boldsymbol{r_2}) \psi(\boldsymbol{r_3}) d^3r_1 d^3r_2 d^3r_3 \\
&\qquad\vdots
\end{aligned} \tag{1.41}$$

Using this formalism, the potential, $V(\boldsymbol{r_1}, \boldsymbol{r_2}, \cdots, \boldsymbol{r_N})$, of the Hamiltonian in Equation (1.36) can be reduced to a two-particle operator defined as the sum of the potentials between particle pairs,

$$V(\boldsymbol{r_1}, \boldsymbol{r_2}, \cdots, \boldsymbol{r_N}) = \sum_{i<j} v(\boldsymbol{r_i}, \boldsymbol{r_j}). \tag{1.42}$$

Then, the Hamiltonian that represents the many body system in terms of creation and annihilation operators in the Fock space yields

$$H = -\frac{1}{2m} \int \psi^{\dagger}(\boldsymbol{r}) \boldsymbol{\nabla}^2 \psi(\boldsymbol{r}) d^3\boldsymbol{r} + \frac{1}{2} \int \psi^{\dagger}(\boldsymbol{r_1}) \psi^{\dagger}(\boldsymbol{r_2}) v(\boldsymbol{r_1}, \boldsymbol{r_2}) \psi(\boldsymbol{r_2}) \psi(\boldsymbol{r_1}) d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2. \tag{1.43}$$

1.3.2 The quantum field as an N-particle system

In order to show the relationship between the quantum field and a system with many identical particles, an operator whose eigenvalue is the number of particles in a given state vector is first defined,

$$\hat{N} = \int \psi^\dagger(\boldsymbol{r})\psi(\boldsymbol{r})d^3\boldsymbol{r}, \tag{1.44}$$

this operator, known as the number operator, is a Hermitian operator and, therefore, holds the following commutation relations[11]:

$$\begin{aligned} \left[\hat{N}, H\right] &= 0 \\ \left[\psi(\boldsymbol{r}), \hat{N}\right] &= \psi(\boldsymbol{r}) \\ \left[\psi^\dagger(\boldsymbol{r}), \hat{N}\right] &= -\psi^\dagger(\boldsymbol{r}). \end{aligned} \tag{1.45}$$

These commutation relations indicate that applying the operator $\psi(\boldsymbol{r})$ on an eigenstate of $\hat{N}$ will decrease the eigenvalue by 1, whereas $\psi^\dagger(\boldsymbol{r})$ will increase the eigenvalue by 1. Consequently, the vacuum state is the eigenstate of the operator $\hat{N}$ whose eigenvalue is equal to zero. This implies, then, that the vacuum state can be annihilated by consecutively applying $\psi(\boldsymbol{r})$ onto it,

$$\psi(\boldsymbol{r})|0\rangle = 0, \tag{1.46}$$

analogously, applying $\psi^\dagger(\boldsymbol{r})$ repeatedly to the vacuum state will generate non–negative integers eigenvalues for $\hat{N}$. Thus, the function belonging to the complete set of states $|E, N\rangle$ of a quantum field are eigenstates of H and $\hat{N}$,

$$\begin{aligned} H|E, N\rangle &= E|E, N\rangle \\ \hat{N}|E, N\rangle &= N|E, N\rangle. \end{aligned} \tag{1.47}$$

Then, the N-particle wave function $\Psi_E(\boldsymbol{r_1}, \boldsymbol{r_2} \cdots, \boldsymbol{r_N})$ of a many identical particle system is equivalent to the complete set of states $|E, N\rangle$,

$$\Psi_E(\boldsymbol{r_1}, \boldsymbol{r_2} \cdots, \boldsymbol{r_N}) \equiv \frac{1}{\sqrt{N!}}\langle 0|\psi(\boldsymbol{r_1}) \cdots \psi(\boldsymbol{r_N})|E, N\rangle. \tag{1.48}$$

In this sense, the probability amplitude that describes the N particles at the positions $\boldsymbol{r_1}, \boldsymbol{r_2} \cdots, \boldsymbol{r_N}$ can be formed by evaluating the overlap between the vacuum state and the state resulting from annihilating the particles at the $\boldsymbol{r_1}, \boldsymbol{r_2} \cdots, \boldsymbol{r_N}$ positions from

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[11] These commutation relations can be easily demonstrated by using the expressions in equations (1.38) and (1.39)

$|E, N\rangle$. Therefore, a quantum field may be equivalent to a system with N identical particles.

1.3.3 The $\psi(\boldsymbol{r})$ and $\psi^\dagger(\boldsymbol{r})$ field operators

The $\psi(\boldsymbol{r})$ and $\psi^\dagger(\boldsymbol{r})$ field operators act onto ket vectors states that are characterized for having particles whose wave function are δ-functions. It was shown in section 1.1 that δ-functions, in general, can be expressed as a linear superposition of a complete set of functions. Thus, $\psi(\boldsymbol{r})$ and $\psi^\dagger(\boldsymbol{r})$ may be expressed as a linear combination of operators that creates or annihilates particles with a specific wave function type. Furthermore, if $u_k(\boldsymbol{r})$ is defined as a member of a complete single particle set of orthonormal wave function such that

$$\int u_k^*(\boldsymbol{r}) u_{k'}(\boldsymbol{r}) d^3\boldsymbol{r} = \delta_{kk'} \tag{1.49}$$

and

$$\sum_k u(\boldsymbol{r}) u^*(\boldsymbol{r}) d^3\boldsymbol{r} = \delta^3(r - r'), \tag{1.50}$$

then, the expansion of the creation and annihilation field operators with respect to such a basis yields

$$\begin{aligned} \psi(\boldsymbol{r}) &= \sum_k u_k(\boldsymbol{r}) a_k \\ \psi^\dagger(\boldsymbol{r}) &= \sum_k u_k^*(\boldsymbol{r}) a_k^\dagger. \end{aligned} \tag{1.51}$$

Due to the orthonormality of the function $u_k(\boldsymbol{r})$ and the commutator relations defined for $\psi(\boldsymbol{r})$ and $\psi^\dagger(\boldsymbol{r})$, the operators a_k and $a_k^\dagger$ satisfy commutation relations for Bosons,

$$\begin{aligned} \left[a_k, a_{k'}^\dagger\right] &= \delta_{kk'} \\ \left[a_k, a_{k'}\right] &= 0 \\ \left[a_k^\dagger, a_{k'}^\dagger\right] &= 0, \end{aligned} \tag{1.52}$$

whereas for Fermions they satisfy anticommutation relations,

$$\begin{aligned} \{a_k, a_{k'}^\dagger\} &= \delta_{kk'} \\ \{a_k, a_{k'}\} &= 0 \\ \{a_k^\dagger, a_{k'}^\dagger\} &= 0. \end{aligned} \tag{1.53}$$

Using these commutation and anticommutation relations, it may be concluded that for each k state the eigenvalues of $a_k^\dagger, a_k$ are integer numbers,

$$\begin{aligned} a_k^\dagger a_k|n\rangle &= n_k|n\rangle \\ \langle n_k|m_k\rangle &= \delta_{n_k,m_k}. \end{aligned} \tag{1.54}$$

These integers numbers, n_k, correspond to the occupation numbers of the single-particle state k. The allowed values of n_k for identical particles are:

$$n_k = \begin{cases} \text{For Bosons :} & 0, 1, 2, \cdots, \infty. \\ \text{For Fermions :} & 0, 1. \end{cases} \tag{1.55}$$

Then, the general actions of the operators a and $a^\dagger$ may be expressed as:

$$\begin{aligned} a|n\rangle &= \sqrt{n}|n-1\rangle \\ a^\dagger|n\rangle &= \sqrt{1 \pm n}|n+1\rangle \end{aligned} \tag{1.56}$$

where the positive sign corresponds to Bosons and the negative sign to Fermions. These expressions indicate that a particle in the state with wave function $u(\boldsymbol{r})$ will be annihilated when the operator a is applied, whereas such a particle will be created if $a^\dagger$ is applied. Therefore, if one simultaneously diagonalizes $a_k^\dagger a_k$ for all k, the obtained eigenstates will be a set of occupation numbers, $\{n_0, n_1, \cdots, n_k\}$. This set of occupation numbers will constitute a valid basis for the Fock space. The string of operators $a_k^\dagger a_k$ can be defined as the occupation-number operator, $\hat{N}_k$, and hence the number operator $\hat{N}$ defined in Equation (1.44) can be given in terms of this occupation-number operator

$$\hat{N} = \sum_{k=1}^{n} \hat{N}_k. \tag{1.57}$$

This stresses the fact that the total number of particles present is known by adding up the elements of a given occupation number vector,

$$N = \sum_k n_k. \tag{1.58}$$

1.3.4 Change of base for operators

The creation and annihilation fields operators act on a set of states that are a basis of $\boldsymbol{H}$. This implies that the representation of these operators is determined by the chosen state basis. Therefore, an equivalent representation of these field operators could be given by using more than one basis. To illustrate this idea, one may imagine a case of plane waves of Fermion particles propagating through a region of volume Ω. Starting from a plane wave basis,

$$|\phi\rangle = \sum_n |n\rangle\langle n|\phi\rangle, \tag{1.59}$$

a given state ϕ can be expressed in the momentum basis by simply performing a change of basis such that

$$|k_i\rangle = \sum_i |k_i\rangle\langle k_i|\phi\rangle. \tag{1.60}$$

Now, suppose a well–defined x position state that when expressed in terms of the momentum basis yields:

$$|x\rangle = \sum_i |k_i\rangle\langle k_i|x\rangle. \tag{1.61}$$

Since this is a well-defined position state, the amplitude for this state is known and its inner product of the momentum k_i state is expressed as:

$$\langle k_i|x\rangle \sim e^{-ik_i x}. \tag{1.62}$$

Therefore, equation 1.61 can be rewritten as the ket that corresponds to a particle in a definite position x in the basis of plane wave momentum eigenstates

$$|x\rangle = \sum_i |k_i\rangle e^{-ik_i x}, \tag{1.63}$$

where, this particle at position x can be created by applying a creation operator to the vacuum

$$\psi^\dagger(x)|0\rangle = \sum_i a^\dagger_{k_i}|0\rangle e^{-ik_i x}. \tag{1.64}$$

Therefore, the operator that creates a particle at a position x may be expressed as

$$\psi^\dagger(x) = \sum_i a^\dagger_{k_i} e^{-ik_i x} \tag{1.65}$$

1.3.5 Describing interactions

The description of the interactions of a particle can be outlined by using the physical and mathematical tools developed in quantum field theory. Let's say one wants to describe a scattering process where a particle comes in with some initial momentum $|k_i\rangle$ and scatters to end up with some final momentum $|k_f\rangle$, see figure 1.5. If the interaction

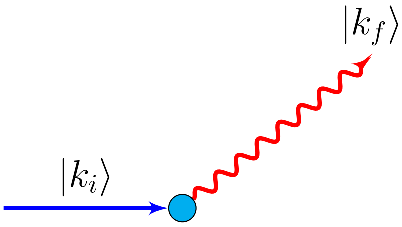

Fig. 1.5.: Scattering at a definite place

Hamiltonian that destroys a particle with momentum k_m and creates a particle with momentum k_l is expressed as

$$\hat{H}_i \sim \sum_{lm} V_{lm} a^\dagger_{k_l} a_{k_m}, \tag{1.66}$$

then, the incoming particle with momentum k_i can be expressed as

$$|k_i\rangle = a^\dagger_{k_i}|0\rangle \tag{1.67}$$

whereas, the outgoing particle with momentum k_f is expressed as

$$|k_f\rangle = a^\dagger_{k_f}|0\rangle \rightarrow \langle k_f| = \langle 0|a_{k_f}. \tag{1.68}$$

The amplitude of a particle with momentum k_f after an interaction starting with momentum k_i can be, then, described with the matrix element between the incoming wave, the interaction potential V_{lm} and outgoing wave,

$$\langle k_f|\hat{H}_i|k_f\rangle \sim \sum_{lm} V_{lm}\langle 0|a_{k_f} a^\dagger_{k_l} a_{k_m} a^\dagger_{k_i}|0\rangle. \tag{1.69}$$

This matrix is just the sum over the interaction potential and the creation and annihilation operators acting on the vacuum state.

1.3.6 Energy and momentum conservation

Now, let's extend the discussion to consider particle decay, a process where a single particle with one initial incoming state ended up with more than one final state. The simplest decay process may be represented in figure 1.6, where a particle with an initial state $|k\rangle$ ends up with two states, $|l\rangle$ and $|m\rangle$. If this decay occurs in a defined place but an unknown time, this transition may be described by using Fermi's golden rule[41, 50,

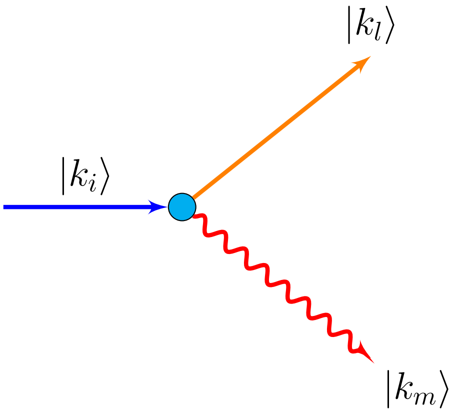

Fig. 1.6.: Decay process at a definite place

51]. The probability of the decay is proportional to the integral of the matrix elements of the perturbation between the initial and final states,

$$\int_t \langle lm|\psi^\dagger\psi^\dagger\psi|k\rangle dt. \tag{1.70}$$

where in the plane wave representation, the ψ operator can be expressed as superpositions of creation and annihilation operators written as

$$\psi \sim \sum_k a e^{ikx+\omega_k t} \tag{1.71}$$

and

$$\psi^\dagger \sim \sum_k a^\dagger e^{-ikx+\omega_k t}. \tag{1.72}$$

The substitution of the ψ and $\psi^\dagger$ operators in equation (1.70) and a definite position, $x = 0$, yield

$$\int_t e^{i(\omega_l+\omega_m-\omega_k)t} dt. \tag{1.73}$$

Since the time is unknown, the consideration of all possible times, and, therefore, the integration over all these times yields

$$\delta(\omega_l + \omega_m - \omega_k). \tag{1.74}$$

This last result in terms of a $delta$-function ensures one of the most relevant consequences of the invariance under time, the conservation of energy. In other words, when conservation of energy is ensured, energy at the end of the scattering experiment is ensured to be the same as it was at the beginning of the experiment[12]. Similarly, for the

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[12] Energy can neither be created nor destroyed.

case of a definite time but an unknown position x the final expression obtained is in terms of a δ-function

$$\int_x \langle lm|\psi^\dagger\psi^\dagger\psi|k\rangle dx. \tag{1.75}$$

If $t = 0$

$$\sim \int_x e^{-i(k_l+k_m-k_k)x}dx \tag{1.76}$$

then,

$$\sim \delta(k_l + k_m - k_k). \tag{1.77}$$

Therefore, integration over all the possible positions ensures conservation of momentum. It is important to mention that in quantum mechanics the position and momentum of a particle cannot be simultaneously measured with precision. Therefore, when the position was definite, one needed to consider all possible times to obtain equation (1.74), whereas in the case of a definite time all possible positions were considered to obtain equation (1.77). This points out the most important idea in quantum mechanics, the Heisenberg uncertainty principle[43, 52].

1.4 The Many–Body Green's function

Following the ideas presented in section (1.3) let us consider a single particle Hamiltonian h_1 whose eigenstates and eigenvalues are

$$h_1|\phi_n\rangle = \varepsilon_n|\phi_n\rangle. \tag{1.78}$$

In general, a particle located in a given $|\phi_n\rangle$ would always remain in the same state. However, let's imagine one could prepare the system in a generic trial state denoted by $|\psi_x\rangle$ and follow its time evolution. When the trial state is created at time $t = 0$, the wavefunction at a later time t may be expressed as

$$\begin{aligned} |\psi(t)\rangle &= e^{-\frac{ih_1 t}{\hbar}}|\psi_x\rangle \\ &= \sum_n |\phi_n\rangle e^{-\frac{i\varepsilon_n t}{\hbar}}\langle\phi_n|\psi_x\rangle. \end{aligned} \tag{1.79}$$

Thus, if one knows the eigenstates $|\phi_n\rangle$, the time evolution of the trial state can be obtained by expanding the trial state, $|\psi_x\rangle$, into the $|\phi_n\rangle$ basis and letting every component to propagate independently. Then, the probability amplitude that a measurement would find the particle at position $\boldsymbol{r}$ yields

$$\begin{aligned}
\langle \boldsymbol{r}|\psi(t)\rangle &= \langle \boldsymbol{r}|e^{-\frac{ih_1 t}{\hbar}}|\psi_x\rangle \\
&= \int d\boldsymbol{r'}\langle \boldsymbol{r}|e^{-\frac{ih_1 t}{\hbar}}|\boldsymbol{r'}\rangle\langle \boldsymbol{r'}|\psi_x\rangle \\
&= \int d\boldsymbol{r'}\sum_n \langle \boldsymbol{r}|\phi_n\rangle e^{-\frac{i\varepsilon_n t}{\hbar}}\langle\phi_n|\boldsymbol{r'}\rangle\langle\boldsymbol{r'}|\psi_x\rangle \\
&\equiv \int d\boldsymbol{r'} G(\boldsymbol{r},\boldsymbol{r'};t)\psi_x(\boldsymbol{r'}),
\end{aligned} \tag{1.80}$$

which involves the propagator G. In general, the time evolution of any initial state can be calculated if $G(\boldsymbol{r},\boldsymbol{r'};t)$ is known. In a single glance, it may seem that the only information contained in the propagator G is related only to time evolution of a given initial state, but this is not true. The propagator G defined in equation (1.80) also contains information about the energy and probability associated with placing a particle at position $\boldsymbol{r}$, these quantities are given by the braket $\langle\phi_n|\boldsymbol{r'}\rangle = \langle\phi_n|\psi^\dagger(\boldsymbol{r'})|0\rangle$. Furthermore, the time evolution is a superposition of waves propagating with different energies. Therefore, applying the Fourier transform to the propagator G would allow to obtain the full eigenvalue spectrum related to the evolution over time of a particle which moves from an initial position $\boldsymbol{r}$ to a final position $\boldsymbol{r'}$.

1.4.1 One–particle Green's function

Let us express the annihilation and creation field operators in the Heisenberg description as

$$\begin{aligned}
\psi_i(\boldsymbol{r},t) &= e^{\frac{iHt}{\hbar}}\psi_i(\boldsymbol{r})e^{-\frac{iHt}{\hbar}} \\
\psi_j^\dagger(\boldsymbol{r},t) &= e^{\frac{iHt}{\hbar}}\psi_j^\dagger(\boldsymbol{r})e^{-\frac{iHt}{\hbar}}
\end{aligned} \tag{1.81}$$

where H is the full Hamiltonian of the system and the field operator subscripts i and j indicate possible internal degrees of freedom (spin, isospin, etc). By using the Heisenberg representation of the field operators, the one-particle Green's function can be defined as the expectation value of the time ordered product of an annihilation and a creation field operator with respect to the exact ground state wave-function of a N-particle system, $|\Psi_0^N\rangle$. Then, the one-particle Green's function or one-particle propagator is mathematically expressed as

$$G_{ij}(\boldsymbol{r}t;\boldsymbol{r'}t') = -\frac{i}{\hbar}\langle\Psi_0^N|T[\psi_i(\boldsymbol{r},t)\psi_j^\dagger(\boldsymbol{r'},t')]|\Psi_0^N\rangle, \tag{1.82}$$

where T is Wick's time-ordering operator which orders the field operators in chronological order with times increasing from right to left. If the chronological order is an odd permutation of the original order, then, a multiplicative factor of -1 needs to be added. Consequently, if the Hamiltonian does not depend on time, by introducing a unit step function[13], θ, the propagator in equation (1.82) becomes

$$\begin{aligned} G_{ij}(\boldsymbol{r},\boldsymbol{r'};t-t') = &-\frac{i}{\hbar}\theta(t-t')\langle\Psi_0^N|[\psi_i(\boldsymbol{r})e^{-i(H-E_o^N)\frac{(t-t')}{\hbar}}\psi_j^\dagger(\boldsymbol{r'})]|\Psi_0^N\rangle \\ &\mp\frac{i}{\hbar}\theta(t'-t)\langle\Psi_0^N|[\psi_j^\dagger(\boldsymbol{r'})e^{i(H-E_o^N)\frac{(t-t')}{\hbar}}\psi_i(\boldsymbol{r})]|\Psi_0^N\rangle. \end{aligned} \tag{1.83}$$

In general, the propagator definition presented in equations (1.82) and (1.83) may be valid for any orthonormal basis. Therefore, a more general expression for equation (1.83) may be written as

$$G_{ij}(t,t') = -i[\theta(t-t')\langle\Psi_0^N|[\psi_i(t)\psi_j^\dagger(t')]|\Psi_0^N\rangle - \theta(t'-t)\langle\Psi_0^N|[\psi_j^\dagger(t)\psi_i(t')]|\Psi_0^N\rangle] \tag{1.84}$$

where $\psi_i(t)$ and $\psi_j^\dagger(t)$ now represent a more general single-particle basis and one lets $\hbar = 1$. The terms of the Green's function in equation (1.84) represent the propagation of a particle (first right hand side term) and the propagation of a hole (second right hand side term). When the particles described are electrons, the propagation of a particle describes the addition of an electron to the system, whereas the propagation of a hole the removal of an electron from the system. The one-particle Green function can be considered as a time-dependent generalization of the one-particle density matrix

$$\rho_{ij} = \langle\Psi_0^N|\psi_j^\dagger\psi_i|\Psi_0^N\rangle = -iG_{ij}(t,t^+), \tag{1.85}$$

where t^+ is defined by adding an infinitesimal positive shift η^+ to the time t, $t^+ = t+\eta^+$. Therefore, one may obtain the one-particle density by setting $\boldsymbol{r} = \boldsymbol{r'}$ and summing over the spin coordinate

$$\rho(\boldsymbol{r}) = -i\int d\sigma_s G(\boldsymbol{r},s,t;\boldsymbol{r},s,t^+). \tag{1.86}$$

In the case of electrons, if the many-body system is invariant under time translation[14] the Green's function would only depend on $\tau = t - t'$. Then, by introducing the

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[13] Heaviside step function [53]

[14] A system is invariant under time translation if there are no time–dependent external potentials.

completeness relations for the $(N-1)$– and $(N+1)$–electronic states the one-particle Green's function yields

$$\begin{aligned}G(\boldsymbol{r},\boldsymbol{r'};\tau) = -\frac{i}{\hbar}[\theta(\tau)\sum_a \langle N|\psi(\boldsymbol{r})|N+1,a\rangle\langle N+1,a|\psi^\dagger(\boldsymbol{r'})|N\rangle e^{-i(E_{N+1,a}-E_N)\tau} \\ - \theta(-\tau)\sum_i \langle N|\psi^\dagger(\boldsymbol{r'})|N-1,i\rangle\langle N-1,i|\psi(\boldsymbol{r})|N\rangle e^{-i(E_N-E_{N-1,i})\tau}]\end{aligned} \tag{1.87}$$

where E_N denotes the energy of the N-electron ground state $|N\rangle$, $E_{N+1,a}$ the energy of the a-th $(N{+}1)$-electron state $|N{+}1,a\rangle$, and $E_{N-1,i}$ the energy of the i-th $(N{-}1)$-electron state $|N{-}1,i\rangle$.

1.5 Green function and Photoelectron emission

In the photoelectron (PE) emission experiment [40, 43], the photocurrent is measured as function of the kinetic energy of the ejected electrons, E_e. The photocurrent measurement is proportional to the magnitude of the external field over many orders of magnitude of E_e. The ejection energy E_e, according to the Einstein's photoelectric relation is proportional to the difference between the photon energy $(\hbar\omega_0)$ and the binding energy I,

$$E_e = \hbar\omega_0 - I. \tag{1.88}$$

If one uses the same principles as in the case of the one–photon scattering process, the photoelectron emission can be calculated by using the Fermi's golden rule. Thus, the transition rate at a given energy ω is given by

$$P(\omega) = \frac{2\pi e^2}{m^2c^2\hbar}\sum_F \Big|\langle F|\sum_n \mathbf{A}_n\cdot\mathbf{P}_n|\Psi_0^N\rangle\Big|^2 \delta(\omega-E_e)\delta(E_F-E_0^N-\hbar\omega_0) \tag{1.89}$$

where $|F\rangle$ and $|\Psi_0^N\rangle$ are the final and initial states of the N–electron atom or molecule under study, consequently, E_F and E_0 are the energies for this states. On the other hand, $\mathbf{A}_n\cdot\mathbf{P}_n$ is the scalar product of the external field at the nth electron and the momentum of this electron. In terms of creation and annihilation operators, a_k and $a_k^\dagger$, for a one particle state $|\phi_k\rangle$ the transition probability $P(\omega)$ may be expressed as

$$\begin{aligned}P(\omega) &= \frac{2\pi e^2}{m^2c^2\hbar}\sum_F \Big|\langle F|\sum_{k,l}\tau_{kl}a_k^\dagger a_l|\Psi_0^N\rangle\Big|^2 \delta(\omega-E_e)\delta(E_F-E_0^N-\hbar\omega_0) \\ &= -\frac{2e^2}{m^2c^2\hbar}\sum_{k,l,m,n}\tau_{mn}^*\tau_{kl}\mathrm{Im}\{iG_{lkmn}(-\hbar\omega_0-i\eta)\}\delta(\omega-E_e)\end{aligned} \tag{1.90}$$

where

$$\tau_{ij} = \langle \phi_i | \mathbf{A} \cdot \mathbf{P} | \phi_j \rangle \tag{1.91}$$

and $G_{lkmn}(-\hbar\omega_0 - i\eta)$ is the Fourier transform of the particle–hole component of the two–body Green's function[15]. In this formalism, all the internal properties such as the spin–orbit coupling, the vibrational, rotational and electronic interactions that are needed to describe the photoelectron spectrum of atoms and molecules are contained in the Green's function. Thus, the complete description of the measured photoelectron spectrum may be obtained by computing the two–body Green's function, but this is not always feasible. On the other hand, the τ_{ij} matrix contains the information that pertains to the angular distribution of the photoelectrons as well as the information about the relative intensities of different photoelectron spectrum bands as a function of the photon energy. When an orthogonal spin–orbital basis, such as the Hartree–Fock spin–orbitals (ϕ_i^{HF}), is used, τ_{ij} may be calculated as the matrix elements of the scalar product $\mathbf{A}_n \cdot \mathbf{P}_n$ between the ϕ_i^{HF} and ϕ_j^{HF} Hartree–Fock orbitals. Although Green's functions provide a natural theoretical approach for the elucidation of a measured photoelectron spectrum, the accurate evaluation of the exact Green's function is a non–trivial and computational costly task. Thereof, reasonable approximations need to be made in order to compute practical $P(\omega)$ values.

1.5.1 Approximation to the final state

In equation (1.90), the final state $|F\rangle$ may be approximated by an antisymmetrized product of a $(N-1)$–electron state, $|\psi_s^{N-1}\rangle$, with a one–electron continuum state $|e\rangle$. The contribution of the continuum state $|e\rangle$ to the initial state $|\psi_0^N\rangle$ is close to zero. Therefore, when E_e is large, in order to obtain a nonvanishing value for $P(\omega)$ the operator a_k must annihilate an electron in $|e\rangle$ in the final state $|F\rangle$. Equation (1.90) becomes

$$P(\omega) = \frac{2e^2}{m^2c^2\hbar} \sum_{e,n,l} \tau_{en}^* \tau_{el} \mathrm{Im}\{G_{ln}(\omega - \hbar\omega_0 - i\eta)\}\delta(\omega - E_e) \tag{1.92}$$

where the Fourier transform of the advanced one-electron Green's function yields

$$G_{ln}(\omega - i\eta) = \sum_s \frac{\langle \Psi_0^N | a_n^\dagger | \Psi_s^{N-1} \rangle \langle \Psi_s^{N-1} | a_l | \Psi_0^N \rangle}{\omega - E_s^{N-1} - E_0^N - i\eta}. \tag{1.93}$$

Although the ansatz for the final state, $|F\rangle = |e\rangle|\psi_s^{N-1}\rangle$, implies that the ejected electron is not correlated with the other electrons in the ionic system, this does not mean that the state $|e\rangle$ is in general a plane wave or only describes a free electron. To the contrary,

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[15] In this expression η is a positive parameter that approaches zero as required for the Fourier transform.

the ejected electron feels the other electrons, but its influence on these other electrons is neglected. Furthermore, one could construct the optimum one–electron state $|e\rangle$ that best describes the system under study. Conversely, in order to accurately describe the photoelectron emission process, one may need to consider the different effects that the remaining electrons in the ionic system exert on the ejected electron. For instance, for the case $\hbar\omega_0 \gg I$, the ejected electron is usually considered free and $|e\rangle$ is taken as a plane wave with the appropriate symmetry, whereas for the case $\hbar\omega_0 - I \leq I$, Coulomb-type waves describing the interaction of the electron with the static charge distribution of the ion should be considered. Finally, ionizations at the $\hbar\omega_0 \approx I$ threshold are correctly characterized by the two–particle Green's function. The transition probability $P(\omega)$ may be expressed in terms of the eigenvalues $D_k(\omega)$ of the Green's function matrix $\mathbf{G}(\omega)$ as

$$P(\omega) = \frac{2e^2}{m^2c^2\hbar}\text{Im}\{\sum_e \text{tr}\left[\widetilde{\boldsymbol{D}}(\omega - \hbar\omega_0 - i\eta)\right]\delta(\omega - E_e)\}, \tag{1.94}$$

with

$$\widetilde{D}_{ij} = |\tau_{ei}(\omega)|^2 D_i(\omega)\delta_{ij}, \tag{1.95}$$

and

$$\tau_{ei}(\omega) = \sum_j \tau_{ej} S_{ij}(\omega), \tag{1.96}$$

where S_{ij} are the elements of the eigenvector matrix of $\mathbf{G}(\omega)$. After considering the Fourier transform one finds

$$\text{Im}\{D_k(\omega - i\eta)\} = \pi \sum_s P_k(s)\delta(\omega + E_s^{N-1} - E_0^N) \tag{1.97}$$

with

$$0 \leq P_k \leq 1. \tag{1.98}$$

The $P_k(s)$ quantities are known as pole strengths. Since these quantities can only have positive values, it follows that for all ω values the transition probability $P(\omega)$ will be always positive.

The binding energy of the ejected electron may be expressed as $I_s = E_s^{N-1} - E_0^N$ and $\tau_{ej}\delta(\omega - E_e)$ becomes $\tau_{e_s j}\delta(\omega - E_e)$.Therefore a further symplification of equation (1.95) yields

$$P(\omega) = \frac{2\pi e^2}{m^2c^2\hbar}\sum_{s,k}|\tau_{e,k}(\hbar\omega_0 - I_s)|^2 P_k(s)\delta(\omega + I_s - \hbar\omega_0). \tag{1.99}$$

If the correlation of the electrons in the atom or molecule is neglected, the Green's function becomes the free Green's function $\boldsymbol{G_0}$. When the Green's function matrix $\boldsymbol{G_0}$ is diagonal, the transition probability reads

$$P^0(\omega) = \frac{2\pi e^2}{m^2 c^2 \hbar} \sum_{k \leq N/2} |\tau_{e_k,k}|^2 \delta(\omega - \varepsilon_k - \hbar\omega_0), \tag{1.100}$$

where ε_k is energy of the kth orbital of the atom of molecule. This last equation indicates that for the case of a N electron closed-shell system the number of bands that one can expect is at most $N/2$. This assertion, however, is not in agreement with the photoionization experimental reality. In the photoionization process, simultaneous excitation or the ionization of a second electron in the same atom or molecule are events with high probability. These excitations accompanying the ionization event are the so–called shake–up and shake–off processes. These last processes can only be contemplated when electron correlation effects are considered in the treatment of the system. For instance, consider $G_{ln}(\omega - i\eta)$ in equations (1.92) and (1.93). If the configuration interaction is negleted, the final ionic state $|\Psi_s^{N-1}\rangle$, whose electron configuration differs from that of the reference ground state by the occupation of more than one orbital, would not be observed. However, if the configuration interaction is taken into account (the full $G_{ln}(\omega - i\eta)$ is considered), the final ionic state will borrow intensity from the other states giving it a suitable electronic configuration and symmetry that would allow this ionic state to be observed. In general, for atoms and molecules the features in the photoelectron spectrum that are invariant to the experiment conditions can be determinated by computing the one– or two–body Green's function together with $|e\rangle$. Furthermore, the information related to the binding energies and the vibrational structure of the bands of the system in consideration is contained in the one–body Green's function.

2

The Electron Propagator

> *Will you understand what I'm going to tell you? . . .*
> *No, you're not going to be able to understand it. . . .*
> *That is because I don't understand it. Nobody does.*
>
> — **Richard Phillips Feynman**
> (QED: The Strange Theory of Light and Matter)

After Feynman introduced the ideas and foundations of the free electron propagator into quantum field theory [35, 37], Schwinger extended Feynman's discussion to many–particle systems [54, 55]. Subsequently, Martin and Schwinger [56] introduced what is, perhaps, the most significant work in the development of what is known today as the many-particle propagator theory. The first application of the many-particle propagator to finite systems and the basis of the theory for atoms and molecules were introduced by Linderberg and Öhrn [12, 13]; subsequent contributions to the propagator theory and methodology were made by several authors, such as Cederbaum [9], von Niessen [57], Schirmer [58], Yeager [59], Simons [60], Ortiz [15] and others [14, 16, 61, 62]. The capabilities and usefulness of the many-particle propagators are of great relevance for the prediction and study of stationary and transition properties. Many-particle propagators are direct methods for the determination of theoretical photoelectron spectra of atoms and molecules. In the framework of electronic structure theory and *ab–initio* methods, many–body propagators, in particular the one–electron propagator, have been stressed as the best direct method to obtain and predict accurate electron binding energies, due to their solid mathematical foundations[62].

2.1 Electron propagator concepts

In electron propagator (EP) theory, binding energies, Dyson orbitals and one–electron properties are contained in the poles and residues of the one–electron Green's function[15, 16]. Poles are energies where singularities of the one–electron Green's function lie, whereas residues are the coefficients of the terms responsible for those singularities.

In the spin–orbital basis, the spectral form for the p–q element of the EP matrix [2, 15, 16] reads

$$G_{pq}(E) = \lim_{\eta \to 0} \{ \sum_n \frac{\langle N|a_p|N+1,n\rangle\langle N+1,n|a_q^\dagger|N\rangle}{E - E_n^{N+1} + E_0^N + i\eta} + \sum_n \frac{\langle N|a_q^\dagger|N-1,n\rangle\langle N-1,n|a_p|N\rangle}{E + E_n^{N-1} - E_0^N - i\eta} \}, \tag{2.1}$$

where p and q are general spin–orbital indices, and $|N\rangle$ is the exact non–degenerate ground state of an N–electron system with energy E_0^N. $E^{N\pm1}$ and $|N \pm 1, n\rangle$ denote energies and states with $N \pm 1$ electrons. η is a positive infinitesimal constant that guarantees the convergence of the Fourier transform from the time–dependent expression. For a finite, orthonormal and discrete spin–orbital basis, the $G_{pq}(E)$ matrix has only simple poles in the frequency domain, *i.e.* poles are only located in the energy plane. When η approaches zero these poles are all on the real energy axis, with values equal to the difference between the total energy of the N–electron stationary ground state and the $N \pm 1$–electron final state. The overlap amplitudes [63] between the N– and $N \pm 1$–electron states are known as the Feynman–Dyson amplitudes (FDAs). These amplitudes are defined according to the spin–orbital basis and the creation, $a_q^\dagger$, and annihilation, a_p, electron field operators [15, 16, 63],

$$\begin{aligned} f_n(q) &= \langle N+1,n|a_q^\dagger|N\rangle \\ g_n(p) &= \langle N-1,n|a_p|N\rangle. \end{aligned} \tag{2.2}$$

FDAs are a reflection of the corrections to the one–electron unperturbed state upon the introduction of a perturbation. This perturbation corresponds to the propagation of the self interaction of the electron by the means of an effective potential. This results in the propagator self–energy taking effectively into account many–body effects such as the interaction of the electron with the vacuum state and with the other electrons of the system, improving the overall description of the unperturbed wave–function. FDAs are fundamental for the calculation of intensities in photoelectron spectrometry for principal and satellite structures [2, 15, 16, 63, 64]. Furthermore, FDAs provide means to construct the overlap function between the reference–state wave–function with N–electrons and a final state with $N \pm 1$ electrons

$$\begin{aligned} \phi_n^{Dyson}(x_1) &= N^{1/2} \int dx_2 dx_3 ... dx_N \Psi_N(x_1, x_2, x_3, ..., x_N) \Psi^*_{N-1,n}(x_2, x_3, ..., x_N), \\ \phi_n^{Dyson}(x_1) &= (N+1)^{1/2} \int dx_2 dx_3 ... dx_{N+1} \Psi_{N+1,n}(x_1, x_2, x_3, ..., x_{N+1}) \Psi^*_N(x_2, x_3, ..., x_{N+1}). \end{aligned} \tag{2.3}$$

These overlap functions are defined as the Dyson orbitals for the electron detachment ($N-1$ electron final state), and attachment ($N+1$ electron final state), processes.

Dyson orbitals are mathematical entities that have been proven to be powerful tools for the phenomenological description and prediction of electron detachment–attachment processes in atoms and molecules [2, 64]. Moreover, photoionization cross sections and many kinds of transition probabilities depend on Dyson orbitals. The normalization factors of the Dyson orbitals are known as the pole strengths:

$$P_n = \int |\phi_n^{Dyson}(x_1)| dx_1. \tag{2.4}$$

Pole strengths are quantities with values between zero and unity. Pole strengths are used as a criterion of the importance of many–electron processes and electron correlation in the description of a transition from N to $N \pm 1$ electrons.

2.2 Electron propagator formalism

The basis of the electron propagator theory (EPT) was first introduced by Linderberg and Öhrn [12, 13]. The superoperator formalism for EPT was advanced by Goscinski and Lukman [65]. Although the superoperator formalism is the most mathematically rigorous form of deriving the equations of EPT, it may be also, in some cases, the most tedious and challenging approach. An alternative to the superoperator formalism of EPT may be the diagrammatic approach [16, 66] which represents the diverse terms and functions of the EPT equations by pictorial symbols. While the diagrammatic approach may look at first to be a more convenient way to produce EPT equations, this approach is not ideal for developing propagators in which a precise control over the intermediate terms which produce the final EPT equations is needed. Also, in the diagrammatic approach, it can be difficult to guarantee that all the diagrams needed to take into account all the electronic effects have been considered and not double counted. Therefore, the diagrammatic approach for the formulation of electron propagator methods may produce wrong propagator equations, see for example reference [67] where some terms are missing for the expressions of some of the field operator couplings. In this respect the superoperator formalism is, in several cases, the most accurate and flexible approach for deriving new electron propagator methods [68].

2.2.1 Second quantization concepts

In electronic structure theory, the foundation for the treatment of atoms and molecules is based on second–quantization concepts and the definition of operators and vector states[48]. In second quantization the many–electron Hamiltonian can be expressed as

$$H = \sum_{PQ} h_{PQ} a_P^\dagger a_Q + \frac{1}{4} \sum_{PQRS} \langle PQ||RS \rangle a_P^\dagger a_Q^\dagger a_S a_R, \tag{2.5}$$

where

$$\langle PQ||RS \rangle = \int \Psi_P^*(1) \Psi_Q^*(2) r_{12}^{-1} (1 - P_{12}) \Psi_R(1) \Psi_S(2) d_1 d_2 \tag{2.6}$$

represent the antisymmetric two–electron integrals. This Hamiltonian operates in the Fock space spanned by all the independent eigenstates of the number operator of the total number of electrons, which is constructed within a given spin–orbital basis. If the chosen spin–orbital basis diagonalizes the Fock operator such that

$$F_{PQ} = h_{PQ} + \sum_{RS} \langle PR||QS \rangle \langle a_R^\dagger a_S \rangle = \varepsilon_P \delta_{PQ}, \tag{2.7}$$

where

$$\langle a_R^\dagger a_S \rangle = \langle \text{ground state} | a_R^\dagger a_S | \text{ground state} \rangle, \tag{2.8}$$

then, the Hamiltonian may be partitioned as

$$H = H_0 + (H - H_0), \tag{2.9}$$

where H_0 is taken as the unperturbed operator defined as

$$H_0 = \sum_P \varepsilon_P a_P^\dagger a_P. \tag{2.10}$$

In electron propagator theory, the electron propagator defined by only using the uncorrelated electron dynamics characterized by H_0 is denoted as $\boldsymbol{G}_0$. The matrix elements of $\boldsymbol{G}_0$ in a given spin–orbital basis are expressed in the same fashion as the full electron propagator, equation (2.1). However, $|N\rangle$ is now interpreted as the Hartree–Fock ground state

$$|N\rangle = a_i^\dagger a_j^\dagger \cdots a_N^\dagger |\mathbf{0}\rangle \equiv |\text{HF}\rangle \tag{2.11}$$

where $|\mathbf{0}\rangle$ is the nondegenerate eigenstate of the electron number operator corresponding to the eigenvalue zero. The ground state energy may be defined as

$$E_0(E) = \sum_i^{Occ} \varepsilon_j \tag{2.12}$$

and the expression of the energy of the $N-1$ state yields

$$E_j(N-1) = E_0(N) - \varepsilon_j, \tag{2.13}$$

whereas for the $N+1$ state

$$E_a(N+1) = E_0(N) + \varepsilon_a \tag{2.14}$$

with

$$|N-1, j\rangle = \prod_{i \neq j}^{Occ} a_i^\dagger |\mathbf{0}\rangle \tag{2.15}$$

and

$$|N+1, a\rangle = \prod_{i}^{Occ} a_i^\dagger a_a^\dagger |\mathbf{0}\rangle, \tag{2.16}$$

respectively. The normalized determinant states and the anticommutation relations

$$[a_1, a_2]_+ = [a_1^\dagger, a_2^\dagger]_+ = [a_1, a_2^\dagger]_+ - \delta_{1,2} = 0 \tag{2.17}$$

yield the following expressions for the overlap amplitudes:

$$f_p(j) = \langle N+1, p | a_j^\dagger | N \rangle = \pm\delta_{pj} \tag{2.18}$$

and

$$g_b(i) = \langle N-1, b | a_i | N \rangle = \pm\delta_{bi}. \tag{2.19}$$

2.2.2 Propagator couplings and superoperator theory

The full electron propagator G_{pq} expressed in equation (2.1) depends on the electron field operators a_p and $a_q^\dagger$. Therefore an alternative notation for this propagator[15, 16, 63] may be

$$G_{pq} = \langle\langle a_p; a_q^\dagger \rangle\rangle_E. \tag{2.20}$$

By using this notation, the expression for $G_{pq}(E)$ in equation (2.1) may be rearranged in the following way:

$$E(E - E_n^{N+1} + E_0^N)^{-1} = 1 + (E_n^{N+1} - E_0^N)(E - E_n^{N+1} + E_0^N)^{-1}, \tag{2.21}$$

where, for the left hand side of equation 2.1 one may obtain

$$\langle N | a_p | N+1, n \rangle (E_n^{N+1} - E_0^N) = \langle N | [a_p, H] | N+1, n \rangle, \tag{2.22}$$

a similar expression is obtained for the right hand side of the equation (2.1). After the manipulations of the propagator equation, the final expression is

$$E\langle\langle a_p; a_q^\dagger\rangle\rangle_E = \langle|N[a_p, a_q^\dagger]_+|N\rangle + \langle\langle[a_p, H]; a_q^\dagger\rangle\rangle_E \tag{2.23}$$

which is the equation of motion of the electron propagator. Equation (2.23) may be regarded as the first instance of a chain of equations, since the more complicated propagator $\langle\langle[a_p, H]; a_q^\dagger\rangle\rangle_E$ has an analogous definition to the one of $\langle\langle a_p; a_q^\dagger\rangle\rangle_E$:

$$\langle\langle a_p; a_q^\dagger\rangle\rangle_E = E^{-1}\langle[a_p, a_q^\dagger]_+\rangle + E^{-2}\langle[[a_p, H], a_q^\dagger]_+\rangle + E^{-3}\langle[[[a_p, H], H], a_q^\dagger]_+\rangle + \dots \tag{2.24}$$

where the expectation values $\langle\dots\rangle$ are taken with respect to the ground state $|N\rangle$ (or a suitable ensemble) and evaluated as the trace of the density operator of the ensemble. This last equation may be defined in terms of the superoperators acting on a space of electron field operators $\mathbf{f}$,

$$\mathbf{f} = \{\mathbf{f}_1, \mathbf{f}_3, \mathbf{f}_5, \dots, \mathbf{f}_n\} \text{ with } n = \{2k+1 : k \in \mathbb{Z}\}. \tag{2.25}$$

If $\mathbf{X}$ and $\mathbf{Y}$ are general elements of this linear space of electron field operators, the identity superoperator $\hat{\boldsymbol{I}}$ and the Hamiltonian superoperator $\hat{\boldsymbol{H}}$ yield the following relations

$$\begin{aligned} \hat{\boldsymbol{I}}\mathbf{X} &= \mathbf{X} \\ \hat{\boldsymbol{H}}\mathbf{X} &= [\mathbf{X}, \boldsymbol{H}], \end{aligned} \tag{2.26}$$

and their scalar product reads

$$(\mathbf{X}|\mathbf{Y}) = \langle\ [\mathbf{Y}, \mathbf{X}^\dagger]_+\ \rangle. \tag{2.27}$$

A more succinct notation for the full propagator may be written as

$$G_{pq} \equiv \langle\langle a_p^\dagger; a_q^\dagger\rangle\rangle_E = (a_p^\dagger|(\boldsymbol{E}\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}})^{-1}a_q^\dagger), \tag{2.28}$$

where $(\boldsymbol{E}\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}})^{-1}$ is known as the superoperator resolvent. The matrix elements of the electron propagator are, then, related to the field operator products arising from the superoperator resolvent evaluated with respect to the $|N\rangle$ reference state. Thus, Dyson orbitals as well as the electron binding energies calculated using electron propagators are properties of the reference state that is being for used for the calculation.

2.2.3 Partitioning and the inner projection basis

In electron propagator calculations, the elements of the superoperator resolvent matrix may be calculated by considering the polynomial expansions in $\hat{\boldsymbol{H}}$ and E. However, the techniques of inner projection and partitioning[62, 69, 70] may offer a more efficient approach for the systematic approximate treatment of the electron propagator. Starting with the expression for the full propagator in equation (2.28) and introducing vector arrays of electron field operators, the matrix expression for the electron propagator yields

$$\boldsymbol{G}(E) = \langle\langle \boldsymbol{a}; \boldsymbol{a}^\dagger \rangle\rangle_E = (\boldsymbol{a}^\dagger | (\boldsymbol{E}\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}})^{-1} \boldsymbol{a}^\dagger). \tag{2.29}$$

The inner projection of $\boldsymbol{G}(E)$ can be easily defined by following the ideas by Pickup and Goscinski[62]. For positive definite operators

$$A' = A^{1/2} \hat{O}_b A^{1/2} \tag{2.30}$$

where $\hat{O}_b$ is a projection operator in the $|\boldsymbol{b}\rangle$ basis defined as

$$\hat{O}_b = |\boldsymbol{b}\rangle\langle\boldsymbol{b}|\boldsymbol{b}\rangle^{-1}\langle\boldsymbol{b}|. \tag{2.31}$$

Therefore, it can be proven that $\hat{O}_b^2 = \hat{O}_b$:

$$\begin{aligned} \hat{O}_b^2 &= |\boldsymbol{b}\rangle\langle\boldsymbol{b}|\boldsymbol{b}\rangle^{-1}\langle\boldsymbol{b}|\boldsymbol{b}\rangle\langle\boldsymbol{b}|\boldsymbol{b}\rangle^{-1}\langle\boldsymbol{b}| \\ &= |\boldsymbol{b}\rangle\langle\boldsymbol{b}|\boldsymbol{b}\rangle^{-1}\langle\boldsymbol{b}| = \hat{O}_b. \end{aligned} \tag{2.32}$$

Since $\langle\boldsymbol{b}|\boldsymbol{b}\rangle$ is real and $(\langle\boldsymbol{b}|\boldsymbol{b}\rangle^{-1})^\dagger = \langle\boldsymbol{b}|\boldsymbol{b}\rangle^{-1}$, the operator $\hat{O}_b$ is self-adjoint,

$$\begin{aligned} \hat{O}_b^\dagger &= (\langle\boldsymbol{b}|)^\dagger(\langle\boldsymbol{b}|\boldsymbol{b}\rangle^{-1})^\dagger(|\boldsymbol{b}\rangle)^\dagger \\ &= |\boldsymbol{b}\rangle\langle\boldsymbol{b}|\boldsymbol{b}\rangle^{-1}\langle\boldsymbol{b}| = \hat{O}_b. \end{aligned} \tag{2.33}$$

If the basis $|\boldsymbol{b}\rangle$ is complete, the operator $\hat{O}_b$ is the identity operator and therefore, the inner projection is exact:

$$A' = A^{1/2}\hat{\boldsymbol{I}}A^{1/2} = A. \tag{2.34}$$

Then, if $A \geq 0$, since $0 \leq \hat{O}_b \leq 1$, the following operator inequality holds

$$0 \leq A' \leq A \tag{2.35}$$

Alternate forms of the inner projection may be obtained by the Bazley [70, 71] transformation

$$|\boldsymbol{f}\rangle = A^{1/2}|\boldsymbol{b}\rangle \tag{2.36}$$

and Aronszajn [70, 72] transformation

$$|\boldsymbol{g}\rangle = A^{-1/2}|\boldsymbol{b}\rangle. \tag{2.37}$$

Using the former one may obtain

$$A' = |\mathbf{f}\rangle\langle\mathbf{f}|A^{-1}\mathbf{f}\rangle^{-1}\langle\mathbf{f}|. \tag{2.38}$$

If the operator A has N negative eigenvalues, the relation

$$A \geq |\mathbf{f}\rangle\langle\mathbf{f}|A\mathbf{f}\rangle^{-1}\langle\mathbf{f}| \tag{2.39}$$

is valid provided that $\langle\mathbf{f}|A\mathbf{f}\rangle$ also has N negative eigenvalues. Even when the operator A has no unique sign, the inner projection will reach convergence in the limit of completeness [73, 74]. Thus, the need of a resolvent operator in equation (2.29) may be eliminated by substituting

$$A = E - \hat{H} \tag{2.40}$$

in equation (2.39) or by substituting

$$A^{-1} = E - \hat{H} \tag{2.41}$$

in equation (2.38). The superoperator inverse is turned into a matrix inverse and the expression for the $\boldsymbol{G}(E)$ matrix becomes

$$\boldsymbol{G}(E) = (\boldsymbol{a}^{\dagger}|\boldsymbol{h})(\boldsymbol{h}|(\boldsymbol{E}\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}})\boldsymbol{h})^{-1}(\boldsymbol{h}|\boldsymbol{a}^{\dagger}) \tag{2.42}$$

where $\boldsymbol{h}$ is a manifold of element from the linear space of electron field operators. The manifold of operators $\boldsymbol{h}$ may be partitioned into a set of simple field operators, $\boldsymbol{a}^{\dagger}$, and an orthogonal complementary set $\mathbf{f}$ such that the orthogonal conditions between these sets of operators are:

$$\begin{aligned}
(\boldsymbol{a}^{\dagger}|\boldsymbol{a}^{\dagger}) &= \mathbf{1}_{\boldsymbol{a}},\\
(\mathbf{f}|\mathbf{f}) &= \mathbf{1}_{\boldsymbol{a}\times\mathbf{f}},\\
(\mathbf{f}|\boldsymbol{a}^{\dagger}) &= \mathbf{0}_{\mathbf{f}\times\boldsymbol{a}},\\
(\boldsymbol{a}^{\dagger}|\mathbf{f}) &= \mathbf{0}_{\mathbf{f}}.
\end{aligned} \tag{2.43}$$

When $\boldsymbol{h} = \{\boldsymbol{a}^\dagger; \mathbf{f}\}$, $\boldsymbol{a}^\dagger \equiv \mathbf{f_1}$ is denoted as the primary space or sector, whereas $\mathbf{f} \equiv \{\mathbf{f_3}; \mathbf{f_5}; \mathbf{f_7}; \cdots; \mathbf{f}_{\boldsymbol{n}}\}$, where $\boldsymbol{n}$ is a positive odd integer, is denoted as the secondary space or sector. Then, the partitioned form of the propagator matrix may be expressed as

$$\boldsymbol{G}(E) = \begin{bmatrix} (\boldsymbol{a}^\dagger|\boldsymbol{a}^\dagger) & (\boldsymbol{a}^\dagger|\mathrm{f}) \end{bmatrix} \begin{bmatrix} (\boldsymbol{a}^\dagger|E\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}}|\boldsymbol{a}^\dagger) & (\boldsymbol{a}^\dagger|E\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}}|\mathrm{f}) \\ (\mathrm{f}|E\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}}|\boldsymbol{a}^\dagger) & (\mathrm{f}|E\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}}|\mathrm{f}) \end{bmatrix}^{-1} \begin{bmatrix} (\boldsymbol{a}^\dagger|\boldsymbol{a}^\dagger) \\ (\boldsymbol{a}^\dagger|\mathrm{f}) \end{bmatrix}, \tag{2.44}$$

which reduces to

$$\boldsymbol{G}(E) = \begin{bmatrix} \mathbf{1} & \mathbf{0} \end{bmatrix} \begin{bmatrix} E\mathbf{1} - (\boldsymbol{a}^\dagger|\hat{\boldsymbol{H}}\boldsymbol{a}^\dagger) & -(\boldsymbol{a}^\dagger|\hat{\boldsymbol{H}}\mathbf{f}) \\ -(\mathbf{f}|\hat{\boldsymbol{H}}\boldsymbol{a}^\dagger) & (\mathbf{f}|\hat{\boldsymbol{H}}\mathbf{f}) \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \end{bmatrix}. \tag{2.45}$$

Poles of the propagator, therefore, occur at values of E that are equal to the eigenvalues, $\boldsymbol{\omega}$, of the superoperator Hamiltonian matrix

$$\mathbf{U}\omega = \hat{\boldsymbol{H}}\mathbf{U} \tag{2.46}$$

expressed as

$$\boldsymbol{\omega}_n \begin{bmatrix} \boldsymbol{U}_{a,n} \\ \boldsymbol{U}_{f,n} \end{bmatrix} = \begin{bmatrix} (\boldsymbol{a}^\dagger|\hat{\boldsymbol{H}}\boldsymbol{a}^\dagger) & (\boldsymbol{a}^\dagger|\hat{\boldsymbol{H}}\mathbf{f}) \\ (\mathbf{f}|\hat{\boldsymbol{H}}\boldsymbol{a}^\dagger) & (\mathbf{f}|\hat{\boldsymbol{H}}\mathbf{f}) \end{bmatrix}^{-1} \begin{bmatrix} \boldsymbol{U}_{a,n} \\ \boldsymbol{U}_{f,n} \end{bmatrix}. \tag{2.47}$$

In the basis of operators one may express the propagator matrix as

$$\boldsymbol{G}(E) = \begin{bmatrix} \mathbf{1} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \boldsymbol{U}(E\mathbf{1} - \boldsymbol{\omega})^{-1}\boldsymbol{U}^\dagger \end{bmatrix} \begin{bmatrix} \mathbf{1} \\ \mathbf{0} \end{bmatrix}. \tag{2.48}$$

The residues corresponding to the $\boldsymbol{n}^{th}$ electron binding energy, $\boldsymbol{\omega}_n$, are defined as

$$\boldsymbol{Res}(\boldsymbol{\omega}_n) = \lim_{E \to \omega_n} G_{pq}(E)(E - \boldsymbol{\omega}_n) = \boldsymbol{U}_{p,n}\boldsymbol{U}^*_{q,n}. \tag{2.49}$$

The Dyson orbitals corresponding to the same pole may be expressed as

$$\phi_n^{Dyson} = \sum_p \phi_p \boldsymbol{U}^*_{p,n}. \tag{2.50}$$

Due to the orthogonalization of the primary and secondary operator space, only the diagonal of the primary block of the inverse of $(\boldsymbol{h}|(\boldsymbol{E}\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}})\boldsymbol{h})$ is needed to determine the propagator matrix $\boldsymbol{G}(E)$. The inverse of the propagator matrix may be expressed as[62, 75]

$$\begin{aligned} \boldsymbol{G}^{-1}(E) &= (\boldsymbol{a}^\dagger|(E\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}})\boldsymbol{a}^\dagger) - (\boldsymbol{a}^\dagger|\hat{\boldsymbol{H}}\mathbf{f})(\mathbf{f}|(E\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}})\mathbf{f})^{-1}(\mathbf{f}|\boldsymbol{a}^\dagger) \\ &= E\mathbf{1}_{\boldsymbol{a}} - \hat{\mathbf{H}}_{\mathbf{aa}} - \hat{\mathbf{H}}_{\mathbf{af}}(E\mathbf{1}_{\boldsymbol{a}} - \hat{\mathbf{H}}_{\mathbf{ff}})^{-1}\hat{\mathbf{H}}_{\mathbf{fa}}. \end{aligned} \tag{2.51}$$

The contributions from the secondary space of the eigenvectors, $\boldsymbol{U}_\mathrm{f}$ do not appear in the residues.Therefore, the search of poles and residues requires only the solution of equation (2.46). Thus, the usual matrix diagonalization techniques used in configuration interactions calculations may be applied to the electron propagator, where instead of configurations, operators are used to form the basis. In the case of ionization energies (electron detachments), in addition to the usual CI-like operator for occupied orbitals (one–hole, h, and two–hole one–particle, $2hp$ operators for shakeup processes) operators corresponding to virtual orbitals (one–particle, p, and two–particle one–hole, $2ph$, for the shakeon processes) may contribute to the eigenvector, $\boldsymbol{U}$, to generate the $N-1$–electron states in the Hilbert space. These operators are also needed in the case of electron affinities (electron attachments); electron attachment operators also have h, p, $2hp$ and $2ph$ constituents.

2.2.4 Hartree–Fock orbitals and binding energies

In quantum chemistry, the ground state Hartree–Fock spin–orbital basis is the most commonly used basis for calculations regarding atoms and molecules. According to the Koopmans's theorem[5], KT, Hartree–Fock *ab–initio* orbital energies may be good measures of the valence electron binding energies of atoms and molecules. Although Hartree–Fock orbital energies may give an acceptable qualitative description of the ionization of valence electrons, these energies are a poor representation of the core ionization energies. In order to go beyond the qualitative results of Koopmans's theorem, the addition of correction terms are necessary. These corrections terms may be separated into two classes, relaxation terms and correlation terms. The relaxation terms may be obtained by performing separate Hartree–Fock calculations on the N–electron ground state and the $N \pm 1$–electron final state corresponding to the ionic state of an electron detachment or attachment process. The difference between the total energies calculated for the N–electron ground state and its corresponding ion state yields the approximate electron binding energy with full account of the relaxation process. This procedure of approximating the binding energies is known as the ΔE_{SCF} procedure. On the other hand, correlation terms are more complicated to generate and require a deeper analysis that can be found in great detail elsewhere [76]. In the calculation of accurate binding energies, both correlation and relaxation terms need to be balanced for each system under consideration. Furthermore, this equilibrium between the correlation and relaxation terms varies a great deal from the core to the valence region. Finding the delicate stability between the correlation and relaxation terms, which is unique for each system under consideration, is what makes the problem of calculating electron binding energies challenging. The qualitative classification of the electron detachment and attachment processes may be done in terms of molecular orbital (MO) configurations. For one–electron detachment processes, a hole may be created in a formerly doubly occupied MO reference determinantal wave–function. The one–electron detachment energy can be viewed as a Koopmans's theorem value adjusted by the final–state orbital relaxation and electron correlations. In the transition process that describes the detachment of one electron, in addition to the creation of a hole in the reference state, the shakeup processes may also be considered by two electrons leaving occupied MOs with the attachment of an electron to a virtual MO as shown in figure 2.1. In general, the one–hole, $1h$, and one–particle, $1p$ configurations correspond to qualitative Koopmans pictures for the description of the electron detachment and attachment processes. However, in order to obtain quantitative results, configurations such as $2ph$, $2hp$, $3ph$, $3hp$, $\ldots$, $np(n-1)h$, $nh(n-1)p$, where n is an positive odd integer, need to be considered.

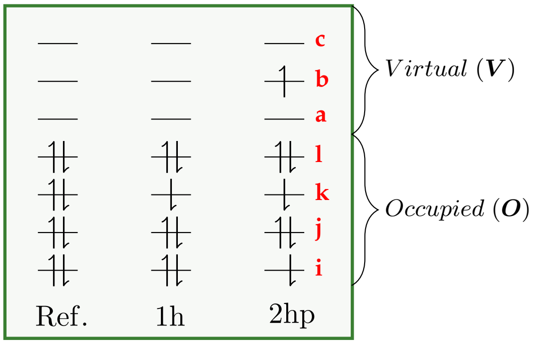


Fig. 2.1.: Electron detachment from a closed-shell reference state.

2.3 Dyson equation

The usual approximation procedure to evaluate the EP involves a perturbation expansion. Poles of an unperturbed one–electron propagator, $\boldsymbol{G_0}(E)$, where

$$[G_0(E)]_{pq} = \delta_{pq}(E - \varepsilon_p)^{-1}, \tag{2.52}$$

equal canonical Hartree–Fock orbital energies, ε_p. The latter are eigenvalues obtained through self–consistent solution of the Hartree–Fock equations, which in canonical form read

$$F\phi_p^{HF} = \varepsilon_p \phi_p^{HF}, \tag{2.53}$$

where ϕ_p^{HF} is a canonical Hartree–Fock orbital. In the frozen–orbital, single–determinant approximation employed in Koopmans's theorem, ionization energies are related to occupied orbital energies by

$$I_p = -\varepsilon_p. \tag{2.54}$$

Results at the Koopmans's theorem level usually are quantitatively inadequate and often produce erroneous orderings of cationic states because they neglect electron correlation and orbital relaxation in final states. With the introduction of an energy–dependent, non–local potential known as the self–energy, $\boldsymbol{\Sigma}(E)$, an improved electron propagator can be obtained from $\boldsymbol{G_0}(E)$ by employing the Dyson equation, which in its inverse, matrix form reads

$$\boldsymbol{G}^{-1}(E) = \boldsymbol{G_0}^{-1}(E) - \boldsymbol{\Sigma}(E). \tag{2.55}$$

The propagator poles may be computed from the equivalent expression [2, 15]

$$[\boldsymbol{F} + \boldsymbol{\Sigma}(E_p)]\phi_p^{Dyson} \equiv \Gamma(E_p)\phi_p^{Dyson} = E_p\phi_p^{Dyson}, \tag{2.56}$$

where $\boldsymbol{F}$ is the Fock operator of equation 2.53 that is generated by the one–electron density matrix of the reference state,

$$(a_p^\dagger|(E\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}})a_q^\dagger) = E\delta_{pq} - h_{pq} - \Sigma_{rs}\langle pr||qs\rangle\langle N,0|a_r^\dagger a_s|N,0\rangle \equiv E_p\delta_{pq} - F_{pq}, \tag{2.57}$$

which may be correlated. E_p is a pole of $\boldsymbol{G}(E)$ which satisfies the Dyson equation and the eigenfunctions are the Dyson orbitals. Hence, the inverse of the Dyson equation may be written as

$$\boldsymbol{G}^{-1}(E) = E\mathbf{1} - \boldsymbol{F} - \boldsymbol{\Sigma}(E_p). \tag{2.58}$$

Thus, by demanding that $\boldsymbol{G}^{-1}(E) = 0$ the poles of the electron propagator may be obtained. A more succinct expression for equation (2.56) in which the condition of $\boldsymbol{G}^{-1}(E)$ having a zero eigenvalue is imposed may be expressed by

$$[\boldsymbol{F} + \boldsymbol{\Sigma}(\boldsymbol{E})]\boldsymbol{C} = \boldsymbol{C}\boldsymbol{E}. \tag{2.59}$$

This expression can be thought as a generalization of the canonical Hartree–Fock equations, where the exchange and Coulomb terms in the Fock operator are subject to a correlated one–electron density matrix, and the orbital relaxation as well as correlation in the final states are described by the self–energy operator. In electron propagator theory, all the contributions from the correlated motion of the electrons are collected into the self–energy matrix. This matrix has energy–dependent and energy–independent (also known as constant) components

$$\boldsymbol{\Sigma}(E) = \boldsymbol{\sigma}(E) + \boldsymbol{\Sigma}(\infty). \tag{2.60}$$

When E approaches infinity, the energy–dependent terms vanishes and only the constant terms of the self–energy matrix remain,

$$\Sigma_{pq}(E) = \Sigma_{rs}\langle pr||qs\rangle\rho_{rs}^{corr}. \tag{2.61}$$

3

Electron Propagator Approximations

> *Although many of the artifices employed in the works before mentioned are remarkable for their elegance, it is easy to see they are adapted only to particular objects, and that some general method, capable of being employed in every case, is still wanting.*
>
> — **George Green**
> (The mathematical theory of electricity)

In electron propagator theory, all relaxation and correlation effects reside in the self–energy operator. Although the exact form of the self–energy operator is known, it is seldom feasible to employ. (Full configuration interaction calculation has similar difficulties.) The energy–dependent, non–local form of the self–energy operator may be systematically improved by increasing its flexibility with perturbation theory procedures. Different propagator approximations are attained by choosing different approximate ground states (*i.e.* the Hartree–Fock ground state, Kohn–Sham ground state, multiconfigurational reference states, etc.), and by truncation of the inner projection superoperator manifold $\mathbf{f}$. Furthermore, the accuracy of the electron propagator approximations may be systematically increased by enlargement of basis sets. Although electron propagator theory allows the construction of several convenient *ab–initio* propagator approximations, the exact one–electron propagator is not one of them. In the derivation of the one–electron propagator no approximations have been made, and therefore the one–electron propagator is exact so far. It is not until the introduction of an approximate wave–function, usually a Hartree–Fock determinant, that an approximation into the one–electron propagator equations is for the first time included.

3.1 Propagator approximations

In electron propagator theory, approximations to $\boldsymbol{F} + \boldsymbol{\Sigma}(E)$ are generally needed to calculate useful data. Propagators with approximate forms of $\boldsymbol{\Sigma}(E)$ that assume a canonical, Hartree–Fock basis of orbitals have been introduced for the calculation of binding energies of atoms and molecules [10, 15]. The formalism of many of these propagators employ a closed–shell reference determinant that in most cases can be extended to the unrestricted Hartree–Fock spin orbital basis. When the superoperator Hamiltonian matrix $\hat{\mathbf{H}}$ is partitioned as

$$\hat{\mathbf{H}} = \hat{\boldsymbol{H}}_0 + (\hat{\boldsymbol{H}} - \hat{\boldsymbol{H}}_0), \tag{3.1}$$

the same techniques as in Raleigh–Schrödinger perturbation theory can be implemented. Thus, one may identify the zeroth–order propagator,

$$\boldsymbol{G}_0^{-1}(E) = (\boldsymbol{a}^\dagger|(E\hat{\boldsymbol{I}} - \hat{\boldsymbol{H}}_0)\boldsymbol{a}^\dagger). \tag{3.2}$$

The metric corresponding to the superoperator space is defined by

$$(\mathbf{X}|\mathbf{Y}) = \langle N|[\mathbf{X}^\dagger, \mathbf{Y}]_+|N\rangle = Tr[\rho[X^\dagger, Y]_+] \tag{3.3}$$

where the reference density operator is defined as:

$$\rho = |N\rangle\langle N|. \tag{3.4}$$

To obtain $\boldsymbol{G}(E)$, the inner projection[69, 70] with a complete manifold of operators$\mathbf{X}$ allows the replacement of the superoperator resolvent by an inverse matrix, resulting in

$$\boldsymbol{G}(E) = (\boldsymbol{a}^\dagger|\mathbf{X})(\mathbf{X}|(E\hat{I} - \hat{H})\mathbf{X})^{-1}(\mathbf{X}|\boldsymbol{a}^\dagger). \tag{3.5}$$

The projection manifold may be partitioned into the set of simple field operators and an orthonormalized complementary set, $\mathbf{f}$,

$$(\boldsymbol{a}^\dagger|\mathbf{X}) = [(\boldsymbol{a}^\dagger|\boldsymbol{a}^\dagger)\ (\boldsymbol{a}^\dagger|\mathbf{f})] = [\mathbf{1}_a\ \mathbf{0}_{a,\mathrm{f}}]. \tag{3.6}$$

When the reference determinant is defined by the approximate ground state expressed as

$$|N\rangle = |\mathrm{HF}\rangle + |\mathrm{Correlation}\rangle, \tag{3.7}$$

the inverse of the full electron propagator matrix $\boldsymbol{G}(E)$ may be expressed as

$$\boldsymbol{G}^{-1}(E) = \boldsymbol{G}_0^{-1}(E) - \boldsymbol{\Sigma}(E). \tag{3.8}$$

In this manner, $\boldsymbol{G}_0^{-1}(E)$ is the so–called Hartree–Fock propagator:

$$[\boldsymbol{G}_0^{-1}(E)]_{pq} = (E - \varepsilon_p)\delta_{pq}, \tag{3.9}$$

where ε_p are the elements of the diagonal Hartree–Fock matrix, *i.e.* the Hartree–Fock orbital energies. Therefore, the elements of the inverse form of the Dyson equation for the full electron propagator may be expressed as:

$$G_{pq}^{-1}(E) = (E - \varepsilon_p)\delta_{pq} - \Sigma_{pq}(E). \tag{3.10}$$

3.2 Perturbative improvements to the Self–energy

The elements of the many electron propagator satisfy

$$G_{pq}^{-1}(E) = (E - \varepsilon_p)\delta_{pq} - \Sigma_{pq}(E), \tag{3.11}$$

where the determinant of the inverse propagator matrix $det(G^{-1})$ vanishes at values of the energy parameter corresponding to electron binding energies. These electron binding energies correspond to the energy parameter E and satisfy the relation

$$det[(E\mathbf{1} - \boldsymbol{\varepsilon}) - \boldsymbol{\Sigma}(E)] = 0 \tag{3.12}$$

or

$$E = \boldsymbol{C}^{\dagger}(E)[\boldsymbol{\varepsilon} - \boldsymbol{\Sigma}(E)]\boldsymbol{C}(E) \tag{3.13}$$

If the inner projection manifold $\mathbf{f}$ is neglected and, corrections to the ground state beyond $|\mathrm{HF}\rangle$ are not considered, the self–energy vanishes and the electron binding energies are given as the negative of the pth orbital energy, ε_p. Since neither relaxation nor correlation effects are considered, this approximation to the values of the electron binding energies is the so–called frozen orbital approximation obtained by the Koopmans's theorem. In electron propagator theory, the values obtained by Koopmans's theorem, the Hartree–Fock orbital energies, are the poles of the zeroth–order electron propagator matrix $\boldsymbol{G}_0(E)$. Koopmans's theorem results may be improved by means of perturbative corrections that account for final–state orbital relaxation and electron correlation. These corrections to the Koopmans's theorem results are contained in the self–energy matrix, $\mathbf{\Sigma}(E)$. The partition of the Hamiltonian presented in equation (3.1) may be rewritten as

$$\hat{\mathbf{H}} = \hat{\boldsymbol{H}}_0 + \hat{\boldsymbol{W}}, \tag{3.14}$$

where $\hat{\boldsymbol{W}}$ is defined as the fluctuation potential. After applying the usual perturbation theory techniques,the Hamiltonian partition may be expressed as

$$\hat{\mathbf{H}} = \hat{\boldsymbol{H}}_0 + \lambda\hat{\boldsymbol{W}}, \tag{3.15}$$

where λ is a dimensionless parameter with continuous values between zero (no perturbation) and unity(full perturbation). If the density operator is expressed as a Maclaurin power series[1] in λ,

$$\rho = \rho_0 + \lambda\rho_1 + \lambda^2\rho_2 + \cdots + \lambda^k\rho_k, \tag{3.16}$$

the following commutator relation holds for the density operator and the unperturbed Hamiltonian operator:

$$[H_0, \rho_0] = 0. \tag{3.17}$$

Thus, for the full Hamiltonian, one may obtain the following commutator relationship:

$$[H_0, \rho_k] + [W, \rho_{k-1}] = 0. \tag{3.18}$$

When the superoperator Hamiltonian matrix is partitioned into primary ($\mathbf{P}$) and secondary ($\mathbf{Q}$) sectors,

$$\hat{\mathbf{H}} = \left[\begin{array}{c|c} \mathbf{P} & \mathbf{Q} \\ \hline \mathbf{Q} & \mathbf{Q} \end{array}\right], \tag{3.19}$$

each of the blocks of the superoperator Hamiltonian matrix $\hat{\mathbf{H}}$ may be evaluated in various orders of the fluctuation potential. For example, when the superoperator matrix $\hat{\mathbf{H}}$ is expressed in terms of the field operators $\boldsymbol{a}$ and $\mathbf{f}$,

$$\hat{\mathbf{H}} = \begin{bmatrix} (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a}) & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\mathbf{f}) \\ (\mathbf{f}|\hat{\boldsymbol{H}}|\boldsymbol{a}) & (\mathbf{f}|\hat{\boldsymbol{H}}|\mathbf{f}) \end{bmatrix}, \tag{3.20}$$

---

[1] Taylor series at zero are also called Maclaurin series. This special case of Taylor series was named after the Scottish mathematician Colin Maclaurin, who made extensive use of them in the 18th century.

the evaluation of any of the blocks of the superoperator Hamiltonian in a given order n will be defined as the sum of the n constituents that define that order. In this respect, for the primary operator block evaluated to the $n\mathrm{th}$ order, the expression obtained is

$$(\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})^n = (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})_0 + (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})_1 + (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})_2 + \cdots + (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})_n. \tag{3.21}$$

Inclusion of all self–energy terms through a given order is generally accomplished by improving the reference density operator. The superoperator matrix elements that are needed to recover all self-energy terms up to fifth order for the usual case with a Hartree–Fock reference density operator are reported in table 3.1.

n	$(\boldsymbol{a}\|\hat{H}\|\boldsymbol{a})$	$(\mathbf{f_3}\|\hat{H}\|\boldsymbol{a})$	$(\mathbf{f_3}\|\hat{H}\|\mathbf{f_3})$	$(\mathbf{f_5}\|\hat{H}\|\boldsymbol{a})$	$(\mathbf{f_5}\|\hat{H}\|\mathbf{f_3})$	$(\mathbf{f_5}\|\hat{H}\|\mathbf{f_5})$
1	1	-	-	-	-	-
2	2	1	0	-	-	-
3	3	2	1	-	-	-
4	4	3	2	2	1	0
5	5	4	3	3	2	1

Tab. 3.1.: Superoperator Hamiltonian requirements for $\boldsymbol{\Sigma}^n$.

3.2.1 Hermiticity

Non–Hermitian terms in the superoperator Hamiltonian matrix may be present when the anti–commutator, $[Y^\dagger, X]_+$, in

$$(Y|\hat{H}X) - (X|\hat{H}Y)^* = Tr([H,\rho][Y^\dagger, X]_+), \tag{3.22}$$

does not vanish [75]. Such terms appear in the superoperator couplings of the type $(\mathbf{f_n}|\hat{H}\mathbf{f_m})$ where n and $\mathrm{m} \in \mathbb{Z}$ with $\mathrm{n} > \mathrm{m}$. These Non–Hermitian terms of these superoperator couplings are absent in the adjoint matrices, and involve elements of the Fock operator. For instance, in $(\mathbf{f_1}|\hat{H}\mathbf{f_5})$, the non–Hermitian terms involve electron repulsion integrals that occur in the first–order, Møller–Plesset amplitudes. Linderberg observed that non–Hermitian terms may be systematically eliminated via perturbative improvements to the reference density operator[75]. For instance, after making the usual assumptions of perturbation theory, for the relationship expressed in equation (3.18), when the reference density operator ρ is correct through order k,

$$(Y|\hat{H}X) - (X|\hat{H}Y)^* = Tr([W,\rho_k][Y^\dagger, X]_+), \tag{3.23}$$

and the non–Hermitian terms are of order $k+1$. Inclusion of first–order corrections to the reference density operator suffices for Hermiticity in the superoperator Hamiltonian matrix through first order.

3.3 The second–order electron propagator

The first correction to the self–energy matrix in the one–electron propagator occurs at the second order of perturbation. The superoperator Hamiltonian matrix that recovers the poles of the second order self–energy may be expressed as

$$\hat{\mathbf{H}} = \begin{bmatrix} (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(0)} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)} \\ (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(1)} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(0)} \end{bmatrix}, \tag{3.24}$$

where $\mathbf{f_3}$ is the vector of $2hp$ and $2ph$ operators defined with respect to the reference determinant. The second–order approximation to the self–energy has the simplest expressions for the superoperator Hamiltonian matrix blocks. These blocks may be expressed in terms of creation and annihilation field operators as

$$\begin{aligned}
&(\mathbf{a}|\widehat{\mathbf{H}}\mathbf{a}) : (a_\iota|\widehat{\mathbf{H}}a_\kappa) = \langle ref|[a_\iota[a_\kappa, \mathbf{H}]]_+|ref\rangle \\
&(\mathbf{f_3}|\widehat{\mathbf{H}}\mathbf{f_3}) : (a_\iota^\dagger a_s a_t|\widehat{\boldsymbol{H}}a_\kappa^\dagger a_p a_q) = \langle ref|[a_t^\dagger a_s^\dagger a_\iota[a_\kappa^\dagger a_p a_q, \mathbf{H}]]_+|ref\rangle \\
&(\mathbf{a}|\widehat{\mathbf{H}}\mathbf{f_3}) : (a_u|\widehat{\mathbf{H}}a_\kappa^\dagger a_p a_q) = \langle ref|[a_u^\dagger[a_\kappa^\dagger a_p a_q, \mathbf{H}]]_+|ref\rangle \\
&(\mathbf{f_3}|\widehat{\mathbf{H}}\mathbf{a}) : (a_\iota^\dagger a_s a_t|\widehat{\mathbf{H}}a_r) = \langle ref|[a_t^\dagger a_s^\dagger a_\iota[a_r, \mathbf{H}]]_+|ref\rangle
\end{aligned} \tag{3.25}$$

where $|ref\rangle$ is the reference determinant used for the superoperator coupling expansion. The indices of the creation and annihilation field operators are general indices, *i.e.* correspond to either a hole or a particle. The expressions for these field operator coupling are obtained by applying each set of field operator into the reference determinant that has been selected to represent the reference–state of the molecular system. In quantum chemistry, the Hartree–Fock reference–state may be the simplest determinant that could be used. In most cases, the Hartree–Fock reference determinant will suffice for the correct description of atoms and molecules. However, no all the important electronic interaction nor electronic quantum effects can be described by a single Hartree–Fock wave–function. The Hartree–Fock wave–function corresponds to the portrait of a particular case of several electronic quantum states that may be important for the correct description of the molecular system and its properties. Therefore, the evaluation of the superoperators coupling using a more general reference–state brings the advantage of achieving more general expressions that can be adapted to describe cases in which several particular determinants are needed. In this regard,

H. H. Corzo and J. V. Ortiz have deduced and introduced more general expressions for the superoperator coupling of equation (3.25)[11]. The expression reported by H. H. Corzo and J. V. Ortiz were derived using as the reference–state the true vacuum state[48], $|\boldsymbol{vac}\rangle$. These expressions correspond to a more general determinant than the Hartree-Fock determinant and may be used in the description of more complicated types of molecular systems and electronic processes.

3.3.1 Primary–Primary block

When a general determinant is employed, the expansion of the operator vectors corresponding to the zeroth order Primary–Primary block of superoperator Hamiltonian matrix ($\widehat{\mathbf{H}}^{(\mathbf{0})}_{\mathbf{PP}}$) yields

$$(a_\iota|\widehat{\mathrm{H}}^{(0)}a_\kappa) = \mathbf{F}_{\kappa\iota}. \tag{3.26}$$

The elements of the $\widehat{\mathbf{H}}^{(\mathbf{0})}_{\mathbf{PP}}$ block in the canonical Hartree–Fock orbital spin–basis read

$$(a_\iota|\widehat{\mathrm{H}}a_\kappa)^{(0)} = \delta_{\kappa\iota}\varepsilon_\iota. \tag{3.27}$$

These elements are the diagonal elements of the Fock matrix, and therefore, they represent the one–electron energies, or Hartree–Fock orbital energies, obtained after solving the Roothaan equations.

3.3.2 Primary–Secondary and Secondary–Primary blocks

The expansion of the terms in first order for the Primary–Secondary block ($\widehat{\mathbf{H}}^{(\mathbf{1})}_{\mathbf{PQ}}$) yields

$$(a_u|\widehat{\mathrm{H}}a^\dagger_\kappa a_p a_q)^{(1)} = \delta_{up}\mathbf{F}_{\kappa q}(n_\kappa - n_q) + \delta_{uq}\mathbf{F}_{\kappa p}(n_\kappa - n_p) - \langle pq\|u\kappa\rangle[(1-n_\kappa)n_p n_q + n_\kappa(1-n_p)(1-n_q)] \tag{3.28}$$

whereas for the Secondary-Primary block ($\widehat{\mathbf{H}}^{(\mathbf{1})}_{\mathbf{QP}}$) the expression is

$$(a^\dagger_\iota a_s a_t|\widehat{\mathrm{H}}a_r)^{(1)} = \langle\iota r\|st\rangle[(1-n_\iota)n_s n_t + n_\iota(1-n_s)(1-n_t)]. \tag{3.29}$$

In $\widehat{\mathbf{H}}^{(\mathbf{1})}_{\mathbf{PQ}}$, the terms that depend on the Fock operator are non–Hermitian. These terms may be omitted [11, 75]. Therefore, the expressions for the Primary–Secondary block may be rewritten as

$$(a_u|\widehat{\mathrm{H}}a^\dagger_\kappa a_p a_q)^{(1)} = -\langle pq\|u\kappa\rangle[(1-n_\kappa)n_p n_q + n_\kappa(1-n_p)(1-n_q)] \tag{3.30}$$

3.3.3 Secondary–Secondary block

The expansion of the Secondary–Secondary block of superoperator Hamiltonian matrix ($\widehat{\mathbf{H}}_{\mathbf{QQ}}$) reads

$$\begin{aligned}
(a_\iota^\dagger a_s a_t|\widehat{H} a_\kappa^\dagger a_p a_q) = {} & \mathbf{F}_{qt}\delta_{\iota\kappa}\delta_{sp}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& - \mathbf{F}_{qs}\delta_{\kappa\iota}\delta_{tp}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& - \mathbf{F}_{pt}\delta_{qs}\delta_{\kappa\iota}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& + \mathbf{F}_{ps}\delta_{\iota\kappa}\delta_{tq}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& + \mathbf{F}_{\iota\kappa}[\delta_{tp}\delta_{sq} - \delta_{ps}\delta_{tq}][(1-n_\iota)n_s n_t + n_\iota(1-n_s)(1-n_t)] \\
& + \langle \iota q \| \kappa t\rangle \delta_{sp}[(1-n_\iota)n_s n_t + n_\iota(1-n_s)(1-n_t)](n_q - n_\kappa) \\
& + \langle \iota p \| \kappa t\rangle \delta_{sq}[(1-n_\iota)n_s n_t + n_\iota(1-n_s)(1-n_t)](n_\kappa - n_p) \\
& + \langle \iota q \| \kappa s\rangle \delta_{tp}[(1-n_\iota)n_s n_t + n_\iota(1-n_s)(1-n_t)](n_\kappa - n_q) \\
& + \langle p \iota \| s \kappa\rangle \delta_{tq}[(1-n_\iota)n_s n_t + n_\iota(1-n_s)(1-n_t)](n_p - n_\kappa) \\
& + \langle pq \| ts\rangle \delta_{\kappa\iota}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)](n_p + n_q - 1).
\end{aligned} \tag{3.31}$$

Since the full many–body Hamiltonian was used for the derivation of this superoperator coupling, this last expression corresponds to the first order superoperator coupling evaluation. In zeroth order, however, only terms that depend on the Fock operator do not vanish,

$$\begin{aligned}
(a_\iota^\dagger a_s a_t|\widehat{H} a_\kappa^\dagger a_p a_q)^{(0)} = {} & \mathbf{F}_{qt}\delta_{\iota\kappa}\delta_{sp}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& - \mathbf{F}_{qs}\delta_{\kappa\iota}\delta_{tp}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& - \mathbf{F}_{pt}\delta_{qs}\delta_{\kappa\iota}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& + \mathbf{F}_{ps}\delta_{\iota\kappa}\delta_{tq}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& + \mathbf{F}_{\iota\kappa}[\delta_{tp}\delta_{sq} - \delta_{ps}\delta_{tq}][(1-n_\iota)n_s n_t + n_\iota(1-n_s)(1-n_t)].
\end{aligned} \tag{3.32}$$

When a grand–canonical Hartree–Fock spin–orbital basis is used the above expression reduces to

$$\begin{aligned}
(a_\iota^\dagger a_s a_t|\widehat{H} a_\kappa^\dagger a_p a_q)^{(0)} = {} & \varepsilon_t\delta_{qt}\delta_{\iota\kappa}\delta_{sp}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& - \varepsilon_s\delta_{qs}\delta_{\kappa\iota}\delta_{tp}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& - \varepsilon_t\delta_{pt}\delta_{qs}\delta_{\kappa\iota}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& + \varepsilon_s\delta_{ps}\delta_{\iota\kappa}\delta_{tq}[(1-n_\kappa)n_s n_t + n_\kappa(1-n_s)(1-n_t)] \\
& + \varepsilon_\kappa\delta_{\iota\kappa}[\delta_{tp}\delta_{sq} - \delta_{ps}\delta_{tq}][(1-n_\iota)n_s n_t + n_\iota(1-n_s)(1-n_t)],
\end{aligned} \tag{3.33}$$

that may be reduced as

$$(a^{\dagger}_{\iota}a_{s}a_{t}|\widehat{H}a^{\dagger}_{\kappa}a_{p}a_{q})^{(0)} = (\varepsilon_{t}+\varepsilon_{s}-\varepsilon_{\iota})[\delta_{qt}\delta_{sp}-\delta_{tp}\delta_{sq}][(1-n_{\kappa})n_{s}n_{t}+n_{\kappa}(1-n_{s})(1-n_{t})]\delta_{\iota\kappa}. \tag{3.34}$$

The expression in equation (3.34) depends on a difference of products of Dirac deltas that are related by exchanging their indices. This relationship between the Dirac deltas resembles the determinant of a two by two matrix. Therefore, further simplification of equation (3.34) may be obtained by means of matrix algebra notation[11]. However, for the sake of simplicity, equation (3.34) will be simplified by setting the logical condition that a single index can not be associated to two different particles, *i.e.*, the operators are unique operators. A creation or annihilation operator acts on a specific particle at a given time. Therefore, if $s > t$ and $p > q$ implies that $\delta_{sq}\ \delta_{tp}$ is equal to zero. Therefore the expression in equation 3.34 reduces to

$$(a^{\dagger}_{\iota}a_{s}a_{t}|\widehat{H}a^{\dagger}_{\kappa}a_{p}a_{q})^{(0)} = (\varepsilon_{t}+\varepsilon_{s}-\varepsilon_{\iota})[(1-n_{\kappa})n_{s}n_{t}+n_{\kappa}(1-n_{s})(1-n_{t})]\delta_{qt}\delta_{sp}\delta_{\iota\kappa}. \tag{3.35}$$

Finally, for a grand–canonical Hartree–Fock basis the expression for $\widehat{\mathbf{H}}^{\mathbf{(0)}}_{\mathbf{QQ}}$ yields

$$(a^{\dagger}_{\iota}a_{s}a_{t}|\widehat{H}a^{\dagger}_{\kappa}a_{p}a_{q})^{(0)} = (\varepsilon_{t}+\varepsilon_{s}-\varepsilon_{\iota})[(1-n_{\kappa})n_{s}n_{t}+n_{\kappa}(1-n_{s})(1-n_{t})]. \tag{3.36}$$

3.3.4 Second–Order Self–Energy

The Dyson equation that express the second order self–energy yields

$$\mathbf{\Sigma}^{(2)}(E) = (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f_3})^{(1)}[E\mathbf{1}-(\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{f_3})^{(0)}]^{-1}(\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{a})^{(1)}. \tag{3.37}$$

Taking this definition of the second order self–energy and replacing each of the super-operator couplings by their general expressions, the elements of the $\mathbf{\Sigma}^{(2)}(E)$ may be expressed as

$$\mathbf{\Sigma}^{(2)}_{ru}(E) = \sum_{\iota,\kappa,p,q,s,t} N_{\iota st}\langle \iota r\|st\rangle\Big[N_{\iota st}[E\mathbf{1}+\mathbf{F}_{\iota\kappa}\delta_{ps}\delta_{tq}-\mathbf{F}_{qt}\delta_{\iota\kappa}\delta_{sp}-\mathbf{F}_{ps}\delta_{\iota\kappa}\delta_{tq}]\Big]^{-1}N_{\kappa pq}\langle pq\|\kappa u\rangle, \tag{3.38}$$

where,

$$N_{\kappa pq} = [(1-n_{\kappa})n_{p}n_{q}+n_{\kappa}(1-n_{p})(1-n_{q})] \tag{3.39}$$

and

$$N_{\iota st} = [(1 - n_\kappa)n_s n_t + n_\kappa(1 - n_s)(1 - n_t)] \tag{3.40}$$

are the normalization factors of in terms of the occupational numbers. The second–order self–energy matrix with a grand canonical, Hartree–Fock reference density operator, when $p = s$, $q = t$ and $\iota = \kappa$, yields

$$\Sigma^{(2)}_{ru}(E) = \sum_{\iota,p<q} \frac{N_{\iota pq}\langle r\iota\|pq\rangle\langle pq\|u\iota\rangle}{E\mathbf{1} + \varepsilon_\iota - \varepsilon_p - \varepsilon_q}, \tag{3.41}$$

Using the above expression, the $2hp$ and $2ph$ terms for the second order propagator can be easily infer when the correct indices convention and values of the occupation numbers are adopted. If the indices a, b, c are set for virtual orbitals, i, j, k for occupied orbitals and κ, ι, ν for either virtual or occupied orbitals, then the $2hp$ term is obtained when $n_\iota = 0$ and $n_p = n_q = 1$, whereas, the $2ph$ term is obtained when $n_\iota = 1$ and $n_p = n_q = 0$. Therefore, the elements of the second–order self–energy matrix may be written as

$$\Sigma^{(2)}_{\iota\kappa}(E) = \sum_{a,i<j} \frac{\langle\iota a\|ij\rangle\langle ij\|\kappa a\rangle}{E + \varepsilon_a - \varepsilon_i - \varepsilon_j} + \sum_{i,a<b} \frac{\langle\iota i\|ab\rangle\langle ab\|\kappa i\rangle}{E + \varepsilon_i - \varepsilon_a - \varepsilon_b} \tag{3.42}$$

This last expression of the self–energy matrix contains the largest corrections to Koopmans's theorem. The second–order self–energy may be sufficient for a qualitative correct ordering of the valance electron final states in the photoelectron spectra, especially when a good quality basis set is used.

3.3.5 Second–order relaxation correction terms

When computing ionization energies, the indices of the second order self–energy matrix, $\Sigma^{(2)}_{\iota\kappa}(E)$ will correspond to occupied orbitals in the Hartree–Fock reference determinant, *i.e.* $\mathbf{\Sigma}^{(2)}_{pp}(E)$. If one isolates the terms in the second sum of equation (3.42) that results when the indices a or b are equal to i one obtains

$$\Sigma^{R(2)}_{pp}(E) = -\sum_{ai} \frac{|\langle ap\|ip\rangle|^2}{\varepsilon_a - \varepsilon_i}. \tag{3.43}$$

This last expression is precisely the second–order contribution to the ionization energy calculated as the self–consistent field (SCF) difference

$$-I_p(\Delta SCF) = E_{HF}(N) - E^p_{HF}(N-1) \tag{3.44}$$

with

$$E_{HF}(N) = \sum_a \varepsilon_a - \frac{1}{2}\sum_{ab} \langle ab||ab\rangle. \tag{3.45}$$

In equation (3.44), $E^p_{HF}(N-1)$ is the total energy obtained from a separate SCF calculation on the state characterized by the spin–orbital p being removed from the electron configuration of the Hartree–Fock N–electron reference state. This ΔSCF approximation is defined as the relaxation correction of the ionization energy. Thus, equation (3.43) displays the second–order relaxation correction terms. Similarly, the relaxation correction terms of the self–energy matrix in any order of perturbation may be identified. Furthermore, rules for the separation of the self–energy relaxation (Σ^R_{pp}) and correlation (Σ^C_{pp}) terms have been given in the literature [77].

3.4 Diagonal approximations

In the basis of Hartree–Fock spin–orbitals, the self–energy includes all relaxation and correlation corrections. Hartree–Fock orbitals can be a reasonable approximation to the Dyson orbitals. Under this idea, one may neglect the off–diagonal elements of the second–order self–energy matrix,

$$\Sigma^{(2)}_{pq}(E) = \frac{1}{2}\sum_{aij} \frac{\langle pa||ij\rangle\langle ij||qa\rangle}{E+\varepsilon_a-\varepsilon_i-\varepsilon_j} + \frac{1}{2}\sum_{iab} \frac{\langle pi||ab\rangle\langle ab||qi\rangle}{E+\varepsilon_i-\varepsilon_a-\varepsilon_b}, \tag{3.46}$$

where $i, j, k, ...$ are occupied (h) spin–orbital indices, $a, b, c, ...$ are virtual (p) spin–orbital indices and anti–symmetrized electron repulsion integrals are represented in Dirac notation. This diagonal, or quasiparticle, approximation of the self–energy assumes that Koopmans's theorem provides a qualitatively reasonable description of an ionizing transition and leads to a simplified form of the Dyson equation that reads

$$E = \varepsilon_p + \Sigma_{pp}(E) \tag{3.47}$$

where the correlation contributions to the matrix elements of the Fock operator of the Dyson quasiparticle equation $[\boldsymbol{F} + \boldsymbol{\Sigma}(E_r)]\phi^{Dyson}_r = E_r\phi^{Dyson}_r$ are absorbed into $\boldsymbol{\Sigma}(E)$. In this way, corrections to the results of Koopmans's theorem may be calculated for each canonical Hartree–Fock orbital. In the diagonal approximation, Dyson orbitals become proportional to normalized, canonical Hartree–Fock orbitals such that

$$\phi^{Dyson}_p = \sqrt{\pi_p}\phi^{HF}_p, \tag{3.48}$$

where pole strengths are evaluated by the formula

$$\pi_p = (1 - \frac{d\Sigma_{pp}(E)}{dE})^{-1}. \tag{3.49}$$

The derivative of $\Sigma_{pp}(E)$ with respect to E is evaluated at the pole (*i.e.* the self–consistent value of E in equation (3.47)). These derivatives may also serve to accelerate the search for poles in equation (3.47) by use of Newton's numerical method for finding the roots of a function of a single variable. Diagonal self–energy approximations have been exploited in a wide variety of applications [22, 25, 78–80]. Employment of equation (3.47) with the second–order self–energy of equation (3.46) defines the diagonal, second–order, or D2, approximation. The D2 approximation may be the most efficient electron propagator approximation for the calculation of vertical detachment energies of atoms and molecules. In the canonical Hartree–Fock basis, the D2 approximation requires a relatively small set of four–index electron repulsion integrals where one index corresponds to a canonical orbital of interest for each of the detachment energy calculation. The other three indices correspond to $2hp$ or $2ph$ operators. The D2 lengthiest calculation has an arithmetic scaling factor of OV^2.

3.4.1 The D3 approximation

In the canonical Hartree–fock spin–orbital basis, the diagonal elements of the third–order self–energy matrix [81, 82] read

$$\begin{gathered}\Sigma^{(3)}_{pp}(E) = \Sigma^{(3)}_{pp}(\infty) + \\ \sum_{aij} \frac{[Y_{paij} + \frac{1}{2}U_{paij}(E)]\langle pa||ij\rangle}{E + \epsilon_a - \epsilon_i - \epsilon_j} + \sum_{iab} \frac{[Y_{piab} + \frac{1}{2}U_{piab}(E)]\langle pi||ab\rangle}{E + \epsilon_i - \epsilon_a - \epsilon_b},\end{gathered} \tag{3.50}$$

where

$$E = \epsilon_p + \Sigma_{pp}(E). \tag{3.51}$$

$$U_{paij}(E) = -\frac{1}{2}\sum_{kl} \frac{\langle pa||kl\rangle\langle kl||ij\rangle}{E + \epsilon_a - \epsilon_k - \epsilon_l} - (1 - P_{ij})\sum_{bk} \frac{\langle pb||jk\rangle\langle ak||bi\rangle}{E + \epsilon_b - \epsilon_j - \epsilon_k}. \tag{3.52}$$

$$U_{piab}(E) = \frac{1}{2}\sum_{cd} \frac{\langle pi||cd\rangle\langle cd||ab\rangle}{E + \epsilon_i - \epsilon_c - \epsilon_d} + (1 - P_{ab})\sum_{jc} \frac{\langle pj||bc\rangle\langle ic||ja\rangle}{E + \epsilon_j - \epsilon_b - \epsilon_c} \tag{3.53}$$

$$Y_{paij} = \frac{1}{2}\sum_{bc}\langle pa||bc\rangle t_{ijbc} + (1 - P_{ij})\sum_{kb}\langle pk||bj\rangle t_{ikab} \tag{3.54}$$

$$Y_{piab} = \frac{1}{2}\sum_{jk}\langle pi||jk\rangle t_{jkab} + (1 - P_{ab})\sum_{jc}\langle pc||jb\rangle t_{ijac} \tag{3.55}$$

and where P_{ij} and P_{ab} are spin–orbital permutation operators. The Y matrices are second–order intermediates that depend on first–order wavefunction amplitudes defined by

$$t_{ijab} = \frac{\langle ij||ab\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \tag{3.56}$$

The constant (or energy–independent) self–energy term,

$$\Sigma_{pp}^{(3)}(\infty) = \sum_{tu} \langle pt||pu\rangle \rho_{tu}^{(2)}, \tag{3.57}$$

arises from the Fock operator in the Dyson quasiparticle equation and depends on the second–order density matrix, $\rho^{(2)}$. The use of the third–order self-energy $\Sigma_{pp}^{(3)}$ for the calculation of binding energies in atoms and molecules defines the so–called D3 approximation. In the D3 approximation, the arithmetic bottleneck occurs in the evaluation of the $U_{piab}(E)$ intermediate (see equation 3.53), where for every p, a summation that involves electron repulsion integrals with four virtual indices has OV^4 scaling. This step must be repeated for every iteration with respect to E. The latter integrals may be calculated and stored or may be regenerated as needed in a semi–direct algorithm [83, 84].

3.4.2 OVGF

The Outer valence Green function (OVGF) approximations assume a diagonal self–energy matrix and describe low–energy transitions [81, 85]. All versions of OVGF are based on the third–order expansion of the self–energy and include estimates of higher–order contributions. Three frequently applied procedures have been denominated as versions A, B and C [81, 85, 86]. OVGF version A corrects canonical HF orbital energies with

$$\Sigma_{pp}^{OVGF-A}(E) = \Sigma_{pp}^{(2)}(E) + (1 + X_p)^{-1}\Sigma_{pp}^{(3)}(E), \tag{3.58}$$

where E is the pole obtained with diagonal second–order and third–order self–energy terms. The scaling coefficient for the third order–terms in the latter equation depends on X_p, which is defined by

$$X_p = -2\frac{\sigma_{pp}^{(3)}(E)}{\Sigma_{pp}^{(2)}(E)}, \tag{3.59}$$

where the numerator has $2hp$ and $2ph$ contributions such that

$$\sigma_{pp}^{(3)}(E) = \frac{1}{2}\sum_{aij} \frac{\langle pa||ij\rangle Y_{paij}}{E + \varepsilon_a - \varepsilon_i - \varepsilon_j} + \frac{1}{2}\sum_{iab} \frac{\langle pi||ab\rangle Y_{piab}}{E + \varepsilon_i - \varepsilon_a - \varepsilon_b}. \tag{3.60}$$

The B version [9] is similar, but separates the energy–dependent $2ph$ and $2hp$ contributions to $\sigma_{pp}^{(3)}$ through

$$\Sigma_{pp}^{OVGF-B}(E) = \Sigma_{pp}^{(2)}(E)+\Sigma_{pp}^{(3)}(\infty)+(1+X_p^{2hp})^{-1}\Sigma_{pp}^{(3-2hp)}(E)+(1+X_p^{2ph})^{-1}\Sigma_{pp}^{(3-2ph)}(E), \tag{3.61}$$

where

$$X_p^{2hp} = -2\frac{\sigma_{pp}^{(3-2hp)}(E)}{\Sigma_{pp}^{2-2hp}}, \tag{3.62}$$

$$X_p^{2ph} = -2\frac{\sigma_{pp}^{(3-2ph)}(E)}{\Sigma_{pp}^{2-2ph}}. \tag{3.63}$$

In version C, the self–energy correction reads

$$\Sigma_{pp}^{OVGF-C}(E) = \Sigma_{pp}^{(2)}(E) + (1 + X_p^C)^{-1}\Sigma_{pp}^{(3)}(E), \tag{3.64}$$

where

$$X_p^C = \frac{X_p^{2hp}\Sigma_{pp}^{3-2hp}(E) + X_p^{2ph}\Sigma_{pp}^{3-2ph}(E)}{\Sigma_{pp}^{3-2hp}(E) + \Sigma_{pp}^{3-2ph}(E)}. \tag{3.65}$$

An algorithm that introduces several numerical criteria for the choosing among these alternatives has been developed and implemented for the OVGF approximation [81, 85, 86]. The OVGF approximation requires a full integral transformation and has an iterative, bottleneck step with OV^4 scaling. Although the A, B and C versions of OVGF introduce no numerical parameters, the OVGF selection procedure does.

3.4.3 P3 and P3+

The arithmetic bottleneck and efficiency problems for computing binding energies in the D3 and OVGF approximations may be avoided with the P3 and P3+ approximations. The P3 approximation, also known as partial third–order quasiparticle theory [82, 87], is an approach in which several terms in $\Sigma^{(3)}(E)$ are omitted from the calculations. The P3 self–energy for electron detachment energies reads

$$\Sigma^{P3}(E)_{kk} = \frac{1}{2}\sum_{iab}\frac{\langle ki||ab\rangle\langle ab||ki\rangle}{E+\varepsilon_i-\varepsilon_a-\varepsilon_b} + \frac{1}{2}\sum_{aij}\frac{\langle ka||ij\rangle[W_{kaij}+U_{kaij}(E)]}{E+\varepsilon_a-\varepsilon_i-\varepsilon_j}, \tag{3.66}$$

where

$$W_{kaij} = \langle ka||ij\rangle + Y_{kaij}. \tag{3.67}$$

This approximation retains all second order terms and has some 2h1p terms in third order. The arithmetic bottleneck occurs in the evaluation of Y_{kaij} intermediates. Here, the first term in equation 3.54 requires electron repulsion integrals with three virtual indices and has an arithmetic scaling factor of O^2V^3. No transformed electron repulsion integrals with four virtual indices are required in calculations of vertical ionization energies. On the other hand, the renormalized partial third order, or P3+, method is obtained by introducing a renormalization factor such that [88],

$$\Sigma^{P3+}(E)_{kk} = \frac{1}{2}\sum_{iab}\frac{\langle ki||ab\rangle\langle ab||ki\rangle}{E+\epsilon_i-\epsilon_a-\epsilon_b} + [1+\Lambda_k]^{-1}\frac{1}{2}\sum_{aij}\frac{\langle ka||ij\rangle[W_{kaij}+U_{kaij}(E)]}{E+\varepsilon_a-\varepsilon_i-\varepsilon_j}, \tag{3.68}$$

where Λ_k reads

$$\Lambda_k = -\frac{1}{2}[\Sigma^{(2)}_{kk}(E)]^{-1}\times\sum_{aij}\frac{\langle ka||ij\rangle Y_{kaij}}{E+\varepsilon_a-\varepsilon_i-\varepsilon_j}. \tag{3.69}$$

This simple procedure avoids exaggeration of final state relaxation effects with virtually no additional computational effort. The P3+ approximation has a single O^2V^3 step and iterations with O^3V^2 scaling. P3+ has a need for transformed integrals with three virtual indices only in a single step and independence of integrals with four virtual indices.

3.5 Non–diagonal approximations

Electron propagator approximations in which the complete self–energy matrix is considered for the calculation of the binding energies are sometimes referred to as the non–diagonal electron propagator approximations. In these electron propagator approximations, self–energy terms in all orders of the fluctuation potential are procured by considering the eigenvalues and eigenvectors of the super operator Hamiltonian matrix, $\hat{\mathbf{H}}\boldsymbol{\Omega} = \boldsymbol{\Omega}\boldsymbol{\omega}$. The simplest non–diagonal approximations is, perhaps, the so–called non–diagonal second–order propagator (ND2). For the ND2 approximation all the elements corresponding to second–order superoperator Hamiltonian matrix and the occupied and virtual spin–orbitals (*i.e.* the occupied–occupied, occupied–virtual, virtual–occupied, and virtual–virtual blocks) are considered. In this respect, in the basis of Hartree–Fock spin–orbitals, the self–energy matrix for the ND2 method is equal to $\Sigma^{(2)}_{\iota\kappa}(E)$ of equation (3.42). Similarly, this fashion, several approximations in which the diagonal self–energy approximation has not been made may be developed.

3.5.1 The $2ph-\mathrm{TDA}$ approximation

The second–order electron propagator approximation may be applied for the calculation of outer valence ionization energies which are far from the poles of the self–energy. Usually, these ionization energies have pole strengths close to unity, thus, one may expect a single line in the photoelectron spectrum for each molecular orbital. However, in the inner valence region the one–particle picture of ionization may break down completely, and satellite lines with small relative intensities may accompany the ionization main lines. These satellite lines as well as the inner valence ionization energies lie in the pole region of the self–energy. The two–particle, one–hole, Tamm–Dancoff ($2ph-\mathrm{TDA}$) approximation, which takes the pole structure of the self–energy into account, was introduced by Cederbaum and coworkers [85, 89, 90] in order to calculate inner valence ionization energies and their satellite lines. The $2ph-\mathrm{TDA}$ approximation is a renormalized method that employs a Hartree–Fock reference state and considers all first–order couplings among h, p, $2hp$, and $2ph$ operators. This propagator approximation may be advantageous over the ND2 approximation for the calculation of ionization energies of electrons in which the one–electron concepts useful for the description of the outer valence and core electrons are not longer valid. The $2ph-\mathrm{TDA}$ approximation is equivalent to the choice

$$\hat{\mathbf{H}} = \begin{bmatrix} (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(0)} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)} \\ (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(1)} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)} \end{bmatrix}. \tag{3.70}$$

Thus, the $2ph-\mathrm{TDA}$ self–energy may be expressed as

$$\boldsymbol{\Sigma}^{(2ph-\mathrm{TDA})}(E) = (\mathbf{a}|\widehat{\mathbf{H}}\mathbf{f_3})^{(1)}[E\mathbf{1} - (\mathbf{f_3}|\widehat{\mathbf{H}}\mathbf{f_3})^{(1)}]^{-1}(\mathbf{f_3}|\widehat{\mathbf{H}}\mathbf{a})^{(1)}. \tag{3.71}$$

The $2ph-\mathrm{TDA}$ self–energy differs from the second–order self–energy in the secondary–secondary block of the superoperator Hamiltonian [15, 91]. In the $2ph-\mathrm{TDA}$ approximation, the $\widehat{\mathbf{H}}_{\mathbf{QQ}}$ is evaluated in first order. When considering the $(\mathbf{f_3}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)}$ superoperator coupling, and the indexes hierarchy to represent the occupied and virtual nature of the orbitals, that is $\iota > s > t$ and $\kappa > p > q$, the $\widehat{\mathbf{H}}^{(\mathbf{1})}_{\mathbf{QQ}}$ block may be expressed as

$$
\begin{aligned}
(\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{f_3})^{(1)} &= (a^{\dagger}_{\iota}a_s a_t|\widehat{H}a^{\dagger}_{\kappa}a_p a_q)\\
&= \mathbf{F}_{qt}\delta_{\iota\kappa}\delta_{sp}[(1-n_{\kappa})n_s n_t + n_{\kappa}(1-n_s)(1-n_t)]\\
&\quad + \mathbf{F}_{ps}\delta_{\iota\kappa}\delta_{tq}[(1-n_{\kappa})n_s n_t + n_{\kappa}(1-n_s)(1-n_t)]\\
&\quad - \mathbf{F}_{\iota\kappa}\delta_{ps}\delta_{tq}[(1-n_{\iota})n_s n_t + n_{\iota}(1-n_s)(1-n_t)]\\
&\quad + \langle \iota q\|\kappa t\rangle\delta_{sp}[(1-n_{\iota})n_s n_t + n_{\iota}(1-n_s)(1-n_t)](n_q - n_{\kappa})\\
&\quad + \langle p\iota\|s\kappa\rangle\delta_{tq}[(1-n_{\iota})n_s n_t + n_{\iota}(1-n_s)(1-n_t)](n_p - n_{\kappa})\\
&\quad + \langle pq\|ts\rangle\delta_{\kappa\iota}[(1-n_{\kappa})n_s n_t + n_{\kappa}(1-n_s)(1-n_t)](n_p + n_q - 1)
\end{aligned}
\quad . \tag{3.72}
$$

Therefore, the $\widehat{\mathbf{H}}^{(\mathbf{1})}_{\mathbf{QQ}}$ superoperator Hamiltonian block for the $2hp$ superoperator coupling yields

$$
(a^{\dagger}_{\iota}a_s a_t|\widehat{H}a^{\dagger}_{\kappa}a_p a_q)_{\mathbf{2hp}} = \mathbf{F}_{qt}\delta_{\iota\kappa}\delta_{sp} + \mathbf{F}_{ps}\delta_{\iota\kappa}\delta_{tq} - \mathbf{F}_{\iota\kappa}\delta_{ps}\delta_{tq} + \langle \iota q\|\kappa t\rangle\delta_{sp} + \langle p\iota\|s\kappa\rangle\delta_{tq} + \langle pq\|ts\rangle\delta_{\kappa\iota}, \tag{3.73}
$$

whereas for the $2ph$ case the expression is

$$
(a^{\dagger}_{\iota}a_s a_t|\widehat{H}a^{\dagger}_{\kappa}a_p a_q)_{\mathbf{2ph}} = \mathbf{F}_{qt}\delta_{\iota\kappa}\delta_{sp} + \mathbf{F}_{ps}\delta_{\iota\kappa}\delta_{tq} - \mathbf{F}_{\iota\kappa}\delta_{ps}\delta_{tq} - \langle \iota q\|\kappa t\rangle\delta_{sp} - \langle p\iota\|s\kappa\rangle\delta_{tq} - \langle pq\|ts\rangle\delta_{\kappa\iota}. \tag{3.74}
$$

When the expressions of each of the blocks of the $\mathbf{\Sigma}^{(2ph-\mathrm{TDA})}$ of equation (3.71) are considered, the final expression for the $2ph-\mathrm{TDA}$ self–energy matrix in the Hartree-Fock canonical spin–orbital basis reads

$$
\begin{aligned}
\mathbf{\Sigma}^{(2ph-TDA)}_{\iota\kappa}(E) = &\sum_{a,i<j,b,k<l}\langle \iota a\|ij\rangle\left[(E\mathbf{1}-\hat{\boldsymbol{H}})^{-1}\right]_{aij,bkl}\langle kl\|\kappa b\rangle\\
+ &\sum_{i,a<b,j,c<d}\langle \iota i\|ab\rangle\left[(E\mathbf{1}-\hat{\boldsymbol{H}})^{-1}\right]_{iab,jcd}\langle cd\|\kappa j\rangle
\end{aligned}
\tag{3.75}
$$

A diagonal variation of the $2ph-$TDA self–energy may be obtained if the off–diagonal elements are neglected. The self–energy matrix elements of this approximation denoted as the $D2ph-$TDA reads

$$\Sigma_{\iota\kappa}^{(D2ph-TDA)}(E) = \sum_{a,i<j} \frac{\langle \iota a \| ij \rangle \langle ij \| \kappa a \rangle}{E + \varepsilon_a - \varepsilon_i - \varepsilon_j + \langle ij \| ij \rangle - \langle ai \| ai \rangle - \langle aj \| aj \rangle} + \sum_{i,a<b} \frac{\langle \iota i \| ab \rangle \langle ab \| \kappa i \rangle}{E + \varepsilon_i - \varepsilon_a - \varepsilon_b - \langle ab \| ab \rangle + \langle ia \| ia \rangle + \langle ib \| ib \rangle} \tag{3.76}$$

A more succinct expression for the above equation may be rewritten as

$$\boldsymbol{\Sigma}_{\iota\kappa}^{(D2ph-TDA)}(E) = \sum_{r,p,q} \frac{N_{rpq} \langle \iota r \| pq \rangle \langle pq \| \kappa r \rangle}{E + \varepsilon_r - \varepsilon_p - \varepsilon_q + \Delta_{rpq}}, \tag{3.77}$$

where

$$N_{rpq} = [(1 - n_r) n_p n_q + n_r (1 - n_p)(1 - n_q)] \tag{3.78}$$

and

$$\Delta_{rpq} = \frac{1}{2} \langle pq \| pq \rangle (n_p + n_q - 1) - \langle rq \| rq \rangle (n_q - n_r) - \langle rp \| rp \rangle (n_p - n_r). \tag{3.79}$$

It is important to point out that for the self–energy matrix of the $2ph-$TDA approximation the $\widehat{\mathbf{H}}_{\mathbf{QQ}}$ block is no longer diagonal. Since the $\boldsymbol{\Sigma}^{(2ph-\mathrm{TDA})}$ retains first order terms in the $(\mathbf{F_3}|\widehat{\mathrm{H}}\mathbf{F_3})$ superoperator coupling, the $\widehat{\mathbf{H}}_{\mathbf{QQ}}$ block of the superoperator Hamiltonian contains off–diagonal terms that depends on two electron integrals. Therefore, the inversion of the $\widehat{\mathbf{H}}_{\mathbf{QQ}}$ is not longer trivial as in the case of the second–order self–energy matrix. Although several methods and algorithm have been reported to obtain the inverse of a matrix [92], the nature of the $\widehat{\mathbf{H}}_{\mathbf{QQ}}$ block makes the binomial series expansion the simplest and most ideal method for the determination of the inverse matrix in equation (3.71). The terms in the $(\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{f_3})^{(1)}$ coupling may be separated in the zeroth–order terms that depend on the unperturbed part of the superoperator Hamiltonian and the terms that are corrected through first order,

$$(\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{f_3})^{(1)} = (\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{f_3})_{(0)} + (\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{f_3})_{(1)} = (\mathbf{f_3}|\widehat{\mathrm{H}}_0\mathbf{f_3})^{(0)} + (\mathbf{f_3}|\widehat{\mathrm{W}}\mathbf{f_3})^{(1)} \tag{3.80}$$

In general, terms that depends on the fluctuation operator $\widehat{\mathrm{W}}$ are smaller than the terms that depends on the $\widehat{\mathrm{H}}_0$, therefore the $(\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{f_3})^{(1)}$ matrix may be assumed to be a diagonal dominant matrix. The inversion of the $\widehat{\mathbf{H}}_{\mathbf{QQ}}^{\mathbf{1}}$ matrix in the Dyson equation may be approximated through a power series equivalent to

$$\frac{1}{(\boldsymbol{A} - \boldsymbol{B})} = \boldsymbol{A}^{-1} + \boldsymbol{A}^{-1}\boldsymbol{B}\boldsymbol{A}^{-1} + \boldsymbol{A}^{-1}\boldsymbol{B}\boldsymbol{A}^{-1}\boldsymbol{B}\boldsymbol{A}^{-1} + ..., \tag{3.81}$$

where the matrix $\boldsymbol{A}$ is equal to the zeroth order diagonal matrix $(\mathbf{f_3}|\widehat{\mathrm{H}}_0\mathbf{f_3})^{(0)}$ and the matrix $\boldsymbol{B}$ is equal to the skew–symmetric matrix $(\mathbf{f_3}|\widehat{\mathrm{W}}\mathbf{f_3})^{(1)}$. Thus, the $\mathbf{\Sigma}^{(2ph-\mathrm{TDA})}$ self–energy matrix may be rewritten as an expansion of the form

$$\begin{aligned}\mathbf{\Sigma}^{(2ph-\mathrm{TDA})}(E) = {} & (\mathbf{a}|\widehat{\mathbf{H}}\mathbf{f_3})^{(1)}[E\mathbf{1} - (\mathbf{f_3}|\widehat{\mathbf{H}}_0\mathbf{f_3})^{(0)}]^{-1}(\mathbf{f_3}|\widehat{\mathbf{H}}\mathbf{a})^{(1)} \\ & + (\mathbf{a}|\widehat{\mathbf{H}}\mathbf{f_3})^{(1)}[E\mathbf{1} - (\mathbf{f_3}|\widehat{\mathbf{H}}_0\mathbf{f_3})^{(0)}]^{-1}(\mathbf{f_3}|\widehat{\mathrm{V}}\mathbf{f_3})^{(1)} \times [E\mathbf{1} - (\mathbf{f_3}|\widehat{\mathbf{H}}_0\mathbf{f_3})^{(0)}]^{-1}(\mathbf{f_3}|\widehat{\mathbf{H}}\mathbf{a})^{(1)} \\ & + (\mathbf{a}|\widehat{\mathbf{H}}\mathbf{f_3})^{(1)}[E\mathbf{1} - (\mathbf{f_3}|\widehat{\mathbf{H}}_0\mathbf{f_3})^{(0)}]^{-1}(\mathbf{f_3}|\widehat{\mathrm{V}}\mathbf{f_3})^{(1)} \times [E\mathbf{1} - (\mathbf{f_3}|\widehat{\mathbf{H}}_0\mathbf{f_3})^{(0)}]^{-1}(\mathbf{f_3}|\widehat{\mathrm{V}}\mathbf{f_3})^{(1)} \\ & \times [E\mathbf{1} - (\mathbf{f_3}|\widehat{\mathbf{H}}_0\mathbf{f_3})^{(0)}]^{-1}(\mathbf{f_3}|\widehat{\mathbf{H}}\mathbf{a})^{(1)} + \cdots .\end{aligned} \tag{3.82}$$

In the Hartree–Fock basis, where the usual notation for particles (p or virtual orbitals with indices $a, b, c, \ldots$) and holes (h or occupied orbitals with indices $i, j, k, \ldots$) have been adopted. The zeroth order contributions to the primary–secondary couplings vanish. The resulting first–order terms for the $2ph-\mathrm{TDA}$ approximation may be expressed as

$$\begin{aligned}(a_a^\dagger a_i a_j|\hat{H}a_\kappa)_{(0)} &= \langle \kappa a|ji\rangle \\ (a_i^\dagger a_a a_b|\hat{H}a_\kappa)_{(0)} &= \langle \kappa i|ba\rangle.\end{aligned} \tag{3.83}$$

The zeroth order terms that depend only on the unperturbed part of the superoperator Hamiltonian for the $2hp$–$2hp$ coupling yields

$$(a_a^\dagger a_i a_j|H_0 a_b^\dagger a_k a_l)_{(0)} = \delta_{ab}\delta_{ik}\delta_{jl}(\varepsilon_i + \varepsilon_j - \varepsilon_a), \tag{3.84}$$

whereas the term that is corrected through first order in V is given by

$$(a_a^\dagger a_i a_j|V a_b^\dagger a_k a_l)_{(0)} = -\delta_{ab}\langle kl|ij\rangle + (1 - P_{ij})(1 - P_{kl})\delta_{ik}\langle al|bj\rangle, \tag{3.85}$$

for $i < j$ and $k < l$. The $2ph$–$2ph$ couplings through first order in V are given by

$$(a_i^\dagger a_a a_b|H_0 a_j^\dagger a_c a_d)_{(0)} = \delta_{ij}\delta_{ac}\delta_{bd}(\varepsilon_a + \varepsilon_b - \varepsilon_i) \tag{3.86}$$

and

$$(a_i^\dagger a_a a_b|V a_j^\dagger a_c a_d)_{(0)} = -\delta_{ij}\langle cd|ab\rangle + (1 - P_{ab})(1 - P_{cd})\delta_{ac}\langle id|jb\rangle \tag{3.87}$$

with $a < b$ and $c < d$. The chief arithmetic bottleneck in $2ph-\mathrm{TDA}$ calculations scales as OV^4, where O is the number of occupied orbitals and V the number of virtual orbitals. This arithmetic bottleneck arises from matrix multiplications that involve $2ph$–$2ph$ couplings. The $2ph-\mathrm{TDA}$ approximation has been applied extensively in making quantitative assignments of inner–valence features in photoelectron spectra. Initially, the $2ph-\mathrm{TDA}$ approximation was developed with the idea that by taking into consideration the detailed pole structure of the self–energy one may overcome the wrong ordering of states produced by Koopmans's approximation for molecules with strong correlation effects (*i.e.* N_2O_4, H_2CO, HCOOH, N_2, CO, CS, butatriene, etc. [93–97]). In the expansion of the $\mathbf{\Sigma}^{(2ph-TDA)}$ matrix, not all the third order terms are taken into account fully. Only, higher order terms, the so–called renormalization terms, which introduce an effective interaction are summed to infinite order. Thus, with iterations having an arithmetic scaling bottleneck of OV^4 the $2ph-\mathrm{TDA}$ approximation is more computationally demanding than the ND2 approximation. In general, the quality of $2ph-\mathrm{TDA}$ results improve steadily with larger basis sets, but it is not an efficient approximation for the purpose of estimating basis set effects.

3.5.2 The 3+ and ADC(3) approximations

In the same manner as in the diagonal approximations, a non–diagonal approximation that resembles third order terms can be defined. The superoperator Hamiltonian matrix that recovers all the third order terms for the self–energy may be expressed as

$$\hat{\mathbf{H}} = \begin{bmatrix} (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(3)} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(2)} \\ (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(2)} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)} \end{bmatrix}. \tag{3.88}$$

This superoperator Hamiltonian matrix recovers all the terms in all orders for the calculation of the poles. When all the high order h, p, $2hp$, $2ph$ couplings that suffice to include all third–order terms are calculated for the self–energy, the so–called 3+ propagator approximation is produced [81, 85]. Certain types of higher order terms also are included in 3+. The third-order algebraic diagrammatic construction, or ADC(3), propagator approximation retains these terms and also adds fourth–order and some higher order terms in the energy–independent part of the self–energy matrix[81]. The non–diagonal ADC(3) and 3+ approximations require contractions with O^2V^4 scaling; iterative OV^4 steps and a full integral transformation are needed as well.

3.5.3 The NR2 approximation

The nondiagonal, renormalized, second–order (NR2) approximation [98], is a variation of the ND2 and $2ph-\mathrm{TDA}$ approximations which retains some third-order and higher order terms. The NR2 self–energy is complete only in second order, and is defined in terms of the first–order, double–substitution operator ($T_2^{(1)}$). For the attachment process, the NR2 self–energy is derived by the superoperator metric

$$(\mathbf{X}|\mathbf{Y})_{N+1} = \langle N|[\mathbf{X}^\dagger, \mathbf{Y}]_+(1 + T_2^{(1)})|N\rangle \tag{3.89}$$

whereas for the detachment process the superoperator metric reads

$$(\mathbf{X}|\mathbf{Y})_{N-1} = \langle N|(1 + T_2^{(1)})[\mathbf{X}^\dagger, \mathbf{Y}]_+|N\rangle. \tag{3.90}$$

If the operator manifold spans h, p, $2hp$ and $2ph$ operators, second–order terms in the superoperator Hamiltonian appear only if $\mathbf{Y}$ is a $2ph$ operator and $\mathbf{X}$ is a $2hp$ operator for electron detachments. In the case electron attachments, the roles of p and h are reversed. Numerical examination of the self–energy terms indicate that only the second–order terms in the $\hat{\mathbf{H}}_{2hp-h}$ block may not be neglected. These results also indicate that first–order $2ph$-$2ph$ terms are unimportant. The NR2 ionization energies are obtained after Hermitizing and diagonalizing the $\hat{\mathbf{H}}$ superoperator matrix:

$$\hat{\mathbf{H}} = \begin{bmatrix} (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(0)}_{hh} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(0)}_{hp} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)}_{h-2hp} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)}_{h-2ph} \\ (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(0)}_{ph} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(0)}_{pp} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)}_{p-2hp} & (\boldsymbol{a}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(1)}_{p-2ph} \\ (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(2)}_{2hp-h} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(1)}_{2hp-p} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{f_3})^{(1)}_{2hp-2hp} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(0)}_{2hp-2ph} \\ (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(1)}_{2ph-h} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{a})^{(1)}_{2ph-p} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\boldsymbol{f_3})^{(0)}_{2ph-2hp} & (\mathbf{f_3}|\hat{\boldsymbol{H}}|\mathbf{f_3})^{(0)}_{2ph-2ph} \end{bmatrix}. \tag{3.91}$$

In the NR2 approximation, all first–order couplings between simple and triple operators and zeroth-order couplings between triple operators are present, therefore both second–order terms in the self–energy are conserved. As in the $2ph-$TDA self–energy, $2hp$ ring and ladder terms of the $2hp$ type are present in third and higher orders. NR2 reduces the formally sixth–power dependence of the second–order couplings between h and $2hp$ operators thorough matrix–vector multiplications. For the calculation of ionization energies, the NR2 approximation has a formal arithmetic scaling of the fifth–power, in which no electron repulsion integrals with four virtual–orbital indices are needed. NR2 has a O^2V^3 iterative arithmetic bottleneck and a non–iterative arithmetic bottleneck with O^3V^3 scaling. These arithmetic scaling make NR2 computationally more efficient than the ADC(3) and 3+ approximations.

3.6 Comparison among approximations

The arithmetic and storage requirements for the most used electron propagator approximations are shown in table 3.2. In general, diagonal approximations are less computationally intensive than non–diagonal ones. Calculations on a representative set of closed–shell molecules [18] indicates that D2 is the most easily executed electron propagator approximation. When compared with extrapolated coupled–cluster singles and doubles plus perturbative triples calculations, CCSD(T), D2 produces results that steadily rise as basis sets are improved. Although D2 values may improve with the basis set size, its mean errors remain unacceptably large. Among the diagonal approximations, the P3+ approximation is the most accurate of all with values that exhibit the best trends with respect to basis–set saturation. In the case of the non–diagonal approximations, the NR2 approximation yields the most accurate values and displays the best convergence to extrapolated CCSD(T) standards with respect to basis sets.

Method	Iterative Bottleneck	Non–iterative Bottleneck	Storage
D2	OV^2	-	OV^2
OVGF	OV^4	O^2V^3	V^4
P3 (P3+)	O^3V^2	O^2V^3	OV^3
2p–h TDA	OV^4	-	V^4
3+	OV^4	O^2V^4	V^4
ADC(3)	O^2V^4	O^2V^4	V^4
NR2	O^2V^3	O^3V^3	OV^3

Tab. 3.2.: Scaling of Arithmetic and Storage Requirements

3.6.1 Final verdict

Finally, one may conclude that P3+ and NR2 are the recommended electron–propagator approximation for the calculations of vertical ionization energies. Because of its treatment of couplings between $2hp$ operators that is exact through first order, the NR2 method is more likely than P3+ to give a correct description of higher vertical ionization energies with lower pole strengths. The advantages of the NR2 and P3+ methods may be extended by employment of techniques that account for basis–set saturation. A more extensive and detailed discussion about the best utilization practices, the different advantages, disadvantages, numerical performance and recommendations about the different electron propagator approximations may be found elsewhere [14, 18].

4

The Electron Propagator Implementation

> *Brainless users do not care about what is inside the box, as long as the box does what they think they need done.*
>
> — **Rephrasing Jef Raskin**
> about Human Computer Interfaces

In several of the computational implementations of the electron propagator methods, two separate strategies have been employed to obtain the poles of the electron propagator matrix. The first departs from the fact that the electron propagator equations are eigenvalue equations of the superoperator Hamiltonian $\hat{\mathbf{H}}$ acting on simple field operators or on products of field operators that change the number of electrons by one. Therefore, finding a pole may be regarded as solving an eigenvalue problem given by $\hat{\mathbf{H}}\boldsymbol{\nu} = \boldsymbol{\lambda}\boldsymbol{\nu}$, where $\boldsymbol{\nu}^{\dagger}\boldsymbol{\nu} = \mathbf{1}$. Thus, the well known concepts, computational techniques and algorithms from linear algebra are key for solving this eigenvalue problem. The second strategy corresponds to the employment of the Dyson quasiparticle equation in which poles occur when the determinant of the inverse of the electron propagator matrix, $det[\boldsymbol{G}^{-1}(E)]$, is equal to zero. In other words, poles are found when E is one of the eigenvalues of $\boldsymbol{F} + \boldsymbol{\Sigma}(E)$. Provided that the same superoperator Hamiltonian matrix elements were used, the two approaches for obtaining the electron propagator matrix poles are equivalent. Although these two strategies may be equivalent, from the computational point of view, their algorithms may have different strengths and limitations. In this chapter, the some of the most important remarks learned from the implementation of the electron propagator equations will be discussed.

4.1 The eigenvalue problem

The poles of the electron propagator matrix correspond to the eigenvalues of the superoperator Hamiltonian matrix $\hat{\mathbf{H}}$:

$$\begin{bmatrix} \hat{\boldsymbol{H}}_{\mathrm{aa}} & \hat{\boldsymbol{H}}_{\mathrm{af}} \\ \hat{\boldsymbol{H}}_{\mathrm{fa}} & \hat{\boldsymbol{H}}_{\mathrm{ff}} \end{bmatrix}. \tag{4.1}$$

Thus, electron binding energies and the corresponding linear combinations of operators in the primary ($\mathbf{a}$) and secondary ($\mathbf{f}$) spaces may be obtained by diagonalizing $\hat{\boldsymbol{H}}$,

$$\begin{bmatrix} \hat{\boldsymbol{H}}_{\mathrm{aa}} & \hat{\boldsymbol{H}}_{\mathrm{af}} \\ \hat{\boldsymbol{H}}_{\mathrm{fa}} & \hat{\boldsymbol{H}}_{\mathrm{ff}} \end{bmatrix} \begin{bmatrix} \boldsymbol{C}_{\mathrm{ap}} \\ \boldsymbol{C}_{\mathrm{fp}} \end{bmatrix} = \begin{bmatrix} \boldsymbol{C}_{\mathrm{ap}} \\ \boldsymbol{C}_{\mathrm{fp}} \end{bmatrix} E_p. \tag{4.2}$$

Insertion of the eigenvalues obtained in the partitioned form of the electron propagator matrix, $\boldsymbol{G}(E)$, produces the inversion of the matrix with a zero eigenvalue, *i.e.*, this insertion is sufficient to obtain a pole. When large basis set are used, the superoperator Hamiltonian matrix may be of a considerable size, which makes, in several cases, impractical its construction and storage. Therefore, the diagonalization of the full superoperator Hamiltonian to find the binding energies of large molecular systems may be challenging and inefficient.

4.1.1 The Dyson approach

The eigenvalues needed for the description of binding energies may be obtained by solving the Dyson quasiparticle equation self consistently. The Dyson equation approach to the electron propagator allows the reduction of the memory and disk needed for the determination of the poles of the electron propagator matrix. In the Dyson equation formulation of electron propagator, instead of diagonalizing the full superoperator Hamiltonian matrix, $\hat{\mathbf{H}}$, the diagonalization of a smaller matrix formed by the addition of the elements of the primary sector of the superhamiltonian matrix, $\hat{\boldsymbol{H}}_{\mathrm{aa}}$, and the self–energy matrix elements is diagonalized,

$$[\hat{\boldsymbol{H}}_{\mathrm{aa}} + \hat{\boldsymbol{H}}_{\mathrm{af}}(E\mathbf{1}_{\mathrm{f}} - \hat{\boldsymbol{H}}_{\mathrm{ff}})^{-1}\hat{\boldsymbol{H}}_{\mathrm{fa}}]\boldsymbol{C}_{\mathrm{ap}} = [\boldsymbol{F} + \boldsymbol{\Sigma}(E)]\boldsymbol{C}_{\mathrm{ap}} = \boldsymbol{C}_{\mathrm{ap}}E_p. \tag{4.3}$$

The eigenvalues obtained from this diagonalization are used to iteratively solve the equation

$$det\{\boldsymbol{G}^{-1}(E)\} = \{E\mathbf{1} - \boldsymbol{F} - \boldsymbol{\Sigma}(E)\} = 0 \tag{4.4}$$

Thus, finding the self–consistent eigenvalues of the Dyson quasiparticle equation requires the construction of the $\boldsymbol{F}$ and $\boldsymbol{\Sigma}(E)$ matrices. The elements of these matrices are blocked into four sectors that take into consideration the occupied (O) and virtual (V) orbitals of the spin–basis set,

$$\begin{bmatrix} (O,O) & (O,V) \\ (V,O) & (V,V) \end{bmatrix}. \tag{4.5}$$

When the canonical Hartree–Fock spin–orbital basis set is used, the Fock matrix is diagonal, therefore, the Hartree–Fock molecular orbital energies may be used to build up the $\boldsymbol{F}$ matrix,

$$\boldsymbol{F} = \begin{bmatrix} \varepsilon_1^O & & & & \\ & \varepsilon_2^O & & \text{0} & \\ & & \ddots & & \\ & \text{0} & & \varepsilon_1^V & \\ & & & & \varepsilon_n^V \end{bmatrix}. \tag{4.6}$$

The $\boldsymbol{\Sigma}(E)$ matrix, in general, is not diagonal, and its block elements are determined by the indices of the product of the superoperator coupling $H_{af}(EI_f - H_{ff})^{-1}H_{fa}$:

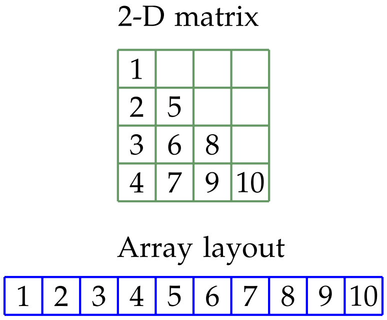
$$\boldsymbol{\Sigma}_{a,a}(E) = \begin{bmatrix} \Sigma(a_O, a_O) & \Sigma(a_O, a_V) \\ \Sigma(a_V, a_O) & \Sigma(a_V, a_V) \end{bmatrix}. \tag{4.7}$$

4.1.2 Hermiticity considerations

The electron propagator superoperator Hamiltonian is Hermitian and so is the self–energy matrix. This Hermiticity may be used in order to further reduce the amount of memory and disk needed for handling and storage of the $[\hat{\boldsymbol{H}}_{\mathrm{aa}} + \hat{\boldsymbol{H}}_{\mathrm{af}}(E\mathbf{1}_{\mathrm{f}} - \hat{\boldsymbol{H}}_{\mathrm{ff}})^{-1}\hat{\boldsymbol{H}}_{\mathrm{fa}}]$ matrix, where only the lower or upper triangular elements of the $\boldsymbol{\Sigma}(E)$ matrix suffice for the construction of this matrix. To illustrate this idea, let's consider a hypothetical molecule with only two occupied (O) molecular orbitals and one virtual (V) orbital. For this hypothetical molecule, full description of binding energies may be obtained by only taking into consideration the lower triangular part of $\boldsymbol{\Sigma}(E)$:

$$\boldsymbol{\Sigma}(\mathbf{E}) = \begin{bmatrix} \Sigma(O_1, O_1) & \Sigma(O_1, O_2) & \Sigma(O_1, V_1) \\ \Sigma(O_2, O_1) & \Sigma(O_2, O_2) & \Sigma(O_2, V_1) \\ \Sigma(V_1, O_1) & \Sigma(V_1, O_2) & \Sigma(V_1, V_1) \end{bmatrix}. \tag{4.8}$$

If N is the total number of occupied and virtual orbitals that need to be considered in the construction of the self–energy matrix, then $N = O + V$. Taking advantage of the Hermiticity of $\mathbf{\Sigma}(E)$ considering only the lower triangular elements of the self–energy matrix reduces the number of elements, operations and storage needed to construct the $\mathbf{\Sigma}(E)$ matrix from N^2 to $\frac{(1+N)N}{2}$. This reduction is significant, especially when large molecules are being considered and modest amounts of computational resources are available. Most of the electron propagator approximations described in this work were implemented, or are being implemented, in Fortran. Thus, one should consider that in Fortran the memory layout for multidimentional arrays is column–major. Therefore, when working with the allocation of arrays for the representation of matrices, these should be allocated as following: This array arrangement for the electron propagator matrices will guarantee a better performance in the access, allocation and management of the data generated. If the electron propagator approximations are implemented in C or C++ one should use row–major layout.



2-D matrix

1			
2	5		
3	6	8	
4	7	9	10

Array layout

1	2	3	4	5	6	7	8	9	10

Fig. 4.1.: Memory allocation for array matrices

4.1.3 Point group considerations

The efficiency of the electron propagator implementation may be improved when the molecular symmetry of the molecule is taking into consideration (when the point group of the molecule is other than C_1, of course). The self–energy matrix, as well as the Fock matrix may be reduced into blocks based on the irreducible representation of the molecular orbital in which the electron is being removed or added. Since the coupling between field operators that correspond to orbitals with different symmetry will vanish, for the construction of the $\boldsymbol{F}$, or the primary sector of the superoperator Hamiltonian, and the $\mathbf{\Sigma}(E)$ matrices, one needs only to take into consideration the occupied and virtual orbitals with the same irreducible representation as the orbital from which the electron will be removed or added. Take for example the water molecule with the C_{2v} point group. The molecular orbitals of the H_2O with the 6-311 basis set may represented as shown in figure 4.2.

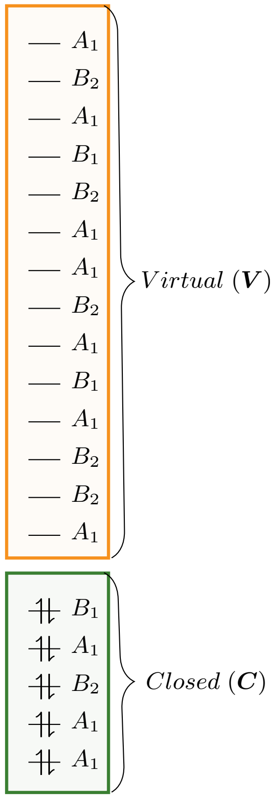


Fig. 4.2.: Molecular orbital configuration for water and the 6-311G basis set

For the case of the ionization of one of the electrons from the highest occupied molecular orbital, (HOMO) of water, whose symmetry is B_1, instead of taking into consideration the 19 molecular orbitals presented in figure 4.2, one may only considered 3 molecular orbitals with B_1 symmetry, see figure 4.3.

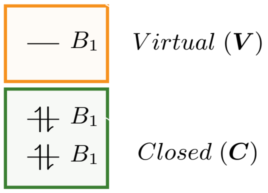


Fig. 4.3.: Molecular orbital to be considered for the detachment energy of the HOMO orbital of H_2O

Since the molecular orbitals whose contributions to the HOMO self–energy are zero or close to zero have been removed, the number of molecular orbitals and two electron integrals that need to be considered have been reduced as well. Therefore, in this case, the use of the molecular point group has reduced the amount of memory and operations needed to compute the pole of the self–energy matrix for the HOMO orbital.

4.2 Pole search methods

Pole searches based on Dyson equation usually converge rapidly with respect to E. Starting with equation (4.4), one may express the unperturbed part of the propagator in terms of the canonical orbital energies ε_p as

$$\boldsymbol{G}_0^{-1}(E) = E\mathbf{1} - \boldsymbol{F} = E\mathbf{1} - \boldsymbol{\varepsilon}, \tag{4.9}$$

such that the Dyson equation reads

$$\boldsymbol{G}^{-1}(E) = \boldsymbol{G}_0^{-1}(E) - \boldsymbol{\Sigma}(E). \tag{4.10}$$

In the Dyson formulae of the electron propagator, E is a pole when $\boldsymbol{G}^{-1}(E)$ has a vanishing eigenvalue. In this regard, one searches for E such that E is an eigenvalue of a function $\boldsymbol{\Gamma}(E)$, where

$$\boldsymbol{\Gamma}(E) = \boldsymbol{\varepsilon} + \boldsymbol{\Sigma}(E). \tag{4.11}$$

The definition of $\boldsymbol{\Gamma}(E)$ indicates that the value of this function is self–consistent. In other words, $\boldsymbol{\Gamma}(E)$ is a function of the form:

$$f(x) = x, \tag{4.12}$$

where the value of the function depends upon the value of the point x. The x point is known as the attractive fixed point of the function f. In the case of $\boldsymbol{\Gamma}(E)$, the value E, the eigenvalue that is being searched, is obtained from the evaluation of the self–energy function $\Gamma(E)$. In this regard, E is a fixed point of the function $\boldsymbol{\Gamma}$. In order to find the solution E the evaluation of the function $\Gamma(E)$ may start at a point E_1 in the basin of attraction of E and if $E_{n+1} = \Gamma(E_n)$ for $n \geq 1$, then, the sequence $\{E_n\}_{n\geq 1}$ will converge to the solution E. Therefore, equation (4.11) may be rewritten as

$$E^{k+1} = \Gamma(E^k) = \varepsilon + \Sigma(E^k), \quad k \geq 0. \tag{4.13}$$

Therefore, the self–energy provides a stationary iterative method of solving a linear system that generates an approximation of the exact value E and a residual. Thus, the self–energy, $\Sigma(E)$, approximates to itself, forming a correction equation for which the process would be repeated until the residual is minimized to the desired threshold. In principle, faster convergence of a stationary iterative method may be achieved when better estimations of the stationary point value are given between consecutive iterations. Successively better estimations of the stationary point could be made by a root–finding algorithm such as the bisection, Newton–Raphson, or secant numerical methods. If a function $f(E_n)$ is defined as the residual, the difference of the numerical value of two consecutive self–energies that were evaluated at two consecutive points E_i and E_{i+1}, then, this residual function may be expressed as

$$f(E_n) = \Gamma(E^{k+1}) - \varepsilon - \Sigma(E^k), \quad k \in n \geq 0. \tag{4.14}$$

The root of the $f(E_n)$ function corresponds to the case in which the variation between two consecutive iterations is zero or close to zero, and therefore the eigenvalue E of the self–energy $\Gamma(E)$.

4.2.1 Newton–Raphson root–finding algorithm

In electron propagator implementations, the most used numerical method for determining the next guess of the $\Gamma(E)$ function is the Newton–Raphson method [99]. In the Newton–Raphson method, starting with the initial point x_0, the estimation of the following point, x_t, is made by finding the tangent line to x_0, as shown in figure 4.4.

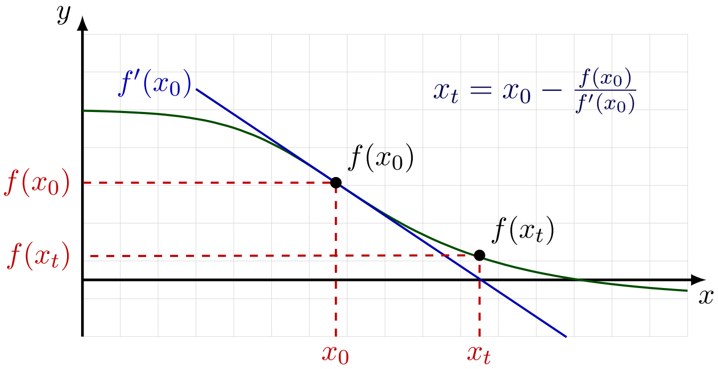


Fig. 4.4.: Graphical representation of the Newton–Rapson method

The x–intercept of this tangent line is the point x_t which usually is a better approximation to the function's root. In the Newton–Raphson method only one point and its evaluation in the function are needed to start the algorithm. However, the function's derivative is also needed, which in some cases is not easy to obtain. By using the

Newton–Raphson equations a new guess for the evaluation of the self–energy may be determined by the following expression:

$$E^{n+1} = \Gamma(E_{n-1}) - \frac{f(E_n)}{f'(E_n)} \quad n > 0, \tag{4.15}$$

where f' stands for derivative of the function with respect of the energy E. If the canonical Hartree–Fock orbital energies are used to build the self–energy of a given electron propagator approximation, equation (4.15) may be expanded as follow:

$$\begin{aligned}
E^{n+1} &= \varepsilon_{HF} + \Sigma(E_{n-1}) - \frac{\varepsilon_{HF} + \Sigma(E_n) - \varepsilon_{HF} - \Sigma(E_{n-1})}{\frac{d\Sigma(E_n)}{dE_n} - 1} \\
&= \varepsilon_{HF} + \Sigma(E_{n-1}) - \frac{\Sigma(E_n) - \Sigma(E_{n-1})}{\frac{d\Sigma(E_n)}{dE_n} - 1} \\
&= \frac{[\varepsilon_{HF} + \Sigma(E_{n-1})][\Sigma'(E_n) - 1]}{\Sigma'(E_n) - 1} - \frac{\Sigma(E_n) - \Sigma(E_{n-1})}{\Sigma'(E_n) - 1} \\
&= \frac{\varepsilon_{HF}\Sigma'(E_n) + \Sigma(E_{n-1})\Sigma'(E_n) - \varepsilon_{HF} - \Sigma(E_{n-1})}{\Sigma'(E_n) - 1} - \frac{\Sigma(E_n) - \Sigma(E_{n-1})}{\Sigma'(E_n) - 1} \\
&= \frac{\varepsilon_{HF}\Sigma'(E_n) + \Sigma(E_{n-1})\Sigma'(E_n) - \varepsilon_{HF} - \Sigma(E_{n-1}) - \Sigma(E_n) + \Sigma(E_{n-1})}{\Sigma'(E_n) - 1} \\
&= \frac{\varepsilon_{HF}\Sigma'(E_n) + \Sigma(E_{n-1})\Sigma'(E_n) - \varepsilon_{HF} - \Sigma(E_n)}{\Sigma'(E_n) - 1} \\
&= \frac{\varepsilon_{HF}\Sigma'(E_n) + \Sigma(E_{n-1})\Sigma'(E_n) - \varepsilon_{HF} - \Sigma(E_n)}{\Sigma'(E_n) - 1} \\
&= \frac{\Gamma(E_{n-1})\Sigma'(E_n) - \Gamma(E_n)}{\Sigma'(E_n) - 1} \\
&= \frac{\Gamma(E_n) - \Gamma(E_{n-1})\Sigma'(E_n)}{1 - \Sigma'(E_n)}
\end{aligned} \tag{4.16}$$

For the general eigenvalue formulae,

$$\mathbf{E}'\mathbf{C}(\mathbf{E}_{old}) = \mathbf{\Gamma}(\mathbf{E}_{old})\mathbf{C}(\mathbf{E}_{old}), \tag{4.17}$$

the Newton–Raphson root finding algorithm for determining the new guess (E^{new}) may be expressed as

$$\mathbf{E}^{new} = \mathbf{E}_{old} - \frac{\mathbf{E}' - \mathbf{E}_{old}}{\mathbf{C}^{\dagger}(\mathbf{E}_{old})\frac{d\mathbf{\Sigma}(E)}{dE}|_{E=E_{old}}\mathbf{C}(\mathbf{E}_{old}) - 1} \tag{4.18}$$

When using the Newton–Raphson algorithm the convergence of eigenvalue E of the function $\Gamma(E)$ is usually found in three to five iterations. However, some problems with the convergence of the self consistent procedure may arise when the initial guess is far from the pole of interest or when the self–energy is not a well behaved smooth function whose derivative may present difficulties. This may be the case for the third–order self–energy and the ND2 as well as the $2ph-\mathrm{TDA}$ approximations in which the number of iterations needed to find the pole of the self–energy may increase considerably and, in some cases, not converge.

4.2.2 Secant root–finding algorithm

Convergence problems sometimes associated with finding the poles of self–energy may be solved by the secant method[100]. This method offers an derivative free alternative for finding the poles of the electron propagator approximations. The secant method may be regarded as a finite–difference approximation of Newton's method. Therefore, the same ideas used in the Newton's method for finding better guesses for the eigenvalue E may also be developed in the secant method framework. In the secant method, at least two points (x_i and x_{i-1}) are needed to start the algorithm, however, only one function evaluation per iteration is needed. Using the secant method, the x_{i+1} root may be approximated as

$$x_{i+1} = x_i - f(x_i)\frac{x_i - x_{i-1}}{f(x_i) - f(x_{i-1})}. \tag{4.19}$$

One of the disadvantages that the secant method has is the order of convergence. Unlike the Newton–Raphson method in which the order of convergence is quadratic, the secant method order of convergence is approximately 1.618. If the residual, $f(E_n)$, is expressed as in equation (4.14), a new guess for the evaluation of the self–energy can be determined by using the following expression:

$$E_{i+1} = E_i - f(E_i)\frac{E_i - E_{i-1}}{f(E_i) - f(E_{i-1})}, \quad i > 0. \tag{4.20}$$

Starting with a given Hartree–Fock orbital energy as initial guess, if one consider that the value of the self–energy depends on the self–energy generated using the previous guess, the sequential process for the self–energy is

$$\begin{array}{ccc} \text{Guess value} \rightarrow & \text{Self–energy} \rightarrow & \text{Output value} \\ \varepsilon_{HF} & \Sigma(\varepsilon_{HF}) & E^1 \\ E^1 & \Sigma(E^1) & E^2 \\ E^2 & \Sigma(E^2) & E^3 \end{array} \tag{4.21}$$

Thus, the expansion of equation (4.20) in terms of the self–energy and the eigenvalue E yields:

$$\begin{aligned}
E^{n+1} &= \Gamma(E_{n-1}) - (\Gamma(E_n) - \Gamma(E_{n-1}))\frac{\Gamma(E_{n-1}) - \Gamma(E_{n-2})}{(\Gamma(E_n) - \Gamma(E_{n-1})) - (\Gamma(E_{n-1}) - \Gamma(E_{n-2}))} \\
&= \Gamma(E_{n-1}) - (\Gamma(E_n) - \Gamma(E_{n-1}))\frac{\Gamma(E_{n-1}) - \Gamma(E_{n-2})}{\Gamma(E_n) - 2\Gamma(E_{n-1}) + \Gamma(E_{n-2})} \\
&= \Gamma(E_{n-1}) - (\Gamma(E_n) - \Gamma(E_{n-1}))\frac{\varepsilon_{HF} + \Sigma(E_{n-1}) - \varepsilon_{HF} - \Sigma(E_{n-2})}{\Gamma(E_n) - 2\Gamma(E_{n-1}) + \Gamma(E_{n-2})} \\
&= \Gamma(E_{n-1}) - (\Sigma(E_n) - \Sigma(E_{n-1}))\frac{\Sigma(E_{n-1}) - \Sigma(E_{n-2})}{\Gamma(E_n) - 2\Gamma(E_{n-1}) + \Gamma(E_{n-2})} \\
&= \Gamma(E_{n-1}) - (\Sigma(E_n) - \Sigma(E_{n-1}))\frac{\Sigma(E_{n-1}) - \Sigma(E_{n-2})}{\Sigma(E_n) - 2\Sigma(E_{n-1}) + \Sigma(E_{n-2})} \\
&= \Gamma(E_{n-1}) - \frac{\Sigma(E_n)\Sigma(E_{n-1}) - \Sigma(E_n)\Sigma(E_{n-2}) - \Sigma(E_{n-1})^2 + \Sigma(E_{n-1})\Sigma(E_{n-2})}{\Sigma(E_n) - 2\Sigma(E_{n-1}) + \Sigma(E_{n-2})} \\
&= \varepsilon_{HF} + \Sigma(E_{n-1}) - \frac{\Sigma(E_n)\Sigma(E_{n-1}) - \Sigma(E_n)\Sigma(E_{n-2}) - \Sigma(E_{n-1})^2 + \Sigma(E_{n-1})\Sigma(E_{n-2})}{\Sigma(E_n) - 2\Sigma(E_{n-1}) + \Sigma(E_{n-2})} \\
&= \varepsilon_{HF} + \frac{\Sigma(E_n)\Sigma(E_{n-2}) - \Sigma(E_{n-1})^2}{\Sigma(E_n) - 2\Sigma(E_{n-1}) + \Sigma(E_{n-2})},
\end{aligned} \tag{4.22}$$

where $\Sigma(E_{n-2}) = E^1$, $\Sigma(E_{n-1}) = E^2$ and $\Sigma(E_{n-1}) = E^3$. When the secant method is compared with the Newton–Raphson method, the number of iterations needed for the convergence of the second–order self–energy increases by two due to the order of convergence and number of points needed for the secant algorithm. In other words, while the Newton–Raphson method may need three iteration to converge to the pole, the secant method needs five iterations. However, for the second–order non-diagonal self–energy, there were cases in which the Newton–Raphson method could not find the pole whereas the secant method found the pole after 8-15 iterations.

4.2.3 Improvement to the Secant root–finding algorithm

The order of convergence and number of points needed for the secant algorithm may be improved by using the parametric equation of a circle [101]. By introducing the parametric equation of the circle tangent to the abscissa axis in the point x_0 of a given function, the diameter of the circle is given by the line segment $[x_0, f(x_0)]$ as shown in figure 4.6. The improvement of the secant method consists in the generation of this circle tangent to the initial point x_0 whose center is located at $[x = x_0, y = \frac{f(x_0)}{2}]$. The coordinates of this first circle are used to generate a second circle tangent to the abscissa axis in x_t, see figure 4.7. This second circle has its diameter defined by the

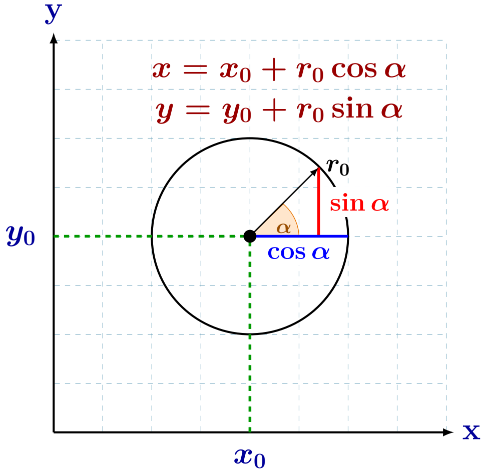


Fig. 4.5.: Parametric equation of a circle

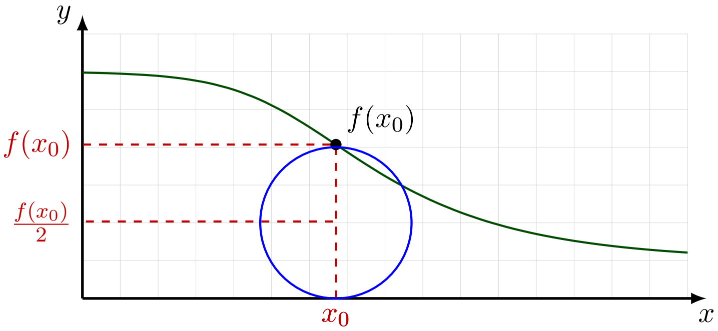


Fig. 4.6.: Parametric equation of a circle tangent to the first point of a function $f(x)$

line segment $[x_t, f(x_t)]$ and its center located at $(x_t = x_0 + r_0, y = \frac{f(x_t)}{2})$. A line is constructed through the $f(x_0)$ and $f(x_t)$ points. The intersection of this line with the x axis generates the next guess point, figure 4.8.

Thus, the secant method may be now expressed as

$$x_{n+1} = x_n + \frac{|f(x_n)|}{2} - \frac{|f(x_n)|}{2}\left[\frac{f(x_n + \frac{|f(x_n)|}{2})}{f(x_n + \frac{|f(x_n)|}{2}) - f(x_n)}\right]. \tag{4.23}$$

This formulation for the secant method only requires one point to start the algorithm and two function evaluations for iteration and has a quadratic convergence. Similarly to the Newton–Raphson and normal secant algorithms, this process is repeated until convergence is reached. If a function $f(E_n)$ is defined as the residual expressed in

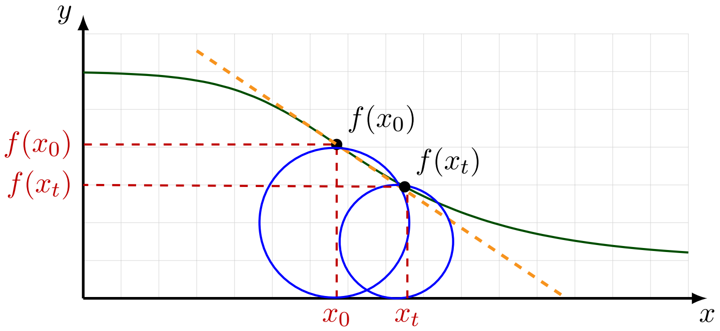


Fig. 4.7.: Improvement to the secant method

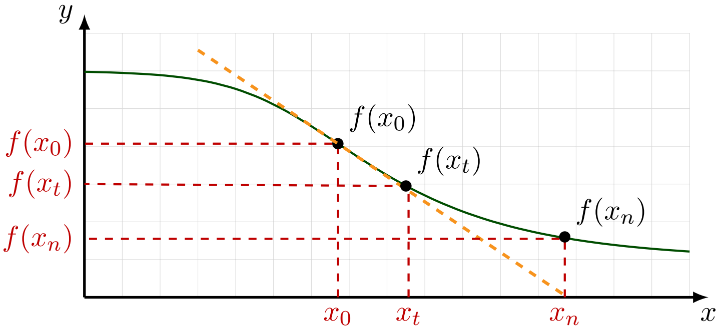


Fig. 4.8.: Generation of the next guess point x_n

equation (4.14), using this variation of the secant method for a new guess for the evaluation of the self–energy can be determined by

$$E_{i+1} = 2\Gamma(E_{i-1}) + |\Gamma(E_i) - \Gamma(E_{i-1})| - \Gamma(E_i), \quad i > 0. \tag{4.24}$$

4.2.4 Pole strengths

The pole strength of the self–energy is the norm of the primary space's component of the eigenvector such that

$$\Gamma_p^{\text{P.S.}} = \left[1 - \boldsymbol{C}^\dagger(E_{pole})\frac{d\boldsymbol{\Sigma}(E)}{dE}|_{E=E_{pole}}\boldsymbol{C}(E_{pole})\right]^{-1} \tag{4.25}$$

Pole strengths are related to the eigenvectors of superoperator Hamiltonian $\hat{\mathbf{H}}$ via

$$\Gamma_p^{\text{P.S.}} = \frac{\boldsymbol{C}_{\text{ap}}^\dagger \boldsymbol{C}_{\text{ap}}}{\boldsymbol{C}_{\text{ap}}^\dagger \boldsymbol{C}_{\text{ap}} + \boldsymbol{C}_{\text{fp}}^\dagger \boldsymbol{C}_{\text{fp}}} = \left[1 + \frac{\boldsymbol{C}_{\text{fp}}^\dagger \boldsymbol{C}_{\text{fp}}}{\boldsymbol{C}_{\text{ap}}^\dagger \boldsymbol{C}_{\text{ap}}}\right]. \tag{4.26}$$

If the derivative of the eigenvalue is defined as

$$\frac{\partial E_p}{\partial E} = \frac{\boldsymbol{C}_{\mathrm{ap}}^{\dagger} \left.\frac{\partial \Sigma(E)}{\partial E}\right|_{E=E_p} \boldsymbol{C}_{\mathrm{ap}}}{\boldsymbol{C}_{\mathrm{ap}}^{\dagger}\boldsymbol{C}_{\mathrm{ap}}}, \tag{4.27}$$

a more succinct notation for the pole strength is

$$\Gamma_p^{\mathrm{P.S.}} = \left(1 - \frac{\partial E_p}{\partial E}\right)^{-1}. \tag{4.28}$$

4.2.5 Derivative

For the calculation of the pole strength, the calculation of the derivative of the self–energy matrix is necessary. This derivative may be calculated analytically for uncomplicated self–energy expressions, such as that of the second–order self–energy. However, analytical expressions are not always possible. In this respect, numerical derivatives may, in some cases, be the most efficient option for the calculation of the derivative of the self–energy, and therefore, its pole strength. In order to compute the derivative of the self–energy, the finite difference method may be used. When the pole of the self–energy is found, a small perturbation, Δ, to the E_p value in the forward direction allows the use of the forward difference,

$$\left(\frac{\partial \Gamma(E)}{\partial E}\right)_{E=E_p} = \frac{\Gamma(E_{p+\Delta_E}) - \Gamma(E_p)}{\Delta_E} \tag{4.29}$$

whereas, if this perturbation is applied to the backward direction, the backward difference may be used,

$$\left(\frac{\partial \Gamma(E)}{\partial E}\right)_{E=E_p} = \frac{\Gamma(E_p) - \Gamma(E_{p-\Delta_E})}{\Delta_E}. \tag{4.30}$$

Since the guess used to the generate the self–energy in which the pole was found may correspond to the evaluation of a previous point in the self–energy[1] the backward difference may be applied without any extra computational cost. However, both the backward and forward differences have a truncation error, or accuracy, of $O(\Delta_E)$. Numerical tests have shown that when compared with the analytical derivative of the self–energy, neither the backward differentiation nor the forward differentiation is reliable. On the other hand, the central difference approximation has been shown to be a reliable option for the calculation of the derivative of the self–energy matrix. The

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[1] This can not be always assumed, therefore in the implementation one always should check the sign of the difference and direction to determine if the previous point value corresponds to the $\Sigma(E_{n-1})$ or $\Sigma(E_{n+1})$.

truncation error of the central difference is of $O(\Delta_E)^2$. For this approximation of the derivative, after the pole of the self–energy is found, a small perturbation of the same size of the pole threshold is applied to both the backward and forward direction of the E_p value (see figure 4.9). Thus, the expression for the derivative of the self–energy

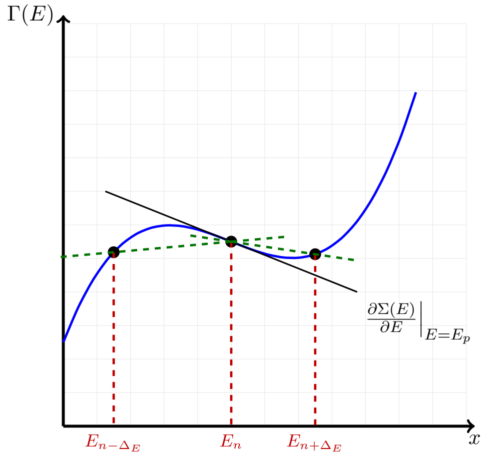

Fig. 4.9.: Self–energy derivative using the central difference

yields

$$\left(\frac{\partial\Gamma(E)}{\partial E}\right)_{E=E_p} = \frac{\Gamma(E_{p+\Delta_E}) - \Gamma(E_{p-\Delta_E})}{2\Delta_E} \tag{4.31}$$

4.2.6 Selection of the Eigenvalue

For the case of the non–diagonal approximations, the Dyson self–energy propagator algorithm generates an array that contains the sum of the Fock and self–energy matrix, $\boldsymbol{F}_{\mu,\nu} + \boldsymbol{\Sigma}(\boldsymbol{E})_{\mu,\nu}$, such that

$$\boldsymbol{F}_{\mu,\nu} + \boldsymbol{\Sigma}_{\mu\nu} = \begin{bmatrix} F_{1,1} & F_{1,2} & F_{1,3} & \dots & F_{1,4} \\ F_{2,1} & F_{2,2} & F_{2,3} & \dots & F_{2,4} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ F_{\mu,1} & F_{\mu,2} & F_{\mu,3} & \dots & F_{\mu,\nu} \end{bmatrix} + \begin{bmatrix} \Sigma_{1,1} & \Sigma_{1,2} & \Sigma_{1,3} & \dots & \Sigma_{1,4} \\ \Sigma_{2,1} & \Sigma_{2,2} & \Sigma_{2,3} & \dots & \Sigma_{2,4} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Sigma_{\mu,1} & \Sigma_{\mu,2} & \Sigma_{\mu,3} & \dots & \Sigma_{\mu,\nu} \end{bmatrix}. \tag{4.32}$$

This array is diagonalized to obtain the array that contains the eigenvalues and eigenvectors. In the generated eigenvalue vector there will the same number of values as the number of occupied and virtual orbitals that were considered for the formation of the $\boldsymbol{F}_{\mu,\nu}$ matrix, whereas the eigenvector matrix will have as much elements as the $\boldsymbol{\Sigma}(\boldsymbol{E})_{\mu,\nu}$ matrix. In order to identify the eigenvalue that needs to be considered for determining the E_p pole, one must be careful about which eigenvector is taken.

The vector of eigenvalues E_μ most of the time has the same canonical order as the orbital energies, however this is not always true. After the relaxation and correlation corrections are considered, the canonical order of the orbitals may changed (this effect is known as a Koopmans's defect). Therefore, a selection of the eigenvalue based on the energy ordering of the canonical orbitals is not always a reliable option. The most trustworthy way to select the eigenvalue that will be used for the determination of the pole is by computing the overlap matrix,

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle = \sum_l \boldsymbol{C}^*_{\mu l} \boldsymbol{C}_{\nu l} = (CC^\dagger)_{\mu\nu}. \tag{4.33}$$

The overlap matrix $S_{\mu\nu}$ is a Gramian matrix used to describe the inter-relationship of a set of basis vectors. The overlap matrix is always a square matrix of size $n \times n$, where n is the number of basis functions used,

$$S_{\mu\nu} = \begin{bmatrix} \langle \chi_1 | \chi_1 \rangle & \langle \chi_1 | \chi_2 \rangle & \langle \chi_1 | \chi_3 \rangle & \cdots & \langle \chi_1 | \chi_\nu \rangle \\ \langle \chi_2 | \chi_1 \rangle & \langle \chi_2 | \chi_2 \rangle & \langle \chi_2 | \chi_3 \rangle & \cdots & \langle \chi_2 | \chi_\nu \rangle \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \langle \chi_\mu | \chi_1 \rangle & \langle \chi_\mu | \chi_2 \rangle & \langle \chi_\mu | \chi_3 \rangle & \cdots & \langle \chi_\mu | \chi_\nu \rangle \end{bmatrix} \tag{4.34}$$

In the implementation of the electron propagator approximations, the overlap matrix is computed between the old eigenvector that corresponds to the E_p value and the eigenvectors generated right after the diagonalization of the $[\boldsymbol{F} + \boldsymbol{\Sigma}(\boldsymbol{E})]$ matrix. For this process, the initial vector used is a unit vector having the same direction as the canonical direction of the orbital ε_p such that

$$V_\mu^{Guess} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \tag{4.35}$$

Using this initial vector, the position of the employed eigenvalue is determined by the position of the eigenvector with the largest overlap, which is usually close to unity.

4.3 Eigenvectors

The primary and secondary components of the eigenvectors obtained after the diagonalization of equation (4.3) contain information that may be used to further describe and interpret electron binding energies, one–electron properties, correlation and relaxation effects, charge and spin densities and total energies of the molecules under study. These eigenvectors indicate the contribution of the field operators in the self–energy. After solving for a pole E_p it is possible to obtain its derivatives with respect to changes in the one–electron part of the many–electron Hamiltonian. Due to the orthogonality conditions of the primary and secondary spaces, contributions of the secondary sector of the eigenvectors do not appear in the residues. Using equation (4.2) the secondary space's component of the eigenvector may be defined as

$$\boldsymbol{C}_{fp} = (E_p \mathbf{1}_f - \hat{\boldsymbol{H}}_{ff})^{-1} \hat{\boldsymbol{H}}_{fa} \boldsymbol{C}_{ap} \tag{4.36}$$

The primary and secondary components of the eigenvectors contain information that may be used to further describe and interpret electron binding energies, one–electron properties, correlation and relaxation effects, charge and spin densities and total energies of the molecules under study.

4.3.1 Dyson orbitals

Dyson orbitals naturally emerge from the inverse form of the Dyson quasiparticle equation. They are inferred from the Feynman–Dyson amplitudes, which are related to the residues of the electron propagator. In the quasi-particle form of the Dyson equation, the pseudo–eigenvalues of the self–energy operator provide eigenfunctions that are proportional to Dyson orbitals. In terms of the Hartree–Fock wave–function, the Dyson orbitals may be expressed as

$$\phi_p^{Dyson} = \sum_{\mathrm{a}} \boldsymbol{C}^{\dagger}_{\mathrm{ap}} \phi_{\mathrm{a}}^{HF}. \tag{4.37}$$

Dyson orbitals may be expressed in terms of molecular coefficients and atomic orbitals. By using this last equation the corresponding change of basis yields

$$\begin{aligned} \phi_p^{Dyson} &= \sum_{\mathrm{a}} \boldsymbol{C}^{\dagger}_{\mathrm{ap}} \sum_{j} \boldsymbol{C}^{M.O.}_{\mathrm{aj}} \chi_{\mathrm{j}}^{A.O.} \\ &= \sum_{j} \big(\sum_{\mathrm{a}} \boldsymbol{C}^{\dagger}_{\mathrm{ap}} \boldsymbol{C}^{M.O.}_{\mathrm{aj}} \big) \chi_{\mathrm{j}}^{A.O.} \\ &= \sum_{\mathrm{j}} \boldsymbol{U}_{\mathrm{pj}} \chi_{\mathrm{j}}^{A.O.}. \end{aligned} \tag{4.38}$$

4.3.2 Charge density

The derivatives of the electron propagator pole, E_p, with respect to changes in the one–electron part of the many–electron Hamiltonian may correspond to external fields or to the field produced by the nuclei arranged in a given way. Let the Dyson equation approach to discovering poles be expressed as

$$E_{pole} = \boldsymbol{C}^{\dagger}(\varepsilon + \boldsymbol{\Sigma}(E)|_{E=E_{pole}})\boldsymbol{C}. \tag{4.39}$$

If γ denotes differentiation with respect to a perturbation, E^{γ}_{pole} then

$$\begin{aligned}\boldsymbol{E}^{\gamma}_{pole} &= \boldsymbol{C}^{\dagger\gamma}(\varepsilon + \boldsymbol{\Sigma}(E)|_{E=E_{pole}})\boldsymbol{C}\\ &+ \boldsymbol{C}^{\dagger}(\varepsilon + \boldsymbol{\Sigma}(E)|_{E=E_{pole}})\boldsymbol{C}^{\gamma}\\ &+ \boldsymbol{C}^{\dagger}\Big(\varepsilon^{\gamma} + \boldsymbol{\Sigma}^{\gamma}(E)\Big|_{E=E_{pole}} + E^{\gamma}_{pole}\frac{\partial \boldsymbol{\Sigma}(E)}{\partial E}\Big|_{E=E_{pole}}\Big)\boldsymbol{C}\end{aligned} \tag{4.40}$$

In the last of the three terms, there are three portions that pertain to the derivatives of the orbital energies, derivatives of the self–energy, where the $\boldsymbol{E}$ parameter is held constant, and derivatives of the self-energy employing the chain rule. Thus, this equation may be rearranged to

$$\begin{aligned}\boldsymbol{E}^{\gamma}_{pole}(1 - \boldsymbol{C}^{\dagger}\frac{\partial \boldsymbol{\Sigma}(E)}{\partial E}\Big|_{E=E_{pole}}\boldsymbol{C}) &= \boldsymbol{C}^{\dagger\gamma}\boldsymbol{C}\boldsymbol{E}_{pole} + \boldsymbol{C}^{\dagger}\boldsymbol{C}^{\gamma}\boldsymbol{E}_{pole}\\ &+ \boldsymbol{C}^{\dagger}(\boldsymbol{\varepsilon}^{\gamma} + \boldsymbol{\Sigma}^{\gamma}(E)\Big|_{E=E_{pole}})\boldsymbol{C}\end{aligned} \tag{4.41}$$

Note that the left side of the previous equation is $\boldsymbol{E}^{\gamma}_{pole}$ divided by the pole strength, $\Gamma^{P.S.}_{pole}$. By using the fact that

$$\boldsymbol{C}^{\dagger}\boldsymbol{C} = 1 \tag{4.42}$$

which implies that

$$\frac{d\boldsymbol{C}^{\dagger}\boldsymbol{C}}{dE} = 0, \tag{4.43}$$

and thus

$$\boldsymbol{C}^{\dagger}\boldsymbol{C}^{\gamma} + \boldsymbol{C}^{\dagger\gamma}\boldsymbol{C} = 0, \tag{4.44}$$

the first two terms on the right side of equation (4.41) vanish. Therefore, equation (4.41) reduces to

$$E^{\gamma}_{pole} = \Gamma^{P.S.}_{pole} \boldsymbol{C}^{\dagger}(\varepsilon^{\gamma} + \boldsymbol{\Sigma}^{\gamma}(E)|_{E=E_{pole}})\boldsymbol{C}. \tag{4.45}$$

A similar conclusion follows by finding poles using the entire superoperator Hamiltonian matrix:

$$\hat{\boldsymbol{H}}\boldsymbol{C} = \boldsymbol{C}E_{pole}. \tag{4.46}$$

Differentiation leads to

$$\hat{\boldsymbol{H}}^{\gamma}\boldsymbol{C}^{\dagger}\hat{\boldsymbol{H}}\boldsymbol{C}^{\gamma} = \boldsymbol{C}^{\gamma}E^{\dagger}_{pole}\boldsymbol{C}E^{\gamma}_{pole}. \tag{4.47}$$

After multiplying both sides by $\boldsymbol{C}^{\dagger}$ this last equation becomes,

$$E^{\gamma}_{pole} = \boldsymbol{C}^{\dagger}\hat{\boldsymbol{H}}^{\gamma}\boldsymbol{C}. \tag{4.48}$$

Using this approach to find the pole, the derivatives of the superoperator Hamiltonian matrix need to be evaluated in order to calculate E^{γ}_{pole}. Connections between the two approaches are facilitated by partitioning the eigenvectors $\boldsymbol{C}$ into their primary ($\mathbf{a}$) and secondary ($\mathbf{f}$) portions:

$$\boldsymbol{C} = [\boldsymbol{C}_{\mathrm{ap}}, \boldsymbol{C}_{\mathrm{fp}}] \tag{4.49}$$

The derivatives of the primary and secondary contributions of superoperator Hamiltonian may be connected to the spin density of the ionized system by:

$$\boldsymbol{\rho}^{Spin}_{\mathrm{pq}} = \boldsymbol{D}^{\alpha}_{\mathrm{pq}} - \boldsymbol{D}^{\beta}_{\mathrm{pq}} \tag{4.50}$$

whereas the charge density of the ionized system may be expressed as:

$$\boldsymbol{\rho}^{Charge}_{\mathrm{pq}} = \boldsymbol{D}^{\alpha}_{\mathrm{pq}} + \boldsymbol{D}^{\beta}_{\mathrm{pq}} \tag{4.51}$$

where $\boldsymbol{D}^{\alpha}_{\mathrm{pq}}$ and $\boldsymbol{D}^{\beta}_{\mathrm{pq}}$ denote the derivatives of the primary or secondary sectors of the superoperator Hamiltonian matrix for the removal of an alpha or beta electron.

Finally, the electron–propagator algorithm may be summarized in the following diagram:

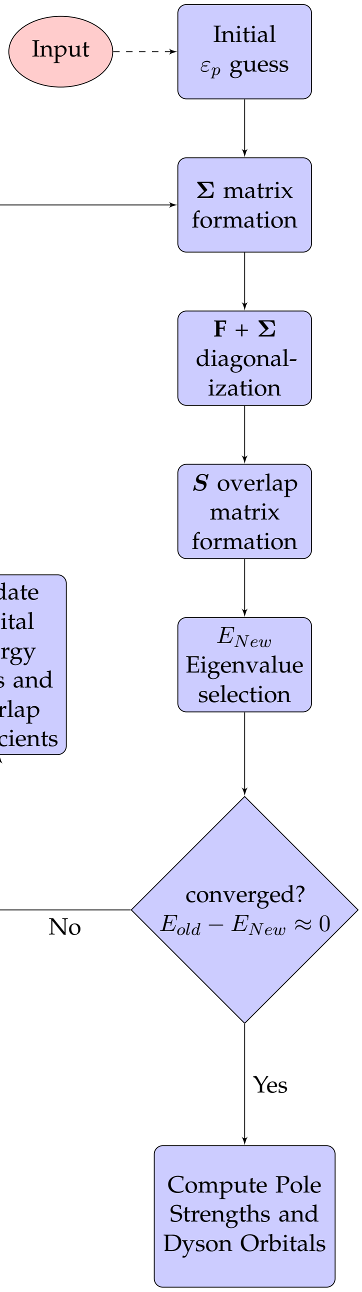

Fig. 4.10.: Electron propagator self consistent algorithm

4.4 Orbital energy threshold recommendation

In the Dyson quasiparticle equation, denominators in the expressions for the self–energy matrix depend on orbital energy differences. For example, for the second–order self–energy matrix,

$$\Sigma^{(2)}_{ru}(E) = \sum_{\iota, p<q} \frac{\langle r\iota \| pq \rangle \langle pq \| u\iota \rangle N_{rpq}}{E + \varepsilon_\iota - \varepsilon_p - \varepsilon_q}, \tag{4.52}$$

the difference $E + \varepsilon_\iota - \varepsilon_p - \varepsilon_q$ depends on three different orbital energy indices. If for the $2ph$ and $2hp$ terms of the self–energy matrix these differences become small, self–consistent field calculations cannot be expected to converge, because of pronounced fluctuations in elements of the virtual–virtual or occupied–occupied blocks of the superoperator Hamiltonian. Such conditions are encountered usually when the binding energy computed corresponds to an occupied, inner-valence spin orbital in which the quasiparticle picture is not longer valid.

5

Restricted open–shell electron propagator

> *I don't know what's the matter with people! They don't learn by understanding; they learn by some other way, by rote or something. Their knowledge is so fragile!*
>
> — **Richard Phillips Feynman**
> (Surely You're Joking, Mr. Feynman!)

A large variety of electronic structure methods can accurately describe only the singlet ground-state of closed–shell systems. The desire of correctly describing molecular systems with open–shell electronic configurations brings the necessity to confront Löwdin's symmetry dilemma [102–105]. In the Sanibel symposium meeting of 1963 [103], Löwdin pointed out that computational chemists are challenged with a dilemma: imposing constraints to enforce correct spin–symmetry properties in the resulting eigenfunctions or increasing the variational parameters to achieve the lowest energy possible. In the case of open–shell systems, enforcement of the correct spin–symmetry results in the formulation of the so–called restricted open–shell methods denoted by an RO prefixed to the method's acronym (*e.g.*, Restricted open-sheell Hartree–Fock (ROHF), Restricted Open–shell Moller–Plesset perturbation theories (ROMPn), Restricted Open–shell Coupledcluster theories (ROCCn), etc.). RO methods preserve spin–symmetry by reducing variational flexibility. It has been shown that RO methods do not provide adequate structures, energies, and spin densities [104–110]. In particular, for the ROHF approximation, whose equations were formulated by Roothaan more than 50 years ago [111], shows that the eigenvalues for the effective Fock operator of the model violate the Aufbau principle. Thus, ROHF orbital energies are not physically meaningful. Therefore, Koopmans's theorem or any phenomenological conclusion based on ROHF orbitals are incorrect. In spite of this very well known and documented ambiguity about the ROHF orbitals, some authors make studies in which wrong or inconsequential conclusions are based on ROHF determinants [106, 110, 112–116]. In this chapter, possible solutions to the ROHF Koopmans's theorem will be summarized and discussed.

5.1 Löwdin's symmetry dilemma

In computational chemistry, restricting each occupied orbital in a closed–shell system to contain only one α and only one β electron is the simplest way to enforce spin symmetry, $\langle \hat{S}^2 \rangle = 0$. This same idea may be extended to open–shell atoms or molecules. In the so–called restricted open–shell (RO) methodologies, each unpaired electron resides only in an α spin–orbital with the remaining β electrons constrained to doubly occupied orbitals. In a single–determinant approximation, the constraints imposed by the RO technique may enforce the generation of eigenstates that are eigenfunctions of $\hat{S}^2$, however these constraints also reduce the variational flexibility. The variational flexibility of the RO methods may be increased by allowing different orbitals for different spins; this generates the so–called unrestricted (U) methods. Furthermore, in a single–determinant approximation the variational flexibility may be maximized when each of the electrons of the system is described as a linear combination of α and β spin orbitals. Methods based on this idea are known as generalized (G) methods. Although the unrestricted and generalized methods increase the variational flexibility of single–determinant approximations, the resulting states are no longer eigenfunctions of $\hat{S}^2$. Choosing between a lower energy solution, and a solution that is an eigenfunction of the spin operator $\hat{S}^2$, and the spatial symmetry operators for the relevant nuclear point group, is exactly what Löwdin's symmetry dilemma requires.

5.2 Symmetry Breaking

The consequences and implications of the Löwdin's symmetry dilemma may be explored in the framework of group theory. The following discussion is based on the published conclusion given by Fukutome, Paldus, Brändas and Goings [104, 105, 108, 117]. Broken symmetry wave–functions may be classified by investigating how they transform under the action of the invariance operators $\hat{g}$ constituting the symmetry group $\mathcal{G}$ of the spin-free electronic Hamiltonian $\hat{H}$,

$$[\hat{g}, \hat{H}] = 0 \quad \forall \hat{g} \in \mathcal{G}, \tag{5.1}$$

or

$$\hat{g}\hat{H}\hat{g}^{-1} = \hat{H}, \tag{5.2}$$

such that $\hat{H}$ is invariant under transformation by any operator $\hat{g}$. In general, when $|\psi\rangle$ is an eigenstate of $\hat{H}$, $\hat{g}|\psi\rangle$ would also be an eigenstate belonging to the same eigenvalue as $|\psi\rangle$. Thus, exact eigenstates of $\hat{H}$ can be chosen to be simultaneous eigenstates of the various symmetries in $\mathcal{G}$. In the case of the approximate variational Hartree–Fock wave–functions, the symmetry requirements represent additional constraints. Although, certain symmetries may be contained in a lowest energy solution, when these symmetries are included in the approximation of the variational Hamiltonian one may only raise the energy, this due to the independent–particle nature of the approximate Hamiltonian. Thus, the more physical constraints are removed from the Hamiltonian the closer the solution will be to the exact solution (lowest energy solution). This dependency between symmetry constraints and energy is reflected in the various broken symmetry subgroups in which the solutions of the single–determinental Hartree–Fock approximation may fall.

5.2.1 Group and subgroups of symmetries

Let $\hat{X}$ be an operator that is invariant with respect to similarity transformations by various subgroups $\mathcal{H} \subset \mathcal{G}$ such that

$$\hat{h}\hat{X}\hat{h}^{-1} = \hat{X}, \quad (\forall \hat{h} \in \mathcal{H} \subset \mathcal{G}). \tag{5.3}$$

For an independent particle model, if the operator $\hat{X}$ is an one body operator, such as the Fock operator, defined in the spinor basis,

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{5.4}$$

and

$$|\alpha\rangle\langle\alpha| = |\beta\rangle\langle\beta| = \boldsymbol{I}_2. \tag{5.5}$$

Any arbitrary spin function may be expressed as

$$|\phi_s\rangle = c_1^s|\alpha\rangle + c_2^s|\beta\rangle = \begin{pmatrix} c_1^s \\ c_2^s \end{pmatrix}. \tag{5.6}$$

Thus, establishing $\hat{X}$ into a spinor basis yields

$$\hat{X} = |i\sigma_1\rangle\langle i\sigma_1|\hat{X}|j\sigma_2\rangle\langle j\sigma_2| = X_{i\sigma_1,j\sigma_2}|i\sigma_i\rangle\langle j\sigma_2| = \begin{pmatrix} X_{\alpha\alpha} & X_{\alpha\beta} \\ X_{\beta\alpha} & X_{\beta\beta} \end{pmatrix} \tag{5.7}$$

with

$$(X_{\sigma_1\sigma_2})_{ij} \in \mathbb{C} \quad \sigma_1, \sigma_2 \in \alpha, \beta. \tag{5.8}$$

In terms of second quantization notation this may be expressed as

$$\hat{X} = \sum_{ij}\sum_{\sigma_1,\sigma 2} X_{i\sigma_1,j\sigma_2} a^\dagger_{i\sigma_1} a_{j\sigma_2} = \sum_{ij}\sum_{\sigma_1,\sigma 2} X_{i\sigma_1,j\sigma_2} \hat{E}^{i\sigma_1}_{j\sigma_2}. \tag{5.9}$$

The transformation properties of $\hat{X}$ under symmetry operations can be determined by examining the transformation of the $U(2n)$ generators $\hat{E}^{i\sigma_1}_{j\sigma_2}$, but for the sake of simplicity only the transformations of a 2×2 block matrix $\boldsymbol{X}$ will be considered. In this case, the problem is reduced to finding the constraints on the $\boldsymbol{X}$ matrix that for any given symmetry operation make the following relation true:

$$\hat{h} \begin{pmatrix} X_{\alpha\alpha} & X_{\alpha\beta} \\ X_{\beta\alpha} & X_{\beta\beta} \end{pmatrix} \hat{h}^{-1} = \begin{pmatrix} X_{\alpha\alpha} & X_{\alpha\beta} \\ X_{\beta\alpha} & X_{\beta\beta} \end{pmatrix}. \tag{5.10}$$

The general invariance group of the spin–free electronic Hamiltonian involves the spin rotation ($SU(2)$) and the time reversal ($\mathcal{T}$) groups. The SU(2) group may be given in terms of spin operators such that[1]

$$\mathrm{SU}(2) = \left\{ U_R(\vec{n}, \theta) = \exp(i\theta \sum_{a=1}^{3} \hat{S}_a \hat{n}_a); \vec{n} = (n_1, n_2, n_3); \vec{n} \in \mathbb{R}^3; ||\vec{n}|| = 1, \theta \in (-2\pi, 2\pi] \right\}. \tag{5.11}$$

Notice that the $SU(2)$ group is a double cover[118], when the spin space is rotated by 2π the sign of the wave–function changes, and if the spin space is rotated again by another 2π the original state is recovered. This behavior is characteristic of fermions. On the other hand, the time reversal group is defined as

$$\mathcal{T} = \left\{ \pm\hat{1}, \pm\hat{\Theta} \right\}, \tag{5.12}$$

where in general $\hat{\Theta}$ is defined in terms of the complex conjugation operator $\hat{K}$,

$$\hat{\Theta} = \hat{U_R}(\vec{e}_2, -\pi)\hat{K} = \exp(-i\pi\hat{S}_2)\hat{K}. \tag{5.13}$$

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[1] The rotations in spin space are quite similar to rotations in 3D space.

It is important to point out that the time reversal does not really mean effects in time per se, but rather changes the direction of movement, be it linear momentum or angular momentum. $\hat{\Theta}$ is just an antiunitary operator [119] that consists of the spin–looking part (unitary part) and then the complex conjugation operator (antiunitary part). Therefore,

$$\hat{\Theta}^{-1} = -\hat{\Theta} = \exp(i\pi\hat{S}_2)\hat{K}. \tag{5.14}$$

Now, consider the unitary transformations of the form $U = e^{i\hat{B}}$, where $\hat{B}$ is a Hermitian operator ($\hat{B} = \hat{B}^{\dagger}$), acting on some operator $\hat{X}$ such that

$$\hat{X} = \hat{U}\hat{X}\hat{U}^{-1} = e^{-i\hat{B}}\hat{X}e^{i\hat{B}}. \tag{5.15}$$

The Baker-Campbell-Hausdorff transformation allows expressing $e^{-i\hat{B}}\hat{X}e^{i\hat{B}}$ as

$$e^{-i\hat{B}}\hat{X}e^{i\hat{B}} = \hat{X} + [\hat{X}, i\hat{B}] + \frac{1}{2!}[[\hat{X}, i\hat{B}], i\hat{B}] + \cdots \tag{5.16}$$

Thus, the constraints on $\hat{X}$ introduced by symmetry operations are satisfied when $[\hat{X}, i\hat{B}] = 0$. Therefore, transformation of the 2×2 matrix $\boldsymbol{X}$ under the Pauli spin matrices defines the $SU(2)$ spin rotation as well as the time–reversal operations. The spin rotation and time–reversal groups are known to contain the following subgroups:

- $\boldsymbol{I}$: There is no symmetry.
- Θ: Symmetric only to time-reversal symmetry.
- K: Symmetric only to complex conjugation.
- S_z: Symmetric only to spin rotations about the z-axis.
- S_z, Θ: Symmetric to both spin rotation about z-axis and time-reversal symmetry.
- S_z, K: Symmetric to both spin rotation about z-axis and complex conjugation.
- S^2: Symmetric to all spin rotations.
- S^2, Θ: Symmetric to both all spin rotations and time reversal symmetries.

Concerning the Hartree–Fock approximation, the differences between the RHF, UHF and GHF may be explored in terms of the different implications and consequences related to imposition of different combinations of symmetry constraints. If the complex Fock matrix is defined as

$$\begin{pmatrix} F_{\alpha\alpha} & F_{\alpha\beta} \\ F_{\beta\alpha} & F_{\beta\beta} \end{pmatrix}, \tag{5.17}$$

for each symmetry or group of symmetries the similarity transformation is given by

$$\hat{h} \begin{pmatrix} F_{\alpha\alpha} & F_{\alpha\beta} \\ F_{\beta\alpha} & F_{\beta\beta} \end{pmatrix} \hat{h}^{-1} = \begin{pmatrix} F_{\alpha\alpha} & F_{\alpha\beta} \\ F_{\beta\alpha} & F_{\beta\beta} \end{pmatrix} \tag{5.18}$$

where $\boldsymbol{h}$ is the symmetry generator.

5.2.2 No symmetry constraints

The simplest transformation on the Fock matrix is given when there are no symmetry constraints. In this case, the similarity transformation is given by

$$\hat{I} \begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & \boldsymbol{F}_{\alpha\beta} \\ \boldsymbol{F}_{\beta\alpha} & \boldsymbol{F}_{\beta\beta} \end{pmatrix} \hat{I}^{-1} = \begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & \boldsymbol{F}_{\alpha\beta} \\ \boldsymbol{F}_{\beta\alpha} & \boldsymbol{F}_{\beta\beta} \end{pmatrix}. \tag{5.19}$$

Since no symmetry constraints are imposed the electron spin can mix. The values of the elements of the Fock matrix may be real or complex. This first result corresponds to the structure of the complex generalized Hartree–Fock (GHF) Fock matrix.

5.2.3 Complex conjugation symmetry constraints

On the other hand, when the complex conjugation symmetry is imposed, the transformation on the Fock matrix yields

$$\hat{K} \begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & \boldsymbol{F}_{\alpha\beta} \\ \boldsymbol{F}_{\beta\alpha} & \boldsymbol{F}_{\beta\beta} \end{pmatrix} \hat{K} = \begin{pmatrix} \boldsymbol{F}^*_{\alpha\alpha} & \boldsymbol{F}^*_{\alpha\beta} \\ \boldsymbol{F}^*_{\beta\alpha} & \boldsymbol{F}^*_{\beta\beta} \end{pmatrix}, \tag{5.20}$$

which corresponds to the structure of the real GHF Fock matrix where the values of this Fock matrix have to be identical on complex conjugation. Notice that for this case K is its own inverse and can only act to either the left or the right.

5.2.4 Time–reversal symmetry constraints

For this case, let the $\boldsymbol{\sigma}_2$ matrix be the Pauli matrix expressed as:

$$\boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{5.21}$$

If the $\hat{S}_2$ operator yields

$$-\,i \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \hat{K} \begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & \boldsymbol{F}_{\alpha\beta} \\ \boldsymbol{F}_{\beta\alpha} & \boldsymbol{F}_{\beta\beta} \end{pmatrix} i\hat{K} \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} = \begin{pmatrix} \boldsymbol{F}^{*}_{\beta\beta} & -\boldsymbol{F}^{*}_{\beta\alpha} \\ -\boldsymbol{F}^{*}_{\alpha\beta} & \boldsymbol{F}^{*}_{\alpha\alpha} \end{pmatrix}, \tag{5.22}$$

then the imposition of time reversal symmetry only introduces two constraints. Thus, by eliminating $\boldsymbol{F}_{\beta\alpha}$ and $\boldsymbol{F}_{\beta\beta}$ the Fock matrix for the paired GHF approximation is obtained:

$$\begin{pmatrix} \boldsymbol{F}_{\beta\beta} & \boldsymbol{F}_{\alpha\beta} \\ -\boldsymbol{F}^{*}_{\alpha\beta} & \boldsymbol{F}^{*}_{\alpha\alpha} \end{pmatrix}. \tag{5.23}$$

5.2.5 z-axis rotation symmetry constraints

Now, if the Pauli matrix $\boldsymbol{\sigma}_3$ is defined as

$$\boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{5.24}$$

one can show that

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \hat{K} \begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & \boldsymbol{F}_{\alpha\beta} \\ \boldsymbol{F}_{\beta\alpha} & \boldsymbol{F}_{\beta\beta} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & -\boldsymbol{F}_{\alpha\beta} \\ -\boldsymbol{F}_{\beta\alpha} & \boldsymbol{F}_{\beta\beta} \end{pmatrix} \tag{5.25}$$

is satisfied only if

$$\boldsymbol{F} = \begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & 0 \\ 0 & \boldsymbol{F}_{\beta\beta} \end{pmatrix} \tag{5.26}$$

Thus, invariance with respect to S_z results in two separate spin blocks. These spin blocks have no restriction in their dimensions and may take real or complex values. This case corresponds to the complex version of the UHF approximation.

5.2.6 Time–reversal and z-axis rotation symmetry constraints

In order to examine the effect of invariance to multiple symmetry operations, one should remember that when considering multiple symmetry operations the order in which the symmetry operations is performed matters. In general, symmetry operations do not commute. However, since each symmetry operation returns the system to its original state, each symmetry operation can be considered separately. For instance, consider two symmetry operations on F parameterized by A and B such that

$$e^{-i\hat{A}}e^{-i\hat{B}}\hat{F}e^{i\hat{B}}e^{i\hat{A}} = e^{-i\hat{A}}[\hat{F}+[\hat{F},i\hat{B}]+\cdots]e^{i\hat{A}} = e^{-i\hat{A}}\hat{F}e^{i\hat{A}} = [\hat{F}+[\hat{F},i\hat{A}]+\cdots]. \tag{5.27}$$

This last is true if and only if

$$[\hat{F},i\hat{A}] = [\hat{F},i\hat{B}] = 0 \tag{5.28}$$

Therefore, for our purposes, multiple symmetry operations only give us more constraints in which the order of each of the symmetry operation does not matter. Thus, in the case of the time reversal and z-axial spin symmetry one obtains

$$\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\hat{K}\begin{pmatrix}F_{\alpha\alpha} & F_{\alpha\beta}\\ -F^*_{\alpha\beta} & F^*_{\alpha\alpha}\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = \begin{pmatrix}F_{\alpha\alpha} & -F_{\alpha\beta}\\ -F^*_{\alpha\beta} & F^*_{\alpha\alpha}\end{pmatrix} \tag{5.29}$$

where the off–diagonal elements of the Fock matrix must go to zero,

$$\begin{pmatrix}F_{\alpha\alpha} & 0\\ 0 & F^*_{\alpha\alpha}\end{pmatrix}. \tag{5.30}$$

This result corresponds to the UHF approximation.

5.2.7 Complex conjugation and z-axis rotation symmetry constraints

The preservation of the rotation about spin z-axis and the complex conjugation symmetry yields

$$\begin{pmatrix}F_{\alpha\alpha} & 0\\ 0 & F_{\beta\beta}\end{pmatrix}, \quad (F \in \mathbb{R}) \tag{5.31}$$

Since symmetry with respect to complex conjugation forces all matrix elements to be real, this results corresponds to the real version of UHF approximation.

5.2.8 All spin axis rotation symmetry constraints

For this case is important to point out that even when S^2 does have an operator representation, it is not a symmetry operation. The S^2 operator may be regarded as the identity, therefore invariance with respect to S^2 can be interpreted as invariance with respect to the whole spin rotation group, S_x, S_y, S_z. However, while S_z is already a part of the total spin rotation group, invariance with respect S_z does not imply invariance with respect to S^2, but invariance with respect S^2 does, in general, imply invariance with respect to S_z. Invariance with respect to the spin group may be shown by considering any two spin rotations, since each spin operator may be generated by the commutator of the other two. Therefore, the invariance with respect to all spin axes may be evaluated by employing the result of S_z and applying the generator S_x defined by Pauli matrix $\boldsymbol{\sigma}_1$. If the Pauli matrix $\boldsymbol{\sigma}_1$ is expressed as

$$\boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{5.32}$$

Applying the generator S_x on the result of S_z yields

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{F}_{\alpha\alpha} & 0 \\ 0 & \boldsymbol{F}_{\beta\beta} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} \boldsymbol{F}_{\beta\beta} & 0 \\ 0 & \boldsymbol{F}_{\alpha\alpha} \end{pmatrix} \tag{5.33}$$

which implies that $\boldsymbol{F}_{\alpha\alpha} = \boldsymbol{F}_{\beta\beta}$ or

$$\boldsymbol{F} = \begin{pmatrix} \boldsymbol{F}_R & 0 \\ 0 & \boldsymbol{F}_R \end{pmatrix}, \quad (\boldsymbol{F}_R \in \mathbb{C}) \tag{5.34}$$

Invariance with respect to all spin rotation group results in the complex RHF case, where the α and β spin blocks are equivalent.

5.2.9 Time reversal and all spin axis rotation symmetry constraints

Since the time reversal group contains the $\hat{S}_y$ operator, in order to obtain the expression for this case, one just needs to take the previous results and make them invariant to complex conjugation. Thus, the expression obtained yields:

$$\hat{K} \begin{pmatrix} \boldsymbol{F}_R & 0 \\ 0 & \boldsymbol{F}_R \end{pmatrix} \hat{K} = \begin{pmatrix} \boldsymbol{F}^*_R & 0 \\ 0 & \boldsymbol{F}^*_R \end{pmatrix}. \tag{5.35}$$

Invariance with respect to complex conjugation forces all the elements of the Fock matrix to be real. This last expression corresponds to the real version of the RHF case.

As shown, in the framework of the Hartree–Fock theory, several variations of the Hartree–Fock approximation can be derived from simple symmetry considerations. Furthermore, the RHF and UHF approximations are subgroups of the GHF equations. If GHF equation are restricted to be invariant with respect to spin rotations along the z-axis the UHF equations will emerge, whereas if GHF equations are restricted to be invariant to time-reversal as well as spin rotations along all axes (x, y, z), the real RHF equations are obtained.

5.3 The diverse pictures of the Hartree–Fock theory

In quantum chemistry, most of the *ab–initio* correlated methods and hybrid density functional theory (DFT) methods are built upon the Hartree–Fock approximation. In the Hartree–Fock theory, the N–electron wave–function is denoted by a normalized Slater determinant, Ψ_0, which contains N spin–orbitals ψ_i,

$$\Psi_0 = |\psi_1 \psi_2 \ldots \psi_N\rangle. \tag{5.36}$$

While maintaining a normalized total wave function, these spin–orbitals are optimized to minimize the energy, E, by means of the variational principle,

$$E = \langle \Psi_0 | \boldsymbol{H} | \Psi_0 \rangle. \tag{5.37}$$

In this optimization, the full electronic Hamiltonian after the application of the Born–Openheimer approximation denoted, by $\boldsymbol{H}$, is employed. The minimization of the energy with respect to the spin–orbitals under the constraint of orthonormality yields

$$\boldsymbol{F}_i \psi_i = \varepsilon_i \psi_i \tag{5.38}$$

This last equation corresponds to a one–electron eigenvalue equation in which the F_i operator is known as the effective one–electron operator for the ith electron. This Fock operator is defined as

$$\boldsymbol{F}_i = \boldsymbol{h}_i + \boldsymbol{V}_i^{HF} \tag{5.39}$$

where $\boldsymbol{h}_i$ is the one–electron Hamiltonian operator describing the motion of the ith electron in the electric field generated by the N nuclei each with charge Z_A, thus, $\boldsymbol{h}_i$ may be expressed as:

$$\boldsymbol{h}_i = -\frac{1}{2}\boldsymbol{\Delta}_i^2 - \sum_{A}^{N_{Nuclei}} \frac{Z_A}{\boldsymbol{r}_{iA}}, \tag{5.40}$$

whereas, $\boldsymbol{V}_i^{HF}$ is the mean field potential experienced by the ith electron due to the presence of the other electrons. Thus, $\boldsymbol{V}_i^{HF}$ may be expressed as:

$$\boldsymbol{V}_i^{HF} = \sum_{j}^{N}(\boldsymbol{J}_j - \boldsymbol{K}_j) \tag{5.41}$$

where $\boldsymbol{J}_j$ represent the Coulomb operator, defining the electron–electron repulsion energy due to each of the two electrons in the jth orbital,

$$\boldsymbol{J}_j|\psi_i(1)\rangle = \langle\psi_j(2)|\frac{1}{r_{12}}|\psi_j(2)\rangle|\psi_i(1)\rangle, \tag{5.42}$$

whereas, $\boldsymbol{K}_j$ is the exchange operator, defining the electron exchange energy due to the antisymmetry of the total N–electron wave–function,

$$\boldsymbol{K}_j|\psi_i(1)\rangle = \langle\psi_j(2)|\frac{1}{r_{12}}|\psi_i(2)\rangle|\psi_j(1)\rangle. \tag{5.43}$$

Following the Roothaan[120] and Hall[121] equations, the spatial part, ϕ_i, of each spin–orbital can be written as a linear combination of M basis functions χ_ν,

$$\psi_i = \phi_i(\boldsymbol{r}) = \sum_{\nu}^{M_{basis}} C_{\nu i}\chi_\nu(\boldsymbol{r}). \tag{5.44}$$

Therefore, by considering this last equation, equation (5.38) yields

$$\sum_{\nu}^{M_{basis}} \boldsymbol{F}_i\chi_\nu C_{\nu i} = \varepsilon_i \sum_{\nu}^{M_{basis}} \chi_\nu C_{\nu i}, \tag{5.45}$$

which after the left multiplication by χ_τ and integration becomes

$$\sum_{\nu}^{M_{basis}} [F_{\tau\nu} - \varepsilon_i S_{\tau\nu}]C_{\nu i} = 0 \quad i = 1, 2, \ldots, N \tag{5.46}$$

where

$$F_{\tau\nu} = \langle\chi_{tau}|\boldsymbol{F}|\chi_\nu\rangle \tag{5.47}$$

and

$$S_{\tau\nu} = \langle \chi_\tau | \chi_\nu \rangle. \tag{5.48}$$

5.3.1 The self–consistent field procedure

A more succinct notation for equation (5.46) may be

$$\boldsymbol{FC} = \boldsymbol{SC}\boldsymbol{\varepsilon}. \tag{5.49}$$

where $\boldsymbol{F}$ is the Fock matrix formulation of the Fock operator, $\boldsymbol{C}$ the molecular orbital coefficients matrix, $\boldsymbol{S}$ the overlap matrix between basis functions, and $\boldsymbol{\varepsilon}$ is the diagonal matrix containing the molecular orbital energies. Following the formulation of the Hartree–Fock equations, one may notice that the Fock matrix does not have a linear dependence on the molecular orbital coefficients. The Fock matrix depends on the Coulomb and exchange operators which have a dependency upon the molecular orbital coefficients matrix. Therefore, from a mathematical perspective, spin contamination is a direct manifestation of the nonlinearity of the Fock operator. In computational implementations, the Hartree–Fock method is also referred as the self–consistent field procedure. In the implementation of the self–consistent field algorithm, equation (5.49) is solved in an iterative manner (figure 5.1).

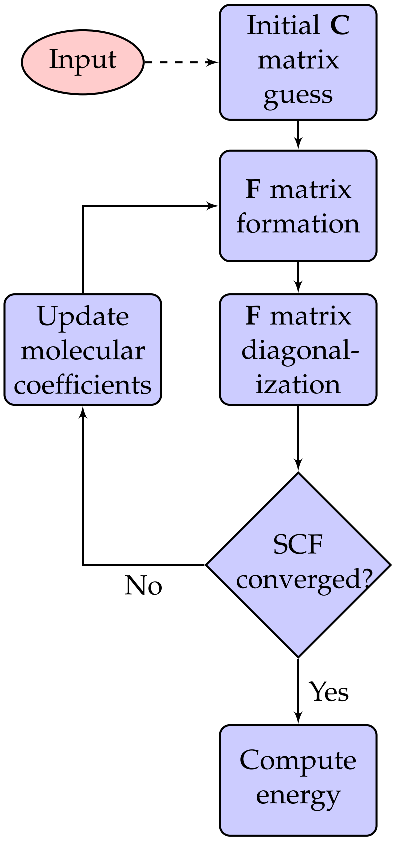


Fig. 5.1.: Hartree–Fock Self consistent field algorithm

Starting with an initial guess for the molecular orbital coefficients, a first Fock matrix $\boldsymbol{F}$ is built. This Fock matrix is used to generate a new set of molecular orbital coefficients from which the a new Fock matrix will be built. This processes of generating $\boldsymbol{C}$ and $\boldsymbol{F}$ matrix is repeated until the change in energies converges below a numeric threshold and self–consistency is achieved. The several physical pictures of the Hartree–Fock approximation (*i.e.*, UHF, RHF, ROHF and GHF) reside in the set of the orthonormal spin–orbital basis used, ψ_i, within the Hartree–Fock equations. In the restricted versions of Hartree–Fock approximation (RHF and ROHF), both the α and β spin–orbitals have the same spatial functions and therefore identical values for the molecular orbital coefficients, $\boldsymbol{C}_{\nu i}$,

$$\psi_i^{\alpha}(\boldsymbol{r}) = \phi_i(\boldsymbol{r})\alpha = \sum_{\nu}^{M_{basis}} C_{\nu i}\chi_{\nu}(\boldsymbol{r})\alpha, \quad \psi_i^{\beta}(\boldsymbol{r}) = \phi_i(\boldsymbol{r})\beta = \sum_{\nu}^{M_{basis}} C_{\nu i}\chi_{\nu}(\boldsymbol{r})\beta. \tag{5.50}$$

The wave–functions generated with the restricted and restricted open–shell Hartree–Fock approximations are eigenfunctions of both the $\hat{S}_z$ and $\hat{S}^2$ operator. In the unrestricted version of the Hartree–Fock approximation (UHF), a spin–orbital basis in which the α and β spin–orbitals may have different spatial functions is used. Therefore, in the UHF approximation, the α and β molecular orbital coefficients, $C^a_{\nu i}$ and $C^b_{\nu i}$, that are used to define the spin–orbitals, are different from each other,

$$\begin{array}{c} \psi_i^{\alpha}(\boldsymbol{r}) = \phi_{ia}^{\alpha} = \phi_{ia}(\boldsymbol{r})\alpha = [\sum_{\nu}^{M_{basis}} C^a_{\nu i}\chi_{\nu}(\boldsymbol{r})]\alpha \\ \psi_i^{\beta}(\boldsymbol{r}) = \phi_{ib}^{\beta} = \phi_{ib}(\boldsymbol{r})\beta = [\sum_{\nu}^{M_{basis}} C^b_{\nu i}\chi_{\nu}(\boldsymbol{r})]\beta \end{array}. \tag{5.51}$$

The resulting wave–functions from the UHF approximation are eigenfunctions of the $\hat{S}_z$ operator but not of the $\hat{S}^2$ operator. Due to the fact that the unrestricted Hartree–Fock formulation has less symmetry constraints than the restricted Hartree–Fock formulation, the unrestricted Hartree–Fock solutions are variationally more flexible than their corresponding restricted Hartree–Fock counterparts. The variational flexibility of the Hartree–Fock solutions is maximized in the generalized Hartree–Fock approximation. In the generalized Hartree–Fock approximation, each of the spin–orbitals is defined as a linear combination of both α and β spin–orbitals[122],

$$\psi_i(\boldsymbol{r}) = \phi_{ia}^{\alpha} + \phi_{ib}^{\beta} = \phi_{ia}(\boldsymbol{r})\alpha + \phi_{ib}(\boldsymbol{r})\beta = \sum_{\nu}^{M_{basis}} \Big\{[C^a_{\nu i}\chi_{\nu}(\boldsymbol{r})]\alpha + [C^b_{\nu i}\chi_{\nu}(\boldsymbol{r})]\beta\Big\}. \tag{5.52}$$

Although the resulting wave–functions from the GHF approximation have the most variational flexibility, they are neither eigenfunctions of the $\hat{S}_z$ operator nor of the

$\hat{S}^2$ operator. Now that the different formulations for the Hartree–Fock method have been presented, let's further analyze Löwdin's symmetry dilemma in a more practical manner. Table 5.1 summaries the spin symmetry and the energy implications of each of the Hartree–Fock approximations. It is important to point out that for all the Hartree–Fock formulations the molecular coefficients can be real or complex. Löwdin pointed out with his symmetry dilemma that every quantum chemist should understand the implications that the symmetry constraints would have in the energy of the system under study. Based on these implications, one should balance variational flexibility versus symmetry constraints. For instant, in the restricted version of the Hartree–Fock approximation one may guarantee correct quantum numbers for the system under study, however, this implies imposing certain constraints in the variational Hamiltonian which would only raise the energy of the system. Therefore, it is not surprising that for open–shell electronic configurations energies computed by post Hartree–Fock methods based on the restricted open–shell version of the Hartree–Fock approximation report larger energies than their counterpart based on the unrestricted Hartree–Fock approximation.

Hartree–Fock methods				
Formulation	$\langle \hat{S}_z \rangle$	$\langle \hat{S}^2 \rangle$	ψ_i^α and ψ_i^β	Energy hierarchy
RHF and ROHF	Yes	Yes	Identical $\boldsymbol{C}_{\nu i}$	The least variational flexibility
UHF	Yes	No	$\boldsymbol{C}_{\nu i}^\alpha$ and $\boldsymbol{C}_{\nu i}^\beta$	$E_{UHF} \leq E_{RHF,ROHF}$
GHF	No	No	$\psi_i(\boldsymbol{r}) = \psi_i^\alpha + \psi_i^\beta$	$E_{GHF} \leq E_{UHF} \leq E_{RHF,ROHF}$

Tab. 5.1.: Hartree–Fock approximations and their constraints–flexibility balancing

For open–shell systems, the restricted open–shell wave–function is a single configuration state function (CSF) and therefore a pure spin state. On the other hand, unrestricted Hartree–Fock energies are lower than restricted open–shell Hartree–Fock energies because for the restricted wave–function the restriction that the α and β orbitals will be the same has been established. However, this may not be clear for some authors that often point out the fact that restricted energies are higher than unrestricted ones and make inconsequential conclusions as if the energy obtained with a restricted method were supposed to be lower than the energy of an unrestricted method. Furthermore, for the cases of open-shell systems, the restricted open–shell solution may not only have higher energies as compared to their unrestricted counterpart but also one needs to be careful in deriving conclusions based on the restricted open–shell molecular orbitals (population analysis, binding energies, etc.) because any conclusion based on ROHF orbitals may be erroneous [106, 110, 112–116]. Since Roothaan's [111] introduction of the Restricted Open–shell Hartree–Fock model, orbital energies do not have physical meaning. Therefore, any conclusions based on the ordering, magnitude or properties of the ROHF molecular orbital without any previous treatment of the orbitals are erroneous [104, 105, 107, 109, 123–126].

5.4 The Restricted Open–shell Hartree–Fock model

The restricted open–shell Hartree–Fock (ROHF) method generates wave–functions that are eigenfunctions of both the $\hat{S}_z$ and $\hat{S}^2$ operator. Therefore, the ROHF approximation is the preferred tool for studying molecules with unpaired electrons. However, the physical picture emerging from Roothaan's open–shell theory have always been somewhat unclear. In the formulation of the ROHF equations, some arbitrariness may be found in the construction of the ROHF total Fock matrix. This generates different coupling schemes for the formation of the ROHF Fock matrix. Although the ROHF wave–function and total energy obtained from these schemes are the same, the resulting orbitals and orbital energies are different and, generally, the post–ROHF results depend on the ROHF coupling scheme used [109, 125–127]. The energy expression for the ROHF energy may be expressed as

$$E_{ROHF} = 2\sum_i f_i h_{ii} + \sum_{ij} f_i f_j (2a_i^j \langle ij|ij\rangle - b_i^j \langle ij|ij\rangle) \tag{5.53}$$

where h_{ij} represent one–electron integrals, $\langle ij||kl\rangle$ the two–electron integrals (in Dirac's notation), a_i^j and b_i^j are the coupling coefficients, and f_i is the orbital occupation number (1 for doubly occupied orbitals and 0 for virtual or unoccupied orbitals). In the case of high–spin open—shell systems, $a = 1$, $b = 2$, and $f = 1/2$ for singly occupied orbitals.

5.4.1 The different ROHF schemes

In ROHF theory Roothaan's effective Fock operator is defined as

$$\widehat{\mathbf{F}}_{\boldsymbol{ROHF}} = \begin{array}{c|ccc|} & Occupied & Open & Virtual \\ \hline Occupied & R_{cc} & F^{\beta}_{co} & F^{cs}_{cv} \\ Open & F^{\beta}_{oc} & R_{oo} & F^{\alpha}_{ov} \\ Virtual & F^{cs}_{vc} & F^{\alpha}_{vo} & R_{vv} \end{array}\,. \tag{5.54}$$

where F^{α} and F^{β} are the UHF α and β Fock matrices and $F^{cs} = (F^{\alpha} + F^{\beta})/2$. At self-consistent field (SCF) convergence, all off–diagonal ROHF Fock matrix elements become zero. The choice of the diagonal elements in equation (5.54) is completely arbitrary within a set of A and B coupling coefficients,

$$\begin{aligned} \boldsymbol{R}_{cc} &= A_{cc}\boldsymbol{F}^{\alpha}_{cc} + B_{cc}\boldsymbol{F}^{\beta}_{cc} \\ \boldsymbol{R}_{oo} &= A_{oo}\boldsymbol{F}^{\alpha}_{oo} + B_{oo}\boldsymbol{F}^{\beta}_{oo} \; . \\ \boldsymbol{R}_{vv} &= A_{vv}\boldsymbol{F}^{\alpha}_{vv} + B_{vv}\boldsymbol{F}^{\beta}_{vv} \end{aligned} \tag{5.55}$$

Different values for these coupling coefficients have been suggested in the literature, see table 5.2. Although all the different ROHF coefficients schemes may converge to the same ROHF energy for a given system, the election of these coefficients may affect the rate of convergence of the self–consistent field algorithm and the orbital energies whose physical meaning is lost due to this dependence. Choices guided to determine "canonical" sets that satisfy Koopmans's theorem may result in violations to the Aufbau principle [123–126]. Among all the methods and techniques proposed for fixing these violations and to obtain a meaningful Koopmans's theorem picture with the ROHF approximation, the method proposed by Plakhutin and Davidson [123–125] may be the most promising one.

ROHF Hamiltonian

A_{cc}	B_{cc}	A_{oo}	B_{oo}	A_{vv}	B_{vv}	Developer
-1/2	3/2	1/2	1/2	3/2	-1/2	Roothaan [111]
1/3	2/3	1/3	1/3	2/3	1/3	McWeeny and Diercksen [128]
1/2	1/2	1	0	1	0	Davison [129]
1/2	1/2	1/2	1/2	1/2	1/2	Guest and Saunders [130]
1/2	1/2	1	0	0	1	Binkley, Pople, and Dobosh [131]
1/2	1/2	1	0	1/2	1/2	Faegri and Manne [132]
1/2	1/2	1/2	0	1/2	1/2	Euler equations [133]
$\frac{2S+1}{2}$	$-\frac{1}{2S}$	1	0	1	0	Canonical ROHF-I [123–125]
0	1	0	1	$-\frac{1}{2S}$	$\frac{2S+1}{2}$	Canonical ROHF-II [123–125]

Tab. 5.2.: Some of the coefficients reported in the literature for equation (5.55) for the systems having a half-filled open electronic shell with all spins parallel.

5.5 Koopmans's theorem in the restricted open-shell Hartree-Fock approximation

Koopmans's theorem is one of the most useful and widely used theorems in quantum chemistry applications. This theorem was first introduced within the framework of the Hartree–Fock method for closed–shell atoms and molecules and establishes that the energy of removing an electron from the ith energy level is equal to the ith eigenvalue (ε_i) of the canonical Hartree–Fock equation. For closed-shell systems, the formulation of the Koopmans's theorem is based on the approximation of "frozen" orbitals, therefore, the calculated one–electron energies ε_i are correlated with the vertical ionization energy. Results derived from Koopmans's theorem for closed–shell systems have been extensively discussed in the literature [134–137]. Although the fundamentals of the Koopmans's theorem are well established, some specific problems arise when applying this theorem to open–shell systems. Among these problems, the most problematic one is related to the validity of Koopmans's theorem in the framework of the restricted open–shell Hartree–Fock method. In the application of Koopmans's theorem in the ROHF approach, the main problems arise from the ambiguity in the one–electron energies derived from ROHF calculations. This problem related to the ambiguity of the one–electron energy definitions in the ROHF method was first pointed out by Roothaan[111] and later discussed by Dodds and McWeeny [138] and other authors [104, 105, 107, 109, 123–127]. In spite of the well known and documented ambiguity of ROHF orbital energies, it is often assumed in present–day that Koopmans's theorem is valid in the ROHF method or that meaningful conclusions can be extracted from ROHF orbital energies. (See for example references [106, 110, 112–116] where in some cases, the wrong use of the ROHF orbital energies leads to contradictory results.) In order to overcome the limitations of Koopmans's theorem in the ROHF approach B. N. Plakhutin *et al* proposed a new scheme for the coupling coefficients of the ROHF Fock matrix [123–125]. The utilization of these coefficients allows the generation of meaningful pseudo–canonical orbital energies that can be used for the calculation of the electron propagator self–energy matrix.

5.5.1 Generation of the correct ROHF couplings coefficients

Using the field superoperator formalism from electron propagator theory, deductions of algebraic expressions for the ROHF Fock matrix may be obtained. Starting with an open–shell determinant with a singly occupied orbital (*e.g.*, a doublet state), the elimination of one particle could produce one singlet or two triplet states, where the singlet and one of the triplet states correspond to linear combinations (sum or difference) of two different determinants. (see figure 5.2.)

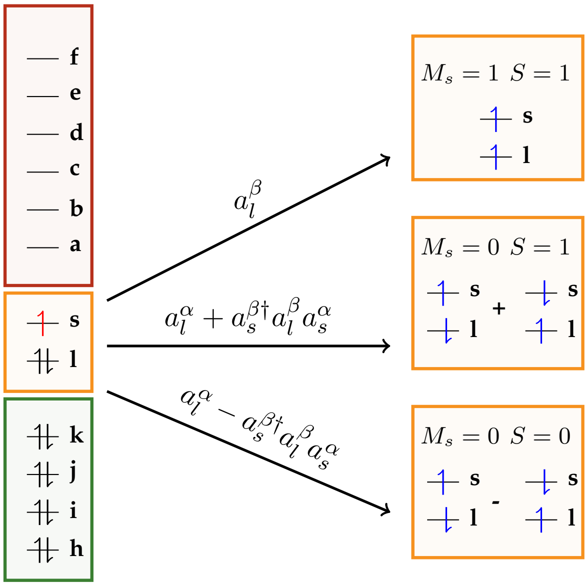


Fig. 5.2.: Generation of singlet and triplet states from a doublet state.

Among the three different states that may be generated with a doublet determinant, the triplet state with quantum numbers $M_s = 1$ and $S = 1$ may be the easiest to generate. This triplet state may be generated through the removal of a β electron from a doubly occupied orbital. This electron removal can be easily described by an annihilation field operator that acts on a doubly occupied orbital. On the other hand, the singlet ($M_s = 0, S = 0$) and the remaining triplet ($M_s = 0, S = 1$) states are generated through the evaluation of simple field annihilation operator and a string of field operators that remove the α electron from the singly occupied orbital s and excites to that orbital a β electron from a doubly occupied orbital. The evaluation of these three superoperator field couplings may generate expressions that correspond to a correct description of Koopmans's theorem in the framework of the ROHF approximation.

5.5.2 Formulation of the first triplet state ($M_s = 1 \; S = 1$)

The triplet state with quantum numbers $M_s = 1$ and $S = 1$, may be generated by removing a β electron from the doubly occupied orbital. In the context of the superoperaor theory this removal of an electron corresponds to the application of an annihilation operator on a doubly occupied orbital. This removal process may be then described as the superoperator coupling:

$$(a_{l\beta}|\widehat{H}a_{l\beta}). \tag{5.56}$$

Using an N-electron determinant as a reference determinant,

$$|\chi\rangle = \prod_{i=1} a_i^\dagger |vac\rangle \tag{5.57}$$

The expansion of the superoperator coupling for the triplet state with quantum numbers $M_s = 1, S = 1$ is described by the Fock matrix:

$$F_{l\beta l\beta} \tag{5.58}$$

5.5.3 Formulation of the second triplet state ($M_s = 0$ $S = 1$)

The second triplet that can be obtained from the doublet reference determinant corresponds to the quantum numbers $M_s = 0$ and $S = 1$. These quantum numbers may be obtained from a linear combinations of two different determinants. This linear combination correspond to the sum of the determinant obtained by the annihilation of an α electron from the reference determinant, and the determinant obtained from the removal of a β electron from a double occupied orbital, and the spin change from α to β of the electron in the singly occupied orbital,

$$(\frac{(a_{l\alpha} + a^\dagger_{S\beta}a_{S\alpha}a_{l\beta})}{\sqrt{2}}|\widehat{H}\frac{(a_{l\alpha} + a^\dagger_{S\beta}a_{S\alpha}a_{l\beta})}{\sqrt{2}}). \tag{5.59}$$

In order to deduce the terms corresponding to the superoperator coupling in equation (5.59), one must consider the superoperator coupling defined by both a simple **a** field operator and an $\mathbf{f}_3$ field operator acting on the reference state. Since this second triplet state is generated by the linear combination of two different determinants, the evaluation of the following superoperator couplings

$$(a_{l\alpha}|\widehat{H}a_{l\alpha}) \tag{5.60}$$

and

$$(a^\dagger_{S\beta}a_{l\beta}a_{S\alpha}|\widehat{H}a^\dagger_{S\beta}a_{l\beta}a_{S\alpha}) \tag{5.61}$$

and their cross terms:

$$(a^\dagger_{S\beta}a_{l\beta}a_{S\alpha}|\widehat{H}a_{l\alpha}), \tag{5.62}$$

and

$$(a_{l\alpha}|\widehat{H}a^{\dagger}_{S\beta}a_{l\beta}a_{S\alpha}). \tag{5.63}$$

are necessary for the correct description of this triplet state. Considering the N-electron determinant (5.57) as a determinant reference, one can easily show that the evaluation of the annihilation of an α electron (5.60) reads:

$$F_{l\alpha l\alpha}. \tag{5.64}$$

On the other hand, the evaluation of the string of operators that represent the annihilation of a beta electron in the double occupied orbital l and the electron spin change in the orbital s (5.61) yields

$$\begin{aligned}
&(F_{S\alpha S\alpha} - F_{S\beta S\beta})[k_{S\alpha}k_{l\beta} - k_{S\beta}k_{S\alpha} + k_{S\beta} - k_{S\beta}k_{l\beta}] + F_{l\beta l\beta}[k_{S\alpha}k_{l\beta} - k_{S\beta}k_{S\alpha} + k_{S\beta} - k_{S\beta}k_{l\beta}] \\
&+ g_{SSSS}[k_{S\beta}k_{l\beta}k_{S\beta} - k_{S\beta}k_{S\beta} - k_{S\alpha}k_{S\beta}k_{S\alpha} + k_{S\alpha}k_{S\beta} + k_{S\alpha}k_{l\beta}k_{S\alpha} - 2k_{S\alpha}k_{l\beta}k_{S\beta} + k_{S\beta}k_{S\alpha}k_{S\beta}] \\
&+ g_{lSlS}[k_{S\beta}k_{S\alpha}k_{S\beta} - k_{S\beta}k_{S\beta} + k_{S\beta}k_{S\alpha}k_{S\alpha} - 2k_{S\beta}k_{S\alpha} - k_{S\alpha}k_{l\beta}k_{S\alpha} + k_{S\beta}k_{l\beta}k_{S\beta} + k_{S\alpha}k_{l\beta} \\
&- k_{S\beta}k_{l\beta} + k_{S\beta}]
\end{aligned} \tag{5.65}$$

where g_{PQRS} represents the two–electron integral given by $\langle PQ||RS\rangle$ (Dirac notation) and k_{x,s_x} represent the occupational number of the orbital x with spin s_x. Considering the fact that in the reference determinant the s orbital is a singly occupied orbital with just one α electron, one may assume that the occupation numbers $k_{S\beta}$ and $k_{S\alpha}$ are equal to zero and one respectively. Therefore, the equation obtained for the superoperator coupling yields

$$(F_{S\alpha S\alpha} - F_{S\beta S\beta})[k_{l\beta}] + F_{l\beta l\beta}[k_{l\beta}] + g_{SSSS}[k_{l\beta}] \tag{5.66}$$

In order to further simplify equation (5.66) one must consider some physical aspect of the system under study. The Fock matrix $F_{S\alpha S\alpha}$ is the term that describes the interactions of the electron α in the orbital S with the electrons located in others orbitals. Thus, one may express $F_{S\beta S\beta}$ matrix by

$$F_{S\beta S\beta} = F_{S\alpha S\alpha} + J_{S\alpha S\alpha}, \tag{5.67}$$

where $J_{S\alpha S\alpha}$ represents a Coulomb repulsion integral[2]. In the same fashion the $F_{l\beta l\beta}$ matrix may be written as

$$F_{l\beta l\beta} = F_{l\alpha l\alpha} + K_{l\alpha S\alpha}, \tag{5.68}$$

---

[2] In Dirac notation the two electron integral may be represented as $\langle ab||ab\rangle = \langle ab|ab\rangle - \langle ab|ba\rangle = J_{ab} - K_{ab}$.

where $K_{l\alpha S\alpha}$ represents an exchange integral. Therefore, equation (5.66) may be reduced to:

$$F_{l\beta l\beta}. \tag{5.69}$$

For the cross terms (5.62) and (5.63), the evaluation of the superoperator couplings read

$$g_{lSSl}[k_{S\alpha}k_{l\beta} + k_{S\beta} - k_{S\beta}k_{l\beta} - k_{S\beta}k_{S\alpha}], \tag{5.70}$$

and

$$g_{lSlS}[k_{S\beta}k_{l\beta} - k_{S\beta} + k_{S\beta}k_{S\alpha} - k_{S\alpha}k_{l\beta}]. \tag{5.71}$$

Finally, after the corresponding algebraic substitutions and taking in account the normalization factor of $\frac{1}{2}$ the equation (5.59) reads

$$F_{l\beta l\beta} \tag{5.72}$$

5.5.4 Formulation of the singlet state ($M_s = 0$ $S = 0$)

The singlet state corresponds to the difference of the two determinants generated by the evaluation of a simple field annihilation operator and a string of field operators that remove the α electron from the singly occupied orbital s and excites to that orbital a β electron from a doubly occupied orbital,

$$((a_{l\alpha} - a^{\dagger}_{S\beta}a_{S\alpha}a_{l\beta})|\widehat{H}(a_{l\alpha} - a^{\dagger}_{S\beta}a_{S\alpha}a_{l\beta})). \tag{5.73}$$

Using similar arguments as the ones used for the deduction of the second triplet state, the coupling that represents the formulation of the singlet state with quantum numbers $M_s = 0$ and $S = 0$ yields

$$((a_{l\alpha} - a^{\dagger}_{S\beta}a_{S\alpha}a_{l\beta})|\widehat{H}(a_{l\alpha} - a^{\dagger}_{S\beta}a_{S\alpha}a_{l\beta})) = \frac{F_{l\alpha l\alpha} - K_{l\alpha S\alpha} - K_{l\alpha S\alpha} + F_{l\beta l\beta} + F_{S\alpha S\alpha} - F_{S\beta S\beta} - J_{l\alpha S\alpha} + J_{S\alpha S\alpha} + J_{S\alpha l\alpha} - K_{S\alpha l\alpha}}{2} \tag{5.74}$$

which reduces to

$$((a_{l\alpha} - a^{\dagger}_{S\beta}a_{S\alpha}a_{l\beta})|\widehat{H}(a_{l\alpha} - a^{\dagger}_{S\beta}a_{S\alpha}a_{l\beta})) = F_{l\beta l\beta} - 2K_{l\alpha S\alpha} \tag{5.75}$$

These deductions obtained using the superoperator theory for the characterization of the ionization process with a single ROHF reference determinant have direct resemblance to the coupling coefficients of the ROHF Fock matrix obtained by B. N. Plakhutin

[123–125]. Therefore, using the Plakhutin ROHF Fock matrix scheme, one may use the ROHF orbital energies to obtain the self–energy matrix of the different electron propagator approximations for the calculation of binding energies in which the spin contamination does not allow the used of a UHF reference determinant. Although the orbital energies obtained by Plakhutin's scheme recover the physical interpretation of the orbital energies such that Koopmans's theorem may be applied in the framework of the ROHF approximation, this approach may not be applicable to all systems or cases. In order to correctly describe the correlation and orbital relaxation effects produced in the electron detachment process a reformulation of the electron propagator self–energy matrix is needed. Therefore, a more general procedure for the generation of orbital correlation and relaxation corrections to improve Koopmans's theorem values for the binding energies of open–shell systems is still needed.

6

Multireference open–shell electron propagator

> *Innovation distinguishes between a leader and a follower.*
>
> — **Steve Jobs**
> (CEO Apple Inc.)

For the proper description of open–shell atoms and molecules, an accurate treatment of non–dynamic (also known as static) correlation is needed. Static correlation results from the interaction of degenerate or near–degenerate configurations. Thus, atoms and molecules that present this type of configurations at certain geometries cannot be described correctly by a single determinant. In quantum chemistry, approximations based on methods such as the second–order Møller–Plesset perturbation theory (MP2) or coupled cluster (CC) theory may capture part of electron correlation that results from the instantaneous interaction between individual electrons (the so–called dynamic correlation). However, these methods are single–reference methods and while they may offer an improvement to the accuracy of the computed result when compared to the experiment, these methods may work only when the reference determinant used is a qualitatively correct first description for the molecular system. Static electron correlation may be accounted for by using multi–determinant methods such as the multi–configurational self–consistent field (MCSCF) [139] method or the complete active space SCF (CASSCF) [140] method. Furthermore, non–dynamic correlation may recoverable via the multi–reference CI (MRCI) [141] or the MRPT [142] method. However, the computational demands for these methods increase exponentially limiting their use for large molecules and basis sets. An alternative may be found in the spin–flip (SF) methods [143–148]. SF methods are multi–reference methods based on the idea that, in principle, in a high–spin reference state there is not entanglement between degenerate open–shell orbitals. Therefore, in SP methods, the electron excitations considered in each of their approaches are spin–flipped from a high–spin $m + 1$ state to give a multi–reference $|s, m\rangle$ state, where s indicates the quantum numbers associated with the $\hat{S}^2$ operator, whereas m is the quantum number associated with the $\hat{S}_z$ operator. In this chapter, a new formulation for the self-energy matrix of the electron–propagator will be presented.This new formulation for the electron propagator is based on the ideas of the spin-flip technique and intended for open–shell molecules in which spin–contamination represents a challenge in the calculation of correct and accurate ionization energies.

6.1 The spin–flip technique

The spin–flip (SF) methods are single–reference electronic structure approximations designed for describing strongly correlated systems. The spin–flip approach allows to formulate and implement any truncated configuration interaction (CI) scheme such that the resulting SF–CI energies are both variational and size–consistent. The spin–flip approach operates under the idea that for many multi–configurational (or strongly correlated) electronic states, there exists a higher spin state that may be higher in energy but that is well described with a single electronic configuration. The simplest spin–flip model employs a self consistent field wave–function for the reference state, and the resulting equations for target states are therefore identical to configuration interaction singles. In the spin–flip approach, however, the Hamiltonian is diagonalized only in the basis of single $\alpha \rightarrow \beta$ excitations from the reference determinant. The most simple SF methods rely on an open–shell high-spin reference determinant ($S = 1$) upon which a series of single spin–flipped excitations that produces a $\Delta S = 1$ are generated. Therefore, unlike a CASSCF(2,2) calculation, in which two active electrons in two active orbitals are needed, the spin–flip approach offers a quasi–two–electron two orbitals active space in the singly occupied orbitals, and allows for double excitations within this active space.

6.1.1 Spin–flip and the spin–contamination problem

Despite the spin–flip approach's advantages, in general, the resultant states from the SP approach are not spin eigenfunctions [146], *i.e*, eigenfunction of the $\hat{S}^2$ operator. It has been observed that excited states, and in many cases the ground state, are significantly spin–contaminated, that is, they are a mixture of $s = m, m+1, m+2, \ldots$. It is well known that large spin–contamination may easily cause not only inaccurate excitation energies but also lead to incorrect assignment of spectrum. This problem prevails even when restricted open–shell Hartree–Fock (ROHF) reference determinants are used. This problem that the SP methods have with spin–contamination may be attributed to the neglect of spin–coupled counterparts of the SF–configuration space.

A spin correct wave function may be obtained by partitioning the orbital space of the reference restricted open–shell Hartree–Fock determinant into three subspaces: the doubly occupied, the singly occupied, and the virtual space, see figure 6.1. Thus, a wave–function that is an eigenfunction of the $\hat{S}^2$ operator may be obtained by imposing the constraint that all determinants in the wave–function have an M_S quantum number equal to zero and allowing the doubly occupied space to lose one electron and the virtual space to gain one electron.

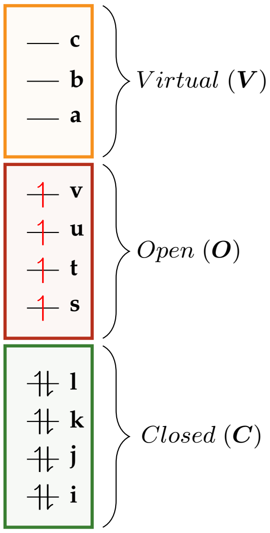


Fig. 6.1.: Partitioned ROHF reference determinant

6.1.2 Spin–flip for ionization energies

The spin–flip ideas for the correct treatment of atoms and molecules with a multi–configurational nature, can be used for the calculation of electron detachment energies. Take for example an open–shell reference state with a singly occupied orbital (*i.e.*, a doublet state), the elimination of one particle may change the z–projection of the total spin moment, ΔS_z , by $\pm\frac{1}{2}$. When $\Delta S_z = -\frac{1}{2}$ the state produced after the electron removal is a singlet. The transition from a doublet to a singlet due to a removal of an electron from a N electronic state to a $N-1$ electronic state may be described by a simple field operator $\mathbf{a}$, and the $\mathbf{f_3}$ field operator that represent the electron removal and a spin–flip excitation, as shown in figure 6.4. In the framework of the electron propagator theory, these two operators may be regarded as a multi–reference Koopmans's theorem picture of the ionization energy. However, in order to further consider orbital relaxation and correlation corrections, a set of field operator that represent higher order excitations need to be consider. Therefore, a new partition of the superoperator Hamiltonian and

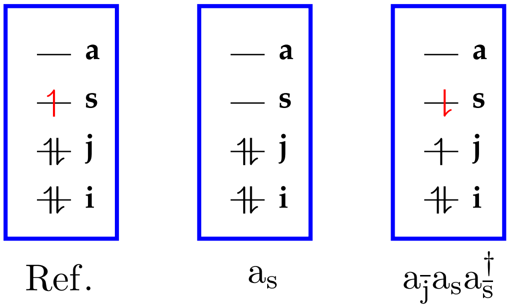


Fig. 6.2.: Doublet reference determinant and the resulting determinants produced after the removal of an electron.

the inclusion of extra spin–flip operators not only of $2hp$ and $2ph$ type but also of the $3h2p$ and $3p2h$ type need to be included.

6.2 Spin–flip in electron propagator theory

In order to introduce the spin–flip technique to the electron propagator formalism, a new partitioning of the superoperator Hamiltonian needs to be formulated. The usual partition of the superoperator Hamiltonian matrix is blocked and divided into a primary space (**P**) and a secondary space with three blocks (**S**),

$$\hat{\mathbf{H}} = \left[\begin{array}{c|c} \mathbf{P} & \mathbf{S} \\ \hline \mathbf{S} & \mathbf{S} \end{array}\right]. \tag{6.1}$$

The primary block of the superoperator Hamiltonian is usually formed by simple field operators $\mathbf{a}$, whereas the secondary block is formed by $\mathbf{f_3}$ field operators. For the introduction of the spin–flip operators, however, the primary space of the superoperator matrix will now contain in addition to the simple field operators, $\mathbf{f_3}$ field operators that corresponds to the single $\alpha \rightarrow \beta$ excitation from the reference determinant formed after the application of the $\mathbf{a}$ operator on the initial reference determinant. Thus, the new partition of the superoperator Hamiltonian takes the form:

$$\hat{\mathbf{H}} = \left[\begin{array}{c|c} \begin{array}{c|c} \mathbf{P} & \mathbf{S} \\ \hline \mathbf{S} & \mathbf{S} \end{array} & \mathbf{S} \\ \hline \mathbf{S} & \mathbf{S} \end{array}\right] \tag{6.2}$$

6.2.1 Redefinition of the primary block

For the new superoperator Hamiltonian, which takes into consideration the spin–flip operator, the primary space is now defined as

$$\hat{\mathbf{H}}_{\boldsymbol{P}} = \begin{bmatrix} (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{a}) & (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f_3}) \\ (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f_3}) & (\mathbf{f_3}|\widehat{\mathrm{H}}\mathbf{f_3}) \end{bmatrix} \tag{6.3}$$

The application of a simple field operator **a** to this reference determinant may remove either an electron from a singly occupied orbital or a doubly occupied orbital, which may produce two different final states: For the definition of the primary space, $\mathbf{f_3}$ spin–flip field operators that only consider the doubly occupied and singly occupied orbital spaces of the original reference determinant will be considered. Thus, this $\mathbf{f_3}$ spin–flip field operator may produce final reference states in which an α electron has been removed from one of the doubly occupied orbitals and one of the open–shell orbitals has changed the spin of its electron from α to β, see figure 6.4.

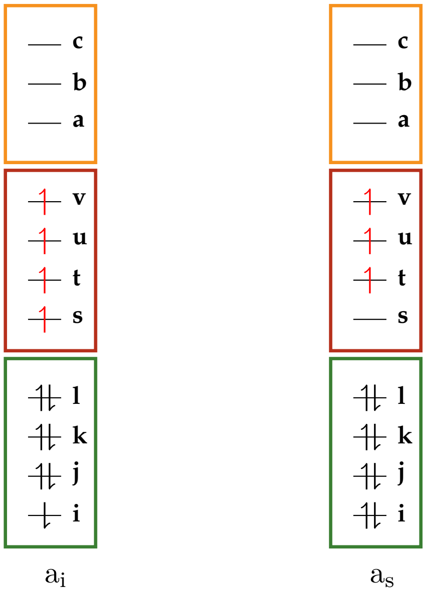


Fig. 6.3.: h field operators for the primary space.

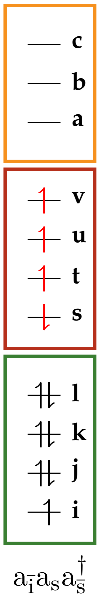


Fig. 6.4.: $2hp$ spin–flip field operator corresponding to the primary space.

Similarly, the complementary one–particle (p) and two–particle one–hole ($2ph$) field operators that need to be considered for the primary sector of the superoperator Hamiltonian may be represented as in figure 6.8. In order to have a correct description

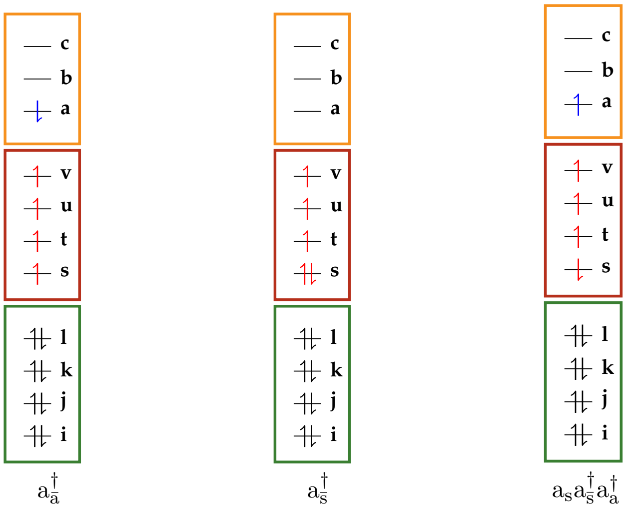


Fig. 6.5.: p and $2ph$ operators for the primary space.

of the important correlation effect for the molecular system, this primary space will be considered in first order. Therefore, a general representation for the primary block of the superoperator Hamiltonian may be expressed as

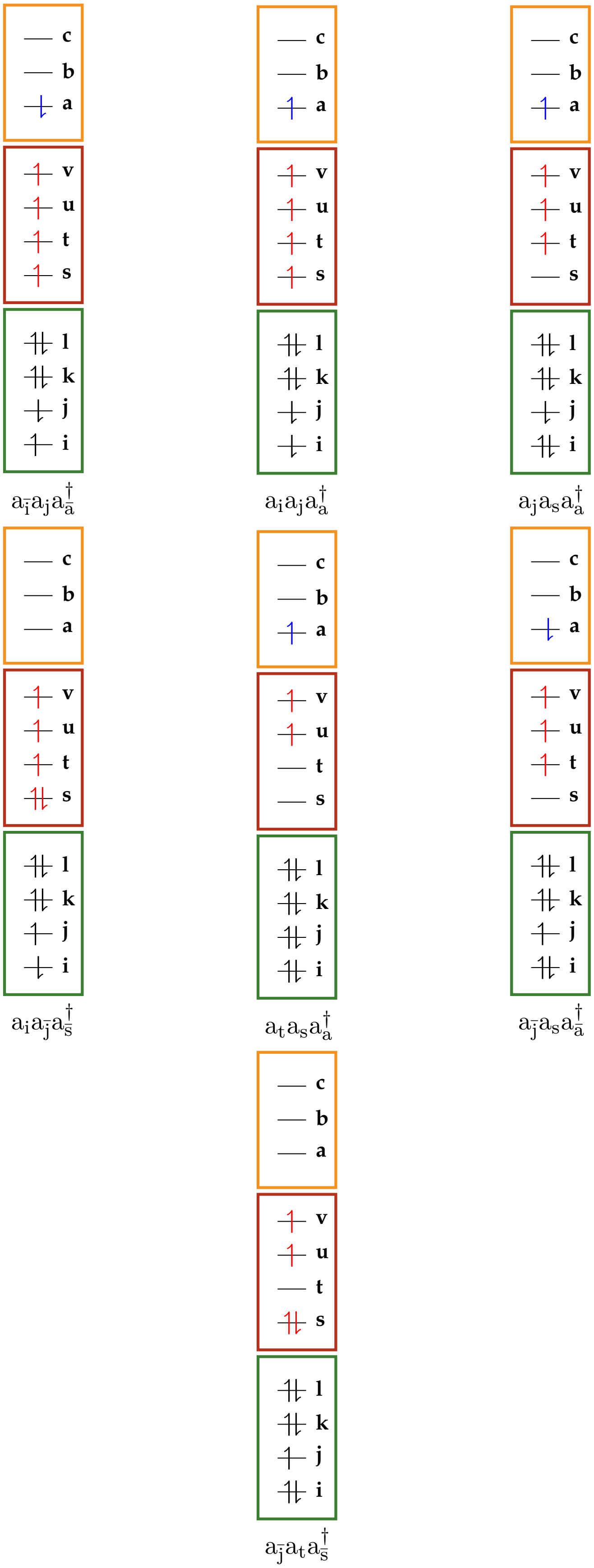
$$\widehat{\mathbf{H}}^{(\mathbf{1})}_{\boldsymbol{PP}} = \begin{array}{c} \\ a_j \\ a^\dagger_{\bar t} a_t a_{\bar j} \\ a_t \\ a_b \end{array} \begin{array}{c} \begin{array}{cccc} a_k & a^\dagger_{\bar u} a_u a_{\bar k} & a_u & a_c \end{array} \\ \begin{pmatrix} F_{kj} & \langle u\bar k \| j\bar u\rangle & F_{uj} & F_{cj} \\ \langle \bar t k \| t\bar j\rangle & (a^\dagger_{\bar t} a_t a_{\bar j} | \widehat{H} a^\dagger_{\bar u} a_u a_{\bar k})^{(1)} & \langle \bar t u \| t\bar j\rangle & \langle \bar t c \| t\bar j\rangle \\ F_{kt} & -\langle u\bar k \| t\bar u\rangle & F_{ut} & F_{ct} \\ F_{kb} & -\langle u\bar k \| b\bar u\rangle & F_{ub} & F_{cb} \end{pmatrix} \end{array} \tag{6.4}$$

When the Brillouin theorem is considered this matrix may be expressed as

$$\widehat{\mathbf{H}}^{(\mathbf{1})}_{\boldsymbol{PP}} = \begin{array}{c} \\ a_j \\ a^\dagger_{\bar t} a_t a_{\bar j} \\ a_t \\ a_b \end{array} \begin{array}{c} \begin{array}{cccc} a_k & a^\dagger_{\bar u} a_u a_{\bar k} & a_u & a_c \end{array} \\ \begin{pmatrix} F_{kj} & \langle u\bar k \| j\bar u\rangle & F_{uj} & 0 \\ \langle \bar t k \| t\bar j\rangle & (a^\dagger_{\bar t} a_t a_{\bar j} | \widehat{H} a^\dagger_{\bar u} a_u a_{\bar k})^{(1)} & \langle \bar t u \| t\bar j\rangle & \langle \bar t c \| t\bar j\rangle \\ F_{kt} & -\langle u\bar k \| t\bar u\rangle & F_{ut} & 0 \\ 0 & -\langle u\bar k \| b\bar u\rangle & 0 & F_{cb} \end{pmatrix} \end{array}. \tag{6.5}$$

6.2.2 Redefinition of the secondary block

In order to achieve a correct description of the final states, determinants corresponding to $2hp$, $2ph$, $3h2p$ and $3p2h$ processes need to be considered. These determinants can only be accessed by the application of $\mathbf{f_3}$ and $\mathbf{f_5}$ field operators to the initial single reference determinant. Thus, in the case of the $\mathbf{f_3}$ field operators, the corresponding $2hp$ operators may be represented as:



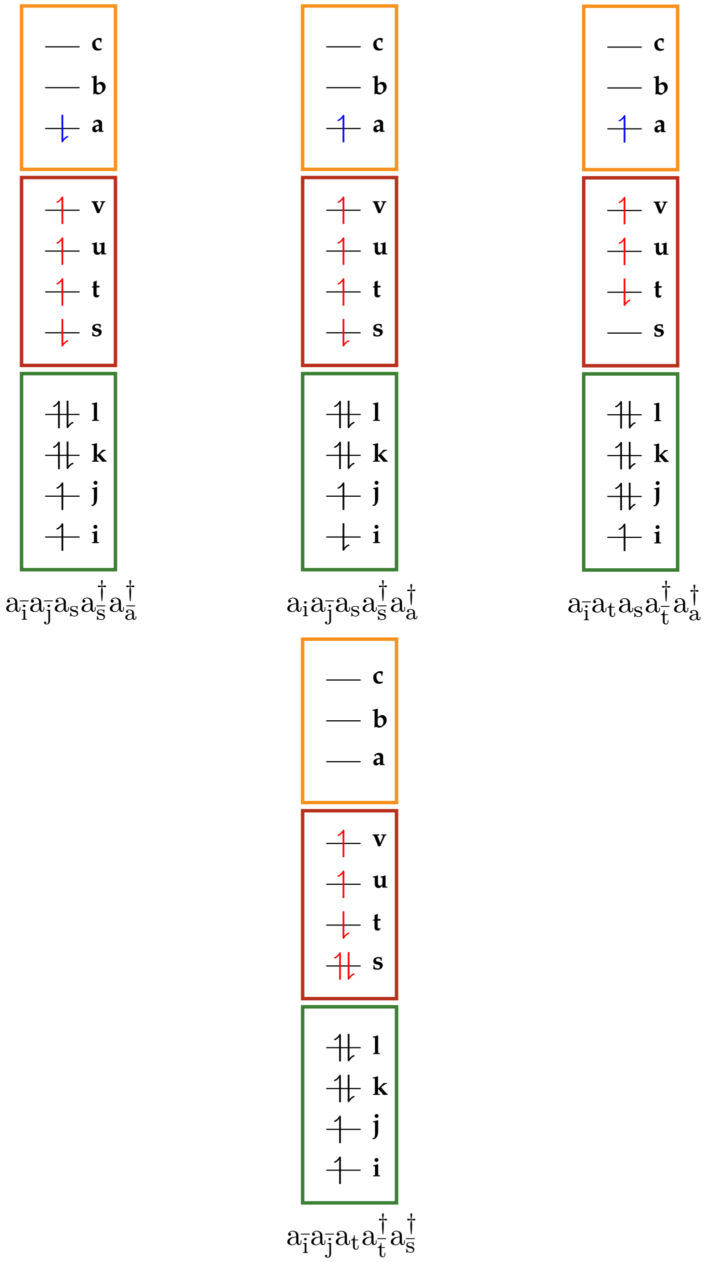
$a_{\bar{i}} a_j a^{\dagger}_{\bar{a}}$ $a_i a_j a^{\dagger}_{a}$ $a_j a_s a^{\dagger}_{a}$

$a_i a_{\bar{j}} a^{\dagger}_{\bar{s}}$ $a_t a_s a^{\dagger}_{a}$ $a_{\bar{j}} a_s a^{\dagger}_{\bar{a}}$

$a_{\bar{j}} a_t a^{\dagger}_{\bar{s}}$

Fig. 6.6.: $2hp$ operators for the secondary space.

On the other hand, for the $3h2p$ processes, which correspond to the $\mathbf{f}_5$ field operators, the field operators needed may be represented as:



$a_{\bar{i}} a_{\bar{j}} a_s a_{\bar{s}}^\dagger a_{\bar{a}}^\dagger$

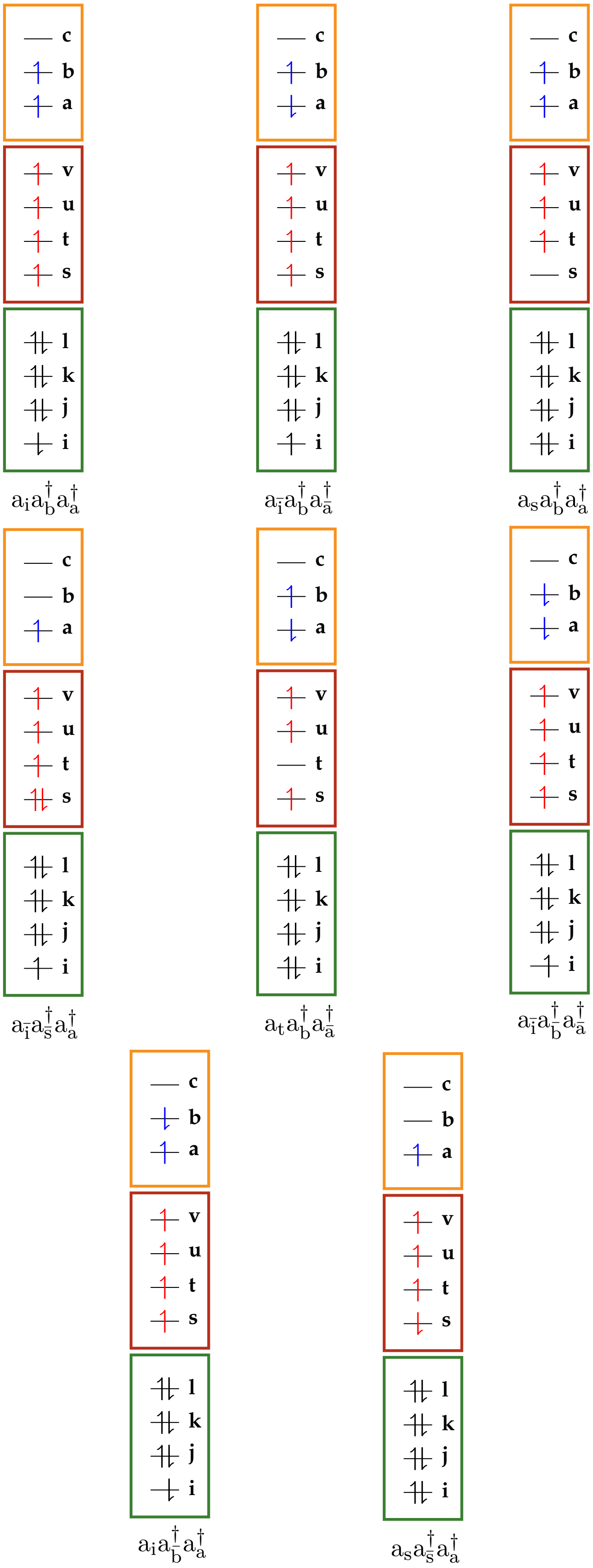
$a_i a_{\bar{j}} a_s a_{\bar{s}}^\dagger a_a^\dagger$

$a_{\bar{i}} a_t a_s a_{\bar{t}}^\dagger a_a^\dagger$

$a_{\bar{i}} a_{\bar{j}} a_t a_{\bar{t}}^\dagger a_{\bar{s}}^\dagger$

Fig. 6.7.: $3h2p$ operators for the secondary space.

Similarly, for the complementary part that corresponds to the two–particle one–hole $\mathbf{F}_3$ field operators, the field operators to be considered are:



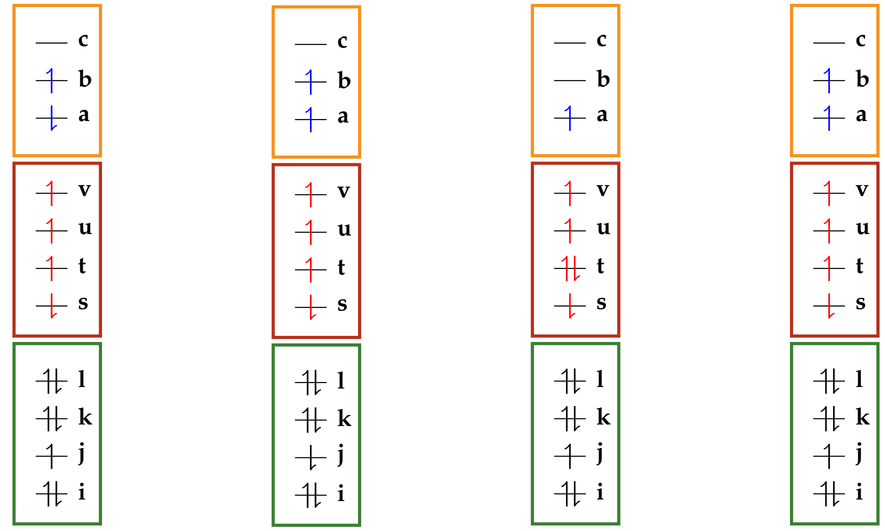
$a_i a_b^\dagger a_a^\dagger$ $a_{\bar{i}} a_b^\dagger a_{\bar{a}}^\dagger$ $a_s a_b^\dagger a_a^\dagger$

$a_{\bar{i}} a_{\bar{s}}^\dagger a_a^\dagger$ $a_t a_b^\dagger a_{\bar{a}}^\dagger$ $a_{\bar{i}} a_{\bar{b}}^\dagger a_{\bar{a}}^\dagger$

$a_i a_{\bar{b}}^\dagger a_a^\dagger$ $a_s a_{\bar{s}}^\dagger a_a^\dagger$

Fig. 6.8.: $2ph$ operators for the secondary space

For the three–particle two–hole operators, the field operators may be represented as



$a_{\bar{j}} a_s a^\dagger_{\bar{s}} a^\dagger_b a^\dagger_{\bar{a}}$ $a_j a_s a^\dagger_{\bar{s}} a^\dagger_b a^\dagger_a$ $a_{\bar{j}} a_s a^\dagger_{\bar{s}} a^\dagger_{\bar{t}} a^\dagger_a$ $a_{\bar{j}} a_s a^\dagger_{\bar{s}} a^\dagger_b a^\dagger_a$

Fig. 6.9.: $3p2h$ operators for the secondary space

6.3 Multi–reference ROHF propagator

The novelty of the new formulation of the electron propagator for computing the ionization energies of open–shell molecules consists in the use of a single reference determinant to access final states with strong multi–configuration character. This single determinant will be improved using the spin–flip technique. The spin–flip operator will allow the consideration of different determinants for the correct description of the final state. As the initial reference determinant, the restricted open–shell Hartree–Fock determinant will be used in order to reduce spin contamination. Correct quantum numbers for the final states will be obtained by allowing doubly occupied orbitals to lose one electron and the virtual space to gain one electron. For obtaining the different correlation and orbital relaxation corrections for the different configurations that may be considered, $\mathbf{f}_3$ and $\mathbf{f}_5$ field operator manifolds will be employed in the superoperator Hamiltonian. However, not all the possible combinations of $\mathbf{f}_3$ and $\mathbf{f}_5$ field operator will be used. Only those operators that generate a $\Delta S_z = -0.5$ with respect to the reference determinant will be used. Also, these field operator manifolds will be restricted to act only on certain orbital blocks of the orbital partition presented in figure 6.1. In this respect, the poles of the corresponding electron propagator may be recovered by the superoperator Hamiltonian matrix:

$$\widehat{\mathbf{H}} = \begin{array}{cccc|c} \mathbf{a} & \mathbf{f_3^P} & \mathbf{f_3^Q} & \mathbf{f_5^Q} & \\ \hline (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{a}) & (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f_3^P}) & (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f_3^Q}) & (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f_5^Q}) & \mathbf{a} \\ (\mathbf{f_3^P}|\widehat{\mathrm{H}}\mathbf{a}) & (\mathbf{f_3^P}|\widehat{\mathrm{H}}\mathbf{f_3^P}) & (\mathbf{f_3^P}|\widehat{\mathrm{H}}\mathbf{f_3^Q}) & (\mathbf{f_3^P}|\widehat{\mathrm{H}}\mathbf{f_5^Q}) & \mathbf{f_3^P} \\ (\mathbf{f_3^Q}|\widehat{\mathrm{H}}\mathbf{a}) & (\mathbf{f_3^Q}|\widehat{\mathrm{H}}\mathbf{f_3^P}) & (\mathbf{f_3^Q}|\widehat{\mathrm{H}}\mathbf{f_3^Q}) & (\mathbf{f_3^Q}|\widehat{\mathrm{H}}\mathbf{f_5^Q}) & \mathbf{f_3^Q} \\ (\mathbf{f_5^Q}|\widehat{\mathrm{H}}\mathbf{a}) & (\mathbf{f_5^Q}|\widehat{\mathrm{H}}\mathbf{f_3^P}) & (\mathbf{f_5^Q}|\widehat{\mathrm{H}}\mathbf{f_3^Q}) & (\mathbf{f_5^Q}|\widehat{\mathrm{H}}\mathbf{f_5^Q}) & \mathbf{f_5^Q} \end{array} \tag{6.6}$$

where the superscripts P and Q indicate the primary and secondary sectors respectively. For the definition of the new electron propagator approach for open–shell molecules, the blocks of the superoperator Hamiltonian matrix will be evaluated using perturbations of different orders. The primary space will be evaluated in its totality in first order of perturbation and only simple field operators, $\mathbf{a}$, that reduce the number of electrons from N to $N-1$ and spin–flip operators $\mathbf{f_3}$ that represent the removal of an electron from a double occupied orbital and the spin change from α to β in a singly occupied orbital will be considered. On the other hand, for the secondary blocks of the superoperator Hamiltonian matrix, the couplings between the primary and secondary blocks will be evaluated in first order, whereas the secondary–secondary block will be evaluated in zeroth order. For the secondary space, the manifold of field operators that will be used consists of seven different types of $\mathbf{f_3}$ field operator and only four types of $\mathbf{f_5}$ field operators. The different string of field operators that will be used for the definition of the secondary block are summarized in table 6.1.

Strings of field operators			
No	ID	Bra	Ket
1	$\mathbf{F_3^{I}}$	$a_{\bar{b}}^{\dagger}a_l a_{\bar{k}}$	$a_{\bar{a}}^{\dagger}a_j a_{\bar{i}}$
2	$\mathbf{F_3^{II}}$	$a_{b}^{\dagger}a_l a_k$	$a_{a}^{\dagger}a_j a_i$
3	$\mathbf{F_3^{III}}$	$a_{b}^{\dagger}a_u a_l$	$a_{a}^{\dagger}a_s a_j$
4	$\mathbf{F_3^{IV}}$	$a_{\bar{u}}^{\dagger}a_k a_{\bar{l}}$	$a_{\bar{s}}^{\dagger}a_i a_{\bar{j}}$
5	$\mathbf{F_3^{V}}$	$a_{b}^{\dagger}a_u a_v$	$a_{a}^{\dagger}a_s a_t$
6	$\mathbf{F_3^{VI}}$	$a_{\bar{b}}^{\dagger}a_u a_{\bar{l}}$	$a_{\bar{a}}^{\dagger}a_s a_{\bar{j}}$
7	$\mathbf{F_3^{VII}}$	$a_{\bar{u}}^{\dagger}a_v a_{\bar{l}}$	$a_{\bar{s}}^{\dagger}a_t a_{\bar{j}}$
8	$\mathbf{F_5^{I}}$	$a_{\bar{b}}^{\dagger}a_{\bar{u}}^{\dagger}a_u a_{\bar{l}} a_{\bar{k}}$	$a_{\bar{a}}^{\dagger}a_{\bar{s}}^{\dagger}a_s a_{\bar{j}} a_{\bar{i}}$
9	$\mathbf{F_5^{II}}$	$a_{b}^{\dagger}a_{\bar{u}}^{\dagger}a_u a_{\bar{l}} a_k$	$a_{a}^{\dagger}a_{\bar{s}}^{\dagger}a_s a_{\bar{j}} a_i$
10	$\mathbf{F_5^{III}}$	$a_{b}^{\dagger}a_{\bar{v}}^{\dagger}a_u a_v a_{\bar{k}}$	$a_{a}^{\dagger}a_{\bar{t}}^{\dagger}a_s a_t a_{\bar{i}}$
11	$\mathbf{F_5^{VI}}$	$a_{\bar{u}}^{\dagger}a_{\bar{v}}^{\dagger}a_v a_{\bar{l}} a_{\bar{k}}$	$a_{\bar{s}}^{\dagger}a_{\bar{t}}^{\dagger}a_t a_{\bar{j}} a_{\bar{i}}$

Tab. 6.1.: $\mathbf{f_3}$ and $\mathbf{f_5}$ operators that will be consider for the definition of the secondary space

Thus, the superoperator Hamiltonian matrix that recovers the poles of this new propagator approximation may be rewritten as

$$\widehat{\mathbf{H}} = \begin{array}{c} \\ \\ \\ \\ \\ \end{array}\begin{array}{cccc} \mathbf{a} & \mathbf{f}_3^{\mathbf{P}} & \mathbf{f}_3^{\mathbf{Q}} & \mathbf{f}_5^{\mathbf{Q}} \end{array}$$

$$\widehat{\mathbf{H}} = \begin{array}{ccccc} \mathbf{a} & \mathbf{f}_3^{\mathbf{P}} & \mathbf{f}_3^{\mathbf{Q}} & \mathbf{f}_5^{\mathbf{Q}} & \\ (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{a})^{(1)} & (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f}_3^{\mathbf{P}})^{(1)} & (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f}_3^{\mathbf{Q}})^{(1)} & (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f}_5^{\mathbf{Q}})^{(1)} & \mathbf{a} \\ (\mathbf{f}_3^{\mathbf{P}}|\widehat{\mathrm{H}}\mathbf{a})^{(1)} & (\mathbf{f}_3^{\mathbf{P}}|\widehat{\mathrm{H}}\mathbf{f}_3^{\mathbf{P}})^{(1)} & (\mathbf{f}_3^{\mathbf{P}}|\widehat{\mathrm{H}}\mathbf{f}_3^{\mathbf{Q}})^{(1)} & (\mathbf{f}_3^{\mathbf{P}}|\widehat{\mathrm{H}}\mathbf{f}_5^{\mathbf{Q}})^{(1)} & \mathbf{f}_3^{\mathbf{P}} \\ (\mathbf{f}_3^{\mathbf{Q}}|\widehat{\mathrm{H}}\mathbf{a})^{(1)} & (\mathbf{f}_3^{\mathbf{Q}}|\widehat{\mathrm{H}}\mathbf{f}_3^{\mathbf{P}})^{(1)} & (\mathbf{f}_3^{\mathbf{Q}}|\widehat{\mathrm{H}}\mathbf{f}_3^{\mathbf{Q}})^{(0)} & (\mathbf{f}_3^{\mathbf{Q}}|\widehat{\mathrm{H}}\mathbf{f}_5^{\mathbf{Q}})^{(0)} & \mathbf{f}_3^{\mathbf{Q}} \\ (\mathbf{f}_5^{\mathbf{Q}}|\widehat{\mathrm{H}}\mathbf{a})^{(1)} & (\mathbf{f}_5^{\mathbf{Q}}|\widehat{\mathrm{H}}\mathbf{f}_3^{\mathbf{P}})^{(1)} & (\mathbf{f}_5^{\mathbf{Q}}|\widehat{\mathrm{H}}\mathbf{f}_3^{\mathbf{Q}})^{(0)} & (\mathbf{f}_5^{\mathbf{Q}}|\widehat{\mathrm{H}}\mathbf{f}_5^{\mathbf{Q}})^{(0)} & \mathbf{f}_5^{\mathbf{Q}} \end{array} \tag{6.7}$$

For this superoperator Hamiltonian matrix, the expression of the different terms resulting from the coupling of the field operators used in defining the primary space are reported in table 6.2. Using the operators listed in table 6.1 the secondary–secondary block of the superoperator Hamiltonian may be represented as in equation (6.8). Since a single ROHF determinant is used as a reference determinant, due to the effects of the Brillouin theorem, several of the field operator couplings vanish in zeroth order as shown in table 6.3. The expressions obtained for the couplings of the different set of field operators are reported in tables 6.4–6.7. For the coupling between the primary and the secondary field operator spaces, the expressions for the superoperator Hamiltonian matrix terms depend on the Fock matrices and two electron–integrals. The expressions for these couplings are reported in tables 6.8–6.10. Complete deduction and details about the notation of the coupling terms between field operators are given in appendices A, B and C

F		$\mathbf{a}$			$\mathbf{f}_3^{\mathbf{P}}$
		a_i	a_s	a_a	$a^\dagger_{\bar{s}}a_s a_{\bar{i}}$
$\mathbf{a}$	a_k	F_{ik}	F_{sk}	F_{ak}	$-\langle s\bar{i}\|k\bar{s}\rangle$
	a_u	F_{iu}	F_{su}	F_{au}	$-\delta_{us}\mathbf{F}_{\bar{s}\bar{i}} - \langle s\bar{i}\|u\bar{s}\rangle$
	a_b	F_{ib}	F_{sb}	F_{ab}	$-\langle s\bar{i}\|b\bar{s}\rangle$
$\mathbf{f}_3^{\mathbf{P}}$	$a^\dagger_{\bar{u}}a_u a_{\bar{k}}$	$\langle \bar{u}i\|u\bar{k}\rangle$	$\langle \bar{u}s\|u\bar{k}\rangle$	$\langle \bar{u}a\|u\bar{k}\rangle$	$\mathbf{F}_{\bar{i}\bar{k}}\delta_{\bar{u}\bar{s}}\delta_{us} + \mathbf{F}_{su}\delta_{\bar{u}\bar{s}}\delta_{\bar{k}\bar{i}} - \mathbf{F}_{\bar{u}\bar{s}}\delta_{su}\delta_{\bar{k}\bar{i}}$ $+ \langle s\bar{i}\|\bar{k}u\rangle\delta_{\bar{s}\bar{u}} + \langle \bar{u}\bar{i}\|\bar{s}\bar{k}\rangle\delta_{us} + \langle s\bar{u}\|u\bar{s}\rangle\delta_{\bar{k}\bar{i}}$

Tab. 6.2.: Primary Space terms

$$\hat{\mathbf{H}}_{QQ} = \begin{bmatrix}
(\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{V}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{VI}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_3^{\mathbf{VII}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_5^{\mathbf{I}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_5^{\mathbf{II}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_5^{\mathbf{III}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}}) \\
(\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{I}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{II}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{III}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{IV}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{V}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VI}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_3^{\mathbf{VII}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{I}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{II}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{III}}) & (\mathbf{F}_5^{\mathbf{IV}}|\hat{\mathbf{H}}\mathbf{F}_5^{\mathbf{IV}})
\end{bmatrix} \tag{6.8}$$

Structure of the Secondary Space in zero order

F	$a^\dagger_{\bar{a}}a_ja_{\bar{i}}$	$a^\dagger_a a_j a_i$	$a^\dagger_a a_s a_j$	$a^\dagger_{\bar{s}}a_i a_{\bar{j}}$	$a^\dagger_a a_s a_t$	$a^\dagger_{\bar{a}}a_s a_{\bar{j}}$	$a^\dagger_{\bar{s}}a_t a_{\bar{j}}$	$a^\dagger_{\bar{a}}a^\dagger_{\bar{s}}a_s a_{\bar{j}}a_{\bar{i}}$	$a^\dagger_a a^\dagger_{\bar{s}}a_s a_{\bar{j}}a_i$	$a^\dagger_a a^\dagger_{\bar{t}}a_s a_t a_{\bar{i}}$	$a^\dagger_{\bar{s}}a^\dagger_{\bar{t}}a_t a_{\bar{j}}a_{\bar{i}}$
$a^\dagger_{\bar{b}}a_l a_{\bar{k}}$	T	0	0	T	0	T	T	0	0	0	0
$a^\dagger_b a_l a_k$	0	T	T	0	0	0	0	0	0	0	0
$a^\dagger_b a_u a_l$	0	T	T	0	T	0	0	0	0	0	0
$a^\dagger_{\bar{u}}a_k a_{\bar{l}}$	T	0	0	T	0	T	T	0	0	0	0
$a^\dagger_b a_u a_v$	0	0	T	0	T	0	0	0	0	0	0
$a^\dagger_{\bar{b}}a_u a_{\bar{l}}$	T	0	0	0	0	T	T	0	0	0	0
$a^\dagger_{\bar{u}}a_v a_{\bar{l}}$	0	0	0	T	0	T	T	0	0	0	0
$a^\dagger_{\bar{b}}a^\dagger_{\bar{u}}a_u a_{\bar{l}}a_{\bar{k}}$	0	0	0	0	0	0	0	T	0	0	T
$a^\dagger_b a^\dagger_{\bar{u}}a_u a_{\bar{l}}a_k$	0	0	0	0	0	0	0	0	T	T	0
$a^\dagger_b a^\dagger_{\bar{v}}a_u a_v a_{\bar{k}}$	0	0	0	0	0	0	0	0	T	T	0
$a^\dagger_{\bar{u}}a^\dagger_{\bar{v}}a_v a_{\bar{l}}a_{\bar{k}}$	0	0	0	0	0	0	0	T	0	0	T

Tab. 6.3.: In the secondary–secondary block, the only couplings that do not banished are in green

$(\mathbf{f^Q}_3|\widehat{H}\mathbf{f^Q}_3)$ and $(\mathbf{f^Q}_3|\widehat{H}\mathbf{f^Q}_3)$ Terms

Coupling	Terms
$(a^\dagger_{\bar b} a_l a_{\bar k}\|\widehat{H} a^\dagger_{\bar a} a_j a_{\bar i})$	$\mathbf{F}_{\bar i\bar k}\delta_{\bar b\bar a}\delta_{lj} + \mathbf{F}_{jl}\delta_{\bar b\bar a}\delta_{\bar k\bar i} - \mathbf{F}_{\bar b\bar a}\delta_{jl}\delta_{\bar k\bar i}$ $+ \langle j\bar i\\|\bar k l\rangle\delta_{\bar a\bar b} + \langle \bar b\bar i\\|\bar a\bar k\rangle\delta_{lj} + \langle j\bar b\\|l\bar a\rangle\delta_{\bar k\bar i}$
$(a^\dagger_{\bar b} a_l a_{\bar k}\|\widehat{H} a^\dagger_{a} a_j a_{i})$	$\langle \bar b i\\|a\bar k\rangle\delta_{lj} - \langle \bar b j\\|a\bar k\rangle\delta_{li}$
$(a^\dagger_{\bar b} a_l a_{\bar k}\|\widehat{H} a^\dagger_{a} a_s a_{j})$	$\langle \bar b j\\|a\bar k\rangle\delta_{ls} - \langle \bar b s\\|a\bar k\rangle\delta_{lj}$
$(a^\dagger_{\bar b} a_l a_{\bar k}\|\widehat{H} a^\dagger_{\bar s} a_i a_{\bar j})$	$-\mathbf{F}_{\bar b\bar s}\delta_{il}\delta_{\bar k\bar j} + \langle \bar b\bar j\\|\bar s\bar k\rangle\delta_{li} + \langle i\bar b\\|l\bar s\rangle\delta_{\bar k\bar j}$
$(a^\dagger_{\bar b} a_l a_{\bar k}\|\widehat{H} a^\dagger_{a} a_s a_{t})$	0
$(a^\dagger_{\bar b} a_l a_{\bar k}\|\widehat{H} a^\dagger_{\bar a} a_s a_{\bar j})$	$\mathbf{F}_{sl}\delta_{\bar b\bar a}\delta_{\bar k\bar j} + \langle s\bar j\\|\bar k l\rangle\delta_{\bar a\bar b} + \langle s\bar b\\|l\bar a\rangle\delta_{\bar k\bar j}$
$(a^\dagger_{\bar b} a_l a_{\bar k}\|\widehat{H} a^\dagger_{\bar s} a_t a_{\bar j})$	$\langle t\bar b\\|l\bar s\rangle\delta_{\bar k\bar j}$
$(a^\dagger_{b} a_l a_{k}\|\widehat{H} a^\dagger_{\bar a} a_j a_{\bar i})$	$\langle b\bar i\\|\bar a k\rangle\delta_{lj} - \langle b\bar i\\|\bar a l\rangle\delta_{kj}$
$(a^\dagger_{b} a_l a_{k}\|\widehat{H} a^\dagger_{a} a_j a_{i})$	$\mathbf{F}_{ik}\delta_{ba}\delta_{lj} - \mathbf{F}_{il}\delta_{ab}\delta_{kj} - \mathbf{F}_{jk}\delta_{il}\delta_{ab} + \mathbf{F}_{jl}\delta_{ba}\delta_{ki} + \mathbf{F}_{ba}[-\delta_{jl}\delta_{ki} + \delta_{kj}\delta_{li}]$ $+ \langle ji\\|kl\rangle\delta_{ab} + \langle bi\\|ak\rangle\delta_{lj} - \langle bj\\|ak\rangle\delta_{li} - \langle bi\\|al\rangle\delta_{kj} + \langle jb\\|la\rangle\delta_{ki}$
$(a^\dagger_{b} a_l a_{k}\|\widehat{H} a^\dagger_{a} a_s a_{j})$	$-\mathbf{F}_{sk}\delta_{jl}\delta_{ab} + \mathbf{F}_{sl}\delta_{ba}\delta_{kj} + \langle sj\\|kl\rangle\delta_{ab} - \langle bs\\|ak\rangle\delta_{lj} + \langle sb\\|la\rangle\delta_{kj}$
$(a^\dagger_{b} a_l a_{k}\|\widehat{H} a^\dagger_{\bar s} a_i a_{\bar j})$	$\langle b\bar j\\|\bar s k\rangle\delta_{li} - \langle b\bar j\\|\bar s l\rangle\delta_{ki}$
$(a^\dagger_{b} a_l a_{k}\|\widehat{H} a^\dagger_{a} a_s a_{t})$	$\langle st\\|kl\rangle\delta_{ab}$
$(a^\dagger_{b} a_l a_{k}\|\widehat{H} a^\dagger_{\bar a} a_s a_{\bar j})$	0
$(a^\dagger_{b} a_l a_{k}\|\widehat{H} a^\dagger_{\bar s} a_t a_{\bar j})$	0
$(a^\dagger_{b} a_u a_{l}\|\widehat{H} a^\dagger_{\bar a} a_j a_{\bar i})$	$-\langle b\bar i\\|\bar a u\rangle\delta_{lj}$
$(a^\dagger_{b} a_u a_{l}\|\widehat{H} a^\dagger_{a} a_j a_{i})$	$-\mathbf{F}_{iu}\delta_{ab}\delta_{lj} + \mathbf{F}_{ju}\delta_{ba}\delta_{li} + \langle ji\\|lu\rangle\delta_{ab} - \langle bi\\|au\rangle\delta_{lj} + \langle jb\\|ua\rangle\delta_{li}$
$(a^\dagger_{b} a_u a_{l}\|\widehat{H} a^\dagger_{a} a_s a_{j})$	$\mathbf{F}_{jl}\delta_{ba}\delta_{us} + \mathbf{F}_{su}\delta_{ba}\delta_{lj} - \mathbf{F}_{ba}\delta_{su}\delta_{lj} + \langle sj\\|lu\rangle\delta_{ab} + \langle bj\\|al\rangle\delta_{us} + \langle sb\\|ua\rangle\delta_{lj}$
$(a^\dagger_{b} a_u a_{l}\|\widehat{H} a^\dagger_{\bar s} a_i a_{\bar j})$	$-\langle b\bar j\\|\bar s u\rangle\delta_{li}$
$(a^\dagger_{b} a_u a_{l}\|\widehat{H} a^\dagger_{a} a_s a_{t})$	$\mathbf{F}_{tl}\delta_{ba}\delta_{us} - \mathbf{F}_{sl}\delta_{tu}\delta_{ab} + \langle st\\|lu\rangle\delta_{ab} + \langle bt\\|al\rangle\delta_{us} - \langle bs\\|al\rangle\delta_{ut}$
$(a^\dagger_{b} a_u a_{l}\|\widehat{H} a^\dagger_{\bar a} a_s a_{\bar j})$	$\langle b\bar j\\|\bar a l\rangle\delta_{us}$
$(a^\dagger_{b} a_u a_{l}\|\widehat{H} a^\dagger_{\bar s} a_t a_{\bar j})$	$\langle b\bar j\\|\bar s l\rangle\delta_{ut}$

Tab. 6.4.: Secundary–Secundary for the $\mathbf{f}_3$–$\mathbf{f}_3$ blocks

$(\mathbf{f}^{\mathbf{Q}}{}_3\vert\widehat{H}\mathbf{f}^{\mathbf{Q}}{}_3)$ and $(\mathbf{f}^{\mathbf{Q}}{}_3\vert\widehat{H}\mathbf{f}^{\mathbf{Q}}{}_3)$ Terms	
Coupling	Terms
$(a^\dagger_{\bar u}a_k a_{\bar l}\vert\widehat{H}a^\dagger_{\bar a}a_j a_{\bar i})$	$-\mathbf{F}_{\bar u\bar a}\delta_{jk}\delta_{\bar l\bar i} + \langle\bar u\bar i\Vert\bar a\bar l\rangle\delta_{kj} + \langle j\bar u\Vert k\bar a\rangle\delta_{\bar l\bar i}$
$(a^\dagger_{\bar u}a_k a_{\bar l}\vert\widehat{H}a^\dagger_{a}a_j a_{i})$	$\langle\bar u i\Vert a\bar l\rangle\delta_{kj} - \langle\bar u j\Vert a\bar l\rangle\delta_{ki}$
$(a^\dagger_{\bar u}a_k a_{\bar l}\vert\widehat{H}a^\dagger_{a}a_s a_{j})$	$-\langle\bar u s\Vert a\bar l\rangle\delta_{kj}$
$(a^\dagger_{\bar u}a_k a_{\bar l}\vert\widehat{H}a^\dagger_{\bar s}a_i a_{\bar j})$	$\mathbf{F}_{\bar j\bar l}\delta_{\bar u\bar s}\delta_{ki} + \mathbf{F}_{ik}\delta_{\bar u\bar s}\delta_{\bar l\bar j} - \mathbf{F}_{\bar u\bar s}\delta_{ik}\delta_{\bar l\bar j} + \langle i\bar j\Vert\bar l k\rangle\delta_{\bar s\bar u} + \langle\bar u\bar j\Vert\bar s\bar l\rangle\delta_{ki} + \langle i\bar u\Vert k\bar s\rangle\delta_{\bar l\bar j}$
$(a^\dagger_{\bar u}a_k a_{\bar l}\vert\widehat{H}a^\dagger_{a}a_s a_{t})$	0
$(a^\dagger_{\bar u}a_k a_{\bar l}\vert\widehat{H}a^\dagger_{\bar a}a_s a_{\bar j})$	$\mathbf{F}_{sk}\delta_{\bar u\bar a}\delta_{\bar l\bar j} + \langle s\bar u\Vert k\bar a\rangle\delta_{\bar l\bar j}$
$(a^\dagger_{\bar u}a_k a_{\bar l}\vert\widehat{H}a^\dagger_{\bar s}a_t a_{\bar j})$	$\mathbf{F}_{tk}\delta_{\bar u\bar s}\delta_{\bar l\bar j} + \langle t\bar j\Vert\bar l k\rangle\delta_{\bar s\bar u} + \langle t\bar u\Vert k\bar s\rangle\delta_{\bar l\bar j}$
$(a^\dagger_{b}a_u a_v\vert\widehat{H}a^\dagger_{\bar a}a_j a_{\bar i})$	0
$(a^\dagger_{b}a_u a_v\vert\widehat{H}a^\dagger_{a}a_j a_{i})$	$\langle ji\Vert vu\rangle\delta_{ab}$
$(a^\dagger_{b}a_u a_v\vert\widehat{H}a^\dagger_{a}a_s a_{j})$	$\mathbf{F}_{jv}\delta_{ba}\delta_{us} - \mathbf{F}_{ju}\delta_{ab}\delta_{vs} + \langle sj\Vert vu\rangle\delta_{ab} + \langle bj\Vert av\rangle\delta_{us} - \langle bj\Vert au\rangle\delta_{vs}$
$(a^\dagger_{b}a_u a_v\vert\widehat{H}a^\dagger_{\bar s}a_i a_{\bar j})$	0
$(a^\dagger_{b}a_u a_v\vert\widehat{H}a^\dagger_{a}a_s a_{t})$	$\mathbf{F}_{tv}\delta_{ba}\delta_{us} - \mathbf{F}_{tu}\delta_{ab}\delta_{vs} - \mathbf{F}_{sv}\delta_{tu}\delta_{ab} + \mathbf{F}_{su}\delta_{ba}\delta_{vt} + \mathbf{F}_{ba}[-\delta_{su}\delta_{vt} + \delta_{vs}\delta_{ut}]$ $+ \langle st\Vert vu\rangle\delta_{ab} + \langle bt\Vert av\rangle\delta_{us} - \langle bs\Vert av\rangle\delta_{ut} - \langle bt\Vert au\rangle\delta_{vs} + \langle sb\Vert ua\rangle\delta_{vt}$
$(a^\dagger_{b}a_u a_v\vert\widehat{H}a^\dagger_{\bar a}a_s a_{\bar j})$	$\langle b\bar j\Vert\bar a v\rangle\delta_{us} - \langle b\bar j\Vert\bar a u\rangle\delta_{vs}$
$(a^\dagger_{b}a_u a_v\vert\widehat{H}a^\dagger_{\bar s}a_t a_{\bar j})$	$\langle b\bar j\Vert\bar s v\rangle\delta_{ut} - \langle b\bar j\Vert\bar s u\rangle\delta_{vt}$
$(a^\dagger_{\bar b}a_u a_{\bar l}\vert\widehat{H}a^\dagger_{\bar a}a_j a_{\bar i})$	$\mathbf{F}_{ju}\delta_{\bar b\bar a}\delta_{\bar l\bar i} + \langle j\bar i\Vert\bar l u\rangle\delta_{\bar a\bar b} + \langle j\bar b\Vert u\bar a\rangle\delta_{\bar l\bar i}$
$(a^\dagger_{\bar b}a_u a_{\bar l}\vert\widehat{H}a^\dagger_{a}a_j a_{i})$	0
$(a^\dagger_{\bar b}a_u a_{\bar l}\vert\widehat{H}a^\dagger_{a}a_s a_{j})$	$\langle\bar b j\Vert a\bar l\rangle\delta_{us}$
$(a^\dagger_{\bar b}a_u a_{\bar l}\vert\widehat{H}a^\dagger_{\bar s}a_i a_{\bar j})$	$\langle i\bar b\Vert u\bar s\rangle\delta_{\bar l\bar j}$
$(a^\dagger_{\bar b}a_u a_{\bar l}\vert\widehat{H}a^\dagger_{a}a_s a_{t})$	$\langle\bar b t\Vert a\bar l\rangle\delta_{us} - \langle\bar b s\Vert a\bar l\rangle\delta_{ut}$
$(a^\dagger_{\bar b}a_u a_{\bar l}\vert\widehat{H}a^\dagger_{\bar a}a_s a_{\bar j})$	$\mathbf{F}_{\bar j\bar l}\delta_{\bar b\bar a}\delta_{us} + \mathbf{F}_{su}\delta_{\bar b\bar a}\delta_{\bar l\bar j} - \mathbf{F}_{\bar b\bar a}\delta_{su}\delta_{\bar l\bar j} + \langle s\bar j\Vert\bar l u\rangle\delta_{\bar a\bar b} + \langle\bar b\bar j\Vert\bar a\bar l\rangle\delta_{us} + \langle s\bar b\Vert u\bar a\rangle\delta_{\bar l\bar j}$
$(a^\dagger_{\bar b}a_u a_{\bar l}\vert\widehat{H}a^\dagger_{\bar s}a_t a_{\bar j})$	$-\mathbf{F}_{\bar b\bar s}\delta_{tu}\delta_{\bar l\bar j} + \langle\bar b\bar j\Vert\bar s\bar l\rangle\delta_{ut} + \langle t\bar b\Vert u\bar s\rangle\delta_{\bar l\bar j}$

Tab. 6.5.: Secundary–Secundary for the $\mathbf{f}_3$–$\mathbf{f}_3$ blocks

$(\mathbf{f^Q}_3\vert\widehat{H}\mathbf{f^Q}_3)$ and $(\mathbf{f^Q}_3\vert\widehat{H}\mathbf{f^Q}_3)$ Terms	
Coupling	Terms
$(a_{\bar{u}}^{\dagger}a_{v}a_{\bar{l}}\vert\widehat{H}a_{\bar{a}}^{\dagger}a_{j}a_{\bar{i}})$	$\langle j\bar{u}\Vert v\bar{a}\rangle\delta_{\bar{l}\bar{i}}$
$(a_{\bar{u}}^{\dagger}a_{v}a_{\bar{l}}\vert\widehat{H}a_{a}^{\dagger}a_{j}a_{i})$	0
$(a_{\bar{u}}^{\dagger}a_{v}a_{\bar{l}}\vert\widehat{H}a_{a}^{\dagger}a_{s}a_{j})$	$\langle\bar{u}j\Vert a\bar{l}\rangle\delta_{vs}$
$(a_{\bar{u}}^{\dagger}a_{v}a_{\bar{l}}\vert\widehat{H}a_{\bar{s}}^{\dagger}a_{i}a_{\bar{j}})$	$\mathbf{F}_{iv}\delta_{\bar{u}\bar{s}}\delta_{\bar{l}\bar{j}} + \langle i\bar{j}\Vert\bar{l}v\rangle\delta_{\bar{s}\bar{u}} + \langle i\bar{u}\Vert v\bar{s}\rangle\delta_{\bar{l}\bar{j}}$
$(a_{\bar{u}}^{\dagger}a_{v}a_{\bar{l}}\vert\widehat{H}a_{a}^{\dagger}a_{s}a_{t})$	$\langle\bar{u}t\Vert a\bar{l}\rangle\delta_{vs} - \langle\bar{u}s\Vert a\bar{l}\rangle\delta_{vt}$
$(a_{\bar{u}}^{\dagger}a_{v}a_{\bar{l}}\vert\widehat{H}a_{\bar{a}}^{\dagger}a_{s}a_{\bar{j}})$	$-\mathbf{F}_{\bar{u}\bar{a}}\delta_{sv}\delta_{\bar{l}\bar{j}} + \langle\bar{u}\bar{j}\Vert\bar{a}\bar{l}\rangle\delta_{vs} + \langle s\bar{u}\Vert v\bar{a}\rangle\delta_{\bar{l}\bar{j}}$
$(a_{\bar{u}}^{\dagger}a_{v}a_{\bar{l}}\vert\widehat{H}a_{\bar{s}}^{\dagger}a_{t}a_{\bar{j}})$	$\mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{u}\bar{s}}\delta_{vt} + \mathbf{F}_{tv}\delta_{\bar{u}\bar{s}}\delta_{\bar{l}\bar{j}} - \mathbf{F}_{\bar{u}\bar{s}}\delta_{tv}\delta_{\bar{l}\bar{j}} + \langle t\bar{j}\Vert\bar{l}v\rangle\delta_{\bar{s}\bar{u}} + \langle\bar{u}\bar{j}\Vert\bar{s}\bar{l}\rangle\delta_{vt} + \langle t\bar{u}\Vert v\bar{s}\rangle\delta_{\bar{l}\bar{j}}$

Tab. 6.6.: Secundary–Secundary for the $\mathbf{f}_3$–$\mathbf{f}_3$ blocks

$(\mathbf{f^{Q}}_5\vert\widehat{H}\mathbf{f^{Q}}_5)$ and $(\mathbf{f^{Q}}_5\vert\widehat{H}\mathbf{f^{Q}}_5)$ Terms	
Coupling	Terms
$(a^\dagger_{\bar b}a^\dagger_{\bar u}a_u a_{\bar l}a_{\bar k}\vert Ha^\dagger_{\bar a}a^\dagger_{\bar s}a_s a_{\bar j}a_{\bar i})$	$F_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{su}\delta_{\bar a\bar b}\delta_{\bar s\bar u} - F_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{su}\delta_{\bar a\bar b}\delta_{\bar s\bar u} - F_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{su}\delta_{\bar a\bar b}\delta_{\bar s\bar u} + F_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{su}\delta_{\bar a\bar b}\delta_{\bar s\bar u} - F_{su}\delta_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{\bar a\bar b}\delta_{\bar s\bar u} + F_{su}\delta_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{\bar a\bar b}\delta_{\bar s\bar u} - F_{\bar b\bar a}\delta_{\bar u\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{su} + F_{\bar b\bar a}\delta_{\bar u\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{su} - F_{\bar u\bar s}\delta_{\bar b\bar a}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{su} + F_{\bar u\bar s}\delta_{\bar b\bar a}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{su}$
$(a^\dagger_{\bar b}a^\dagger_{\bar u}a_u a_{\bar l}a_{\bar k}\vert Ha^\dagger_{a}a^\dagger_{\bar s}a_s a_{\bar j}a_{i})$	0
$(a^\dagger_{\bar b}a^\dagger_{\bar u}a_u a_{\bar l}a_{\bar k}\vert Ha^\dagger_{a}a^\dagger_{\bar t}a_s a_t a_{\bar i})$	0
$(a^\dagger_{\bar b}a^\dagger_{\bar u}a_u a_{\bar l}a_{\bar k}\vert Ha^\dagger_{\bar s}a^\dagger_{\bar t}a_t a_{\bar j}a_{\bar i})$	$-F_{\bar b\bar s}\delta_{\bar u\bar t}[\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tu} - \delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tu}] + F_{\bar b\bar t}\delta_{\bar u\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tu}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tu})]$
$(a^\dagger_{b}a^\dagger_{\bar u}a_u a_{\bar l}a_{k}\vert Ha^\dagger_{\bar a}a^\dagger_{\bar s}a_s a_{\bar j}a_{\bar i})$	0
$(a^\dagger_{b}a^\dagger_{\bar u}a_u a_{\bar l}a_{k}\vert Ha^\dagger_{a}a^\dagger_{\bar s}a_s a_{\bar j}a_{i})$	$F_{ik}\delta_{\bar j\bar l}\delta_{su}\delta_{ab}\delta_{\bar s\bar u} - F_{ba}\delta_{\bar u\bar s}\delta_{ik}\delta_{\bar j\bar l}\delta_{su} - F_{\bar u\bar s}\delta_{ba}\delta_{ik}\delta_{\bar j\bar l}\delta_{su}$
$(a^\dagger_{b}a^\dagger_{\bar u}a_u a_{\bar l}a_{k}\vert Ha^\dagger_{a}a^\dagger_{\bar t}a_s a_t a_{\bar i})$	$-F_{tk}\delta_{\bar i\bar l}\delta_{su}\delta_{ab}\delta_{\bar t\bar u} + F_{sk}\delta_{\bar i\bar l}\delta_{tu}\delta_{ab}\delta_{\bar t\bar u}$
$(a^\dagger_{b}a^\dagger_{\bar u}a_u a_{\bar l}a_{k}\vert Ha^\dagger_{\bar s}a^\dagger_{\bar t}a_t a_{\bar j}a_{\bar i})$	0
$(a^\dagger_{b}a^\dagger_{\bar v}a_u a_v a_{\bar k}\vert Ha^\dagger_{\bar a}a^\dagger_{\bar s}a_s a_{\bar j}a_{\bar i})$	0
$(a^\dagger_{b}a^\dagger_{\bar v}a_u a_v a_{\bar k}\vert Ha^\dagger_{a}a^\dagger_{\bar s}a_s a_{\bar j}a_{i})$	$-F_{iv}\delta_{\bar j\bar k}\delta_{su}\delta_{ab}\delta_{\bar s\bar v} + F_{iu}\delta_{\bar j\bar k}\delta_{sv}\delta_{ab}\delta_{\bar s\bar v}$
$(a^\dagger_{b}a^\dagger_{\bar v}a_u a_v a_{\bar k}\vert Ha^\dagger_{a}a^\dagger_{\bar t}a_s a_t a_{\bar i})$	$F_{\bar i\bar k}\delta_{tv}\delta_{su}\delta_{ab}\delta_{\bar t\bar v} - F_{\bar i\bar k}\delta_{sv}\delta_{tu}\delta_{ab}\delta_{\bar t\bar v} + F_{tv}\delta_{\bar i\bar k}\delta_{su}\delta_{ab}\delta_{\bar t\bar v} - F_{tu}\delta_{\bar i\bar k}\delta_{sv}\delta_{ab}\delta_{\bar t\bar v} - F_{sv}\delta_{tu}\delta_{\bar i\bar k}\delta_{ab}\delta_{\bar t\bar v} + F_{su}\delta_{tv}\delta_{\bar i\bar k}\delta_{ab}\delta_{\bar t\bar v} - F_{ba}\delta_{\bar v\bar t}\delta_{\bar i\bar k}\delta_{tv}\delta_{su} + F_{ba}\delta_{\bar v\bar t}\delta_{\bar i\bar k}\delta_{sv}\delta_{tu} - F_{\bar v\bar t}\delta_{ba}\delta_{\bar i\bar k}\delta_{tv}\delta_{su} + F_{\bar v\bar t}\delta_{ba}\delta_{\bar i\bar k}\delta_{sv}\delta_{tu}$
$(a^\dagger_{b}a^\dagger_{\bar v}a_u a_v a_{\bar k}\vert Ha^\dagger_{\bar s}a^\dagger_{\bar t}a_t a_{\bar j}a_{\bar i})$	0
$(a^\dagger_{\bar u}a^\dagger_{\bar v}a_v a_{\bar l}a_{\bar k}\vert Ha^\dagger_{\bar a}a^\dagger_{\bar s}a_s a_{\bar j}a_{\bar i})$	$-F_{\bar u\bar a}\delta_{\bar v\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{sv} + F_{\bar u\bar a}\delta_{\bar v\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{sv} + F_{\bar v\bar a}\delta_{\bar u\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{sv} - F_{\bar v\bar a}\delta_{\bar u\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{sv}$
$(a^\dagger_{\bar u}a^\dagger_{\bar v}a_v a_{\bar l}a_{\bar k}\vert Ha^\dagger_{a}a^\dagger_{\bar s}a_s a_{\bar j}a_{i})$	0
$(a^\dagger_{\bar u}a^\dagger_{\bar v}a_v a_{\bar l}a_{\bar k}\vert Ha^\dagger_{a}a^\dagger_{\bar t}a_s a_t a_{\bar i})$	0
$(a^\dagger_{\bar u}a^\dagger_{\bar v}a_v a_{\bar l}a_{\bar k}\vert Ha^\dagger_{\bar s}a^\dagger_{\bar t}a_t a_{\bar j}a_{\bar i})$	$F_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv}\delta_{\bar s\bar u}\delta_{\bar t\bar v} - F_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv}\delta_{\bar s\bar v}\delta_{\bar t\bar u} - F_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv}\delta_{\bar s\bar u}\delta_{\bar t\bar v} + F_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv}\delta_{\bar s\bar v}\delta_{\bar t\bar u} - F_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{tv}\delta_{\bar s\bar u}\delta_{\bar t\bar v} + F_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{tv}\delta_{\bar s\bar v}\delta_{\bar t\bar u} + F_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{tv}\delta_{\bar s\bar u}\delta_{\bar t\bar v} - F_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{tv}\delta_{\bar s\bar v}\delta_{\bar t\bar u} - F_{tv}\delta_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{\bar s\bar u}\delta_{\bar t\bar v} + F_{tv}\delta_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{\bar s\bar v}\delta_{\bar t\bar u} + F_{tv}\delta_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{\bar s\bar u}\delta_{\bar t\bar v} - F_{tv}\delta_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{\bar s\bar v}\delta_{\bar t\bar u} - F_{\bar u\bar s}\delta_{\bar v\bar t}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv} + F_{\bar u\bar s}\delta_{\bar v\bar t}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv} + F_{\bar v\bar s}\delta_{\bar u\bar t}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv} - F_{\bar v\bar s}\delta_{\bar u\bar t}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv} + F_{\bar u\bar t}\delta_{\bar v\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv} - F_{\bar u\bar t}\delta_{\bar v\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv} - F_{\bar v\bar t}\delta_{\bar u\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv} + F_{\bar v\bar t}\delta_{\bar u\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv}$

Tab. 6.7.: Secundary–Secundary $\mathbf{f}_5$–$\mathbf{f}_5$ blocks

$(\mathbf{a}\vert\widehat{H}\mathbf{f^Q}_3)$ and $(\mathbf{f^Q}_3\vert\widehat{H}\mathbf{a})$ Terms	
Coupling	Terms
$(a_\kappa\vert\widehat{H}a^\dagger_{\bar{a}}a_j a_{\bar{i}})$	$-\delta_{\kappa j}\mathbf{F}_{\bar{a}\bar{i}} - \delta_{\kappa\bar{i}}\mathbf{F}_{\bar{a}j} - \langle j\bar{i}\Vert\kappa\bar{a}\rangle$
$(a_\kappa\vert\widehat{H}a^\dagger_{a}a_j a_{i})$	$-\delta_{\kappa j}\mathbf{F}_{ai} - \delta_{\kappa i}\mathbf{F}_{aj} - \langle ji\Vert\kappa a\rangle$
$(a_\kappa\vert\widehat{H}a^\dagger_{a}a_s a_{j})$	$-\delta_{\kappa s}\mathbf{F}_{aj} - \delta_{\kappa j}\mathbf{F}_{as} - \langle sj\Vert\kappa a\rangle$
$(a_\kappa\vert\widehat{H}a^\dagger_{\bar{s}}a_i a_{\bar{j}})$	$-\delta_{\kappa i}\mathbf{F}_{\bar{s}\bar{j}} - \delta_{\kappa\bar{j}}\mathbf{F}_{\bar{s}i} - \langle i\bar{j}\Vert\kappa\bar{s}\rangle$
$(a_\kappa\vert\widehat{H}a^\dagger_{a}a_s a_{t})$	$-\delta_{\kappa s}\mathbf{F}_{at} - \delta_{\kappa t}\mathbf{F}_{as} - \langle st\Vert\kappa a\rangle$
$(a_\kappa\vert\widehat{H}a^\dagger_{\bar{a}}a_s a_{\bar{j}})$	$-\delta_{\kappa s}\mathbf{F}_{\bar{a}\bar{j}} - \delta_{\kappa\bar{j}}\mathbf{F}_{\bar{a}s} - \langle s\bar{j}\Vert\kappa\bar{a}\rangle$
$(a_\kappa\vert\widehat{H}a^\dagger_{\bar{s}}a_t a_{\bar{j}})$	$-\delta_{\kappa t}\mathbf{F}_{\bar{s}\bar{j}} - \delta_{\kappa\bar{j}}\mathbf{F}_{\bar{s}t} - \langle t\bar{j}\Vert\kappa\bar{s}\rangle$
$(a^\dagger_{\bar{b}}a_l a_{\bar{k}}\vert\widehat{H}a_\iota)$	$\langle\bar{b}\iota\Vert l\bar{k}\rangle$
$(a^\dagger_{b}a_l a_{k}\vert\widehat{H}a_\iota)$	$\langle b\iota\Vert lk\rangle$
$(a^\dagger_{b}a_u a_{l}\vert\widehat{H}a_\iota)$	$\langle b\iota\Vert ul\rangle$
$(a^\dagger_{\bar{u}}a_k a_{\bar{l}}\vert\widehat{H}a_\iota)$	$\langle\bar{u}\iota\Vert k\bar{l}\rangle$
$(a^\dagger_{b}a_u a_{v}\vert\widehat{H}a_\iota)$	$\langle b\iota\Vert uv\rangle$
$(a^\dagger_{\bar{b}}a_u a_{\bar{l}}\vert\widehat{H}a_\iota)$	$\langle\bar{b}\iota\Vert u\bar{l}\rangle$
$(a^\dagger_{\bar{u}}a_v a_{\bar{l}}\vert\widehat{H}a_\iota)$	$\langle\bar{u}\iota\Vert v\bar{l}\rangle$

Tab. 6.8.: Primary–Secundary and Secundary–Primary for the **a**–$\mathbf{f}_3$–**a** blocks

$(\mathbf{f^P}_3\vert\widehat{H}\mathbf{f^Q}_3)$ and $(\mathbf{f^Q}_3\vert\widehat{H}\mathbf{f^P}_3)$ Terms	
Coupling	Terms
$(a^\dagger_{\bar u}a_u a_{\bar k}\vert\widehat{H}a^\dagger_{\bar a}a_j a_{\bar i})$	$\langle j\bar u\Vert u\bar a\rangle\delta_{\bar k\bar i}$
$(a^\dagger_{\bar u}a_u a_{\bar k}\vert\widehat{H}a^\dagger_{a}a_j a_{i})$	0
$(a^\dagger_{\bar u}a_u a_{\bar k}\vert\widehat{H}a^\dagger_{a}a_s a_{j})$	$\langle \bar u j\Vert a\bar k\rangle\delta_{us}$
$(a^\dagger_{\bar u}a_u a_{\bar k}\vert\widehat{H}a^\dagger_{\bar s}a_i a_{\bar j})$	$\mathbf{F}_{iu}\delta_{\bar u\bar s}\delta_{\bar k\bar j} + \langle i\bar j\Vert\bar k u\rangle\delta_{\bar s\bar u} + \langle i\bar u\Vert u\bar s\rangle\delta_{\bar k\bar j}$
$(a^\dagger_{\bar u}a_u a_{\bar k}\vert\widehat{H}a^\dagger_{a}a_s a_{t})$	$\langle\bar u t\Vert a\bar k\rangle\delta_{us} - \langle\bar u s\Vert a\bar k\rangle\delta_{ut}$
$(a^\dagger_{\bar u}a_u a_{\bar k}\vert\widehat{H}a^\dagger_{\bar a}a_s a_{\bar j})$	$-\mathbf{F}_{\bar u\bar a}\delta_{su}\delta_{\bar k\bar j} + \langle\bar u\bar j\Vert\bar a\bar k\rangle\delta_{us} + \langle s\bar u\Vert u\bar a\rangle\delta_{\bar k\bar j}$
$(a^\dagger_{\bar u}a_u a_{\bar k}\vert\widehat{H}a^\dagger_{\bar s}a_t a_{\bar j})$	$\mathbf{F}_{\bar j\bar k}\delta_{\bar u\bar s}\delta_{ut} + \mathbf{F}_{tu}\delta_{\bar u\bar s}\delta_{\bar k\bar j} - \mathbf{F}_{\bar u\bar s}\delta_{tu}\delta_{\bar k\bar j} + \langle t\bar j\Vert\bar k u\rangle\delta_{\bar s\bar u} + \langle\bar u\bar j\Vert\bar s\bar k\rangle\delta_{ut} + \langle t\bar u\Vert u\bar s\rangle\delta_{\bar k\bar j}$
$(a^\dagger_{\bar b}a_l a_{\bar k}\vert\widehat{H}a^\dagger_{\bar s}a_s a_{\bar i})$	$\langle s\bar b\Vert l\bar s\rangle\delta_{\bar k\bar i}$
$(a^\dagger_{b}a_l a_{k}\vert\widehat{H}a^\dagger_{\bar s}a_s a_{\bar i})$	0
$(a^\dagger_{b}a_u a_{l}\vert\widehat{H}a^\dagger_{\bar s}a_s a_{\bar i})$	$\langle b\bar i\Vert\bar s l\rangle\delta_{us}$
$(a^\dagger_{\bar u}a_k a_{\bar l}\vert\widehat{H}a^\dagger_{\bar s}a_s a_{\bar i})$	$\mathbf{F}_{sk}\delta_{\bar u\bar s}\delta_{\bar l\bar i} + \langle s\bar i\Vert\bar l k\rangle\delta_{\bar s\bar u} + \langle s\bar u\Vert k\bar s\rangle\delta_{\bar l\bar i}$
$(a^\dagger_{b}a_u a_{v}\vert\widehat{H}a^\dagger_{\bar s}a_s a_{\bar i})$	$\langle b\bar i\Vert\bar s v\rangle\delta_{us} - \langle b\bar i\Vert\bar s u\rangle\delta_{vs}$
$(a^\dagger_{\bar b}a_u a_{\bar l}\vert\widehat{H}a^\dagger_{\bar s}a_s a_{\bar i})$	$-\mathbf{F}_{\bar b\bar s}\delta_{su}\delta_{\bar l\bar i} + \langle\bar b\bar i\Vert\bar s\bar l\rangle\delta_{us} + \langle s\bar b\Vert u\bar s\rangle\delta_{\bar l\bar i}$
$(a^\dagger_{\bar u}a_v a_{\bar l}\vert\widehat{H}a^\dagger_{\bar s}a_s a_{\bar i})$	$\mathbf{F}_{\bar i\bar l}\delta_{\bar u\bar s}\delta_{vs} + \mathbf{F}_{sv}\delta_{\bar u\bar s}\delta_{\bar l\bar i} - \mathbf{F}_{\bar u\bar s}\delta_{sv}\delta_{\bar l\bar i} + \langle s\bar i\Vert\bar l v\rangle\delta_{\bar s\bar u} + \langle\bar u\bar i\Vert\bar s\bar l\rangle\delta_{vs} + \langle s\bar u\Vert v\bar s\rangle\delta_{\bar l\bar i}$

Tab. 6.9.: Primary–Secundary and Secundary–Primary $\mathbf{f}_3$–$\mathbf{f}_3$ blocks

$(\mathbf{f^P}_3|\widehat{H}\mathbf{f^Q}_5)$ and $(\mathbf{f^Q}_5|\widehat{H}\mathbf{f^P}_3)$ Terms

Coupling	Terms
$(a^\dagger_{\bar u} a_u a_{\bar k}\|H a^\dagger_{\bar a} a^\dagger_{\bar s} a_s a_{\bar j} a_{\bar i})$	$\delta_{\bar s\bar u}[-\delta_{su}(\bar j\bar k\|\|\bar i\bar a) - \delta_{\bar i\bar k}(\bar j u\|\|s\bar a) - \delta_{\bar j\bar k}(su\|\|\bar i\bar a)]$ $-(\bar u\bar a\|\|\bar i\bar s)\delta_{us}\delta_{\bar k\bar j} + (\bar u\bar a\|\|\bar j\bar s)\delta_{us}\delta_{\bar k\bar i}$
$(a^\dagger_{\bar u} a_u a_{\bar k}\|H a^\dagger_{a} a^\dagger_{\bar s} a_s a_{\bar j} a_i)$	$\delta_{\bar s\bar u}[-\delta_{su}(\bar j\bar k\|\|ia) - \delta_{\bar j\bar k}(su\|\|ia)]$ $-(\bar u a\|\|i\bar s)\delta_{us}\delta_{\bar k\bar j} + (\bar u a\|\|s\bar s)\delta_{ui}\delta_{\bar k\bar j}$
$(a^\dagger_{\bar u} a_u a_{\bar k}\|H a^\dagger_{a} a^\dagger_{\bar t} a_s a_t a_{\bar i})$	$\delta_{\bar t\bar u}[-\delta_{su}(t\bar k\|\|\bar i a) - \delta_{\bar i\bar k}(tu\|\|sa) + \delta_{tu}(s\bar k\|\|\bar i a)]$ $+(\bar u a\|\|t\bar t)\delta_{us}\delta_{\bar k\bar i} - (\bar u a\|\|s\bar t)\delta_{ut}\delta_{\bar k\bar i}$
$(a^\dagger_{\bar u} a_u a_{\bar k}\|H a^\dagger_{\bar s} a^\dagger_{\bar t} a_t a_{\bar j} a_{\bar i})$	$\delta_{\bar s\bar u}[\delta_{tu}(\bar j\bar k\|\|\bar i\bar t) + \delta_{\bar i\bar k}(\bar j u\|\|t\bar t) + \delta_{\bar j\bar k}(tu\|\|\bar i\bar t)]$ $+\delta_{\bar t\bar u}[-\delta_{tu}(\bar j\bar k\|\|\bar i\bar s) - \delta_{\bar i\bar k}(\bar j u\|\|t\bar s) - \delta_{\bar j\bar k}(tu\|\|\bar i\bar s)]$ $-(\bar u\bar s\|\|\bar i\bar t)\delta_{ut}\delta_{\bar k\bar j} + (\bar u\bar s\|\|\bar j\bar t)\delta_{ut}\delta_{\bar k\bar i}$
$(a^\dagger_{b} a^\dagger_{\bar u} a_u a_{\bar l} a_{\bar k}\|H a^\dagger_{\bar s} a_s a_{\bar i})$	$-\delta_{\bar u\bar s}[(\bar u\bar k\|\|\bar i\bar l)\delta_{su} - (\bar u\bar l\|\|\bar i\bar k)\delta_{su} + (\bar u u\|\|s\bar l)\delta_{\bar i\bar k}]$ $-(\bar u\bar k\|\|b\bar s)\delta_{su}\delta_{\bar i\bar l} + (\bar u\bar l\|\|b\bar s)\delta_{su}\delta_{\bar i\bar k}$
$(a^\dagger_{b} a^\dagger_{\bar u} a_u a_{\bar l} a_k\|H a^\dagger_{\bar s} a_s a_{\bar i})$	$-\delta_{\bar u\bar s}[(\bar u k\|\|\bar i\bar l)\delta_{su} - (\bar u\bar l\|\|\bar i k)\delta_{su} + (\bar u\bar l\|\|sk)\delta_{\bar i u}]$ $-(\bar u k\|\|b\bar s)\delta_{su}\delta_{\bar i\bar l} + (\bar u u\|\|b\bar s)\delta_{sk}\delta_{\bar i\bar l}$
$(a^\dagger_{b} a^\dagger_{\bar v} a_u a_v a_{\bar k}\|H a^\dagger_{\bar s} a_s a_{\bar i})$	$-\delta_{\bar v\bar s}[(\bar v\bar k\|\|\bar i v)\delta_{su} - (\bar v v\|\|\bar i\bar k)\delta_{su} + (\bar v u\|\|sv)\delta_{\bar i\bar k}]$ $+(\bar v v\|\|b\bar s)\delta_{su}\delta_{\bar i\bar k} - (\bar v u\|\|b\bar s)\delta_{sv}\delta_{\bar i\bar k}$
$(a^\dagger_{\bar u} a^\dagger_{\bar v} a_v a_{\bar l} a_{\bar k}\|H a^\dagger_{\bar s} a_s a_{\bar i})$	$\delta_{\bar u\bar s}[(\bar v\bar k\|\|\bar i q)\delta_{sv} - (\bar v\bar l\|\|\bar i\bar k)\delta_{sv} + (\bar v v\|\|s\bar l)\delta_{\bar i\bar k}]$ $-\delta_{\bar v\bar s}[(\bar v\bar k\|\|\bar i\bar l)\delta_{sv} - (\bar v\bar l\|\|\bar i\bar k)\delta_{sv} + (\bar v v\|\|s\bar l)\delta_{\bar i\bar k}]$ $-(\bar v\bar k\|\|\bar u\bar s)\delta_{sv}\delta_{\bar i\bar l} + (\bar v\bar l\|\|\bar u\bar s)\delta_{sv}\delta_{\bar i\bar k}$

Tab. 6.10.: Primary–Secundary and Secundary–Primary $\mathbf{f}_3$–$\mathbf{f}_5$–$\mathbf{f}_3$ blocks

6.3.1 Self–energy reformulation

For the electron detachment energies, the Dyson electron propagator approximation that uses a single ROHF determinant as the reference determinant may be expressed as

$$\mathbf{e}+\mathbf{\Sigma}(E) = (\mathbf{h}|\widehat{\mathrm{H}}\mathbf{h}) + (\mathbf{h}|\widehat{\mathrm{H}}\mathbf{f_Q})^{(1)}[E\mathbf{1} - (\mathbf{f_Q}|\widehat{\mathrm{H}}\mathbf{f_Q})^{(0)}]^{-1}(\mathbf{f_Q}|\widehat{\mathrm{H}}\mathbf{h})^{(1)} \tag{6.9}$$

where $\mathbf{h}$ represents the field operators corresponding to the new partition of the primary space, whereas $\mathbf{f_Q}$ are the field operators corresponding to the secondary space. Thus, the repartitioned primary space may be expressed as

$$(\mathbf{h}|\widehat{\mathrm{H}}\mathbf{h}) = (\mathbf{a}+\mathbf{f_3^P}|\widehat{\mathrm{H}}|\mathbf{a}+\mathbf{f_3^P}) = (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{a}) + (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{f_3^P}) + (\mathbf{f_3^P}|\widehat{\mathrm{H}}\mathbf{a}) + (\mathbf{f_3^P}|\widehat{\mathrm{H}}\mathbf{f_3^P}) \tag{6.10}$$

On the other hand, the self–energy matrix for this repartitioned electron propagator may be expressed as

$$\mathbf{\Sigma}(E) = (\mathbf{h}|\widehat{\mathrm{H}}\mathbf{f_Q})^{(1)}[E\mathbf{1} - (\mathbf{f_Q}|\widehat{\mathrm{H}}\mathbf{f_Q})^{(0)}]^{-1}(\mathbf{f_Q}|\widehat{\mathrm{H}}\mathbf{h})^{(1)} \tag{6.11}$$

This new expression for the self–energy matrix would now holds products between the $\mathbf{H}_{3,3}$, $\mathbf{H}_{5,5}$, $\mathbf{H}_{3,5}$ and $\mathbf{H}_{5,3}$ matrices. Thus in the implementation of this electron propagator, both the primary and secondary block would need to be allocated as a 2×2 blocked matrix instead of as a simple array. Hence, $\Gamma(E)$ may be expressed as

$$\Gamma(E)_{2\times 2} = (\mathbf{h}|\widehat{\mathrm{H}}\mathbf{h})_{2\times 2} + \mathbf{\Sigma}(E)_{2\times 2} \tag{6.12}$$

This is relevant to mention in order to clearly understand that after the diagonalization of the $\Gamma(E)_{2\times 2}$ matrix the resulting eigenvectors and values would now have dimension corresponding to two times the number of orbitals that are being considered, $2\times N$ where $N = \mathrm{Occupied\quad orbitals} + \mathrm{Virtual\quad orbitals}$. Therefore, the overlap algorithm that is usually used for the selection of the eigenvalue that will correspond to the next iteration may need to be adapted. In general, the initial guess overlap vector has only one element different from zero. (The element that corresponds to the orbital from which an electron in being removed or added) For the case of the spin–flip propagator, the initial guess overlap vector may have two of its elements with values different than zero. The position of these elements is related to the final determinants that are considered for the description of the final state. For example, if the initial reference determinant is a doublet, then the initial guess vector will be divided into two different sectors of size N,

$$V_{\mu}^{Guess} = \left[\begin{array}{c} i \\ j \\ k \\ s \\ a \\ \vdots \\ N \\ \hline i \\ j \\ k \\ s \\ a \\ \vdots \\ N \end{array}\right] . \tag{6.13}$$

In this vector, the different sectors may be regarded as the different determinants needed to form the final state. Thus, the only elements different than zero would be those corresponding to the orbitals from which an electron need to be removed from the reference determinant to produce the relevant configurations for the final state,

$$V_{\mu}^{Guess} = \left[\begin{array}{c} i \\ j \\ \frac{1}{\sqrt{2}} \\ s \\ a \\ \vdots \\ N \\ \hline i \\ j \\ \frac{1}{\sqrt{2}} \\ s \\ a \\ \vdots \\ N \end{array}\right] . \tag{6.14}$$

In the case of a doublet reference determinant, in which a singlet and a triplet state may be obtained by a linear combination of two determinants, one may be able to distinguish between these two states by inspecting the overlap coefficient values and their signs,

$$V_{\mu}^{Guess} = \left[\begin{array}{c} i \\ j \\ \frac{1}{\sqrt{2}} \\ s \\ a \\ \vdots \\ N \\ \hline i \\ j \\ \pm\frac{1}{\sqrt{2}} \\ s \\ a \\ \vdots \\ N \end{array}\right]. \tag{6.15}$$

If the two overlap coefficients with the closest value to unity have the same sign, then the state obtained is a triplet state otherwise is a singlet state. Advancement of the implementation and development of the algorithm for this electron propagator are still in progress.

A

Primary block field operator couplings

The couplings for the primary block are based on the superoperator Hamiltonian matrix:

$$\widehat{\mathbf{H}}_{\boldsymbol{PP}} = \begin{bmatrix} (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{a}) & (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{F_3}) \\ (\mathbf{a}|\widehat{\mathrm{H}}\mathbf{F_3}) & (\mathbf{F_3}|\widehat{\mathrm{H}}\mathbf{F_3}) \end{bmatrix} \tag{A.1}$$

The terms of this matrix are evaluated in first order. The indices and coupling for field operators that are used for building the $\widehat{\mathbf{H}}_{\boldsymbol{PP}}$ matrix are as follow:

$$\widehat{\mathbf{H}}^{(\mathbf{1})}_{\boldsymbol{PP}} = \begin{array}{ccccc} & a_k & a^\dagger_{\bar{u}} a_u a_{\bar{k}} & a_u & a_c \\ a_j & F_{kj} & \langle u\bar{k} \| j\bar{u} \rangle & F_{uj} & F_{cj} \\ a^\dagger_{\bar{t}} a_t a_{\bar{j}} & \langle \bar{t}k \| t\bar{j} \rangle & (a^\dagger_{\bar{t}} a_t a_{\bar{j}} | \widehat{H} a^\dagger_{\bar{u}} a_u a_{\bar{k}}) & \langle \bar{t}u \| t\bar{j} \rangle & \langle \bar{t}c \| t\bar{j} \rangle \\ a_t & F_{kt} & -\langle u\bar{k} \| t\bar{u} \rangle & F_{ut} & F_{ct} \\ a_b & F_{kb} & -\langle u\bar{k} \| b\bar{u} \rangle & F_{ub} & F_{cb} \end{array} \tag{A.2}$$

A.1 Deduction of the matrix elements for the primary–primary block

$$(a_j|\widehat{\mathrm{H}}a_k) = F_{kj} \tag{A.3}$$

$$(a_t|\widehat{\mathrm{H}}a_k) = F_{kt} \tag{A.4}$$

$$(a_b|\widehat{\mathrm{H}}a_k) = F_{kb} \tag{A.5}$$

$$(a_j|\widehat{\mathrm{H}}a_u) = F_{uj} \tag{A.6}$$

$$(a_t|\widehat{\mathrm{H}}a_u) = F_{ut} \tag{A.7}$$

$$(a_b|\widehat{\mathrm{H}}a_u) = F_{ub} \tag{A.8}$$

$$(a_j|\widehat{\mathrm{H}}a_c) = F_{cj} \tag{A.9}$$

$$(a_t|\widehat{\mathrm{H}}a_c) = F_{ct} \tag{A.10}$$

$$(a_b|\widehat{\mathrm{H}}a_c) = F_{cb} \tag{A.11}$$

$$\begin{aligned}(a_\kappa^\dagger a_p a_q|\widehat{\mathrm{H}}a_r) &= \langle \kappa r \| pq \rangle(-n_p n_\kappa - n_\kappa n_q + n_p n_q + n_\kappa)\\ &= \langle \kappa r \| pq \rangle(+1)\\ &= \langle \kappa r \| pq \rangle\end{aligned} \tag{A.12}$$

$$\begin{aligned}(a_{\bar{u}}^\dagger a_u a_{\bar{k}}|\widehat{\mathrm{H}}a_j) &= \langle \bar{u} j \| u\bar{k} \rangle(-n_u n_{\bar{u}} - n_{\bar{u}} n_{\bar{k}} + n_u n_{\bar{k}} + n_{\bar{u}})\\ &= \langle \bar{u} j \| u\bar{k} \rangle(+1)\\ &= \langle \bar{u} j \| u\bar{k} \rangle\end{aligned} \tag{A.13}$$

$$\begin{aligned}(a_{\bar{t}}^\dagger a_t a_{\bar{j}}|\widehat{\mathrm{H}}a_k) &= \langle \bar{t} k \| t\bar{j} \rangle(-n_t n_{\bar{t}} - n_{\bar{t}} n_{\bar{j}} + n_t n_{\bar{j}} + n_{\bar{t}})\\ &= \langle \bar{t} k \| t\bar{j} \rangle(+1)\\ &= \langle \bar{t} k \| t\bar{j} \rangle\end{aligned} \tag{A.14}$$

$$
\begin{aligned}
(a^{\dagger}_{\bar{t}} a_t a_{\bar{j}} | \widehat{\mathrm{H}} a_u) &= \langle \bar{t}u \| t\bar{j} \rangle (-n_t n_{\bar{t}} - n_{\bar{t}} n_{\bar{j}} + n_t n_{\bar{j}} + n_{\bar{t}}) \\
&= \langle \bar{t}u \| t\bar{j} \rangle (+1) \\
&= \langle \bar{t}u \| t\bar{j} \rangle
\end{aligned}
\tag{A.15}
$$

$$
\begin{aligned}
(a^{\dagger}_{\bar{t}} a_t a_{\bar{j}} | \widehat{\mathrm{H}} a_c) &= \langle \bar{t}c \| t\bar{j} \rangle (-n_t n_{\bar{t}} - n_{\bar{t}} n_{\bar{j}} + n_t n_{\bar{j}} + n_{\bar{t}}) \\
&= \langle \bar{t}c \| t\bar{j} \rangle (+1) \\
&= \langle \bar{t}c \| t\bar{j} \rangle
\end{aligned}
\tag{A.16}
$$

$$
\begin{aligned}
(a_t | \widehat{\mathrm{H}} a^{\dagger}_{\bar{u}} a_u a_{\bar{k}}) &= \delta_{tu} \mathbf{F}_{\bar{u}\bar{k}} (n_{\bar{u}} - n_{\bar{k}}) + \delta_{t\bar{k}} \mathbf{F}_{\bar{u}u} (n_{\bar{u}} - n_u) + \langle u\bar{k} \| t\bar{u} \rangle (n_u n_{\bar{u}} + n_{\bar{u}} n_{\bar{k}} - n_u n_{\bar{k}} - n_{\bar{u}}) \\
&= \delta_{tu} \mathbf{F}_{\bar{u}\bar{k}} (-1) + \delta_{t\bar{k}} \mathbf{F}_{\bar{u}u} (-1) + \langle u\bar{k} \| t\bar{u} \rangle (-1) \\
&= -\delta_{tu} \mathbf{F}_{\bar{u}\bar{k}} - \delta_{t\bar{k}} \mathbf{F}_{\bar{u}u} - \langle u\bar{k} \| t\bar{u} \rangle
\end{aligned}
\tag{A.17}
$$

$$
\begin{aligned}
(a_b | \widehat{\mathrm{H}} a^{\dagger}_{\bar{u}} a_u a_{\bar{k}}) &= \delta_{bu} \mathbf{F}_{\bar{u}\bar{k}} (n_{\bar{u}} - n_{\bar{k}}) + \delta_{b\bar{k}} \mathbf{F}_{\bar{u}u} (n_{\bar{u}} - n_u) + \langle u\bar{k} \| t\bar{u} \rangle (n_u n_{\bar{u}} + n_{\bar{u}} n_{\bar{k}} - n_u n_{\bar{k}} - n_{\bar{u}}) \\
&= \delta_{bu} \mathbf{F}_{\bar{u}\bar{k}} (-1) + \delta_{b\bar{k}} \mathbf{F}_{\bar{u}u} (-1) + \langle u\bar{k} \| t\bar{u} \rangle (-1) \\
&= -\delta_{bu} \mathbf{F}_{\bar{u}\bar{k}} - \delta_{b\bar{k}} \mathbf{F}_{\bar{u}u} - \langle u\bar{k} \| b\bar{u} \rangle
\end{aligned}
\tag{A.18}
$$

$$
\begin{aligned}
(a^{\dagger}_{\bar{t}} a_t a_{\bar{j}} | \widehat{H} a^{\dagger}_{\bar{u}} a_u a_{\bar{k}}) = {} & \mathbf{F}_{\bar{k}\bar{j}} \delta_{\bar{t}\bar{u}} \delta_{tu} - \mathbf{F}_{\bar{k}t} \delta_{\bar{u}\bar{t}} \delta_{\bar{j}u} - \mathbf{F}_{u\bar{j}} \delta_{\bar{k}t} \delta_{\bar{u}\bar{t}} + \mathbf{F}_{ut} \delta_{\bar{t}\bar{u}} \delta_{\bar{j}\bar{k}} + \mathbf{F}_{\bar{t}\bar{u}} [-\delta_{ut} \delta_{\bar{j}\bar{k}} + \delta_{\bar{j}u} \delta_{t\bar{k}}] \\
& + \langle u\bar{k} \| \bar{j}t \rangle \delta_{\bar{u}\bar{t}} + \langle \bar{t}\bar{k} \| \bar{u}\bar{j} \rangle \delta_{tu} - \langle \bar{t}u \| \bar{u}\bar{j} \rangle \delta_{t\bar{k}} - \langle \bar{t}\bar{k} \| \bar{u}t \rangle \delta_{\bar{j}u} + \langle u\bar{t} \| t\bar{u} \rangle \delta_{\bar{j}\bar{k}}
\end{aligned}
\tag{A.19}
$$

B

Secondary block field operator couplings

The difference between the $2hp$ and $2ph$ terms is reflected in the occupation numbers. By using the general deductions expressions, the $2hp$ and $2ph$ are related through a sign change and the nature of the indices, the indices that were set for occupied orbitals now represent virtual orbitals an vice-versa. Therefore, In this expression we only focus on $2ph$ terms that can be transform to $2hp$ by changing multiplying the $2ph$ by -1. In some cases,the two electron integrals have been change from the Dirac notation to the Mulliken notation. The change of notation of the two electron integral was done in order to further reduce the long expressions that were obtained using matrix notation. The relations between the two notations is:

$$\begin{aligned} \langle ij||kl\rangle &= \langle ij|kl\rangle - \langle ij|lk\rangle \\ &= (ik|jl) - (il|jk) \end{aligned} \tag{B.1}$$

B.1 General term for $(F_3|\widehat{H}F_3)$ for the 2ph terms in first order

The field operator $(F_3|\widehat{H}F_3)$ coupling general expression reads

$$\begin{aligned} (a_\iota^\dagger a_s a_t|\widehat{H}a_\kappa^\dagger a_p a_q) = {} & \mathbf{F}_{qt}\delta_{\iota\kappa}\delta_{sp} - \mathbf{F}_{qs}\delta_{\kappa\iota}\delta_{tp} - \mathbf{F}_{pt}\delta_{qs}\delta_{\kappa\iota} + \mathbf{F}_{ps}\delta_{\iota\kappa}\delta_{tq} + \mathbf{F}_{\iota\kappa}[-\delta_{ps}\delta_{tq} + \delta_{tp}\delta_{sq}] \\ & + \langle pq||ts\rangle\delta_{\kappa\iota} + \langle \iota q||\kappa t\rangle\delta_{sp} - \langle \iota p||\kappa t\rangle\delta_{sq} - \langle \iota q||\kappa s\rangle\delta_{tp} + \langle p\iota||s\kappa\rangle\delta_{tq} \end{aligned} \tag{B.2}$$

B.1.1 $a_{\bar{b}}^{\dagger} a_l a_{\bar{k}}$

$$
\begin{aligned}
(a_{\bar{b}}^{\dagger} a_l a_{\bar{k}} | \widehat{H} a_{\bar{a}}^{\dagger} a_j a_{\bar{i}}) &= \mathbf{F}_{\bar{i}\bar{k}} \delta_{\bar{b}\bar{a}} \delta_{lj} - \mathbf{F}_{\bar{i}l} \delta_{\bar{a}\bar{b}} \delta_{\bar{k}j} - \mathbf{F}_{j\bar{k}} \delta_{\bar{i}l} \delta_{\bar{a}\bar{b}} + \mathbf{F}_{jl} \delta_{\bar{b}\bar{a}} \delta_{\bar{k}\bar{i}} + \mathbf{F}_{\bar{b}\bar{a}} [-\delta_{jl} \delta_{\bar{k}\bar{i}} + \delta_{\bar{k}j} \delta_{l\bar{i}}] \\
&\quad + \langle j\bar{i} \| \bar{k}l \rangle \delta_{\bar{a}\bar{b}} + \langle \bar{b}\bar{i} \| \bar{a}\bar{k} \rangle \delta_{lj} - \langle \bar{b}j \| \bar{a}\bar{k} \rangle \delta_{l\bar{i}} - \langle \bar{b}\bar{i} \| \bar{a}l \rangle \delta_{\bar{k}j} + \langle j\bar{b} \| l\bar{a} \rangle \delta_{\bar{k}\bar{i}} \\
&= \mathbf{F}_{\bar{i}\bar{k}} \delta_{\bar{b}\bar{a}} \delta_{lj} + \mathbf{F}_{jl} \delta_{\bar{b}\bar{a}} \delta_{\bar{k}\bar{i}} - \mathbf{F}_{\bar{b}\bar{a}} \delta_{jl} \delta_{\bar{k}\bar{i}} + \langle j\bar{i} \| \bar{k}l \rangle \delta_{\bar{a}\bar{b}} + \langle \bar{b}\bar{i} \| \bar{a}\bar{k} \rangle \delta_{lj} + \langle j\bar{b} \| l\bar{a} \rangle \delta_{\bar{k}\bar{i}}
\end{aligned}
\tag{B.3}
$$

$$
\begin{aligned}
(a_{\bar{b}}^{\dagger} a_l a_{\bar{k}} | \widehat{H} a_{a}^{\dagger} a_j a_i) &= \mathbf{F}_{i\bar{k}} \delta_{\bar{b}a} \delta_{lj} - \mathbf{F}_{il} \delta_{a\bar{b}} \delta_{\bar{k}j} - \mathbf{F}_{j\bar{k}} \delta_{il} \delta_{a\bar{b}} + \mathbf{F}_{jl} \delta_{\bar{b}a} \delta_{\bar{k}i} + \mathbf{F}_{\bar{b}a} [-\delta_{jl} \delta_{\bar{k}i} + \delta_{\bar{k}j} \delta_{li}] \\
&\quad + \langle ji \| \bar{k}l \rangle \delta_{a\bar{b}} + \langle \bar{b}i \| a\bar{k} \rangle \delta_{lj} - \langle \bar{b}j \| a\bar{k} \rangle \delta_{li} - \langle \bar{b}i \| al \rangle \delta_{\bar{k}j} + \langle j\bar{b} \| la \rangle \delta_{\bar{k}i} \\
&= \langle \bar{b}i \| a\bar{k} \rangle \delta_{lj} - \langle \bar{b}j \| a\bar{k} \rangle \delta_{li}
\end{aligned}
\tag{B.4}
$$

$$
\begin{aligned}
(a_{\bar{b}}^{\dagger} a_l a_{\bar{k}} | \widehat{H} a_{a}^{\dagger} a_s a_j) &= \mathbf{F}_{j\bar{k}} \delta_{\bar{b}a} \delta_{ls} - \mathbf{F}_{jl} \delta_{a\bar{b}} \delta_{\bar{k}s} - \mathbf{F}_{s\bar{k}} \delta_{jl} \delta_{a\bar{b}} + \mathbf{F}_{sl} \delta_{\bar{b}a} \delta_{\bar{k}j} + \mathbf{F}_{\bar{b}a} [-\delta_{sl} \delta_{\bar{k}j} + \delta_{\bar{k}s} \delta_{lj}] \\
&\quad + \langle sj \| \bar{k}l \rangle \delta_{a\bar{b}} + \langle \bar{b}j \| a\bar{k} \rangle \delta_{ls} - \langle \bar{b}s \| a\bar{k} \rangle \delta_{lj} - \langle \bar{b}j \| al \rangle \delta_{\bar{k}s} + \langle s\bar{b} \| la \rangle \delta_{\bar{k}j} \\
&= \langle \bar{b}j \| a\bar{k} \rangle \delta_{ls} - \langle \bar{b}s \| a\bar{k} \rangle \delta_{lj}
\end{aligned}
\tag{B.5}
$$

$$
\begin{aligned}
(a_{\bar{b}}^{\dagger} a_l a_{\bar{k}} | \widehat{H} a_{\bar{s}}^{\dagger} a_i a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{k}} \delta_{\bar{b}\bar{s}} \delta_{li} - \mathbf{F}_{\bar{j}l} \delta_{\bar{s}\bar{b}} \delta_{\bar{k}i} - \mathbf{F}_{i\bar{k}} \delta_{\bar{j}l} \delta_{\bar{s}\bar{b}} + \mathbf{F}_{il} \delta_{\bar{b}\bar{s}} \delta_{\bar{k}\bar{j}} + \mathbf{F}_{\bar{b}\bar{s}} [-\delta_{il} \delta_{\bar{k}\bar{j}} + \delta_{\bar{k}i} \delta_{l\bar{j}}] \\
&\quad + \langle i\bar{j} \| \bar{k}l \rangle \delta_{\bar{s}\bar{b}} + \langle \bar{b}\bar{j} \| \bar{s}\bar{k} \rangle \delta_{li} - \langle \bar{b}i \| \bar{s}\bar{k} \rangle \delta_{l\bar{j}} - \langle \bar{b}\bar{j} \| \bar{s}l \rangle \delta_{\bar{k}i} + \langle i\bar{b} \| l\bar{s} \rangle \delta_{\bar{k}\bar{j}} \\
&= -\mathbf{F}_{\bar{b}\bar{s}} \delta_{il} \delta_{\bar{k}\bar{j}} + \langle \bar{b}\bar{j} \| \bar{s}\bar{k} \rangle \delta_{li} + \langle i\bar{b} \| l\bar{s} \rangle \delta_{\bar{k}\bar{j}}
\end{aligned}
\tag{B.6}
$$

$$
\begin{aligned}
(a_{\bar{b}}^{\dagger} a_l a_{\bar{k}} | \widehat{H} a_{a}^{\dagger} a_s a_t) &= \mathbf{F}_{t\bar{k}} \delta_{\bar{b}a} \delta_{ls} - \mathbf{F}_{tl} \delta_{a\bar{b}} \delta_{\bar{k}s} - \mathbf{F}_{s\bar{k}} \delta_{tl} \delta_{a\bar{b}} + \mathbf{F}_{sl} \delta_{\bar{b}a} \delta_{\bar{k}t} + \mathbf{F}_{\bar{b}a} [-\delta_{sl} \delta_{\bar{k}t} + \delta_{\bar{k}s} \delta_{lt}] \\
&\quad + \langle st \| \bar{k}l \rangle \delta_{a\bar{b}} + \langle \bar{b}t \| a\bar{k} \rangle \delta_{ls} - \langle \bar{b}s \| a\bar{k} \rangle \delta_{lt} - \langle \bar{b}t \| al \rangle \delta_{\bar{k}s} + \langle s\bar{b} \| la \rangle \delta_{\bar{k}t} \\
&= 0
\end{aligned}
\tag{B.7}
$$

$$
\begin{aligned}
(a^{\dagger}_{\bar{b}} a_l a_{\bar{k}} | \widehat{H} a^{\dagger}_{\bar{a}} a_s a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{k}} \delta_{\bar{b}\bar{a}} \delta_{ls} - \mathbf{F}_{\bar{j}l} \delta_{\bar{a}\bar{b}} \delta_{\bar{k}s} - \mathbf{F}_{s\bar{k}} \delta_{\bar{j}l} \delta_{\bar{a}\bar{b}} + \mathbf{F}_{sl} \delta_{\bar{b}\bar{a}} \delta_{\bar{k}\bar{j}} + \mathbf{F}_{\bar{b}\bar{a}} [-\delta_{sl} \delta_{\bar{k}\bar{j}} + \delta_{\bar{k}s} \delta_{l\bar{j}}] \\
&\quad + \langle s\bar{j} \| \bar{k}l \rangle \delta_{\bar{a}\bar{b}} + \langle \bar{b}\bar{j} \| \bar{a}\bar{k} \rangle \delta_{ls} - \langle \bar{b}s \| \bar{a}\bar{k} \rangle \delta_{l\bar{j}} - \langle \bar{b}\bar{j} \| \bar{a}l \rangle \delta_{\bar{k}s} + \langle s\bar{b} \| l\bar{a} \rangle \delta_{\bar{k}\bar{j}} \\
&= \mathbf{F}_{sl} \delta_{\bar{b}\bar{a}} \delta_{\bar{k}\bar{j}} + \langle s\bar{j} \| \bar{k}l \rangle \delta_{\bar{a}\bar{b}} + \langle s\bar{b} \| l\bar{a} \rangle \delta_{\bar{k}\bar{j}}
\end{aligned}
\tag{B.8}
$$

$$
\begin{aligned}
(a^{\dagger}_{\bar{b}} a_l a_{\bar{k}} | \widehat{H} a^{\dagger}_{\bar{s}} a_t a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{k}} \delta_{\bar{b}\bar{s}} \delta_{lt} - \mathbf{F}_{\bar{j}l} \delta_{\bar{s}\bar{b}} \delta_{\bar{k}t} - \mathbf{F}_{t\bar{k}} \delta_{\bar{j}l} \delta_{\bar{s}\bar{b}} + \mathbf{F}_{tl} \delta_{\bar{b}\bar{s}} \delta_{\bar{k}\bar{j}} + \mathbf{F}_{\bar{b}\bar{s}} [-\delta_{tl} \delta_{\bar{k}\bar{j}} + \delta_{\bar{k}t} \delta_{l\bar{j}}] \\
&\quad + \langle t\bar{j} \| \bar{k}l \rangle \delta_{\bar{s}\bar{b}} + \langle \bar{b}\bar{j} \| \bar{s}\bar{k} \rangle \delta_{lt} - \langle \bar{b}t \| \bar{s}\bar{k} \rangle \delta_{l\bar{j}} - \langle \bar{b}\bar{j} \| \bar{s}l \rangle \delta_{\bar{k}t} + \langle t\bar{b} \| l\bar{s} \rangle \delta_{\bar{k}\bar{j}} \\
&= \langle t\bar{b} \| l\bar{s} \rangle \delta_{\bar{k}\bar{j}}
\end{aligned}
\tag{B.9}
$$

B.1.2 $a^{\dagger}_{b} a_l a_k$

$$
\begin{aligned}
(a^{\dagger}_{b} a_l a_k | \widehat{H} a^{\dagger}_{\bar{a}} a_j a_{\bar{i}}) &= \mathbf{F}_{\bar{i}k} \delta_{b\bar{a}} \delta_{lj} - \mathbf{F}_{\bar{i}l} \delta_{\bar{a}b} \delta_{kj} - \mathbf{F}_{jk} \delta_{\bar{i}l} \delta_{\bar{a}b} + \mathbf{F}_{jl} \delta_{b\bar{a}} \delta_{k\bar{i}} + \mathbf{F}_{b\bar{a}} [-\delta_{jl} \delta_{k\bar{i}} + \delta_{kj} \delta_{l\bar{i}}] \\
&\quad + \langle j\bar{i} \| kl \rangle \delta_{\bar{a}b} + \langle b\bar{i} \| \bar{a}k \rangle \delta_{lj} - \langle bj \| \bar{a}k \rangle \delta_{l\bar{i}} - \langle b\bar{i} \| \bar{a}l \rangle \delta_{kj} + \langle jb \| l\bar{a} \rangle \delta_{k\bar{i}} \\
&= \langle b\bar{i} \| \bar{a}k \rangle \delta_{lj} - \langle b\bar{i} \| \bar{a}l \rangle \delta_{kj}
\end{aligned}
\tag{B.10}
$$

$$
\begin{aligned}
(a^{\dagger}_{b} a_l a_k | \widehat{H} a^{\dagger}_{a} a_j a_i) &= \mathbf{F}_{ik} \delta_{ba} \delta_{lj} - \mathbf{F}_{il} \delta_{ab} \delta_{kj} - \mathbf{F}_{jk} \delta_{il} \delta_{ab} + \mathbf{F}_{jl} \delta_{ba} \delta_{ki} + \mathbf{F}_{ba} [-\delta_{jl} \delta_{ki} + \delta_{kj} \delta_{li}] \\
&\quad + \langle ji \| kl \rangle \delta_{ab} + \langle bi \| ak \rangle \delta_{lj} - \langle bj \| ak \rangle \delta_{li} - \langle bi \| al \rangle \delta_{kj} + \langle jb \| la \rangle \delta_{ki} \\
&= \mathbf{F}_{ik} \delta_{ba} \delta_{lj} - \mathbf{F}_{il} \delta_{ab} \delta_{kj} - \mathbf{F}_{jk} \delta_{il} \delta_{ab} + \mathbf{F}_{jl} \delta_{ba} \delta_{ki} + \mathbf{F}_{ba} [-\delta_{jl} \delta_{ki} + \delta_{kj} \delta_{li}] \\
&\quad + \langle ji \| kl \rangle \delta_{ab} + \langle bi \| ak \rangle \delta_{lj} - \langle bj \| ak \rangle \delta_{li} - \langle bi \| al \rangle \delta_{kj} + \langle jb \| la \rangle \delta_{ki}
\end{aligned}
\tag{B.11}
$$

$$
\begin{aligned}
(a^{\dagger}_{b} a_l a_k | \widehat{H} a^{\dagger}_{a} a_s a_j) &= \mathbf{F}_{jk} \delta_{ba} \delta_{ls} - \mathbf{F}_{jl} \delta_{ab} \delta_{ks} - \mathbf{F}_{sk} \delta_{jl} \delta_{ab} + \mathbf{F}_{sl} \delta_{ba} \delta_{kj} + \mathbf{F}_{ba} [-\delta_{sl} \delta_{kj} + \delta_{ks} \delta_{lj}] \\
&\quad + \langle sj \| kl \rangle \delta_{ab} + \langle bj \| ak \rangle \delta_{ls} - \langle bs \| ak \rangle \delta_{lj} - \langle bj \| al \rangle \delta_{ks} + \langle sb \| la \rangle \delta_{kj} \\
&= -\mathbf{F}_{sk} \delta_{jl} \delta_{ab} + \mathbf{F}_{sl} \delta_{ba} \delta_{kj} + \langle sj \| kl \rangle \delta_{ab} - \langle bs \| ak \rangle \delta_{lj} + \langle sb \| la \rangle \delta_{kj}
\end{aligned}
\tag{B.12}
$$

$$
\begin{aligned}
(a_b^\dagger a_l a_k|\widehat{H} a_{\bar{s}}^\dagger a_i a_{\bar{j}}) &= \mathbf{F}_{\bar{j}k}\delta_{b\bar{s}}\delta_{li} - \mathbf{F}_{\bar{j}l}\delta_{\bar{s}b}\delta_{ki} - \mathbf{F}_{ik}\delta_{\bar{j}l}\delta_{\bar{s}b} + \mathbf{F}_{il}\delta_{b\bar{s}}\delta_{k\bar{j}} + \mathbf{F}_{b\bar{s}}[-\delta_{il}\delta_{k\bar{j}} + \delta_{ki}\delta_{l\bar{j}}] \\
&\quad + \langle i\bar{j}\|kl\rangle\delta_{\bar{s}b} + \langle b\bar{j}\|\bar{s}k\rangle\delta_{li} - \langle bi\|\bar{s}k\rangle\delta_{l\bar{j}} - \langle b\bar{j}\|\bar{s}l\rangle\delta_{ki} + \langle ib\|l\bar{s}\rangle\delta_{k\bar{j}} \\
&= \langle b\bar{j}\|\bar{s}k\rangle\delta_{li} - \langle b\bar{j}\|\bar{s}l\rangle\delta_{ki}
\end{aligned} \tag{B.13}
$$

$$
\begin{aligned}
(a_b^\dagger a_l a_k|\widehat{H} a_a^\dagger a_s a_t) &= \mathbf{F}_{tk}\delta_{ba}\delta_{ls} - \mathbf{F}_{tl}\delta_{ab}\delta_{ks} - \mathbf{F}_{sk}\delta_{tl}\delta_{ab} + \mathbf{F}_{sl}\delta_{ba}\delta_{kt} + \mathbf{F}_{ba}[-\delta_{sl}\delta_{kt} + \delta_{ks}\delta_{lt}] \\
&\quad + \langle st\|kl\rangle\delta_{ab} + \langle bt\|ak\rangle\delta_{ls} - \langle bs\|ak\rangle\delta_{lt} - \langle bt\|al\rangle\delta_{ks} + \langle sb\|la\rangle\delta_{kt} \\
&= \langle st\|kl\rangle\delta_{ab}
\end{aligned} \tag{B.14}
$$

$$
\begin{aligned}
(a_b^\dagger a_l a_k|\widehat{H} a_{\bar{a}}^\dagger a_s a_{\bar{j}}) &= \mathbf{F}_{\bar{j}k}\delta_{b\bar{a}}\delta_{ls} - \mathbf{F}_{\bar{j}l}\delta_{\bar{a}b}\delta_{ks} - \mathbf{F}_{sk}\delta_{\bar{j}l}\delta_{\bar{a}b} + \mathbf{F}_{sl}\delta_{b\bar{a}}\delta_{k\bar{j}} + \mathbf{F}_{b\bar{a}}[-\delta_{sl}\delta_{k\bar{j}} + \delta_{ks}\delta_{l\bar{j}}] \\
&\quad + \langle s\bar{j}\|kl\rangle\delta_{\bar{a}b} + \langle b\bar{j}\|\bar{a}k\rangle\delta_{ls} - \langle bs\|\bar{a}k\rangle\delta_{l\bar{j}} - \langle b\bar{j}\|\bar{a}l\rangle\delta_{ks} + \langle sb\|l\bar{a}\rangle\delta_{k\bar{j}} \\
&= 0
\end{aligned} \tag{B.15}
$$

$$
\begin{aligned}
(a_b^\dagger a_l a_k|\widehat{H} a_{\bar{s}}^\dagger a_t a_{\bar{j}}) &= \mathbf{F}_{\bar{j}k}\delta_{b\bar{s}}\delta_{lt} - \mathbf{F}_{\bar{j}l}\delta_{\bar{s}b}\delta_{kt} - \mathbf{F}_{tk}\delta_{\bar{j}l}\delta_{\bar{s}b} + \mathbf{F}_{tl}\delta_{b\bar{s}}\delta_{k\bar{j}} + \mathbf{F}_{b\bar{s}}[-\delta_{tl}\delta_{k\bar{j}} + \delta_{kt}\delta_{l\bar{j}}] \\
&\quad + \langle t\bar{j}\|kl\rangle\delta_{\bar{s}b} + \langle b\bar{j}\|\bar{s}k\rangle\delta_{lt} - \langle bt\|\bar{s}k\rangle\delta_{l\bar{j}} - \langle b\bar{j}\|\bar{s}l\rangle\delta_{kt} + \langle tb\|l\bar{s}\rangle\delta_{k\bar{j}} \\
&= 0
\end{aligned} \tag{B.16}
$$

B.1.3 $a_b^\dagger a_u a_l$

$$
\begin{aligned}
(a_b^\dagger a_u a_l|\widehat{H} a_{\bar{a}}^\dagger a_j a_{\bar{i}}) &= \mathbf{F}_{\bar{i}l}\delta_{b\bar{a}}\delta_{uj} - \mathbf{F}_{\bar{i}u}\delta_{\bar{a}b}\delta_{lj} - \mathbf{F}_{jl}\delta_{\bar{i}u}\delta_{\bar{a}b} + \mathbf{F}_{ju}\delta_{b\bar{a}}\delta_{l\bar{i}} + \mathbf{F}_{b\bar{a}}[-\delta_{ju}\delta_{l\bar{i}} + \delta_{lj}\delta_{u\bar{i}}] \\
&\quad + \langle j\bar{i}\|lu\rangle\delta_{\bar{a}b} + \langle b\bar{i}\|\bar{a}l\rangle\delta_{uj} - \langle bj\|\bar{a}l\rangle\delta_{u\bar{i}} - \langle b\bar{i}\|\bar{a}u\rangle\delta_{lj} + \langle jb\|u\bar{a}\rangle\delta_{l\bar{i}} \\
&= -\langle b\bar{i}\|\bar{a}u\rangle\delta_{lj}
\end{aligned} \tag{B.17}
$$

$$
\begin{aligned}
(a_b^\dagger a_u a_l|\widehat{H} a_a^\dagger a_j a_i) &= \mathbf{F}_{il}\delta_{ba}\delta_{uj} - \mathbf{F}_{iu}\delta_{ab}\delta_{lj} - \mathbf{F}_{jl}\delta_{iu}\delta_{ab} + \mathbf{F}_{ju}\delta_{ba}\delta_{li} + \mathbf{F}_{ba}[-\delta_{ju}\delta_{li} + \delta_{lj}\delta_{ui}] \\
&\quad + \langle ji\|lu\rangle\delta_{ab} + \langle bi\|al\rangle\delta_{uj} - \langle bj\|al\rangle\delta_{ui} - \langle bi\|au\rangle\delta_{lj} + \langle jb\|ua\rangle\delta_{li} \\
&= -\mathbf{F}_{iu}\delta_{ab}\delta_{lj} + \mathbf{F}_{ju}\delta_{ba}\delta_{li} + \langle ji\|lu\rangle\delta_{ab} - \langle bi\|au\rangle\delta_{lj} + \langle jb\|ua\rangle\delta_{li}
\end{aligned} \tag{B.18}
$$

$$\begin{aligned}(a_b^\dagger a_u a_l|\widehat{H}a_a^\dagger a_s a_j) &= \mathbf{F}_{jl}\delta_{ba}\delta_{us} - \mathbf{F}_{ju}\delta_{ab}\delta_{ls} - \mathbf{F}_{sl}\delta_{ju}\delta_{ab} + \mathbf{F}_{su}\delta_{ba}\delta_{lj} + \mathbf{F}_{ba}[-\delta_{su}\delta_{lj} + \delta_{ls}\delta_{uj}] \\ &\quad + \langle sj\|lu\rangle\delta_{ab} + \langle bj\|al\rangle\delta_{us} - \langle bs\|al\rangle\delta_{uj} - \langle bj\|au\rangle\delta_{ls} + \langle sb\|ua\rangle\delta_{lj} \\ &= \mathbf{F}_{jl}\delta_{ba}\delta_{us} + \mathbf{F}_{su}\delta_{ba}\delta_{lj} - \mathbf{F}_{ba}\delta_{su}\delta_{lj} + \langle sj\|lu\rangle\delta_{ab} + \langle bj\|al\rangle\delta_{us} + \langle sb\|ua\rangle\delta_{lj}\end{aligned} \tag{B.19}$$

$$\begin{aligned}(a_b^\dagger a_u a_l|\widehat{H}a_{\bar{s}}^\dagger a_i a_{\bar{j}}) &= \mathbf{F}_{\bar{j}l}\delta_{b\bar{s}}\delta_{ui} - \mathbf{F}_{\bar{j}u}\delta_{\bar{s}b}\delta_{li} - \mathbf{F}_{il}\delta_{\bar{j}u}\delta_{\bar{s}b} + \mathbf{F}_{iu}\delta_{b\bar{s}}\delta_{l\bar{j}} + \mathbf{F}_{b\bar{s}}[-\delta_{iu}\delta_{l\bar{j}} + \delta_{li}\delta_{u\bar{j}}] \\ &\quad + \langle i\bar{j}\|lu\rangle\delta_{\bar{s}b} + \langle b\bar{j}\|\bar{s}l\rangle\delta_{ui} - \langle bi\|\bar{s}l\rangle\delta_{u\bar{j}} - \langle b\bar{j}\|\bar{s}u\rangle\delta_{li} + \langle ib\|u\bar{s}\rangle\delta_{l\bar{j}} \\ &= -\langle b\bar{j}\|\bar{s}u\rangle\delta_{li}\end{aligned} \tag{B.20}$$

$$\begin{aligned}(a_b^\dagger a_u a_l|\widehat{H}a_a^\dagger a_s a_t) &= \mathbf{F}_{tl}\delta_{ba}\delta_{us} - \mathbf{F}_{tu}\delta_{ab}\delta_{ls} - \mathbf{F}_{sl}\delta_{tu}\delta_{ab} + \mathbf{F}_{su}\delta_{ba}\delta_{lt} + \mathbf{F}_{ba}[-\delta_{su}\delta_{lt} + \delta_{ls}\delta_{ut}] \\ &\quad + \langle st\|lu\rangle\delta_{ab} + \langle bt\|al\rangle\delta_{us} - \langle bs\|al\rangle\delta_{ut} - \langle bt\|au\rangle\delta_{ls} + \langle sb\|ua\rangle\delta_{lt} \\ &= \mathbf{F}_{tl}\delta_{ba}\delta_{us} - \mathbf{F}_{sl}\delta_{tu}\delta_{ab} + \langle st\|lu\rangle\delta_{ab} + \langle bt\|al\rangle\delta_{us} - \langle bs\|al\rangle\delta_{ut}\end{aligned} \tag{B.21}$$

$$\begin{aligned}(a_b^\dagger a_u a_l|\widehat{H}a_{\bar{a}}^\dagger a_s a_{\bar{j}}) &= \mathbf{F}_{\bar{j}l}\delta_{b\bar{a}}\delta_{us} - \mathbf{F}_{\bar{j}u}\delta_{\bar{a}b}\delta_{ls} - \mathbf{F}_{sl}\delta_{\bar{j}u}\delta_{\bar{a}b} + \mathbf{F}_{su}\delta_{b\bar{a}}\delta_{l\bar{j}} + \mathbf{F}_{b\bar{a}}[-\delta_{su}\delta_{l\bar{j}} + \delta_{ls}\delta_{u\bar{j}}] \\ &\quad + \langle s\bar{j}\|lu\rangle\delta_{\bar{a}b} + \langle b\bar{j}\|\bar{a}l\rangle\delta_{us} - \langle bs\|\bar{a}l\rangle\delta_{u\bar{j}} - \langle b\bar{j}\|\bar{a}u\rangle\delta_{ls} + \langle sb\|u\bar{a}\rangle\delta_{l\bar{j}} \\ &= +\langle b\bar{j}\|\bar{a}l\rangle\delta_{us}\end{aligned} \tag{B.22}$$

$$\begin{aligned}(a_b^\dagger a_u a_l|\widehat{H}a_{\bar{s}}^\dagger a_t a_{\bar{j}}) &= \mathbf{F}_{\bar{j}l}\delta_{b\bar{s}}\delta_{ut} - \mathbf{F}_{\bar{j}u}\delta_{\bar{s}b}\delta_{lt} - \mathbf{F}_{tl}\delta_{\bar{j}u}\delta_{\bar{s}b} + \mathbf{F}_{tu}\delta_{b\bar{s}}\delta_{l\bar{j}} + \mathbf{F}_{b\bar{s}}[-\delta_{tu}\delta_{l\bar{j}} + \delta_{lt}\delta_{u\bar{j}}] \\ &\quad + \langle t\bar{j}\|lu\rangle\delta_{\bar{s}b} + \langle b\bar{j}\|\bar{s}l\rangle\delta_{ut} - \langle bt\|\bar{s}l\rangle\delta_{u\bar{j}} - \langle b\bar{j}\|\bar{s}u\rangle\delta_{lt} + \langle tb\|u\bar{s}\rangle\delta_{l\bar{j}} \\ &= +\langle b\bar{j}\|\bar{s}l\rangle\delta_{ut}\end{aligned} \tag{B.23}$$

B.1.4 $a_{\bar{u}}^\dagger a_k a_{\bar{l}}$

$$\begin{aligned}(a_{\bar{u}}^\dagger a_k a_{\bar{l}}|\widehat{H}a_{\bar{a}}^\dagger a_j a_{\bar{i}}) &= \mathbf{F}_{\bar{i}\bar{l}}\delta_{\bar{u}\bar{a}}\delta_{kj} - \mathbf{F}_{\bar{i}k}\delta_{\bar{a}\bar{u}}\delta_{\bar{l}j} - \mathbf{F}_{j\bar{l}}\delta_{\bar{i}k}\delta_{\bar{a}\bar{u}} + \mathbf{F}_{jk}\delta_{\bar{u}\bar{a}}\delta_{\bar{l}\bar{i}} + \mathbf{F}_{\bar{u}\bar{a}}[-\delta_{jk}\delta_{\bar{l}\bar{i}} + \delta_{\bar{l}j}\delta_{k\bar{i}}] \\ &\quad + \langle j\bar{i}\|\bar{l}k\rangle\delta_{\bar{a}\bar{u}} + \langle \bar{u}\bar{i}\|\bar{a}\bar{l}\rangle\delta_{kj} - \langle \bar{u}j\|\bar{a}\bar{l}\rangle\delta_{k\bar{i}} - \langle \bar{u}\bar{i}\|\bar{a}k\rangle\delta_{\bar{l}j} + \langle j\bar{u}\|k\bar{a}\rangle\delta_{\bar{l}\bar{i}} \\ &= -\mathbf{F}_{\bar{u}\bar{a}}\delta_{jk}\delta_{\bar{l}\bar{i}} + \langle \bar{u}\bar{i}\|\bar{a}\bar{l}\rangle\delta_{kj} + \langle j\bar{u}\|k\bar{a}\rangle\delta_{\bar{l}\bar{i}}\end{aligned} \tag{B.24}$$

$$\begin{aligned}(a^\dagger_{\bar{u}} a_k a_{\bar{l}} | \widehat{H} a^\dagger_a a_j a_i) &= \mathbf{F}_{i\bar{l}} \delta_{\bar{u}a} \delta_{kj} - \mathbf{F}_{ik} \delta_{a\bar{u}} \delta_{\bar{l}j} - \mathbf{F}_{j\bar{l}} \delta_{ik} \delta_{a\bar{u}} + \mathbf{F}_{jk} \delta_{\bar{u}a} \delta_{\bar{l}i} + \mathbf{F}_{\bar{u}a}[-\delta_{jk}\delta_{\bar{l}i} + \delta_{\bar{l}j}\delta_{ki}] \\ &\quad + \langle ji \| \bar{l}k \rangle \delta_{a\bar{u}} + \langle \bar{u}i \| a\bar{l} \rangle \delta_{kj} - \langle \bar{u}j \| a\bar{l} \rangle \delta_{ki} - \langle \bar{u}i \| ak \rangle \delta_{\bar{l}j} + \langle j\bar{u} \| ka \rangle \delta_{\bar{l}i} \\ &= \langle \bar{u}i \| a\bar{l} \rangle \delta_{kj} - \langle \bar{u}j \| a\bar{l} \rangle \delta_{ki}\end{aligned} \tag{B.25}$$

$$\begin{aligned}(a^\dagger_{\bar{u}} a_k a_{\bar{l}} | \widehat{H} a^\dagger_a a_s a_j) &= \mathbf{F}_{j\bar{l}} \delta_{\bar{u}a} \delta_{ks} - \mathbf{F}_{jk} \delta_{a\bar{u}} \delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}} \delta_{jk} \delta_{a\bar{u}} + \mathbf{F}_{sk} \delta_{\bar{u}a} \delta_{\bar{l}j} + \mathbf{F}_{\bar{u}a}[-\delta_{sk}\delta_{\bar{l}j} + \delta_{\bar{l}s}\delta_{kj}] \\ &\quad + \langle sj \| \bar{l}k \rangle \delta_{a\bar{u}} + \langle \bar{u}j \| a\bar{l} \rangle \delta_{ks} - \langle \bar{u}s \| a\bar{l} \rangle \delta_{kj} - \langle \bar{u}j \| ak \rangle \delta_{\bar{l}s} + \langle s\bar{u} \| ka \rangle \delta_{\bar{l}j} \\ &= -\langle \bar{u}s \| a\bar{l} \rangle \delta_{kj}\end{aligned} \tag{B.26}$$

$$\begin{aligned}(a^\dagger_{\bar{u}} a_k a_{\bar{l}} | \widehat{H} a^\dagger_{\bar{s}} a_i a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}} \delta_{\bar{u}\bar{s}} \delta_{ki} - \mathbf{F}_{\bar{j}k} \delta_{\bar{s}\bar{u}} \delta_{\bar{l}i} - \mathbf{F}_{i\bar{l}} \delta_{\bar{j}k} \delta_{\bar{s}\bar{u}} + \mathbf{F}_{ik} \delta_{\bar{u}\bar{s}} \delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{u}\bar{s}}[-\delta_{ik}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}i}\delta_{k\bar{j}}] \\ &\quad + \langle i\bar{j} \| \bar{l}k \rangle \delta_{\bar{s}\bar{u}} + \langle \bar{u}\bar{j} \| \bar{s}\bar{l} \rangle \delta_{ki} - \langle \bar{u}i \| \bar{s}\bar{l} \rangle \delta_{k\bar{j}} - \langle \bar{u}\bar{j} \| \bar{s}k \rangle \delta_{\bar{l}i} + \langle i\bar{u} \| k\bar{s} \rangle \delta_{\bar{l}\bar{j}} \\ &= \mathbf{F}_{\bar{j}\bar{l}} \delta_{\bar{u}\bar{s}} \delta_{ki} + \mathbf{F}_{ik} \delta_{\bar{u}\bar{s}} \delta_{\bar{l}\bar{j}} - \mathbf{F}_{\bar{u}\bar{s}} \delta_{ik} \delta_{\bar{l}\bar{j}} + \langle i\bar{j} \| \bar{l}k \rangle \delta_{\bar{s}\bar{u}} + \langle \bar{u}\bar{j} \| \bar{s}\bar{l} \rangle \delta_{ki} + \langle i\bar{u} \| k\bar{s} \rangle \delta_{\bar{l}\bar{j}}\end{aligned} \tag{B.27}$$

$$\begin{aligned}(a^\dagger_{\bar{u}} a_k a_{\bar{l}} | \widehat{H} a^\dagger_a a_s a_t) &= \mathbf{F}_{t\bar{l}} \delta_{\bar{u}a} \delta_{ks} - \mathbf{F}_{tk} \delta_{a\bar{u}} \delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}} \delta_{tk} \delta_{a\bar{u}} + \mathbf{F}_{sk} \delta_{\bar{u}a} \delta_{\bar{l}t} + \mathbf{F}_{\bar{u}a}[-\delta_{sk}\delta_{\bar{l}t} + \delta_{\bar{l}s}\delta_{kt}] \\ &\quad + \langle st \| \bar{l}k \rangle \delta_{a\bar{u}} + \langle \bar{u}t \| a\bar{l} \rangle \delta_{ks} - \langle \bar{u}s \| a\bar{l} \rangle \delta_{kt} - \langle \bar{u}t \| ak \rangle \delta_{\bar{l}s} + \langle s\bar{u} \| ka \rangle \delta_{\bar{l}t} \\ &= 0\end{aligned} \tag{B.28}$$

$$\begin{aligned}(a^\dagger_{\bar{u}} a_k a_{\bar{l}} | \widehat{H} a^\dagger_{\bar{a}} a_s a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}} \delta_{\bar{u}\bar{a}} \delta_{ks} - \mathbf{F}_{\bar{j}k} \delta_{\bar{a}\bar{u}} \delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}} \delta_{\bar{j}k} \delta_{\bar{a}\bar{u}} + \mathbf{F}_{sk} \delta_{\bar{u}\bar{a}} \delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{u}\bar{a}}[-\delta_{sk}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}s}\delta_{k\bar{j}}] \\ &\quad + \langle s\bar{j} \| \bar{l}k \rangle \delta_{\bar{a}\bar{u}} + \langle \bar{u}\bar{j} \| \bar{a}\bar{l} \rangle \delta_{ks} - \langle \bar{u}s \| \bar{a}\bar{l} \rangle \delta_{k\bar{j}} - \langle \bar{u}\bar{j} \| \bar{a}k \rangle \delta_{\bar{l}s} + \langle s\bar{u} \| k\bar{a} \rangle \delta_{\bar{l}\bar{j}} \\ &= \mathbf{F}_{sk} \delta_{\bar{u}\bar{a}} \delta_{\bar{l}\bar{j}} + \langle s\bar{u} \| k\bar{a} \rangle \delta_{\bar{l}\bar{j}}\end{aligned} \tag{B.29}$$

$$\begin{aligned}(a^\dagger_{\bar{u}} a_k a_{\bar{l}} | \widehat{H} a^\dagger_{\bar{s}} a_t a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}} \delta_{\bar{u}\bar{s}} \delta_{kt} - \mathbf{F}_{\bar{j}k} \delta_{\bar{s}\bar{u}} \delta_{\bar{l}t} - \mathbf{F}_{t\bar{l}} \delta_{\bar{j}k} \delta_{\bar{s}\bar{u}} + \mathbf{F}_{tk} \delta_{\bar{u}\bar{s}} \delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{u}\bar{s}}[-\delta_{tk}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}t}\delta_{k\bar{j}}] \\ &\quad + \langle t\bar{j} \| \bar{l}k \rangle \delta_{\bar{s}\bar{u}} + \langle \bar{u}\bar{j} \| \bar{s}\bar{l} \rangle \delta_{kt} - \langle \bar{u}t \| \bar{s}\bar{l} \rangle \delta_{k\bar{j}} - \langle \bar{u}\bar{j} \| \bar{s}k \rangle \delta_{\bar{l}t} + \langle t\bar{u} \| k\bar{s} \rangle \delta_{\bar{l}\bar{j}} \\ &= \mathbf{F}_{tk} \delta_{\bar{u}\bar{s}} \delta_{\bar{l}\bar{j}} + \langle t\bar{j} \| \bar{l}k \rangle \delta_{\bar{s}\bar{u}} + \langle t\bar{u} \| k\bar{s} \rangle \delta_{\bar{l}\bar{j}}\end{aligned} \tag{B.30}$$

B.1.5 $a^\dagger_b a_u a_v$

$$\begin{aligned}(a^\dagger_b a_u a_v | \widehat{H} a^\dagger_{\bar{a}} a_j a_{\bar{i}}) &= \mathbf{F}_{\bar{i}v} \delta_{b\bar{a}} \delta_{uj} - \mathbf{F}_{\bar{i}u} \delta_{\bar{a}b} \delta_{vj} - \mathbf{F}_{jv} \delta_{\bar{i}u} \delta_{\bar{a}b} + \mathbf{F}_{ju} \delta_{b\bar{a}} \delta_{v\bar{i}} + \mathbf{F}_{b\bar{a}}[-\delta_{ju}\delta_{v\bar{i}} + \delta_{vj}\delta_{u\bar{i}}] \\ &\quad + \langle j\bar{i} \| vu \rangle \delta_{\bar{a}b} + \langle b\bar{i} \| \bar{a}v \rangle \delta_{uj} - \langle bj \| \bar{a}v \rangle \delta_{u\bar{i}} - \langle b\bar{i} \| \bar{a}u \rangle \delta_{vj} + \langle jb \| u\bar{a} \rangle \delta_{v\bar{i}} \\ &= 0\end{aligned} \tag{B.31}$$

$$
\begin{aligned}
(a_b^\dagger a_u a_v|\widehat{H} a_a^\dagger a_j a_i) &= \mathbf{F}_{iv}\delta_{ba}\delta_{uj} - \mathbf{F}_{iu}\delta_{ab}\delta_{vj} - \mathbf{F}_{jv}\delta_{iu}\delta_{ab} + \mathbf{F}_{ju}\delta_{ba}\delta_{vi} + \mathbf{F}_{ba}[-\delta_{ju}\delta_{vi} + \delta_{vj}\delta_{ui}] \\
&\quad + \langle ji\|vu\rangle\delta_{ab} + \langle bi\|av\rangle\delta_{uj} - \langle bj\|av\rangle\delta_{ui} - \langle bi\|au\rangle\delta_{vj} + \langle jb\|ua\rangle\delta_{vi} \\
&= \langle ji\|vu\rangle\delta_{ab}
\end{aligned}
\tag{B.32}
$$

$$
\begin{aligned}
(a_b^\dagger a_u a_v|\widehat{H} a_a^\dagger a_s a_j) &= \mathbf{F}_{jv}\delta_{ba}\delta_{us} - \mathbf{F}_{ju}\delta_{ab}\delta_{vs} - \mathbf{F}_{sv}\delta_{ju}\delta_{ab} + \mathbf{F}_{su}\delta_{ba}\delta_{vj} + \mathbf{F}_{ba}[-\delta_{su}\delta_{vj} + \delta_{vs}\delta_{uj}] \\
&\quad + \langle sj\|vu\rangle\delta_{ab} + \langle bj\|av\rangle\delta_{us} - \langle bs\|av\rangle\delta_{uj} - \langle bj\|au\rangle\delta_{vs} + \langle sb\|ua\rangle\delta_{vj} \\
&= \mathbf{F}_{jv}\delta_{ba}\delta_{us} - \mathbf{F}_{ju}\delta_{ab}\delta_{vs} + \langle sj\|vu\rangle\delta_{ab} + \langle bj\|av\rangle\delta_{us} - \langle bj\|au\rangle\delta_{vs}
\end{aligned}
\tag{B.33}
$$

$$
\begin{aligned}
(a_b^\dagger a_u a_v|\widehat{H} a_{\bar{s}}^\dagger a_i a_{\bar{j}}) &= \mathbf{F}_{\bar{j}v}\delta_{b\bar{s}}\delta_{ui} - \mathbf{F}_{\bar{j}u}\delta_{\bar{s}b}\delta_{vi} - \mathbf{F}_{iv}\delta_{\bar{j}u}\delta_{\bar{s}b} + \mathbf{F}_{iu}\delta_{b\bar{s}}\delta_{v\bar{j}} + \mathbf{F}_{b\bar{s}}[-\delta_{iu}\delta_{v\bar{j}} + \delta_{vi}\delta_{u\bar{j}}] \\
&\quad + \langle i\bar{j}\|vu\rangle\delta_{\bar{s}b} + \langle b\bar{j}\|\bar{s}v\rangle\delta_{ui} - \langle bi\|\bar{s}v\rangle\delta_{u\bar{j}} - \langle b\bar{j}\|\bar{s}u\rangle\delta_{vi} + \langle ib\|u\bar{s}\rangle\delta_{v\bar{j}} \\
&= 0
\end{aligned}
\tag{B.34}
$$

$$
\begin{aligned}
(a_b^\dagger a_u a_v|\widehat{H} a_a^\dagger a_s a_t) &= \mathbf{F}_{tv}\delta_{ba}\delta_{us} - \mathbf{F}_{tu}\delta_{ab}\delta_{vs} - \mathbf{F}_{sv}\delta_{tu}\delta_{ab} + \mathbf{F}_{su}\delta_{ba}\delta_{vt} + \mathbf{F}_{ba}[-\delta_{su}\delta_{vt} + \delta_{vs}\delta_{ut}] \\
&\quad + \langle st\|vu\rangle\delta_{ab} + \langle bt\|av\rangle\delta_{us} - \langle bs\|av\rangle\delta_{ut} - \langle bt\|au\rangle\delta_{vs} + \langle sb\|ua\rangle\delta_{vt} \\
&= \mathbf{F}_{tv}\delta_{ba}\delta_{us} - \mathbf{F}_{tu}\delta_{ab}\delta_{vs} - \mathbf{F}_{sv}\delta_{tu}\delta_{ab} + \mathbf{F}_{su}\delta_{ba}\delta_{vt} + \mathbf{F}_{ba}[-\delta_{su}\delta_{vt} + \delta_{vs}\delta_{ut}] \\
&\quad + \langle st\|vu\rangle\delta_{ab} + \langle bt\|av\rangle\delta_{us} - \langle bs\|av\rangle\delta_{ut} - \langle bt\|au\rangle\delta_{vs} + \langle sb\|ua\rangle\delta_{vt}
\end{aligned}
\tag{B.35}
$$

$$
\begin{aligned}
(a_b^\dagger a_u a_v|\widehat{H} a_{\bar{a}}^\dagger a_s a_{\bar{j}}) &= \mathbf{F}_{\bar{j}v}\delta_{b\bar{a}}\delta_{us} - \mathbf{F}_{\bar{j}u}\delta_{\bar{a}b}\delta_{vs} - \mathbf{F}_{sv}\delta_{\bar{j}u}\delta_{\bar{a}b} + \mathbf{F}_{su}\delta_{b\bar{a}}\delta_{v\bar{j}} + \mathbf{F}_{b\bar{a}}[-\delta_{su}\delta_{v\bar{j}} + \delta_{vs}\delta_{u\bar{j}}] \\
&\quad + \langle s\bar{j}\|vu\rangle\delta_{\bar{a}b} + \langle b\bar{j}\|\bar{a}v\rangle\delta_{us} - \langle bs\|\bar{a}v\rangle\delta_{u\bar{j}} - \langle b\bar{j}\|\bar{a}u\rangle\delta_{vs} + \langle sb\|u\bar{a}\rangle\delta_{v\bar{j}} \\
&= \langle b\bar{j}\|\bar{a}v\rangle\delta_{us} - \langle b\bar{j}\|\bar{a}u\rangle\delta_{vs}
\end{aligned}
\tag{B.36}
$$

$$
\begin{aligned}
(a_b^\dagger a_u a_v|\widehat{H} a_{\bar{s}}^\dagger a_t a_{\bar{j}}) &= \mathbf{F}_{\bar{j}v}\delta_{b\bar{s}}\delta_{ut} - \mathbf{F}_{\bar{j}u}\delta_{\bar{s}b}\delta_{vt} - \mathbf{F}_{tv}\delta_{\bar{j}u}\delta_{\bar{s}b} + \mathbf{F}_{tu}\delta_{b\bar{s}}\delta_{v\bar{j}} + \mathbf{F}_{b\bar{s}}[-\delta_{tu}\delta_{v\bar{j}} + \delta_{vt}\delta_{u\bar{j}}] \\
&\quad + \langle t\bar{j}\|vu\rangle\delta_{\bar{s}b} + \langle b\bar{j}\|\bar{s}v\rangle\delta_{ut} - \langle bt\|\bar{s}v\rangle\delta_{u\bar{j}} - \langle b\bar{j}\|\bar{s}u\rangle\delta_{vt} + \langle tb\|u\bar{s}\rangle\delta_{v\bar{j}} \\
&= \langle b\bar{j}\|\bar{s}v\rangle\delta_{ut} - \langle b\bar{j}\|\bar{s}u\rangle\delta_{vt}
\end{aligned}
\tag{B.37}
$$

B.1.6 $a_{\bar{b}}^{\dagger}a_{u}a_{\bar{l}}$

$$\begin{aligned}(a_{\bar{b}}^{\dagger}a_{u}a_{\bar{l}}|\widehat{H}a_{\bar{a}}^{\dagger}a_{j}a_{\bar{i}}) &= \mathbf{F}_{\bar{i}\bar{l}}\delta_{\bar{b}\bar{a}}\delta_{uj} - \mathbf{F}_{\bar{i}u}\delta_{\bar{a}\bar{b}}\delta_{\bar{l}j} - \mathbf{F}_{j\bar{l}}\delta_{\bar{i}u}\delta_{\bar{a}\bar{b}} + \mathbf{F}_{ju}\delta_{\bar{b}\bar{a}}\delta_{\bar{l}\bar{i}} + \mathbf{F}_{\bar{b}\bar{a}}[-\delta_{ju}\delta_{\bar{l}\bar{i}} + \delta_{\bar{l}j}\delta_{u\bar{i}}] \\ &\quad + \langle j\bar{i}\|\bar{l}u\rangle\delta_{\bar{a}\bar{b}} + \langle\bar{b}\bar{i}\|\bar{a}\bar{l}\rangle\delta_{uj} - \langle\bar{b}j\|\bar{a}\bar{l}\rangle\delta_{u\bar{i}} - \langle\bar{b}\bar{i}\|\bar{a}u\rangle\delta_{\bar{l}j} + \langle j\bar{b}\|u\bar{a}\rangle\delta_{\bar{l}\bar{i}} \\ &= \mathbf{F}_{ju}\delta_{\bar{b}\bar{a}}\delta_{\bar{l}\bar{i}} + \langle j\bar{i}\|\bar{l}u\rangle\delta_{\bar{a}\bar{b}} + \langle j\bar{b}\|u\bar{a}\rangle\delta_{\bar{l}\bar{i}}\end{aligned} \tag{B.38}$$

$$\begin{aligned}(a_{\bar{b}}^{\dagger}a_{u}a_{\bar{l}}|\widehat{H}a_{a}^{\dagger}a_{j}a_{i}) &= \mathbf{F}_{i\bar{l}}\delta_{\bar{b}a}\delta_{uj} - \mathbf{F}_{iu}\delta_{a\bar{b}}\delta_{\bar{l}j} - \mathbf{F}_{j\bar{l}}\delta_{iu}\delta_{a\bar{b}} + \mathbf{F}_{ju}\delta_{\bar{b}a}\delta_{\bar{l}i} + \mathbf{F}_{\bar{b}a}[-\delta_{ju}\delta_{\bar{l}i} + \delta_{\bar{l}j}\delta_{ui}] \\ &\quad + \langle ji\|\bar{l}u\rangle\delta_{a\bar{b}} + \langle\bar{b}i\|a\bar{l}\rangle\delta_{uj} - \langle\bar{b}j\|a\bar{l}\rangle\delta_{ui} - \langle\bar{b}i\|au\rangle\delta_{\bar{l}j} + \langle j\bar{b}\|ua\rangle\delta_{\bar{l}i} \\ &= 0\end{aligned} \tag{B.39}$$

$$\begin{aligned}(a_{\bar{b}}^{\dagger}a_{u}a_{\bar{l}}|\widehat{H}a_{a}^{\dagger}a_{s}a_{j}) &= \mathbf{F}_{j\bar{l}}\delta_{\bar{b}a}\delta_{us} - \mathbf{F}_{ju}\delta_{a\bar{b}}\delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}}\delta_{ju}\delta_{a\bar{b}} + \mathbf{F}_{su}\delta_{\bar{b}a}\delta_{\bar{l}j} + \mathbf{F}_{\bar{b}a}[-\delta_{su}\delta_{\bar{l}j} + \delta_{\bar{l}s}\delta_{uj}] \\ &\quad + \langle sj\|\bar{l}u\rangle\delta_{a\bar{b}} + \langle\bar{b}j\|a\bar{l}\rangle\delta_{us} - \langle\bar{b}s\|a\bar{l}\rangle\delta_{uj} - \langle\bar{b}j\|au\rangle\delta_{\bar{l}s} + \langle s\bar{b}\|ua\rangle\delta_{\bar{l}j} \\ &= \langle\bar{b}j\|a\bar{l}\rangle\delta_{us}\end{aligned} \tag{B.40}$$

$$\begin{aligned}(a_{\bar{b}}^{\dagger}a_{u}a_{\bar{l}}|\widehat{H}a_{\bar{s}}^{\dagger}a_{i}a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{b}\bar{s}}\delta_{ui} - \mathbf{F}_{\bar{j}u}\delta_{\bar{s}\bar{b}}\delta_{\bar{l}i} - \mathbf{F}_{i\bar{l}}\delta_{\bar{j}u}\delta_{\bar{s}\bar{b}} + \mathbf{F}_{iu}\delta_{\bar{b}\bar{s}}\delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{b}\bar{s}}[-\delta_{iu}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}i}\delta_{u\bar{j}}] \\ &\quad + \langle i\bar{j}\|\bar{l}u\rangle\delta_{\bar{s}\bar{b}} + \langle\bar{b}\bar{j}\|\bar{s}\bar{l}\rangle\delta_{ui} - \langle\bar{b}i\|\bar{s}\bar{l}\rangle\delta_{u\bar{j}} - \langle\bar{b}\bar{j}\|\bar{s}u\rangle\delta_{\bar{l}i} + \langle i\bar{b}\|u\bar{s}\rangle\delta_{\bar{l}\bar{j}} \\ &= \langle i\bar{b}\|u\bar{s}\rangle\delta_{\bar{l}\bar{j}}\end{aligned} \tag{B.41}$$

$$\begin{aligned}(a_{\bar{b}}^{\dagger}a_{u}a_{\bar{l}}|\widehat{H}a_{a}^{\dagger}a_{s}a_{t}) &= \mathbf{F}_{t\bar{l}}\delta_{\bar{b}a}\delta_{us} - \mathbf{F}_{tu}\delta_{a\bar{b}}\delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}}\delta_{tu}\delta_{a\bar{b}} + \mathbf{F}_{su}\delta_{\bar{b}a}\delta_{\bar{l}t} + \mathbf{F}_{\bar{b}a}[-\delta_{su}\delta_{\bar{l}t} + \delta_{\bar{l}s}\delta_{ut}] \\ &\quad + \langle st\|\bar{l}u\rangle\delta_{a\bar{b}} + \langle\bar{b}t\|a\bar{l}\rangle\delta_{us} - \langle\bar{b}s\|a\bar{l}\rangle\delta_{ut} - \langle\bar{b}t\|au\rangle\delta_{\bar{l}s} + \langle s\bar{b}\|ua\rangle\delta_{\bar{l}t} \\ &= \langle\bar{b}t\|a\bar{l}\rangle\delta_{us} - \langle\bar{b}s\|a\bar{l}\rangle\delta_{ut}\end{aligned} \tag{B.42}$$

$$\begin{aligned}(a_{\bar{b}}^{\dagger}a_u a_{\bar{l}}|\widehat{H}a_{\bar{a}}^{\dagger}a_s a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{b}\bar{a}}\delta_{us} - \mathbf{F}_{\bar{j}u}\delta_{\bar{a}\bar{b}}\delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}}\delta_{\bar{j}u}\delta_{\bar{a}\bar{b}} + \mathbf{F}_{su}\delta_{\bar{b}\bar{a}}\delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{b}\bar{a}}[-\delta_{su}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}s}\delta_{u\bar{j}}] \\ &\quad + \langle s\bar{j}\|\bar{l}u\rangle\delta_{\bar{a}\bar{b}} + \langle\bar{b}\bar{j}\|\bar{a}\bar{l}\rangle\delta_{us} - \langle\bar{b}s\|\bar{a}\bar{l}\rangle\delta_{u\bar{j}} - \langle\bar{b}\bar{j}\|\bar{a}u\rangle\delta_{\bar{l}s} + \langle s\bar{b}\|u\bar{a}\rangle\delta_{\bar{l}\bar{j}} \\ &= \mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{b}\bar{a}}\delta_{us} + \mathbf{F}_{su}\delta_{\bar{b}\bar{a}}\delta_{\bar{l}\bar{j}} - \mathbf{F}_{\bar{b}\bar{a}}\delta_{su}\delta_{\bar{l}\bar{j}} + \langle s\bar{j}\|\bar{l}u\rangle\delta_{\bar{a}\bar{b}} + \langle\bar{b}\bar{j}\|\bar{a}\bar{l}\rangle\delta_{us} + \langle s\bar{b}\|u\bar{a}\rangle\delta_{\bar{l}\bar{j}}\end{aligned}\tag{B.43}$$

$$\begin{aligned}(a_{\bar{b}}^{\dagger}a_u a_{\bar{l}}|\widehat{H}a_{\bar{s}}^{\dagger}a_t a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{b}\bar{s}}\delta_{ut} - \mathbf{F}_{\bar{j}u}\delta_{\bar{s}\bar{b}}\delta_{\bar{l}t} - \mathbf{F}_{t\bar{l}}\delta_{\bar{j}u}\delta_{\bar{s}\bar{b}} + \mathbf{F}_{tu}\delta_{\bar{b}\bar{s}}\delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{b}\bar{s}}[-\delta_{tu}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}t}\delta_{u\bar{j}}] \\ &\quad + \langle t\bar{j}\|\bar{l}u\rangle\delta_{\bar{s}\bar{b}} + \langle\bar{b}\bar{j}\|\bar{s}\bar{l}\rangle\delta_{ut} - \langle\bar{b}t\|\bar{s}\bar{l}\rangle\delta_{u\bar{j}} - \langle\bar{b}\bar{j}\|\bar{s}u\rangle\delta_{\bar{l}t} + \langle t\bar{b}\|u\bar{s}\rangle\delta_{\bar{l}\bar{j}} \\ &= -\mathbf{F}_{\bar{b}\bar{s}}\delta_{tu}\delta_{\bar{l}\bar{j}} + \langle\bar{b}\bar{j}\|\bar{s}\bar{l}\rangle\delta_{ut} + \langle t\bar{b}\|u\bar{s}\rangle\delta_{\bar{l}\bar{j}}\end{aligned}\tag{B.44}$$

B.1.7 $a_{\bar{u}}^{\dagger}a_u a_{\bar{l}}$

$$\begin{aligned}(a_{\bar{u}}^{\dagger}a_v a_{\bar{l}}|\widehat{H}a_{\bar{a}}^{\dagger}a_j a_{\bar{i}}) &= \mathbf{F}_{\bar{i}\bar{l}}\delta_{\bar{u}\bar{a}}\delta_{\bar{v}j} - \mathbf{F}_{\bar{i}v}\delta_{\bar{a}\bar{u}}\delta_{\bar{l}j} - \mathbf{F}_{j\bar{l}}\delta_{\bar{i}v}\delta_{\bar{a}\bar{u}} + \mathbf{F}_{jv}\delta_{\bar{u}\bar{a}}\delta_{\bar{l}\bar{i}} + \mathbf{F}_{\bar{u}\bar{a}}[-\delta_{jv}\delta_{\bar{l}\bar{i}} + \delta_{\bar{l}j}\delta_{v\bar{i}}] \\ &\quad + \langle j\bar{i}\|\bar{l}v\rangle\delta_{\bar{a}\bar{u}} + \langle\bar{u}\bar{i}\|\bar{a}\bar{l}\rangle\delta_{vj} - \langle\bar{u}j\|\bar{a}\bar{l}\rangle\delta_{v\bar{i}} - \langle\bar{u}\bar{i}\|\bar{a}v\rangle\delta_{\bar{l}j} + \langle j\bar{u}\|v\bar{a}\rangle\delta_{\bar{l}\bar{i}} \\ &= \langle j\bar{u}\|v\bar{a}\rangle\delta_{\bar{l}\bar{i}}\end{aligned}\tag{B.45}$$

$$\begin{aligned}(a_{\bar{u}}^{\dagger}a_v a_{\bar{l}}|\widehat{H}a_{a}^{\dagger}a_j a_i) &= \mathbf{F}_{i\bar{l}}\delta_{\bar{u}a}\delta_{vj} - \mathbf{F}_{iv}\delta_{a\bar{u}}\delta_{\bar{l}j} - \mathbf{F}_{j\bar{l}}\delta_{iv}\delta_{a\bar{u}} + \mathbf{F}_{jv}\delta_{\bar{u}a}\delta_{\bar{l}i} + \mathbf{F}_{\bar{u}a}[-\delta_{jv}\delta_{\bar{l}i} + \delta_{\bar{l}j}\delta_{vi}] \\ &\quad + \langle ji\|\bar{l}v\rangle\delta_{a\bar{u}} + \langle\bar{u}i\|a\bar{l}\rangle\delta_{vj} - \langle\bar{u}j\|a\bar{l}\rangle\delta_{vi} - \langle\bar{u}i\|av\rangle\delta_{\bar{l}j} + \langle j\bar{u}\|va\rangle\delta_{\bar{l}i} \\ &= 0\end{aligned}\tag{B.46}$$

$$\begin{aligned}(a_{\bar{u}}^{\dagger}a_v a_{\bar{l}}|\widehat{H}a_{a}^{\dagger}a_s a_j) &= \mathbf{F}_{j\bar{l}}\delta_{\bar{u}a}\delta_{vs} - \mathbf{F}_{jv}\delta_{a\bar{u}}\delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}}\delta_{jv}\delta_{a\bar{u}} + \mathbf{F}_{sv}\delta_{\bar{u}a}\delta_{\bar{l}j} + \mathbf{F}_{\bar{u}a}[-\delta_{sv}\delta_{\bar{l}j} + \delta_{\bar{l}s}\delta_{vj}] \\ &\quad + \langle sj\|\bar{l}v\rangle\delta_{a\bar{u}} + \langle\bar{u}j\|a\bar{l}\rangle\delta_{vs} - \langle\bar{u}s\|a\bar{l}\rangle\delta_{vj} - \langle\bar{u}j\|av\rangle\delta_{\bar{l}s} + \langle s\bar{u}\|va\rangle\delta_{\bar{l}j} \\ &= \langle\bar{u}j\|a\bar{l}\rangle\delta_{vs}\end{aligned}\tag{B.47}$$

$$\begin{aligned}(a^\dagger_{\bar u} a_v a_{\bar l}|\widehat{H} a^\dagger_{\bar s} a_i a_{\bar j}) &= \mathbf{F}_{\bar j \bar l}\delta_{\bar u \bar s}\delta_{vi} - \mathbf{F}_{\bar j v}\delta_{\bar s \bar u}\delta_{\bar l i} - \mathbf{F}_{i \bar l}\delta_{\bar j v}\delta_{\bar s \bar u} + \mathbf{F}_{iv}\delta_{\bar u \bar s}\delta_{\overline{l\bar j}} + \mathbf{F}_{\bar u \bar s}[-\delta_{iv}\delta_{\overline{l\bar j}} + \delta_{\bar l i}\delta_{v \bar j}] \\ &\quad + \langle i\bar j \| \bar l v\rangle \delta_{\bar s \bar u} + \langle \bar u \bar j \| \bar s \bar l\rangle \delta_{vi} - \langle \bar u i \| \bar s \bar l\rangle \delta_{v \bar j} - \langle \bar u \bar j \| \bar s v\rangle \delta_{\bar l i} + \langle i \bar u \| v \bar s\rangle \delta_{\overline{l\bar j}} \\ &= \mathbf{F}_{iv}\delta_{\bar u \bar s}\delta_{\overline{l\bar j}} + \langle i\bar j \| \bar l v\rangle \delta_{\bar s \bar u} + \langle i \bar u \| v \bar s\rangle \delta_{\overline{l\bar j}}\end{aligned} \tag{B.48}$$

$$\begin{aligned}(a^\dagger_{\bar u} a_v a_{\bar l}|\widehat{H} a^\dagger_{a} a_s a_t) &= \mathbf{F}_{t \bar l}\delta_{\bar u a}\delta_{vs} - \mathbf{F}_{tv}\delta_{a \bar u}\delta_{\bar l s} - \mathbf{F}_{s \bar l}\delta_{tv}\delta_{a \bar u} + \mathbf{F}_{sv}\delta_{\bar u a}\delta_{\bar l t} + \mathbf{F}_{\bar u a}[-\delta_{sv}\delta_{\bar l t} + \delta_{\bar l s}\delta_{vt}] \\ &\quad + \langle st \| \bar l v\rangle \delta_{a \bar u} + \langle \bar u t \| a \bar l\rangle \delta_{vs} - \langle \bar u s \| a \bar l\rangle \delta_{vt} - \langle \bar u t \| a v\rangle \delta_{\bar l s} + \langle s \bar u \| v a\rangle \delta_{\bar l t} \\ &= \langle \bar u t \| a \bar l\rangle \delta_{vs} - \langle \bar u s \| a \bar l\rangle \delta_{vt}\end{aligned} \tag{B.49}$$

$$\begin{aligned}(a^\dagger_{\bar u} a_v a_{\bar l}|\widehat{H} a^\dagger_{\bar a} a_s a_{\bar j}) &= \mathbf{F}_{\bar j \bar l}\delta_{\bar u \bar a}\delta_{vs} - \mathbf{F}_{\bar j v}\delta_{\bar a \bar u}\delta_{\bar l s} - \mathbf{F}_{s \bar l}\delta_{\bar j v}\delta_{\bar a \bar u} + \mathbf{F}_{sv}\delta_{\bar u \bar a}\delta_{\overline{l\bar j}} + \mathbf{F}_{\bar u \bar a}[-\delta_{sv}\delta_{\overline{l\bar j}} + \delta_{\bar l s}\delta_{v \bar j}] \\ &\quad + \langle s\bar j \| \bar l v\rangle \delta_{\bar a \bar u} + \langle \bar u \bar j \| \bar a \bar l\rangle \delta_{vs} - \langle \bar u s \| \bar a \bar l\rangle \delta_{v \bar j} - \langle \bar u \bar j \| \bar a v\rangle \delta_{\bar l s} + \langle s \bar u \| v \bar a\rangle \delta_{\overline{l\bar j}} \\ &= -\mathbf{F}_{\bar u \bar a}\delta_{sv}\delta_{\overline{l\bar j}} + \langle \bar u \bar j \| \bar a \bar l\rangle \delta_{vs} + \langle s \bar u \| v \bar a\rangle \delta_{\overline{l\bar j}}\end{aligned} \tag{B.50}$$

$$\begin{aligned}(a^\dagger_{\bar u} a_v a_{\bar l}|\widehat{H} a^\dagger_{\bar s} a_t a_{\bar j}) &= \mathbf{F}_{\bar j \bar l}\delta_{\bar u \bar s}\delta_{vt} - \mathbf{F}_{\bar j v}\delta_{\bar s \bar u}\delta_{\bar l t} - \mathbf{F}_{t \bar l}\delta_{\bar j v}\delta_{\bar s \bar u} + \mathbf{F}_{tv}\delta_{\bar u \bar s}\delta_{\overline{l\bar j}} + \mathbf{F}_{\bar u \bar s}[-\delta_{tv}\delta_{\overline{l\bar j}} + \delta_{\bar l t}\delta_{v \bar j}] \\ &\quad + \langle t\bar j \| \bar l v\rangle \delta_{\bar s \bar u} + \langle \bar u \bar j \| \bar s \bar l\rangle \delta_{vt} - \langle \bar u t \| \bar s \bar l\rangle \delta_{v \bar j} - \langle \bar u \bar j \| \bar s v\rangle \delta_{\bar l t} + \langle t \bar u \| v \bar s\rangle \delta_{\overline{l\bar j}} \\ &= \mathbf{F}_{\bar j \bar l}\delta_{\bar u \bar s}\delta_{vt} + \mathbf{F}_{tv}\delta_{\bar u \bar s}\delta_{\overline{l\bar j}} - \mathbf{F}_{\bar u \bar s}\delta_{tv}\delta_{\overline{l\bar j}} + \langle t\bar j \| \bar l v\rangle \delta_{\bar s \bar u} + \langle \bar u \bar j \| \bar s \bar l\rangle \delta_{vt} + \langle t \bar u \| v \bar s\rangle \delta_{\overline{l\bar j}}\end{aligned} \tag{B.51}$$

B.2 General term for $(F_5|\widehat{H}F_5)$ for the 2ph terms in zero order

$$
\begin{aligned}
&(a^\dagger_\alpha a^\dagger_\beta a_p a_q a_r|H a^\dagger_\iota a^\dagger_\tau a_s a_t a_u) = \\
&\qquad \mathbf{det(}F_{ur}\delta_{tq}\delta_{sp}\mathbf{)det(}\delta_{\iota\alpha}\delta_{\tau\beta}\mathbf{)} \\
&\qquad - P_{ut}\mathbf{det(}F_{ur}\delta_{tq}\delta_{sp}\mathbf{)det(}\delta_{\iota\alpha}\delta_{\tau\beta}\mathbf{)} \\
&\qquad - P_{us}\mathbf{det(}F_{ur}\delta_{tq}\delta_{sp}\mathbf{)det(}\delta_{\iota\alpha}\delta_{\tau\beta}\mathbf{)} \\
&\qquad - F_{\alpha\iota}\delta_{\beta\tau}\mathbf{det(}\delta_{ur}\delta_{tq}\delta_{sp}\mathbf{)} \\
&\qquad + P_{\alpha\beta}F_{\alpha\iota}\delta_{\beta\tau}\mathbf{det(}\delta_{ur}\delta_{tq}\delta_{sp}\mathbf{)} \\
&\qquad + P_{\iota\tau}F_{\alpha\iota}\delta_{\beta\tau}\mathbf{det(}\delta_{ur}\delta_{tq}\delta_{sp}\mathbf{)} \\
&\qquad - P_{\iota\tau}P_{\alpha\beta}F_{\alpha\iota}\delta_{\beta\tau}\mathbf{det(}\delta_{ur}\delta_{tq}\delta_{sp}\mathbf{)}
\end{aligned}
\tag{B.52}
$$

where

$$
\mathbf{det(}F_{ur}\delta_{tq}\delta_{sp}\mathbf{)} = \begin{vmatrix} F_{ur} & F_{uq} & F_{up} \\ \delta_{tr} & \delta_{tq} & \delta_{tp} \\ \delta_{sr} & \delta_{sq} & \delta_{sp} \end{vmatrix} = F_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - F_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + F_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})
$$

$$
\mathbf{det(}\delta_{\iota\alpha}\delta_{\tau\beta}\mathbf{)} = \begin{vmatrix} \delta_{\iota\alpha} & \delta_{\iota\beta} \\ \delta_{\tau\alpha} & \delta_{\tau\beta} \end{vmatrix} = (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha})
$$

$$
\mathbf{det(}\delta_{ur}\delta_{tq}\delta_{sp}\mathbf{)} = \begin{vmatrix} \delta_{ur} & \delta_{uq} & \delta_{up} \\ \delta_{ar} & \delta_{tq} & \delta_{tp} \\ \delta_{sr} & \delta_{sq} & \delta_{sp} \end{vmatrix} = \delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})
\tag{B.53}
$$

$$
\begin{aligned}
&(a^\dagger_\alpha a^\dagger_\beta a_p a_q a_r | H a^\dagger_\iota a^\dagger_\tau a_s a_t a_u) = \\
&\quad [F_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - F_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + F_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - P_{ut}[F_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - F_{ul}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + F_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - P_{us}[F_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - F_{ul}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + F_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - F_{\alpha\iota}\delta_{\beta\tau}[\delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \\
&\quad + P_{\alpha\beta}F_{\alpha\iota}\delta_{\beta\tau}[\delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \\
&\quad + P_{\iota\tau}F_{\alpha\iota}\delta_{\beta\tau}[\delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \\
&\quad - P_{\iota\tau}P_{\alpha\beta}F_{\alpha\iota}\delta_{\beta\tau}[\delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})]
\end{aligned}
\tag{B.54}
$$

$$
\begin{aligned}
&(a^\dagger_\alpha a^\dagger_\beta a_p a_q a_r | H a^\dagger_\iota a^\dagger_\tau a_s a_t a_u) = \\
&\quad [F_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - F_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + F_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - [F_{tr}(\delta_{uq}\delta_{sp} - \delta_{sq}\delta_{up}) - F_{tl}(\delta_{ur}\delta_{sp} - \delta_{up}\delta_{sr}) + F_{tp}(\delta_{ur}\delta_{sq} - \delta_{uq}\delta_{sr})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - [F_{sr}(\delta_{tq}\delta_{up} - \delta_{uq}\delta_{tp}) - F_{sl}(\delta_{tr}\delta_{up} - \delta_{tp}\delta_{ur}) + F_{sp}(\delta_{tr}\delta_{uq} - \delta_{tq}\delta_{ur})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - F_{\alpha\iota}\delta_{\beta\tau}[\delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \\
&\quad + F_{\beta\iota}\delta_{\alpha\tau}[\delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \\
&\quad + F_{\alpha\tau}\delta_{\beta\iota}[\delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})] \\
&\quad - F_{\beta\tau}\delta_{\alpha\iota}[\delta_{ur}(\delta_{tq}\delta_{sp} - \delta_{sq}\delta_{tp}) - \delta_{uq}(\delta_{tr}\delta_{sp} - \delta_{tp}\delta_{sr}) + \delta_{up}(\delta_{tr}\delta_{sq} - \delta_{tq}\delta_{sr})]
\end{aligned}
\tag{B.55}
$$

General indices

$$
\begin{aligned}
&(a^\dagger_\alpha a^\dagger_\beta a_\pi a_\mu a_\kappa | H a^\dagger_\iota a^\dagger_\tau a_\sigma a_\theta a_\eta) = \\
&\quad [F_{\eta\kappa}(\delta_{\theta\mu}\delta_{\sigma\pi} - \delta_{\sigma\mu}\delta_{\theta\pi}) - F_{\eta\mu}(\delta_{\theta\kappa}\delta_{\sigma\pi} - \delta_{\theta\pi}\delta_{\sigma\kappa}) + F_{\eta\pi}(\delta_{\theta\kappa}\delta_{\sigma\mu} - \delta_{\theta\mu}\delta_{\sigma\kappa})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - [F_{\theta\kappa}(\delta_{\eta\mu}\delta_{\sigma\pi} - \delta_{\sigma\mu}\delta_{\eta\pi}) - F_{\theta\mu}(\delta_{\eta\kappa}\delta_{\sigma\pi} - \delta_{\eta\pi}\delta_{\sigma\kappa}) + F_{\theta\pi}(\delta_{\eta\kappa}\delta_{\sigma\mu} - \delta_{\eta\mu}\delta_{\sigma\kappa})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - [F_{\sigma\kappa}(\delta_{\theta\mu}\delta_{\eta\pi} - \delta_{\eta\mu}\delta_{\theta\pi}) - F_{\sigma\mu}(\delta_{\theta\kappa}\delta_{\eta\pi} - \delta_{\theta\pi}\delta_{\eta\kappa}) + F_{\sigma\pi}(\delta_{\theta\kappa}\delta_{\eta\mu} - \delta_{\theta\mu}\delta_{\eta\kappa})] \times (\delta_{\iota\alpha}\delta_{\tau\beta} - \delta_{\iota\beta}\delta_{\tau\alpha}) \\
&\quad - F_{\alpha\iota}\delta_{\beta\tau}[\delta_{\eta\kappa}(\delta_{\theta\mu}\delta_{\sigma\pi} - \delta_{\sigma\mu}\delta_{\theta\pi}) - \delta_{\eta\mu}(\delta_{\theta\kappa}\delta_{\sigma\pi} - \delta_{\theta\pi}\delta_{\sigma\kappa}) + \delta_{\eta\pi}(\delta_{\theta\kappa}\delta_{\sigma\mu} - \delta_{\theta\mu}\delta_{\sigma\kappa})] \\
&\quad + F_{\beta\iota}\delta_{\alpha\tau}[\delta_{\eta\kappa}(\delta_{\theta\mu}\delta_{\sigma\pi} - \delta_{\sigma\mu}\delta_{\theta\pi}) - \delta_{\eta\mu}(\delta_{\theta\kappa}\delta_{\sigma\pi} - \delta_{\theta\pi}\delta_{\sigma\kappa}) + \delta_{\eta\pi}(\delta_{\theta\kappa}\delta_{\sigma\mu} - \delta_{\theta\mu}\delta_{\sigma\kappa})] \\
&\quad + F_{\alpha\tau}\delta_{\beta\iota}[\delta_{\eta\kappa}(\delta_{\theta\mu}\delta_{\sigma\pi} - \delta_{\sigma\mu}\delta_{\theta\pi}) - \delta_{\eta\mu}(\delta_{\theta\kappa}\delta_{\sigma\pi} - \delta_{\theta\pi}\delta_{\sigma\kappa}) + \delta_{\eta\pi}(\delta_{\theta\kappa}\delta_{\sigma\mu} - \delta_{\theta\mu}\delta_{\sigma\kappa})] \\
&\quad - F_{\beta\tau}\delta_{\alpha\iota}[\delta_{\eta\kappa}(\delta_{\theta\mu}\delta_{\sigma\pi} - \delta_{\sigma\mu}\delta_{\theta\pi}) - \delta_{\eta\mu}(\delta_{\theta\kappa}\delta_{\sigma\pi} - \delta_{\theta\pi}\delta_{\sigma\kappa}) + \delta_{\eta\pi}(\delta_{\theta\kappa}\delta_{\sigma\mu} - \delta_{\theta\mu}\delta_{\sigma\kappa})]
\end{aligned}
\tag{B.56}
$$

B.2.1 $a^\dagger_{\bar b} a^\dagger_{\bar u} a_u a_{\bar l} a_{\bar k}$

$$
\begin{aligned}
&(a^\dagger_{\bar b} a^\dagger_{\bar u} a_u a_{\bar l} a_{\bar k} | H a^\dagger_{\bar a} a^\dagger_{\bar s} a_s a_{\bar j} a_{\bar i}) = \\
&\quad [F_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - F_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + F_{\bar i u}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \times (\delta_{\bar a\bar b}\delta_{\bar s\bar u} - \delta_{\bar a\bar u}\delta_{\bar s\bar b}) \\
&\quad - [F_{\bar j\bar k}(\delta_{\bar i\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar i u}) - F_{\bar j\bar l}(\delta_{\bar i\bar k}\delta_{su} - \delta_{\bar i u}\delta_{s\bar k}) + F_{\bar j u}(\delta_{\bar i\bar k}\delta_{s\bar l} - \delta_{\bar i\bar l}\delta_{s\bar k})] \times (\delta_{\bar a\bar b}\delta_{\bar s\bar u} - \delta_{\bar a\bar u}\delta_{\bar s\bar b}) \\
&\quad - [F_{s\bar k}(\delta_{\bar j\bar l}\delta_{\bar i u} - \delta_{\bar i\bar l}\delta_{\bar j u}) - F_{s\bar l}(\delta_{\bar j\bar k}\delta_{\bar i u} - \delta_{\bar j u}\delta_{\bar i\bar k}) + F_{su}(\delta_{\bar j\bar k}\delta_{\bar i\bar l} - \delta_{\bar j\bar l}\delta_{\bar i\bar k})] \times (\delta_{\bar a\bar b}\delta_{\bar s\bar u} - \delta_{\bar a\bar u}\delta_{\bar s\bar b}) \\
&\quad - F_{\bar b\bar a}\delta_{\bar u\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + \delta_{\bar i u}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar u\bar a}\delta_{\bar b\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + \delta_{\bar i u}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar b\bar s}\delta_{\bar u\bar a}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + \delta_{\bar i u}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad - F_{\bar u\bar s}\delta_{\bar b\bar a}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + \delta_{\bar i u}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad = [F_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{su}) - F_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{su})] \times (\delta_{\bar a\bar b}\delta_{\bar s\bar u}) \\
&\quad - [F_{\bar j\bar k}(\delta_{\bar i\bar l}\delta_{su}) - F_{\bar j\bar l}(\delta_{\bar i\bar k}\delta_{su})] \times (\delta_{\bar a\bar b}\delta_{\bar s\bar u}) \\
&\quad - F_{su}(\delta_{\bar j\bar k}\delta_{\bar i\bar l} - \delta_{\bar j\bar l}\delta_{\bar i\bar k}) \times (\delta_{\bar a\bar b}\delta_{\bar s\bar u}) \\
&\quad - F_{\bar b\bar a}\delta_{\bar u\bar s}[\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{su} - \delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{su}] \\
&\quad - F_{\bar u\bar s}\delta_{\bar b\bar a}[\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{su} - \delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{su}] \\
&\quad = F_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{su}\delta_{\bar a\bar b}\delta_{\bar s\bar u} - F_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{su}\delta_{\bar a\bar b}\delta_{\bar s\bar u} - F_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{su}\delta_{\bar a\bar b}\delta_{\bar s\bar u} + F_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{su}\delta_{\bar a\bar b}\delta_{\bar s\bar u} \\
&\quad - F_{su}\delta_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{\bar a\bar b}\delta_{\bar s\bar u} + F_{su}\delta_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{\bar a\bar b}\delta_{\bar s\bar u} - F_{\bar b\bar a}\delta_{\bar u\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{su} + F_{\bar b\bar a}\delta_{\bar u\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{su} \\
&\quad - F_{\bar u\bar s}\delta_{\bar b\bar a}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{su} + F_{\bar u\bar s}\delta_{\bar b\bar a}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{su}
\end{aligned}
\tag{B.57}
$$

$$
\begin{aligned}
&(a^\dagger_{\bar b} a^\dagger_{\bar u} a_u a_{\bar l} a_{\bar k} | H a^\dagger_{a} a^\dagger_{\bar s} a_s a_{\bar j} a_{i}) = \\
&\quad [F_{i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - F_{i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + F_{iu}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \times (\delta_{a\bar b}\delta_{\bar s\bar u} - \delta_{a\bar u}\delta_{\bar s\bar b}) \\
&\quad - [F_{\bar j\bar k}(\delta_{i\bar l}\delta_{su} - \delta_{s\bar l}\delta_{iu}) - F_{\bar j\bar l}(\delta_{i\bar k}\delta_{su} - \delta_{iu}\delta_{s\bar k}) + F_{\bar j u}(\delta_{i\bar k}\delta_{s\bar l} - \delta_{i\bar l}\delta_{s\bar k})] \times (\delta_{a\bar b}\delta_{\bar s\bar u} - \delta_{a\bar u}\delta_{\bar s\bar b}) \\
&\quad - [F_{s\bar k}(\delta_{\bar j\bar l}\delta_{iu} - \delta_{i\bar l}\delta_{\bar j u}) - F_{s\bar l}(\delta_{\bar j\bar k}\delta_{iu} - \delta_{\bar j u}\delta_{i\bar k}) + F_{su}(\delta_{\bar j\bar k}\delta_{i\bar l} - \delta_{\bar j\bar l}\delta_{i\bar k})] \times (\delta_{a\bar b}\delta_{\bar s\bar u} - \delta_{a\bar u}\delta_{\bar s\bar b}) \\
&\quad - F_{\bar b a}\delta_{\bar u\bar s}[\delta_{i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - \delta_{i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + \delta_{iu}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar u a}\delta_{\bar b\bar s}[\delta_{i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - \delta_{i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + \delta_{iu}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar b\bar s}\delta_{\bar u a}[\delta_{i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - \delta_{i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + \delta_{iu}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad - F_{\bar u\bar s}\delta_{\bar b a}[\delta_{i\bar k}(\delta_{\bar j\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar j u}) - \delta_{i\bar l}(\delta_{\bar j\bar k}\delta_{su} - \delta_{\bar j u}\delta_{s\bar k}) + \delta_{iu}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad = [F_{i\bar k}\delta_{\bar j\bar l}\delta_{su} - F_{i\bar l}\delta_{\bar j\bar k}\delta_{su}] \times (\delta_{a\bar b}\delta_{\bar s\bar u}) = 0
\end{aligned}
\tag{B.58}
$$

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\begin{aligned}
&(a^\dagger_{\bar b} a^\dagger_{\bar u} a_u a_{\bar l} a_{\bar k} | H a^\dagger_a a^\dagger_{\bar t} a_s a_t a_{\bar i}) = \\
&\quad [F_{\bar i\bar k}(\delta_{t\bar l}\delta_{su} - \delta_{s\bar l}\delta_{tu}) - F_{\bar i\bar l}(\delta_{t\bar k}\delta_{su} - \delta_{tu}\delta_{s\bar k}) + F_{\bar iu}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \times (\delta_{a\bar b}\delta_{\bar t\bar u} - \delta_{a\bar u}\delta_{\bar t\bar b}) \\
&\quad - [F_{t\bar k}(\delta_{\bar i\bar l}\delta_{su} - \delta_{s\bar l}\delta_{\bar iu}) - F_{t\bar l}(\delta_{\bar i\bar k}\delta_{su} - \delta_{\bar iu}\delta_{s\bar k}) + F_{tu}(\delta_{\bar i\bar k}\delta_{s\bar l} - \delta_{\bar i\bar l}\delta_{s\bar k})] \times (\delta_{a\bar b}\delta_{\bar t\bar u} - \delta_{a\bar u}\delta_{\bar t\bar b}) \\
&\quad - [F_{s\bar k}(\delta_{t\bar l}\delta_{\bar iu} - \delta_{\bar i\bar l}\delta_{tu}) - F_{s\bar l}(\delta_{t\bar k}\delta_{\bar iu} - \delta_{tu}\delta_{\bar i\bar k}) + F_{su}(\delta_{t\bar k}\delta_{\bar i\bar l} - \delta_{t\bar l}\delta_{\bar i\bar k})] \times (\delta_{a\bar b}\delta_{\bar t\bar u} - \delta_{a\bar u}\delta_{\bar t\bar b}) \\
&\quad - F_{\bar ba}\delta_{\bar u\bar t}[\delta_{\bar i\bar k}(\delta_{t\bar l}\delta_{su} - \delta_{s\bar l}\delta_{tu}) - \delta_{\bar i\bar l}(\delta_{t\bar k}\delta_{su} - \delta_{tu}\delta_{s\bar k}) + \delta_{\bar iu}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar ua}\delta_{\bar b\bar t}[\delta_{\bar i\bar k}(\delta_{t\bar l}\delta_{su} - \delta_{s\bar l}\delta_{tu}) - \delta_{\bar i\bar l}(\delta_{t\bar k}\delta_{su} - \delta_{tu}\delta_{s\bar k}) + \delta_{\bar iu}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar b\bar t}\delta_{\bar ua}[\delta_{\bar i\bar k}(\delta_{t\bar l}\delta_{su} - \delta_{s\bar l}\delta_{tu}) - \delta_{\bar i\bar l}(\delta_{t\bar k}\delta_{su} - \delta_{tu}\delta_{s\bar k}) + \delta_{\bar iu}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \\
&\quad - F_{\bar u\bar t}\delta_{\bar ba}[\delta_{\bar i\bar k}(\delta_{t\bar l}\delta_{su} - \delta_{s\bar l}\delta_{tu}) - \delta_{\bar i\bar l}(\delta_{t\bar k}\delta_{su} - \delta_{tu}\delta_{s\bar k}) + \delta_{\bar iu}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \\
&\quad = 0
\end{aligned}
\tag{B.59}
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\begin{aligned}
&(a^\dagger_{\bar b} a^\dagger_{\bar u} a_u a_{\bar l} a_{\bar k} | H a^\dagger_{\bar s} a^\dagger_{\bar t} a_t a_{\bar j} a_{\bar i}) = \\
&\quad [F_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tu} - \delta_{t\bar l}\delta_{\bar ju}) - F_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tu} - \delta_{\bar ju}\delta_{t\bar k}) + F_{\bar iu}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \times (\delta_{\bar s\bar b}\delta_{\bar t\bar u} - \delta_{\bar s\bar u}\delta_{\bar t\bar b}) \\
&\quad - [F_{\bar j\bar k}(\delta_{\bar i\bar l}\delta_{tu} - \delta_{t\bar l}\delta_{\bar iu}) - F_{\bar j\bar l}(\delta_{\bar i\bar k}\delta_{tu} - \delta_{\bar iu}\delta_{t\bar k}) + F_{\bar ju}(\delta_{\bar i\bar k}\delta_{t\bar l} - \delta_{\bar i\bar l}\delta_{t\bar k})] \times (\delta_{\bar s\bar b}\delta_{\bar t\bar u} - \delta_{\bar s\bar u}\delta_{\bar t\bar b}) \\
&\quad - [F_{t\bar k}(\delta_{\bar j\bar l}\delta_{\bar iu} - \delta_{\bar i\bar l}\delta_{\bar ju}) - F_{t\bar l}(\delta_{\bar j\bar k}\delta_{\bar iu} - \delta_{\bar ju}\delta_{\bar i\bar k}) + F_{tu}(\delta_{\bar j\bar k}\delta_{\bar i\bar l} - \delta_{\bar j\bar l}\delta_{\bar i\bar k})] \times (\delta_{\bar s\bar b}\delta_{\bar t\bar u} - \delta_{\bar s\bar u}\delta_{\bar t\bar b}) \\
&\quad - F_{\bar b\bar s}\delta_{\bar u\bar t}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tu} - \delta_{t\bar l}\delta_{\bar ju}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tu} - \delta_{\bar ju}\delta_{t\bar k}) + \delta_{\bar iu}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \\
&\quad + F_{\bar u\bar s}\delta_{\bar b\bar t}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tu} - \delta_{t\bar l}\delta_{\bar ju}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tu} - \delta_{\bar ju}\delta_{t\bar k}) + \delta_{\bar iu}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \\
&\quad + F_{\bar b\bar t}\delta_{\bar u\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tu} - \delta_{t\bar l}\delta_{\bar ju}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tu} - \delta_{\bar ju}\delta_{t\bar k}) + \delta_{\bar iu}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \\
&\quad - F_{\bar u\bar t}\delta_{\bar b\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tu} - \delta_{t\bar l}\delta_{\bar ju}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tu} - \delta_{\bar ju}\delta_{t\bar k}) + \delta_{\bar iu}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \\
&\quad = -F_{\bar b\bar s}\delta_{\bar u\bar t}[\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tu} - \delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tu}] + F_{\bar b\bar t}\delta_{\bar u\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tu}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tu})]
\end{aligned}
\tag{B.60}
$$

B.2.2 $a_b^\dagger a_{\bar{u}}^\dagger a_u a_{\bar{l}} a_k$

$$
\begin{aligned}
&(a_b^\dagger a_{\bar{u}}^\dagger a_u a_{\bar{l}} a_k | H a_{\bar{a}}^\dagger a_{\bar{s}}^\dagger a_s a_{\bar{j}} a_{\bar{i}}) = \\
&\quad [F_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - F_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + F_{\bar{i}u}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \times (\delta_{\bar{a}b}\delta_{\bar{s}\bar{u}} - \delta_{\bar{a}\bar{u}}\delta_{\bar{s}b}) \\
&\quad - [F_{\bar{j}k}(\delta_{\bar{i}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{i}u}) - F_{\bar{j}\bar{l}}(\delta_{\bar{i}k}\delta_{su} - \delta_{\bar{i}u}\delta_{sk}) + F_{\bar{j}u}(\delta_{\bar{i}k}\delta_{s\bar{l}} - \delta_{\bar{i}\bar{l}}\delta_{sk})] \times (\delta_{\bar{a}b}\delta_{\bar{s}\bar{u}} - \delta_{\bar{a}\bar{u}}\delta_{\bar{s}b}) \\
&\quad - [F_{sk}(\delta_{\bar{j}\bar{l}}\delta_{\bar{i}u} - \delta_{\bar{i}\bar{l}}\delta_{\bar{j}u}) - F_{s\bar{l}}(\delta_{\bar{j}k}\delta_{\bar{i}u} - \delta_{\bar{j}u}\delta_{\bar{i}k}) + F_{su}(\delta_{\bar{j}k}\delta_{\bar{i}\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{\bar{i}k})] \times (\delta_{\bar{a}b}\delta_{\bar{s}\bar{u}} - \delta_{\bar{a}\bar{u}}\delta_{\bar{s}b}) \\
&\quad - F_{b\bar{a}}\delta_{\bar{u}\bar{s}}[\delta_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - \delta_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + \delta_{\bar{i}u}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \\
&\quad + F_{\bar{u}\bar{a}}\delta_{b\bar{s}}[\delta_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - \delta_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + \delta_{\bar{i}u}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \\
&\quad + F_{b\bar{s}}\delta_{\bar{u}\bar{a}}[\delta_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - \delta_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + \delta_{\bar{i}u}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \\
&\quad - F_{\bar{u}\bar{s}}\delta_{b\bar{a}}[\delta_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - \delta_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + \delta_{\bar{i}u}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \\
&\quad = 0
\end{aligned}
\tag{B.61}
$$

$$
\begin{aligned}
&(a_b^\dagger a_{\bar{u}}^\dagger a_u a_{\bar{l}} a_k | H a_{a}^\dagger a_{\bar{s}}^\dagger a_s a_{\bar{j}} a_{i}) = \\
&\quad [F_{ik}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - F_{i\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + F_{iu}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \times (\delta_{ab}\delta_{\bar{s}\bar{u}} - \delta_{a\bar{u}}\delta_{\bar{s}b}) \\
&\quad - [F_{\bar{j}k}(\delta_{i\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{iu}) - F_{\bar{j}\bar{l}}(\delta_{ik}\delta_{su} - \delta_{iu}\delta_{sk}) + F_{\bar{j}u}(\delta_{ik}\delta_{s\bar{l}} - \delta_{i\bar{l}}\delta_{sk})] \times (\delta_{ab}\delta_{\bar{s}\bar{u}} - \delta_{a\bar{u}}\delta_{\bar{s}b}) \\
&\quad - [F_{sk}(\delta_{\bar{j}\bar{l}}\delta_{iu} - \delta_{i\bar{l}}\delta_{\bar{j}u}) - F_{s\bar{l}}(\delta_{\bar{j}k}\delta_{iu} - \delta_{\bar{j}u}\delta_{ik}) + F_{su}(\delta_{\bar{j}k}\delta_{i\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{ik})] \times (\delta_{ab}\delta_{\bar{s}\bar{u}} - \delta_{a\bar{u}}\delta_{\bar{s}b}) \\
&\quad - F_{ba}\delta_{\bar{u}\bar{s}}[\delta_{ik}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - \delta_{i\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + \delta_{iu}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \\
&\quad + F_{\bar{u}a}\delta_{b\bar{s}}[\delta_{ik}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - \delta_{i\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + \delta_{iu}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \\
&\quad + F_{b\bar{s}}\delta_{\bar{u}a}[\delta_{ik}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - \delta_{i\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + \delta_{iu}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \\
&\quad - F_{\bar{u}\bar{s}}\delta_{ba}[\delta_{ik}(\delta_{\bar{j}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{j}u}) - \delta_{i\bar{l}}(\delta_{\bar{j}k}\delta_{su} - \delta_{\bar{j}u}\delta_{sk}) + \delta_{iu}(\delta_{\bar{j}k}\delta_{s\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{sk})] \\
&\quad = F_{ik}\delta_{\bar{j}\bar{l}}\delta_{su}\delta_{ab}\delta_{\bar{s}\bar{u}} - F_{ba}\delta_{\bar{u}\bar{s}}\delta_{ik}\delta_{\bar{j}\bar{l}}\delta_{su} - F_{\bar{u}\bar{s}}\delta_{ba}\delta_{ik}\delta_{\bar{j}\bar{l}}\delta_{su}
\end{aligned}
\tag{B.62}
$$

$$
\begin{aligned}
&(a_b^\dagger a_{\bar{u}}^\dagger a_u a_{\bar{l}} a_k | H a_a^\dagger a_{\bar{t}}^\dagger a_s a_t a_{\bar{i}}) = \\
&\quad [F_{\bar{i}k}(\delta_{t\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{tu}) - F_{\bar{i}\bar{l}}(\delta_{tk}\delta_{su} - \delta_{tu}\delta_{sk}) + F_{\bar{i}u}(\delta_{tk}\delta_{s\bar{l}} - \delta_{t\bar{l}}\delta_{sk})] \times (\delta_{ab}\delta_{\bar{t}\bar{u}} - \delta_{a\bar{u}}\delta_{\bar{t}b}) \\
&\quad - [F_{tk}(\delta_{\bar{i}\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{\bar{i}u}) - F_{t\bar{l}}(\delta_{\bar{i}k}\delta_{su} - \delta_{\bar{i}u}\delta_{sk}) + F_{tu}(\delta_{\bar{i}k}\delta_{s\bar{l}} - \delta_{\bar{i}\bar{l}}\delta_{sk})] \times (\delta_{ab}\delta_{\bar{t}\bar{u}} - \delta_{a\bar{u}}\delta_{\bar{t}b}) \\
&\quad - [F_{sk}(\delta_{t\bar{l}}\delta_{\bar{i}u} - \delta_{\bar{i}\bar{l}}\delta_{tu}) - F_{s\bar{l}}(\delta_{tk}\delta_{\bar{i}u} - \delta_{tu}\delta_{\bar{i}k}) + F_{su}(\delta_{tk}\delta_{\bar{i}\bar{l}} - \delta_{t\bar{l}}\delta_{\bar{i}k})] \times (\delta_{ab}\delta_{\bar{t}\bar{u}} - \delta_{a\bar{u}}\delta_{\bar{t}b}) \\
&\quad - F_{ba}\delta_{\bar{u}\bar{t}}[\delta_{\bar{i}k}(\delta_{t\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{tu}) - \delta_{\bar{i}\bar{l}}(\delta_{tk}\delta_{su} - \delta_{tu}\delta_{sk}) + \delta_{\bar{i}u}(\delta_{tk}\delta_{s\bar{l}} - \delta_{t\bar{l}}\delta_{sk})] \\
&\quad + F_{\bar{u}a}\delta_{b\bar{t}}[\delta_{\bar{i}k}(\delta_{t\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{tu}) - \delta_{\bar{i}\bar{l}}(\delta_{tk}\delta_{su} - \delta_{tu}\delta_{sk}) + \delta_{\bar{i}u}(\delta_{tk}\delta_{s\bar{l}} - \delta_{t\bar{l}}\delta_{sk})] \\
&\quad + F_{b\bar{t}}\delta_{\bar{u}a}[\delta_{\bar{i}k}(\delta_{t\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{tu}) - \delta_{\bar{i}\bar{l}}(\delta_{tk}\delta_{su} - \delta_{tu}\delta_{sk}) + \delta_{\bar{i}u}(\delta_{tk}\delta_{s\bar{l}} - \delta_{t\bar{l}}\delta_{sk})] \\
&\quad - F_{\bar{u}\bar{t}}\delta_{ba}[\delta_{\bar{i}k}(\delta_{t\bar{l}}\delta_{su} - \delta_{s\bar{l}}\delta_{tu}) - \delta_{\bar{i}\bar{l}}(\delta_{tk}\delta_{su} - \delta_{tu}\delta_{sk}) + \delta_{\bar{i}u}(\delta_{tk}\delta_{s\bar{l}} - \delta_{t\bar{l}}\delta_{sk})] \\
&\quad = -F_{tk}\delta_{\bar{i}\bar{l}}\delta_{su}\delta_{ab}\delta_{\bar{t}\bar{u}} + F_{sk}\delta_{\bar{i}\bar{l}}\delta_{tu}\delta_{ab}\delta_{\bar{t}\bar{u}}
\end{aligned}
\tag{B.63}
$$

$$
\begin{aligned}
&(a_b^\dagger a_{\bar{u}}^\dagger a_u a_{\bar{l}} a_k | H a_{\bar{s}}^\dagger a_{\bar{t}}^\dagger a_t a_{\bar{j}} a_{\bar{i}}) = \\
&\quad [F_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{tu} - \delta_{t\bar{l}}\delta_{\bar{j}u}) - F_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{tu} - \delta_{\bar{j}u}\delta_{tk}) + F_{\bar{i}u}(\delta_{\bar{j}k}\delta_{t\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{tk})] \times (\delta_{\bar{s}b}\delta_{\bar{t}\bar{u}} - \delta_{\bar{s}\bar{u}}\delta_{\bar{t}b}) \\
&\quad - [F_{\bar{j}k}(\delta_{\bar{i}\bar{l}}\delta_{tu} - \delta_{t\bar{l}}\delta_{\bar{i}u}) - F_{\bar{j}\bar{l}}(\delta_{\bar{i}k}\delta_{tu} - \delta_{\bar{i}u}\delta_{tk}) + F_{\bar{j}u}(\delta_{\bar{i}k}\delta_{t\bar{l}} - \delta_{\bar{i}\bar{l}}\delta_{tk})] \times (\delta_{\bar{s}b}\delta_{\bar{t}\bar{u}} - \delta_{\bar{s}\bar{u}}\delta_{\bar{t}b}) \\
&\quad - [F_{tk}(\delta_{\bar{j}\bar{l}}\delta_{\bar{i}u} - \delta_{\bar{i}\bar{l}}\delta_{\bar{j}u}) - F_{t\bar{l}}(\delta_{\bar{j}k}\delta_{\bar{i}u} - \delta_{\bar{j}u}\delta_{\bar{i}k}) + F_{tu}(\delta_{\bar{j}k}\delta_{\bar{i}\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{\bar{i}k})] \times (\delta_{\bar{s}b}\delta_{\bar{t}\bar{u}} - \delta_{\bar{s}\bar{u}}\delta_{\bar{t}b}) \\
&\quad - F_{b\bar{s}}\delta_{\bar{u}\bar{t}}[\delta_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{tu} - \delta_{t\bar{l}}\delta_{\bar{j}u}) - \delta_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{tu} - \delta_{\bar{j}u}\delta_{tk}) + \delta_{\bar{i}u}(\delta_{\bar{j}k}\delta_{t\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{tk})] \\
&\quad + F_{\bar{u}\bar{s}}\delta_{b\bar{t}}[\delta_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{tu} - \delta_{t\bar{l}}\delta_{\bar{j}u}) - \delta_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{tu} - \delta_{\bar{j}u}\delta_{tk}) + \delta_{\bar{i}u}(\delta_{\bar{j}k}\delta_{t\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{tk})] \\
&\quad + F_{b\bar{t}}\delta_{\bar{u}\bar{s}}[\delta_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{tu} - \delta_{t\bar{l}}\delta_{\bar{j}u}) - \delta_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{tu} - \delta_{\bar{j}u}\delta_{tk}) + \delta_{\bar{i}u}(\delta_{\bar{j}k}\delta_{t\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{tk})] \\
&\quad - F_{\bar{u}\bar{t}}\delta_{b\bar{s}}[\delta_{\bar{i}k}(\delta_{\bar{j}\bar{l}}\delta_{tu} - \delta_{t\bar{l}}\delta_{\bar{j}u}) - \delta_{\bar{i}\bar{l}}(\delta_{\bar{j}k}\delta_{tu} - \delta_{\bar{j}u}\delta_{tk}) + \delta_{\bar{i}u}(\delta_{\bar{j}k}\delta_{t\bar{l}} - \delta_{\bar{j}\bar{l}}\delta_{tk})] \\
&\quad = 0
\end{aligned}
\tag{B.64}
$$

B.2.3 $a_b^\dagger a_{\bar{v}}^\dagger a_u a_{\bar{v}} a_{\bar{k}}$

$$\begin{aligned}
&(a_b^\dagger a_{\bar{v}}^\dagger a_u a_v a_{\bar{k}} | H a_{\bar{a}}^\dagger a_{\bar{s}}^\dagger a_s a_{\bar{j}} a_{\bar{i}}) = \\
&\quad [F_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - F_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + F_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \times (\delta_{\bar{a}b}\delta_{\bar{s}\bar{v}} - \delta_{\bar{a}\bar{v}}\delta_{\bar{s}b}) \\
&\quad - [F_{\bar{j}\bar{k}}(\delta_{\bar{i}v}\delta_{su} - \delta_{sv}\delta_{\bar{i}u}) - F_{\bar{j}v}(\delta_{\bar{i}\bar{k}}\delta_{su} - \delta_{\bar{i}u}\delta_{s\bar{k}}) + F_{\bar{j}u}(\delta_{\bar{i}\bar{k}}\delta_{sv} - \delta_{\bar{i}v}\delta_{s\bar{k}})] \times (\delta_{\bar{a}b}\delta_{\bar{s}\bar{v}} - \delta_{\bar{a}\bar{v}}\delta_{\bar{s}b}) \\
&\quad - [F_{s\bar{k}}(\delta_{\bar{j}v}\delta_{\bar{i}u} - \delta_{\bar{i}v}\delta_{\bar{j}u}) - F_{sv}(\delta_{\bar{j}\bar{k}}\delta_{\bar{i}u} - \delta_{\bar{j}u}\delta_{\bar{i}\bar{k}}) + F_{su}(\delta_{\bar{j}\bar{k}}\delta_{\bar{i}v} - \delta_{\bar{j}v}\delta_{\bar{i}\bar{k}})] \times (\delta_{\bar{a}b}\delta_{\bar{s}\bar{v}} - \delta_{\bar{a}\bar{v}}\delta_{\bar{s}b}) \\
&\quad - F_{b\bar{a}}\delta_{\bar{v}\bar{s}}[\delta_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - \delta_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + \delta_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \\
&\quad + F_{\bar{v}\bar{a}}\delta_{b\bar{s}}[\delta_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - \delta_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + \delta_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \\
&\quad + F_{b\bar{s}}\delta_{\bar{v}\bar{a}}[\delta_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - \delta_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + \delta_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \\
&\quad - F_{\bar{v}\bar{s}}\delta_{b\bar{a}}[\delta_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - \delta_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + \delta_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \\
&\quad = 0
\end{aligned} \tag{B.65}$$

$$\begin{aligned}
&(a_b^\dagger a_{\bar{v}}^\dagger a_u a_v a_{\bar{k}} | H a_a^\dagger a_{\bar{s}}^\dagger a_s a_{\bar{j}} a_i) = \\
&\quad [F_{i\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - F_{iv}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + F_{iu}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \times (\delta_{ab}\delta_{\bar{s}\bar{v}} - \delta_{a\bar{v}}\delta_{\bar{s}b}) \\
&\quad - [F_{\bar{j}\bar{k}}(\delta_{iv}\delta_{su} - \delta_{sv}\delta_{iu}) - F_{\bar{j}v}(\delta_{i\bar{k}}\delta_{su} - \delta_{iu}\delta_{s\bar{k}}) + F_{\bar{j}u}(\delta_{i\bar{k}}\delta_{sv} - \delta_{iv}\delta_{s\bar{k}})] \times (\delta_{ab}\delta_{\bar{s}\bar{v}} - \delta_{a\bar{v}}\delta_{\bar{s}b}) \\
&\quad - [F_{s\bar{k}}(\delta_{\bar{j}v}\delta_{iu} - \delta_{iv}\delta_{\bar{j}u}) - F_{sv}(\delta_{\bar{j}\bar{k}}\delta_{iu} - \delta_{\bar{j}u}\delta_{i\bar{k}}) + F_{su}(\delta_{\bar{j}\bar{k}}\delta_{iv} - \delta_{\bar{j}v}\delta_{i\bar{k}})] \times (\delta_{ab}\delta_{\bar{s}\bar{v}} - \delta_{a\bar{v}}\delta_{\bar{s}b}) \\
&\quad - F_{ba}\delta_{\bar{v}\bar{s}}[\delta_{i\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - \delta_{iv}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + \delta_{iu}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \\
&\quad + F_{\bar{v}a}\delta_{b\bar{s}}[\delta_{i\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - \delta_{iv}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + \delta_{iu}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \\
&\quad + F_{b\bar{s}}\delta_{\bar{v}a}[\delta_{i\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - \delta_{iv}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + \delta_{iu}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \\
&\quad - F_{\bar{v}\bar{s}}\delta_{ba}[\delta_{i\bar{k}}(\delta_{\bar{j}v}\delta_{su} - \delta_{sv}\delta_{\bar{j}u}) - \delta_{iv}(\delta_{\bar{j}\bar{k}}\delta_{su} - \delta_{\bar{j}u}\delta_{s\bar{k}}) + \delta_{iu}(\delta_{\bar{j}\bar{k}}\delta_{sv} - \delta_{\bar{j}v}\delta_{s\bar{k}})] \\
&\quad = -F_{iv}\delta_{\bar{j}\bar{k}}\delta_{su}\delta_{ab}\delta_{\bar{s}\bar{v}} + F_{iu}\delta_{\bar{j}\bar{k}}\delta_{sv}\delta_{ab}\delta_{\bar{s}\bar{v}}
\end{aligned} \tag{B.66}$$

$$
\begin{aligned}
&(a_b^\dagger a_{\bar{v}}^\dagger a_u a_v a_{\bar{k}}|H a_a^\dagger a_{\bar{t}}^\dagger a_s a_t a_{\bar{i}}) = \\
&\quad [F_{\bar{i}\bar{k}}(\delta_{tv}\delta_{su} - \delta_{sv}\delta_{tu}) - F_{\bar{i}v}(\delta_{t\bar{k}}\delta_{su} - \delta_{tu}\delta_{s\bar{k}}) + F_{\bar{i}u}(\delta_{t\bar{k}}\delta_{sv} - \delta_{tv}\delta_{s\bar{k}})] \times (\delta_{ab}\delta_{\bar{t}\bar{v}} - \delta_{a\bar{v}}\delta_{\bar{t}b}) \\
&\quad - [F_{t\bar{k}}(\delta_{\bar{i}v}\delta_{su} - \delta_{sv}\delta_{\bar{i}u}) - F_{tv}(\delta_{\bar{i}\bar{k}}\delta_{su} - \delta_{\bar{i}u}\delta_{s\bar{k}}) + F_{tu}(\delta_{\bar{i}\bar{k}}\delta_{sv} - \delta_{\bar{i}v}\delta_{s\bar{k}})] \times (\delta_{ab}\delta_{\bar{t}\bar{v}} - \delta_{a\bar{v}}\delta_{\bar{t}b}) \\
&\quad - [F_{s\bar{k}}(\delta_{tv}\delta_{\bar{i}u} - \delta_{\bar{i}v}\delta_{tu}) - F_{sv}(\delta_{t\bar{k}}\delta_{\bar{i}u} - \delta_{tu}\delta_{\bar{i}\bar{k}}) + F_{su}(\delta_{t\bar{k}}\delta_{\bar{i}v} - \delta_{tv}\delta_{\bar{i}\bar{k}})] \times (\delta_{ab}\delta_{\bar{t}\bar{v}} - \delta_{a\bar{v}}\delta_{\bar{t}b}) \\
&\quad - F_{ba}\delta_{\bar{v}\bar{t}}[\delta_{\bar{i}\bar{k}}(\delta_{tv}\delta_{su} - \delta_{sv}\delta_{tu}) - \delta_{\bar{i}v}(\delta_{t\bar{k}}\delta_{su} - \delta_{tu}\delta_{s\bar{k}}) + \delta_{\bar{i}u}(\delta_{t\bar{k}}\delta_{sv} - \delta_{tv}\delta_{s\bar{k}})] \\
&\quad + F_{\bar{v}a}\delta_{b\bar{t}}[\delta_{\bar{i}\bar{k}}(\delta_{tv}\delta_{su} - \delta_{sv}\delta_{tu}) - \delta_{\bar{i}v}(\delta_{t\bar{k}}\delta_{su} - \delta_{tu}\delta_{s\bar{k}}) + \delta_{\bar{i}u}(\delta_{t\bar{k}}\delta_{sv} - \delta_{tv}\delta_{s\bar{k}})] \\
&\quad + F_{b\bar{t}}\delta_{\bar{v}a}[\delta_{\bar{i}\bar{k}}(\delta_{tv}\delta_{su} - \delta_{sv}\delta_{tu}) - \delta_{\bar{i}v}(\delta_{t\bar{k}}\delta_{su} - \delta_{tu}\delta_{s\bar{k}}) + \delta_{\bar{i}u}(\delta_{t\bar{k}}\delta_{sv} - \delta_{tv}\delta_{s\bar{k}})] \\
&\quad - F_{\bar{v}\bar{t}}\delta_{ba}[\delta_{\bar{i}\bar{k}}(\delta_{tv}\delta_{su} - \delta_{sv}\delta_{tu}) - \delta_{\bar{i}v}(\delta_{t\bar{k}}\delta_{su} - \delta_{tu}\delta_{s\bar{k}}) + \delta_{\bar{i}u}(\delta_{t\bar{k}}\delta_{sv} - \delta_{tv}\delta_{s\bar{k}})] \\
&\quad = F_{\bar{i}\bar{k}}\delta_{tv}\delta_{su}\delta_{ab}\delta_{\bar{t}\bar{v}} - F_{\bar{i}\bar{k}}\delta_{sv}\delta_{tu}\delta_{ab}\delta_{\bar{t}\bar{v}} + F_{tv}\delta_{\bar{i}\bar{k}}\delta_{su}\delta_{ab}\delta_{\bar{t}\bar{v}} - F_{tu}\delta_{\bar{i}\bar{k}}\delta_{sv}\delta_{ab}\delta_{\bar{t}\bar{v}} \\
&\quad - F_{sv}\delta_{tu}\delta_{\bar{i}\bar{k}}\delta_{ab}\delta_{\bar{t}\bar{v}} + F_{su}\delta_{tv}\delta_{\bar{i}\bar{k}}\delta_{ab}\delta_{\bar{t}\bar{v}} - F_{ba}\delta_{\bar{v}\bar{t}}\delta_{\bar{i}\bar{k}}\delta_{tv}\delta_{su} + F_{ba}\delta_{\bar{v}\bar{t}}\delta_{\bar{i}\bar{k}}\delta_{sv}\delta_{tu} \\
&\quad - F_{\bar{v}\bar{t}}\delta_{ba}\delta_{\bar{i}\bar{k}}\delta_{tv}\delta_{su} + F_{\bar{v}\bar{t}}\delta_{ba}\delta_{\bar{i}\bar{k}}\delta_{sv}\delta_{tu}
\end{aligned}
\tag{B.67}
$$

$$
\begin{aligned}
&(a_b^\dagger a_{\bar{v}}^\dagger a_u a_v a_{\bar{k}}|H a_{\bar{s}}^\dagger a_{\bar{t}}^\dagger a_t a_{\bar{j}} a_{\bar{i}}) = \\
&\quad [F_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{tu} - \delta_{tv}\delta_{\bar{j}u}) - F_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{tu} - \delta_{\bar{j}u}\delta_{t\bar{k}}) + F_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{tv} - \delta_{\bar{j}v}\delta_{t\bar{k}})] \times (\delta_{\bar{s}b}\delta_{\bar{t}\bar{v}} - \delta_{\bar{s}\bar{v}}\delta_{\bar{t}b}) \\
&\quad - [F_{\bar{j}\bar{k}}(\delta_{\bar{i}v}\delta_{tu} - \delta_{tv}\delta_{\bar{i}u}) - F_{\bar{j}v}(\delta_{\bar{i}\bar{k}}\delta_{tu} - \delta_{\bar{i}u}\delta_{t\bar{k}}) + F_{\bar{j}u}(\delta_{\bar{i}\bar{k}}\delta_{tv} - \delta_{\bar{i}v}\delta_{t\bar{k}})] \times (\delta_{\bar{s}b}\delta_{\bar{t}\bar{v}} - \delta_{\bar{s}\bar{v}}\delta_{\bar{t}b}) \\
&\quad - [F_{t\bar{k}}(\delta_{\bar{j}v}\delta_{\bar{i}u} - \delta_{\bar{i}v}\delta_{\bar{j}u}) - F_{tv}(\delta_{\bar{j}\bar{k}}\delta_{\bar{i}u} - \delta_{\bar{j}u}\delta_{\bar{i}\bar{k}}) + F_{tu}(\delta_{\bar{j}\bar{k}}\delta_{\bar{i}v} - \delta_{\bar{j}v}\delta_{\bar{i}\bar{k}})] \times (\delta_{\bar{s}b}\delta_{\bar{t}\bar{v}} - \delta_{\bar{s}\bar{v}}\delta_{\bar{t}b}) \\
&\quad - F_{b\bar{s}}\delta_{\bar{v}\bar{t}}[\delta_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{tu} - \delta_{tv}\delta_{\bar{j}u}) - \delta_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{tu} - \delta_{\bar{j}u}\delta_{t\bar{k}}) + \delta_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{tv} - \delta_{\bar{j}v}\delta_{t\bar{k}})] \\
&\quad + F_{\bar{v}\bar{s}}\delta_{b\bar{t}}[\delta_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{tu} - \delta_{tv}\delta_{\bar{j}u}) - \delta_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{tu} - \delta_{\bar{j}u}\delta_{t\bar{k}}) + \delta_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{tv} - \delta_{\bar{j}v}\delta_{t\bar{k}})] \\
&\quad + F_{b\bar{t}}\delta_{\bar{v}\bar{s}}[\delta_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{tu} - \delta_{tv}\delta_{\bar{j}u}) - \delta_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{tu} - \delta_{\bar{j}u}\delta_{t\bar{k}}) + \delta_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{tv} - \delta_{\bar{j}v}\delta_{t\bar{k}})] \\
&\quad - F_{\bar{v}\bar{t}}\delta_{b\bar{s}}[\delta_{\bar{i}\bar{k}}(\delta_{\bar{j}v}\delta_{tu} - \delta_{tv}\delta_{\bar{j}u}) - \delta_{\bar{i}v}(\delta_{\bar{j}\bar{k}}\delta_{tu} - \delta_{\bar{j}u}\delta_{t\bar{k}}) + \delta_{\bar{i}u}(\delta_{\bar{j}\bar{k}}\delta_{tv} - \delta_{\bar{j}v}\delta_{t\bar{k}})] \\
&\quad = 0
\end{aligned}
\tag{B.68}
$$

B.2.4 $a^\dagger_{\bar u} a^\dagger_{\bar v} a_v a_{\bar l} a_{\bar k}$

$$
\begin{aligned}
&(a^\dagger_{\bar u} a^\dagger_{\bar v} a_v a_{\bar l} a_{\bar k} | H a^\dagger_{\bar a} a^\dagger_{\bar s} a_s a_{\bar j} a_{\bar i}) = \\
&\quad [F_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - F_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + F_{\bar i v}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \times (\delta_{\bar a\bar u}\delta_{\bar s\bar v} - \delta_{\bar a\bar v}\delta_{\bar s\bar u}) \\
&\quad - [F_{\bar j\bar k}(\delta_{\bar i\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar i v}) - F_{\bar j\bar l}(\delta_{\bar i\bar k}\delta_{sv} - \delta_{\bar i v}\delta_{s\bar k}) + F_{\bar j v}(\delta_{\bar i\bar k}\delta_{s\bar l} - \delta_{\bar i\bar l}\delta_{s\bar k})] \times (\delta_{\bar a\bar u}\delta_{\bar s\bar v} - \delta_{\bar a\bar v}\delta_{\bar s\bar u}) \\
&\quad - [F_{s\bar k}(\delta_{\bar j\bar l}\delta_{\bar i v} - \delta_{\bar i\bar l}\delta_{\bar j v}) - F_{s\bar l}(\delta_{\bar j\bar k}\delta_{\bar i v} - \delta_{\bar j v}\delta_{\bar i\bar k}) + F_{sv}(\delta_{\bar j\bar k}\delta_{\bar i\bar l} - \delta_{\bar j\bar l}\delta_{\bar i\bar k})] \times (\delta_{\bar a\bar u}\delta_{\bar s\bar v} - \delta_{\bar a\bar v}\delta_{\bar s\bar u}) \\
&\quad - F_{\bar u\bar a}\delta_{\bar v\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + \delta_{\bar i v}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar v\bar a}\delta_{\bar u\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + \delta_{\bar i v}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar u\bar s}\delta_{\bar v\bar a}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + \delta_{\bar i v}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad - F_{\bar v\bar s}\delta_{\bar u\bar a}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + \delta_{\bar i v}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad = -F_{\bar u\bar a}\delta_{\bar v\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{sv} + F_{\bar u\bar a}\delta_{\bar v\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{sv} + F_{\bar v\bar a}\delta_{\bar u\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{sv} - F_{\bar v\bar a}\delta_{\bar u\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{sv}
\end{aligned}
\tag{B.69}
$$

$$
\begin{aligned}
&(a^\dagger_{\bar u} a^\dagger_{\bar v} a_v a_{\bar l} a_{\bar k} | H a^\dagger_{a} a^\dagger_{\bar s} a_s a_{\bar j} a_{i}) = \\
&\quad [F_{i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - F_{i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + F_{iv}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \times (\delta_{a\bar u}\delta_{\bar s\bar v} - \delta_{a\bar v}\delta_{\bar s\bar u}) \\
&\quad - [F_{\bar j\bar k}(\delta_{i\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{iv}) - F_{\bar j\bar l}(\delta_{i\bar k}\delta_{sv} - \delta_{iv}\delta_{s\bar k}) + F_{\bar j v}(\delta_{i\bar k}\delta_{s\bar l} - \delta_{i\bar l}\delta_{s\bar k})] \times (\delta_{a\bar u}\delta_{\bar s\bar v} - \delta_{a\bar v}\delta_{\bar s\bar u}) \\
&\quad - [F_{s\bar k}(\delta_{\bar j\bar l}\delta_{iv} - \delta_{i\bar l}\delta_{\bar j v}) - F_{s\bar l}(\delta_{\bar j\bar k}\delta_{iv} - \delta_{\bar j v}\delta_{i\bar k}) + F_{sv}(\delta_{\bar j\bar k}\delta_{i\bar l} - \delta_{\bar j\bar l}\delta_{i\bar k})] \times (\delta_{a\bar u}\delta_{\bar s\bar v} - \delta_{a\bar v}\delta_{\bar s\bar u}) \\
&\quad - F_{\bar u a}\delta_{\bar v\bar s}[\delta_{i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - \delta_{i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + \delta_{iv}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar v a}\delta_{\bar u\bar s}[\delta_{i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - \delta_{i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + \delta_{iv}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar u\bar s}\delta_{\bar v a}[\delta_{i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - \delta_{i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + \delta_{iv}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad - F_{\bar v\bar s}\delta_{\bar u a}[\delta_{i\bar k}(\delta_{\bar j\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar j v}) - \delta_{i\bar l}(\delta_{\bar j\bar k}\delta_{sv} - \delta_{\bar j v}\delta_{s\bar k}) + \delta_{iv}(\delta_{\bar j\bar k}\delta_{s\bar l} - \delta_{\bar j\bar l}\delta_{s\bar k})] \\
&\quad = 0
\end{aligned}
\tag{B.70}
$$

$$
\begin{aligned}
&(a^\dagger_{\bar u} a^\dagger_{\bar v} a_v a_{\bar l} a_{\bar k} | H a^\dagger_a a^\dagger_{\bar t} a_s a_t a_{\bar i}) = \\
&\quad [F_{\bar i\bar k}(\delta_{t\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{tv}) - F_{\bar i\bar l}(\delta_{t\bar k}\delta_{sv} - \delta_{tv}\delta_{s\bar k}) + F_{\bar i v}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \times (\delta_{a\bar u}\delta_{\bar t\bar v} - \delta_{a\bar v}\delta_{\bar t\bar u}) \\
&\quad - [F_{t\bar k}(\delta_{\bar i\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{\bar i v}) - F_{t\bar l}(\delta_{\bar i\bar k}\delta_{sv} - \delta_{\bar i v}\delta_{s\bar k}) + F_{tv}(\delta_{\bar i\bar k}\delta_{s\bar l} - \delta_{\bar i\bar l}\delta_{s\bar k})] \times (\delta_{a\bar u}\delta_{\bar t\bar v} - \delta_{a\bar v}\delta_{\bar t\bar u}) \\
&\quad - [F_{s\bar k}(\delta_{t\bar l}\delta_{\bar i v} - \delta_{\bar i\bar l}\delta_{tv}) - F_{s\bar l}(\delta_{t\bar k}\delta_{\bar i v} - \delta_{tv}\delta_{\bar i\bar k}) + F_{sv}(\delta_{t\bar k}\delta_{\bar i\bar l} - \delta_{t\bar l}\delta_{\bar i\bar k})] \times (\delta_{a\bar u}\delta_{\bar t\bar v} - \delta_{a\bar v}\delta_{\bar t\bar u}) \\
&\quad - F_{\bar u a}\delta_{\bar v\bar t}[\delta_{\bar i\bar k}(\delta_{t\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{tv}) - \delta_{\bar i\bar l}(\delta_{t\bar k}\delta_{sv} - \delta_{tv}\delta_{s\bar k}) + \delta_{\bar i v}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar v a}\delta_{\bar u\bar t}[\delta_{\bar i\bar k}(\delta_{t\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{tv}) - \delta_{\bar i\bar l}(\delta_{t\bar k}\delta_{sv} - \delta_{tv}\delta_{s\bar k}) + \delta_{\bar i v}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \\
&\quad + F_{\bar u\bar t}\delta_{\bar v a}[\delta_{\bar i\bar k}(\delta_{t\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{tv}) - \delta_{\bar i\bar l}(\delta_{t\bar k}\delta_{sv} - \delta_{tv}\delta_{s\bar k}) + \delta_{\bar i v}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \\
&\quad - F_{\bar v\bar t}\delta_{\bar u a}[\delta_{\bar i\bar k}(\delta_{t\bar l}\delta_{sv} - \delta_{s\bar l}\delta_{tv}) - \delta_{\bar i\bar l}(\delta_{t\bar k}\delta_{sv} - \delta_{tv}\delta_{s\bar k}) + \delta_{\bar i v}(\delta_{t\bar k}\delta_{s\bar l} - \delta_{t\bar l}\delta_{s\bar k})] \\
&\quad = 0
\end{aligned}
\tag{B.71}
$$

$$
\begin{aligned}
&(a^\dagger_{\bar u} a^\dagger_{\bar v} a_v a_{\bar l} a_{\bar k} | H a^\dagger_{\bar s} a^\dagger_{\bar t} a_t a_{\bar j} a_{\bar i}) = \\
&\quad [F_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tv} - \delta_{t\bar l}\delta_{\bar j v}) - F_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tv} - \delta_{\bar j v}\delta_{t\bar k}) + F_{\bar i v}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \times (\delta_{\bar s\bar u}\delta_{\bar t\bar v} - \delta_{\bar s\bar v}\delta_{\bar t\bar u}) \\
&\quad - [F_{\bar j\bar k}(\delta_{\bar i\bar l}\delta_{tv} - \delta_{t\bar l}\delta_{\bar i v}) - F_{\bar j\bar l}(\delta_{\bar i\bar k}\delta_{tv} - \delta_{\bar i v}\delta_{t\bar k}) + F_{\bar j v}(\delta_{\bar i\bar k}\delta_{t\bar l} - \delta_{\bar i\bar l}\delta_{t\bar k})] \times (\delta_{\bar s\bar u}\delta_{\bar t\bar v} - \delta_{\bar s\bar v}\delta_{\bar t\bar u}) \\
&\quad - [F_{t\bar k}(\delta_{\bar j\bar l}\delta_{\bar i v} - \delta_{\bar i\bar l}\delta_{\bar j v}) - F_{t\bar l}(\delta_{\bar j\bar k}\delta_{\bar i v} - \delta_{\bar j v}\delta_{\bar i\bar k}) + F_{tv}(\delta_{\bar j\bar k}\delta_{\bar i\bar l} - \delta_{\bar j\bar l}\delta_{\bar i\bar k})] \times (\delta_{\bar s\bar u}\delta_{\bar t\bar v} - \delta_{\bar s\bar v}\delta_{\bar t\bar u}) \\
&\quad - F_{\bar u\bar s}\delta_{\bar v\bar t}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tv} - \delta_{t\bar l}\delta_{\bar j v}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tv} - \delta_{\bar j v}\delta_{t\bar k}) + \delta_{\bar i v}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \\
&\quad + F_{\bar v\bar s}\delta_{\bar u\bar t}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tv} - \delta_{t\bar l}\delta_{\bar j v}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tv} - \delta_{\bar j v}\delta_{t\bar k}) + \delta_{\bar i v}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \\
&\quad + F_{\bar u\bar t}\delta_{\bar v\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tv} - \delta_{t\bar l}\delta_{\bar j v}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tv} - \delta_{\bar j v}\delta_{t\bar k}) + \delta_{\bar i v}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \\
&\quad - F_{\bar v\bar t}\delta_{\bar u\bar s}[\delta_{\bar i\bar k}(\delta_{\bar j\bar l}\delta_{tv} - \delta_{t\bar l}\delta_{\bar j v}) - \delta_{\bar i\bar l}(\delta_{\bar j\bar k}\delta_{tv} - \delta_{\bar j v}\delta_{t\bar k}) + \delta_{\bar i v}(\delta_{\bar j\bar k}\delta_{t\bar l} - \delta_{\bar j\bar l}\delta_{t\bar k})] \\
&\quad = F_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv}\delta_{\bar s\bar u}\delta_{\bar t\bar v} - F_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv}\delta_{\bar s\bar v}\delta_{\bar t\bar u} - F_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv}\delta_{\bar s\bar u}\delta_{\bar t\bar v} + F_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv}\delta_{\bar s\bar v}\delta_{\bar t\bar u} \\
&\quad - F_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{tv}\delta_{\bar s\bar u}\delta_{\bar t\bar v} + F_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{tv}\delta_{\bar s\bar v}\delta_{\bar t\bar u} + F_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{tv}\delta_{\bar s\bar u}\delta_{\bar t\bar v} - F_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{tv}\delta_{\bar s\bar v}\delta_{\bar t\bar u} \\
&\quad - F_{tv}\delta_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{\bar s\bar u}\delta_{\bar t\bar v} + F_{tv}\delta_{\bar j\bar k}\delta_{\bar i\bar l}\delta_{\bar s\bar v}\delta_{\bar t\bar u} + F_{tv}\delta_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{\bar s\bar u}\delta_{\bar t\bar v} - F_{tv}\delta_{\bar j\bar l}\delta_{\bar i\bar k}\delta_{\bar s\bar v}\delta_{\bar t\bar u} \\
&\quad - F_{\bar u\bar s}\delta_{\bar v\bar t}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv} + F_{\bar u\bar s}\delta_{\bar v\bar t}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv} + F_{\bar v\bar s}\delta_{\bar u\bar t}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv} - F_{\bar v\bar s}\delta_{\bar u\bar t}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv} \\
&\quad + F_{\bar u\bar t}\delta_{\bar v\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv} - F_{\bar u\bar t}\delta_{\bar v\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv} - F_{\bar v\bar t}\delta_{\bar u\bar s}\delta_{\bar i\bar k}\delta_{\bar j\bar l}\delta_{tv} + F_{\bar v\bar t}\delta_{\bar u\bar s}\delta_{\bar i\bar l}\delta_{\bar j\bar k}\delta_{tv}
\end{aligned}
\tag{B.72}
$$

C

Primary-Secondary block field operator couplings

The difference between the $2hp$ and $2ph$ terms is reflected in the occupation numbers. By using the general deductions expressions, the $2hp$ and $2ph$ are related through a sign change and the nature of the indices, the indices that were set for occupied orbitals now represent virtual orbitals an vice-versa. Therefore, In this expression we only focus on $2ph$ terms that can be transform to $2hp$ by changing multiplying the $2ph$ by -1. In some cases,the two electron integrals have been change from the Dirac notation to the Mulliken notation. The change of notation of the two electron integral was done in order to further reduce the long expressions that were obtained using matrix notation. The relations between the two notations is:

$$\begin{aligned} \langle ij||kl\rangle &= \langle ij|kl\rangle - \langle ij|lk\rangle \\ &= (ik|jl) - (il|jk) \end{aligned} \tag{C.1}$$

C.1 General definitions

General term for $(F_1|\widehat{H}F_3)$ and $(F_3|\widehat{H}F_1)$ for the 2ph terms

$$(a_b|\widehat{\mathrm{H}}a^\dagger_{\bar{u}}a_u a_{\bar{k}}) = -\delta_{bu}\mathbf{F}_{\bar{u}\bar{k}} - \delta_{b\bar{k}}\mathbf{F}_{\bar{u}u} - \langle u\bar{k}\|b\bar{u}\rangle \tag{C.2}$$

$$(a^\dagger_{\bar{t}}a_t a_{\bar{j}}|\widehat{\mathrm{H}}a_c) = \langle\bar{t}c\|t\bar{j}\rangle \tag{C.3}$$

General term for $(F_3|\widehat{H}F_3)$ for the 2ph terms

$$\begin{aligned}(a^\dagger_{\bar{t}}a_t a_{\bar{j}}|\widehat{H}a^\dagger_{\bar{u}}a_u a_{\bar{k}}) = {} & \mathbf{F}_{\bar{k}\bar{j}}\delta_{\bar{t}\bar{u}}\delta_{tu} - \mathbf{F}_{\bar{k}t}\delta_{\bar{u}\bar{t}}\delta_{\bar{j}u} - \mathbf{F}_{u\bar{j}}\delta_{\bar{k}t}\delta_{\bar{u}\bar{t}} + \mathbf{F}_{ut}\delta_{\bar{t}\bar{u}}\delta_{\bar{j}\bar{k}} + \mathbf{F}_{\bar{t}\bar{u}}[-\delta_{ut}\delta_{\bar{j}\bar{k}} + \delta_{\bar{j}u}\delta_{t\bar{k}}] \\ & + \langle u\bar{k}\|\bar{j}t\rangle\delta_{\bar{u}\bar{t}} + \langle\bar{t}\bar{k}\|\bar{u}\bar{j}\rangle\delta_{tu} - \langle\bar{t}u\|\bar{u}\bar{j}\rangle\delta_{t\bar{k}} - \langle\bar{t}\bar{k}\|\bar{u}t\rangle\delta_{\bar{j}u} + \langle u\bar{t}\|t\bar{u}\rangle\delta_{\bar{j}\bar{k}}\end{aligned} \tag{C.4}$$

$$\begin{aligned}(a^\dagger_{\bar{t}}a_t a_{\bar{j}}|\widehat{H}a^\dagger_{\bar{u}}a_u a_{\bar{k}}) = {} & \mathbf{F}_{\bar{k}\bar{j}}\delta_{\bar{t}\bar{u}}\delta_{tu} - \mathbf{F}_{\bar{k}t}\delta_{\bar{u}\bar{t}}\delta_{\bar{j}u} - \mathbf{F}_{u\bar{j}}\delta_{\bar{k}t}\delta_{\bar{u}\bar{t}} + \mathbf{F}_{ut}\delta_{\bar{t}\bar{u}}\delta_{\bar{j}\bar{k}} + \mathbf{F}_{\bar{t}\bar{u}}[-\delta_{ut}\delta_{\bar{j}\bar{k}} + \delta_{\bar{j}u}\delta_{t\bar{k}}] \\ & + \langle u\bar{k}\|\bar{j}t\rangle\delta_{\bar{u}\bar{t}} + \langle\bar{t}\bar{k}\|\bar{u}\bar{j}\rangle\delta_{tu} - \langle\bar{t}u\|\bar{u}\bar{j}\rangle\delta_{t\bar{k}} - \langle\bar{t}\bar{k}\|\bar{u}t\rangle\delta_{\bar{j}u} + \langle u\bar{t}\|t\bar{u}\rangle\delta_{\bar{j}\bar{k}}\end{aligned} \tag{C.5}$$

General term for $(F_3|\widehat{H}F_5)$ and $(F_5|\widehat{H}F_3)$ for the 2ph terms

$$\begin{aligned}(a^\dagger_\iota a_s a_t|Ha^\dagger_\alpha a^\dagger_\beta a_p a_q a_r) = {} & [1 - P_{\beta\alpha}][1 - P_{rq} - P_{rp}] \times F_{r\beta}\delta_{\alpha\iota}N_{\alpha st}\mathbf{det(}\delta_{sp}\delta_{tq}\mathbf{)}(n_\beta - n_r) \\ & + [1 - P_{\alpha\beta}][1 - P_{rp} - P_{qp}][1 - P_{st}]\delta_{ps}(qt||r\beta)\delta_{\alpha\iota}N_{\iota st}N_{\beta qr} \\ & + N_{\iota st}N_{r\alpha\beta} \times [1 - P_{rq} - P_{rp}](\iota\alpha||r\beta)\mathbf{det(}\delta_{sq}\delta_{tp}\mathbf{)}\end{aligned} \tag{C.6}$$

$$\begin{aligned}& (a^\dagger_\alpha a^\dagger_\beta a_p a_q a_r|Ha^\dagger_\iota a_s a_t) \\ & \quad = [1 - P_{\alpha\beta}] \times \delta_{\alpha\iota}N_{\alpha\beta pqr} \times [1 - P_{rq} - P_{rp}][1 - P_{st}](\beta r||tq)\delta_{sp} \\ & \qquad + N_{\alpha\beta pqr} \times [1 - P_{rq} - P_{rp}](\beta r||\alpha\iota)\mathbf{det(}\delta_{sq}\delta_{tp}\mathbf{)}\end{aligned} \tag{C.7}$$

where

$$\begin{aligned}N_{\alpha st} &= (1 - n_\alpha)n_s n_t + n_\alpha(1 - n_s)(1 - n_t) \\ N_{\alpha\beta pqr} &= (1 - n_\alpha)(1 - n_\beta)n_p n_q n_r + n_\alpha n_\beta(1 - n_p)(1 - n_q)(1 - n_r) \\ \mathbf{det(}\delta_{sp}\delta_{tq}\mathbf{)} &= \begin{vmatrix}\delta_{sp} & \delta_{sq} \\ \delta_{tp} & \delta_{tq}\end{vmatrix} = (\delta_{sp}\delta_{tq} - \delta_{sq}\delta_{tp}) \\ \mathbf{det(}\delta_{sq}\delta_{tp}\mathbf{)} &= \begin{vmatrix}\delta_{sq} & \delta_{sp} \\ \delta_{tq} & \delta_{tp}\end{vmatrix} = (\delta_{sq}\delta_{tp} - \delta_{sp}\delta_{tq})\end{aligned} \tag{C.8}$$

Therefore for 2ph and 3p2h $n_\alpha = n_\beta = n_\iota = 1$

$$\begin{aligned}
(a_\iota^\dagger a_s a_t|Ha_\alpha^\dagger a_\beta^\dagger a_p a_q a_r) &= [1-P_{\beta\alpha}][1-P_{rq}-P_{rp}] \times F_{r\beta}\delta_{\alpha\iota}N_{\alpha st}(\delta_{sp}\delta_{tq}-\delta_{sq}\delta_{tp})(n_\beta-n_r)\\
&+ [1-P_{\alpha\beta}][1-P_{rp}-P_{qp}][1-P_{st}]\delta_{ps}(qt||r\beta)\delta_{\alpha\iota}N_{\iota st}N_{\beta qr}\\
&+ N_{\iota st}N_{r\alpha\beta} \times [1-P_{rq}-P_{rp}](\iota\alpha||r\beta)(\delta_{sq}\delta_{tp}-\delta_{sp}\delta_{tq})\\
&= +\delta_{ps}(qt||r\beta)\delta_{\alpha\iota}N_{\iota st}N_{\beta qr} - \delta_{pt}(qs||r\beta)\delta_{\alpha\iota}N_{\iota ts}N_{\beta qr}\\
&- \delta_{rs}(qt||p\beta)\delta_{\alpha\iota}N_{\iota st}N_{\beta qp} + \delta_{rt}(qs||p\beta)\delta_{\alpha\iota}N_{\iota ts}N_{\beta qp}\\
&- \delta_{qs}(pt||r\beta)\delta_{\alpha\iota}N_{\iota st}N_{\beta pr} + \delta_{qt}(ps||r\beta)\delta_{\alpha\iota}N_{\iota ts}N_{\beta pr}\\
&- \delta_{ps}(qt||r\alpha)\delta_{\beta\iota}N_{\iota st}N_{\alpha qr} + \delta_{pt}(qs||r\alpha)\delta_{\beta\iota}N_{\iota ts}N_{\alpha qr}\\
&+ \delta_{rs}(qt||p\alpha)\delta_{\beta\iota}N_{\iota st}N_{\alpha qp} - \delta_{rt}(qs||p\alpha)\delta_{\beta\iota}N_{\iota ts}N_{\alpha qp}\\
&+ \delta_{qs}(pt||r\alpha)\delta_{\beta\iota}N_{\iota st}N_{\alpha pr} - \delta_{qt}(ps||r\alpha)\delta_{\beta\iota}N_{\iota ts}N_{\alpha pr}]\\
&+ N_{\iota st}N_{r\alpha\beta}(\iota\alpha||r\beta)(\delta_{sq}\delta_{tp}-\delta_{sp}\delta_{tq}) - N_{\iota st}N_{r\alpha\beta}(\iota\alpha||q\beta)(\delta_{sr}\delta_{tp}-\delta_{sp}\delta_{tr})\\
&- N_{\iota st}N_{r\alpha\beta}(\iota\alpha||p\beta)(\delta_{sq}\delta_{tr}-\delta_{sr}\delta_{tq})\\
&= +\delta_{ps}(qt||r\beta)\delta_{\alpha\iota} - \delta_{pt}(qs||r\beta)\delta_{\alpha\iota} - \delta_{rs}(qt||p\beta)\delta_{\alpha\iota} + \delta_{rt}(qs||p\beta)\delta_{\alpha\iota}\\
&- \delta_{qs}(pt||r\beta)\delta_{\alpha\iota} + \delta_{qt}(ps||r\beta)\delta_{\alpha\iota} - \delta_{ps}(qt||r\alpha)\delta_{\beta\iota} + \delta_{pt}(qs||r\alpha)\delta_{\beta\iota}\\
&+ \delta_{rs}(qt||p\alpha)\delta_{\beta\iota} - \delta_{rt}(qs||p\alpha)\delta_{\beta\iota} + \delta_{qs}(pt||r\alpha)\delta_{\beta\iota} - \delta_{qt}(ps||r\alpha)\delta_{\beta\iota}\\
&+ (\iota\alpha||r\beta)(\delta_{sq}\delta_{tp}-\delta_{sp}\delta_{tq}) - (\iota\alpha||q\beta)(\delta_{sr}\delta_{tp}-\delta_{sp}\delta_{tr}) - (\iota\alpha||p\beta)(\delta_{sq}\delta_{tr}-\delta_{sr}\delta_{tq})\\
&= [\delta_{ps}(qt||r\beta) - \delta_{pt}(qs||r\beta) - \delta_{rs}(qt||p\beta)\\
&+ \delta_{rt}(qs||p\beta) - \delta_{qs}(pt||r\beta) + \delta_{qt}(ps||r\beta)]\delta_{\alpha\iota}\\
&+ [-\delta_{ps}(qt||r\alpha) + \delta_{pt}(qs||r\alpha) + \delta_{rs}(qt||p\alpha)\\
&- \delta_{rt}(qs||p\alpha) + \delta_{qs}(pt||r\alpha) - \delta_{qt}(ps||r\alpha)]\delta_{\beta\iota}\\
&+ (\iota\alpha||r\beta)(\delta_{sq}\delta_{tp}-\delta_{sp}\delta_{tq}) - (\iota\alpha||q\beta)(\delta_{sr}\delta_{tp}-\delta_{sp}\delta_{tr}) - (\iota\alpha||p\beta)(\delta_{sq}\delta_{tr}-\delta_{sr}\delta_{tq})
\end{aligned} \tag{C.9}$$

with general indeces

$$\begin{aligned}
(a_\iota^\dagger a_\sigma a_\tau|Ha_\alpha^\dagger a_\beta^\dagger a_\pi a_\kappa a_\rho) &= [\delta_{\pi\sigma}(\kappa\tau||\rho\beta) - \delta_{\pi\tau}(\kappa\sigma||\rho\beta) - \delta_{\rho\sigma}(\kappa\tau||\pi\beta)\\
&+ \delta_{\rho\tau}(\kappa\sigma||\pi\beta) - \delta_{\kappa\sigma}(\pi\tau||\rho\beta) + \delta_{\kappa\tau}(\pi\sigma||\rho\beta)]\delta_{\alpha\iota}\\
&+ [-\delta_{\pi\sigma}(\kappa\tau||\rho\alpha) + \delta_{\pi\tau}(\kappa\sigma||\rho\alpha) + \delta_{\rho\sigma}(\kappa\tau||\pi\alpha)\\
&- \delta_{\rho\tau}(\kappa\sigma||\pi\alpha) + \delta_{\kappa\sigma}(\pi\tau||\rho\alpha) - \delta_{\kappa\tau}(\pi\sigma||\rho\alpha)]\delta_{\beta\iota}\\
&+ (\iota\alpha||\rho\beta)(\delta_{\sigma\kappa}\delta_{\tau\pi} - \delta_{\sigma\pi}\delta_{\tau\kappa}) - (\iota\alpha||\kappa\beta)(\delta_{\sigma\rho}\delta_{\tau\pi} - \delta_{\sigma\pi}\delta_{\tau\rho})\\
&- (\iota\alpha||\pi\beta)(\delta_{\sigma\kappa}\delta_{\tau\rho} - \delta_{\sigma\rho}\delta_{\tau\kappa})
\end{aligned} \tag{C.10}$$

$$
\begin{aligned}
&(a_\alpha^\dagger a_\beta^\dagger a_p a_q a_r | H a_\iota^\dagger a_s a_t) \\
&\qquad = [1 - P_{\alpha\beta}] \times \delta_{\alpha\iota} N_{\alpha\beta pqr} \times [1 - P_{rq} - P_{rp}][1 - P_{st}](\beta r||tq)\delta_{sp} \\
&\qquad\quad + N_{\alpha\beta pqr} \times [1 - P_{rq} - P_{rp}](\beta r||\alpha\iota)(\delta_{sq}\delta_{tp} - \delta_{sp}\delta_{tq})
\end{aligned}
\tag{C.11}
$$

$$
\begin{aligned}
&(a_\alpha^\dagger a_\beta^\dagger a_p a_q a_r | H a_\iota^\dagger a_s a_t) \\
&\qquad = + \delta_{\alpha\iota}[(\beta r||tq)\delta_{sp} - (\beta r||sq)\delta_{tp} - (\beta q||tr)\delta_{sp} \\
&\qquad\quad + (\beta q||sr)\delta_{tp} - (\beta p||tq)\delta_{sr} + (\beta p||sq)\delta_{tr}] \\
&\qquad\quad - \delta_{\beta\iota}[(\beta r||tq)\delta_{sp} - (\beta r||sq)\delta_{tp} - (\beta q||tr)\delta_{sp} \\
&\qquad\quad + (\beta q||sr)\delta_{tp} - (\beta p||tq)\delta_{sr} + (\beta p||sq)\delta_{tr}] \\
&\qquad\quad + \delta_{sq}\delta_{tp}(\beta r||\alpha\iota) - \delta_{sp}\delta_{tq}(\beta r||\alpha\iota) - \delta_{sr}\delta_{tp}(\beta q||\alpha\iota) + \delta_{sp}\delta_{tr}(\beta q||\alpha\iota) \\
&\qquad\quad - \delta_{sq}\delta_{tr}(\beta p||\alpha\iota) + \delta_{sr}\delta_{tq}(\beta p||\alpha\iota)
\end{aligned}
\tag{C.12}
$$

with general indeces

$$
\begin{aligned}
&(a_\alpha^\dagger a_\beta^\dagger a_\pi a_\nu a_\rho | H a_\iota^\dagger a_\sigma a_\kappa) \\
&\qquad = + \delta_{\alpha\iota}[(\beta\rho||\kappa q)\delta_{\sigma\pi} - (\beta\rho||\sigma\nu)\delta_{\kappa\pi} - (\beta\nu||\kappa\rho)\delta_{\sigma\pi} \\
&\qquad\quad + (\beta\nu||\sigma\rho)\delta_{\kappa\pi} - (\beta\pi||\kappa\nu)\delta_{\sigma\rho} + (\beta\pi||\sigma\nu)\delta_{\kappa\rho}] \\
&\qquad\quad - \delta_{\beta\iota}[(\beta\rho||\kappa\nu)\delta_{\sigma\pi} - (\beta\rho||\sigma\nu)\delta_{\kappa\pi} - (\beta\nu||\kappa\rho)\delta_{\sigma\pi} \\
&\qquad\quad + (\beta\nu||\sigma\rho)\delta_{\kappa\pi} - (\beta\pi||\kappa\nu)\delta_{\sigma\rho} + (\beta\pi||\sigma\nu)\delta_{\kappa\rho}] \\
&\qquad\quad + (\beta\rho||\alpha\iota)[\delta_{\sigma\nu}\delta_{\kappa\pi} - \delta_{\sigma\pi}\delta_{\kappa\nu}] \\
&\qquad\quad + (\beta\nu||\alpha\iota)[\delta_{\sigma\pi}\delta_{\kappa\rho} - \delta_{\sigma\rho}\delta_{\kappa\pi}] \\
&\qquad\quad + (\beta\pi||\alpha\iota)[\delta_{\sigma\rho}\delta_{\kappa\nu} - \delta_{\sigma\nu}\delta_{\kappa\rho}]
\end{aligned}
\tag{C.13}
$$

C.2 $(F_1|\widehat{H}F_3)$ Terms

$$(a_b|\widehat{\mathrm{H}}a_{\bar{u}}^{\dagger}a_u a_{\bar{k}}) = -\delta_{bu}\mathbf{F}_{\bar{u}\bar{k}} - \delta_{b\bar{k}}\mathbf{F}_{\bar{u}u} - \langle u\bar{k}\|b\bar{u}\rangle \tag{C.14}$$

$$(a_\kappa|\widehat{\mathrm{H}}a_{\bar{a}}^{\dagger}a_j a_{\bar{i}}) = -\delta_{\kappa j}\mathbf{F}_{\bar{a}\bar{i}} - \delta_{\kappa\bar{i}}\mathbf{F}_{\bar{a}j} - \langle j\bar{i}\|\kappa\bar{a}\rangle \tag{C.15}$$

$$(a_\kappa|\widehat{\mathrm{H}}a_{a}^{\dagger}a_j a_{i}) = -\delta_{\kappa j}\mathbf{F}_{ai} - \delta_{\kappa i}\mathbf{F}_{aj} - \langle ji\|\kappa a\rangle \tag{C.16}$$

$$(a_\kappa|\widehat{\mathrm{H}}a_{a}^{\dagger}a_s a_{j}) = -\delta_{\kappa s}\mathbf{F}_{aj} - \delta_{\kappa j}\mathbf{F}_{as} - \langle sj\|\kappa a\rangle \tag{C.17}$$

$$(a_\kappa|\widehat{\mathrm{H}}a_{\bar{s}}^{\dagger}a_i a_{\bar{j}}) = -\delta_{\kappa i}\mathbf{F}_{\bar{s}\bar{j}} - \delta_{\kappa\bar{j}}\mathbf{F}_{\bar{s}i} - \langle i\bar{j}\|\kappa\bar{s}\rangle \tag{C.18}$$

$$(a_\kappa|\widehat{\mathrm{H}}a_{a}^{\dagger}a_s a_{t}) = -\delta_{\kappa s}\mathbf{F}_{at} - \delta_{\kappa t}\mathbf{F}_{as} - \langle st\|\kappa a\rangle \tag{C.19}$$

$$(a_\kappa|\widehat{\mathrm{H}}a_{\bar{a}}^{\dagger}a_s a_{\bar{j}}) = -\delta_{\kappa s}\mathbf{F}_{\bar{a}\bar{j}} - \delta_{\kappa\bar{j}}\mathbf{F}_{\bar{a}s} - \langle s\bar{j}\|\kappa\bar{a}\rangle \tag{C.20}$$

$$(a_\kappa|\widehat{\mathrm{H}}a^\dagger_{\bar{s}}a_t a_{\bar{j}}) = -\delta_{\kappa t}\mathbf{F}_{\bar{s}\bar{j}} - \delta_{\kappa\bar{j}}\mathbf{F}_{\bar{s}t} - \langle t\bar{j}\|\kappa\bar{s}\rangle \tag{C.21}$$

C.3 $(F_3|\widehat{H}F_1)$ Terms

$$(a^\dagger_{\bar{t}}a_t a_{\bar{j}}|\widehat{\mathrm{H}}a_c) = \langle\bar{t}c\|t\bar{j}\rangle \tag{C.22}$$

$$(a^\dagger_{\bar{b}}a_l a_{\bar{k}}|\widehat{\mathrm{H}}a_\iota) = \langle\bar{b}\iota\|l\bar{k}\rangle \tag{C.23}$$

$$(a^\dagger_{b}a_l a_{k}|\widehat{\mathrm{H}}a_\iota) = \langle b\iota\|lk\rangle \tag{C.24}$$

$$(a^\dagger_{b}a_u a_{l}|\widehat{\mathrm{H}}a_\iota) = \langle b\iota\|ul\rangle \tag{C.25}$$

$$(a^\dagger_{\bar{u}}a_k a_{\bar{l}}|\widehat{\mathrm{H}}a_\iota) = \langle\bar{u}\iota\|k\bar{l}\rangle \tag{C.26}$$

$$(a^\dagger_{b}a_u a_{v}|\widehat{\mathrm{H}}a_\iota) = \langle b\iota\|uv\rangle \tag{C.27}$$

$$(a^\dagger_{\bar{b}} a_u a_{\bar{l}} | \widehat{\mathrm{H}} a_\iota) = \langle \bar{b}\iota \| u\bar{l} \rangle \tag{C.28}$$

$$(a^\dagger_{\bar{u}} a_v a_{\bar{l}} | \widehat{\mathrm{H}} a_\iota) = \langle \bar{u}\iota \| v\bar{l} \rangle \tag{C.29}$$

C.4 $(F^P_3 | \widehat{H} F^Q_3)$ Terms

$$\begin{aligned}(a^\dagger_{\bar{t}} a_t a_{\bar{j}} | \widehat{H} a^\dagger_{\bar{u}} a_u a_{\bar{k}}) &= \mathbf{F}_{\bar{k}\bar{j}}\delta_{\bar{t}\bar{u}}\delta_{tu} - \mathbf{F}_{\bar{k}t}\delta_{\bar{u}\bar{t}}\delta_{\bar{j}u} - \mathbf{F}_{u\bar{j}}\delta_{\bar{k}t}\delta_{\bar{u}\bar{t}} + \mathbf{F}_{ut}\delta_{\bar{t}\bar{u}}\delta_{\bar{j}\bar{k}} + \mathbf{F}_{\bar{t}\bar{u}}[-\delta_{ut}\delta_{\bar{j}\bar{k}} + \delta_{\bar{j}u}\delta_{t\bar{k}}] \\ &\quad + \langle u\bar{k} \| \bar{j}t \rangle \delta_{\bar{u}\bar{t}} + \langle \bar{t}\bar{k} \| \bar{u}\bar{j} \rangle \delta_{tu} - \langle \bar{t}u \| \bar{u}\bar{j} \rangle \delta_{t\bar{k}} - \langle \bar{t}\bar{k} \| \bar{u}t \rangle \delta_{\bar{j}u} + \langle u\bar{t} \| t\bar{u} \rangle \delta_{\bar{j}\bar{k}} \\ &= \mathbf{F}_{\bar{k}\bar{j}}\delta_{\bar{t}\bar{u}}\delta_{tu} + \mathbf{F}_{ut}\delta_{\bar{t}\bar{u}}\delta_{\bar{j}\bar{k}} - \mathbf{F}_{\bar{t}\bar{u}}\delta_{ut}\delta_{\bar{j}\bar{k}} + \langle u\bar{k} \| \bar{j}t \rangle \delta_{\bar{u}\bar{t}} + \langle \bar{t}\bar{k} \| \bar{u}\bar{j} \rangle \delta_{tu} + \langle u\bar{t} \| t\bar{u} \rangle \delta_{\bar{j}\bar{k}}\end{aligned} \tag{C.30}$$

$$\begin{aligned}(a^\dagger_{\bar{u}} a_u a_{\bar{l}} | \widehat{H} a^\dagger_{\bar{a}} a_j a_{\bar{i}}) &= \mathbf{F}_{\bar{i}\bar{l}}\delta_{\bar{u}\bar{a}}\delta_{uj} - \mathbf{F}_{\bar{i}u}\delta_{\bar{a}\bar{u}}\delta_{\bar{l}j} - \mathbf{F}_{j\bar{l}}\delta_{\bar{i}u}\delta_{\bar{a}\bar{u}} + \mathbf{F}_{ju}\delta_{\bar{u}\bar{a}}\delta_{\bar{l}\bar{i}} + \mathbf{F}_{\bar{u}\bar{a}}[-\delta_{ju}\delta_{\bar{l}\bar{i}} + \delta_{\bar{l}j}\delta_{u\bar{i}}] \\ &\quad + \langle j\bar{i} \| \bar{l}u \rangle \delta_{\bar{a}\bar{u}} + \langle \bar{u}\bar{i} \| \bar{a}\bar{l} \rangle \delta_{uj} - \langle \bar{u}j \| \bar{a}\bar{l} \rangle \delta_{u\bar{i}} - \langle \bar{u}\bar{i} \| \bar{a}u \rangle \delta_{\bar{l}j} + \langle j\bar{u} \| u\bar{a} \rangle \delta_{\bar{l}\bar{i}} \\ &= \langle j\bar{u} \| u\bar{a} \rangle \delta_{\bar{l}\bar{i}}\end{aligned} \tag{C.31}$$

$$\begin{aligned}(a^\dagger_{\bar{u}} a_u a_{\bar{l}} | \widehat{H} a^\dagger_{a} a_j a_{i}) &= \mathbf{F}_{i\bar{l}}\delta_{\bar{u}a}\delta_{uj} - \mathbf{F}_{iu}\delta_{a\bar{u}}\delta_{\bar{l}j} - \mathbf{F}_{j\bar{l}}\delta_{iu}\delta_{a\bar{u}} + \mathbf{F}_{ju}\delta_{\bar{u}a}\delta_{\bar{l}i} + \mathbf{F}_{\bar{u}a}[-\delta_{ju}\delta_{\bar{l}i} + \delta_{\bar{l}j}\delta_{ui}] \\ &\quad + \langle ji \| \bar{l}u \rangle \delta_{a\bar{u}} + \langle \bar{u}i \| a\bar{l} \rangle \delta_{uj} - \langle \bar{u}j \| a\bar{l} \rangle \delta_{ui} - \langle \bar{u}i \| au \rangle \delta_{\bar{l}j} + \langle j\bar{u} \| ua \rangle \delta_{\bar{l}i} \\ &= 0\end{aligned} \tag{C.32}$$

$$\begin{aligned}(a^\dagger_{\bar{u}}a_u a_{\bar{l}}|\widehat{H}a^\dagger_a a_s a_j) &= \mathbf{F}_{j\bar{l}}\delta_{\bar{u}a}\delta_{us} - \mathbf{F}_{ju}\delta_{a\bar{u}}\delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}}\delta_{ju}\delta_{a\bar{u}} + \mathbf{F}_{su}\delta_{\bar{u}a}\delta_{\bar{l}j} + \mathbf{F}_{\bar{u}a}[-\delta_{su}\delta_{\bar{l}j} + \delta_{\bar{l}s}\delta_{uj}] \\ &\quad + \langle sj\|\bar{l}u\rangle\delta_{a\bar{u}} + \langle\bar{u}j\|a\bar{l}\rangle\delta_{us} - \langle\bar{u}s\|a\bar{l}\rangle\delta_{uj} - \langle\bar{u}j\|au\rangle\delta_{\bar{l}s} + \langle s\bar{u}\|ua\rangle\delta_{\bar{l}j} \\ &= \langle\bar{u}j\|a\bar{l}\rangle\delta_{us}\end{aligned} \tag{C.33}$$

$$\begin{aligned}(a^\dagger_{\bar{u}}a_u a_{\bar{l}}|\widehat{H}a^\dagger_{\bar{s}} a_i a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{u}\bar{s}}\delta_{ui} - \mathbf{F}_{\bar{j}u}\delta_{\bar{s}\bar{u}}\delta_{\bar{l}i} - \mathbf{F}_{i\bar{l}}\delta_{\bar{j}u}\delta_{\bar{s}\bar{u}} + \mathbf{F}_{iu}\delta_{\bar{u}\bar{s}}\delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{u}\bar{s}}[-\delta_{iu}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}i}\delta_{u\bar{j}}] \\ &\quad + \langle i\bar{j}\|\bar{l}u\rangle\delta_{\bar{s}\bar{u}} + \langle\bar{u}\bar{j}\|\bar{s}\bar{l}\rangle\delta_{ui} - \langle\bar{u}i\|\bar{s}\bar{l}\rangle\delta_{u\bar{j}} - \langle\bar{u}\bar{j}\|\bar{s}u\rangle\delta_{\bar{l}i} + \langle i\bar{u}\|u\bar{s}\rangle\delta_{\bar{l}\bar{j}} \\ &= +\mathbf{F}_{iu}\delta_{\bar{u}\bar{s}}\delta_{\bar{l}\bar{j}} + \langle i\bar{j}\|\bar{l}u\rangle\delta_{\bar{s}\bar{u}} + \langle i\bar{u}\|u\bar{s}\rangle\delta_{\bar{l}\bar{j}}\end{aligned} \tag{C.34}$$

$$\begin{aligned}(a^\dagger_{\bar{u}}a_u a_{\bar{l}}|\widehat{H}a^\dagger_a a_s a_t) &= \mathbf{F}_{t\bar{l}}\delta_{\bar{u}a}\delta_{us} - \mathbf{F}_{tu}\delta_{a\bar{u}}\delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}}\delta_{tu}\delta_{a\bar{u}} + \mathbf{F}_{su}\delta_{\bar{u}a}\delta_{\bar{l}t} + \mathbf{F}_{\bar{u}a}[-\delta_{su}\delta_{\bar{l}t} + \delta_{\bar{l}s}\delta_{ut}] \\ &\quad + \langle st\|\bar{l}u\rangle\delta_{a\bar{u}} + \langle\bar{u}t\|a\bar{l}\rangle\delta_{us} - \langle\bar{u}s\|a\bar{l}\rangle\delta_{ut} - \langle\bar{u}t\|au\rangle\delta_{\bar{l}s} + \langle s\bar{u}\|ua\rangle\delta_{\bar{l}t} \\ &= \langle\bar{u}t\|a\bar{l}\rangle\delta_{us} - \langle\bar{u}s\|a\bar{l}\rangle\delta_{ut}\end{aligned} \tag{C.35}$$

$$\begin{aligned}(a^\dagger_{\bar{u}}a_u a_{\bar{l}}|\widehat{H}a^\dagger_{\bar{a}} a_s a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{u}\bar{a}}\delta_{us} - \mathbf{F}_{\bar{j}u}\delta_{\bar{a}\bar{u}}\delta_{\bar{l}s} - \mathbf{F}_{s\bar{l}}\delta_{\bar{j}u}\delta_{\bar{a}\bar{u}} + \mathbf{F}_{su}\delta_{\bar{u}\bar{a}}\delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{u}\bar{a}}[-\delta_{su}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}s}\delta_{u\bar{j}}] \\ &\quad + \langle s\bar{j}\|\bar{l}u\rangle\delta_{\bar{a}\bar{u}} + \langle\bar{u}\bar{j}\|\bar{a}\bar{l}\rangle\delta_{us} - \langle\bar{u}s\|\bar{a}\bar{l}\rangle\delta_{u\bar{j}} - \langle\bar{u}\bar{j}\|\bar{a}u\rangle\delta_{\bar{l}s} + \langle s\bar{u}\|u\bar{a}\rangle\delta_{\bar{l}\bar{j}} \\ &= -\mathbf{F}_{\bar{u}\bar{a}}\delta_{su}\delta_{\bar{l}\bar{j}} + \langle\bar{u}\bar{j}\|\bar{a}\bar{l}\rangle\delta_{us} + \langle s\bar{u}\|u\bar{a}\rangle\delta_{\bar{l}\bar{j}}\end{aligned} \tag{C.36}$$

$$\begin{aligned}(a^\dagger_{\bar{u}}a_u a_{\bar{l}}|\widehat{H}a^\dagger_{\bar{s}} a_t a_{\bar{j}}) &= \mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{u}\bar{s}}\delta_{ut} - \mathbf{F}_{\bar{j}u}\delta_{\bar{s}\bar{u}}\delta_{\bar{l}t} - \mathbf{F}_{t\bar{l}}\delta_{\bar{j}u}\delta_{\bar{s}\bar{u}} + \mathbf{F}_{tu}\delta_{\bar{u}\bar{s}}\delta_{\bar{l}\bar{j}} + \mathbf{F}_{\bar{u}\bar{s}}[-\delta_{tu}\delta_{\bar{l}\bar{j}} + \delta_{\bar{l}t}\delta_{u\bar{j}}] \\ &\quad + \langle t\bar{j}\|\bar{l}u\rangle\delta_{\bar{s}\bar{u}} + \langle\bar{u}\bar{j}\|\bar{s}\bar{l}\rangle\delta_{ut} - \langle\bar{u}t\|\bar{s}\bar{l}\rangle\delta_{u\bar{j}} - \langle\bar{u}\bar{j}\|\bar{s}u\rangle\delta_{\bar{l}t} + \langle t\bar{u}\|u\bar{s}\rangle\delta_{\bar{l}\bar{j}} \\ &= \mathbf{F}_{\bar{j}\bar{l}}\delta_{\bar{u}\bar{s}}\delta_{ut} + \mathbf{F}_{tu}\delta_{\bar{u}\bar{s}}\delta_{\bar{l}\bar{j}} - \mathbf{F}_{\bar{u}\bar{s}}\delta_{tu}\delta_{\bar{l}\bar{j}} + \langle t\bar{j}\|\bar{l}u\rangle\delta_{\bar{s}\bar{u}} + \langle\bar{u}\bar{j}\|\bar{s}\bar{l}\rangle\delta_{ut} + \langle t\bar{u}\|u\bar{s}\rangle\delta_{\bar{l}\bar{j}}\end{aligned} \tag{C.37}$$

C.5 $(F_3^Q|\widehat{H}F_3^P)$ Terms

$$\begin{aligned}
(a^\dagger_{\bar b} a_l a_{\bar k}|\widehat{H} a^\dagger_{\bar t} a_t a_{\bar j}) &= \mathbf{F}_{\bar j \bar k}\delta_{\bar b \bar t}\delta_{lt} - \mathbf{F}_{\bar j l}\delta_{\bar t \bar b}\delta_{\bar k t} - \mathbf{F}_{t \bar k}\delta_{\bar j l}\delta_{\bar t \bar b} + \mathbf{F}_{tl}\delta_{\bar b \bar t}\delta_{\bar k \bar j} + \mathbf{F}_{\bar b \bar t}[-\delta_{tl}\delta_{\bar k \bar j} + \delta_{\bar k t}\delta_{l \bar j}] \\
&\quad + \langle t\bar j \| \bar k l\rangle \delta_{\bar t \bar b} + \langle \bar b \bar j \| \bar t \bar k\rangle \delta_{lt} - \langle \bar b t \| \bar t \bar k\rangle \delta_{l \bar j} - \langle \bar b \bar j \| \bar t l\rangle \delta_{\bar k t} + \langle t \bar b \| l \bar t\rangle \delta_{\bar k \bar j} \\
&= \langle t \bar b \| l \bar t\rangle \delta_{\bar k \bar j}
\end{aligned} \tag{C.38}$$

$$\begin{aligned}
(a^\dagger_{b} a_l a_{k}|\widehat{H} a^\dagger_{\bar t} a_t a_{\bar j}) &= \mathbf{F}_{\bar j k}\delta_{b \bar t}\delta_{lt} - \mathbf{F}_{\bar j l}\delta_{\bar t b}\delta_{k t} - \mathbf{F}_{t k}\delta_{\bar j l}\delta_{\bar t b} + \mathbf{F}_{tl}\delta_{b \bar t}\delta_{k \bar j} + \mathbf{F}_{b \bar t}[-\delta_{tl}\delta_{k \bar j} + \delta_{k t}\delta_{l \bar j}] \\
&\quad + \langle t\bar j \| k l\rangle \delta_{\bar t b} + \langle b \bar j \| \bar t k\rangle \delta_{lt} - \langle b t \| \bar t k\rangle \delta_{l \bar j} - \langle b \bar j \| \bar t l\rangle \delta_{k t} + \langle t b \| l \bar t\rangle \delta_{k \bar j} \\
&= 0
\end{aligned} \tag{C.39}$$

$$\begin{aligned}
(a^\dagger_{b} a_u a_{l}|\widehat{H} a^\dagger_{\bar t} a_t a_{\bar j}) &= \mathbf{F}_{\bar j l}\delta_{b \bar t}\delta_{ut} - \mathbf{F}_{\bar j u}\delta_{\bar t b}\delta_{l t} - \mathbf{F}_{t l}\delta_{\bar j u}\delta_{\bar t b} + \mathbf{F}_{tu}\delta_{b \bar t}\delta_{l \bar j} + \mathbf{F}_{b \bar t}[-\delta_{tu}\delta_{l \bar j} + \delta_{l t}\delta_{u \bar j}] \\
&\quad + \langle t\bar j \| l u\rangle \delta_{\bar t b} + \langle b \bar j \| \bar t l\rangle \delta_{ut} - \langle b t \| \bar t l\rangle \delta_{u \bar j} - \langle b \bar j \| \bar t u\rangle \delta_{l t} + \langle t b \| u \bar t\rangle \delta_{l \bar j} \\
&= \langle b \bar j \| \bar t l\rangle \delta_{ut}
\end{aligned} \tag{C.40}$$

$$\begin{aligned}
(a^\dagger_{\bar u} a_k a_{\bar l}|\widehat{H} a^\dagger_{\bar t} a_t a_{\bar j}) &= \mathbf{F}_{\bar j \bar l}\delta_{\bar u \bar t}\delta_{kt} - \mathbf{F}_{\bar j k}\delta_{\bar t \bar u}\delta_{\bar l t} - \mathbf{F}_{t \bar l}\delta_{\bar j k}\delta_{\bar t \bar u} + \mathbf{F}_{tk}\delta_{\bar u \bar t}\delta_{\bar l \bar j} + \mathbf{F}_{\bar u \bar t}[-\delta_{tk}\delta_{\bar l \bar j} + \delta_{\bar l t}\delta_{k \bar j}] \\
&\quad + \langle t\bar j \| \bar l k\rangle \delta_{\bar t \bar u} + \langle \bar u \bar j \| \bar t \bar l\rangle \delta_{kt} - \langle \bar u t \| \bar t \bar l\rangle \delta_{k \bar j} - \langle \bar u \bar j \| \bar t k\rangle \delta_{\bar l t} + \langle t \bar u \| k \bar t\rangle \delta_{\bar l \bar j} \\
&= +\mathbf{F}_{tk}\delta_{\bar u \bar t}\delta_{\bar l \bar j} + \langle t\bar j \| \bar l k\rangle \delta_{\bar t \bar u} + \langle t \bar u \| k \bar t\rangle \delta_{\bar l \bar j}
\end{aligned} \tag{C.41}$$

$$\begin{aligned}
(a^\dagger_{b} a_u a_{v}|\widehat{H} a^\dagger_{\bar t} a_t a_{\bar j}) &= \mathbf{F}_{\bar j v}\delta_{b \bar t}\delta_{ut} - \mathbf{F}_{\bar j u}\delta_{\bar t b}\delta_{v t} - \mathbf{F}_{t v}\delta_{\bar j u}\delta_{\bar t b} + \mathbf{F}_{tu}\delta_{b \bar t}\delta_{v \bar j} + \mathbf{F}_{b \bar t}[-\delta_{tu}\delta_{v \bar j} + \delta_{v t}\delta_{u \bar j}] \\
&\quad + \langle t\bar j \| v u\rangle \delta_{\bar t b} + \langle b \bar j \| \bar t v\rangle \delta_{ut} - \langle b t \| \bar t v\rangle \delta_{u \bar j} - \langle b \bar j \| \bar t u\rangle \delta_{v t} + \langle t b \| u \bar t\rangle \delta_{v \bar j} \\
&= +\langle b \bar j \| \bar t v\rangle \delta_{ut} - \langle b \bar j \| \bar t u\rangle \delta_{vt}
\end{aligned} \tag{C.42}$$

$$\begin{aligned}(a^\dagger_{\bar b}a_u a_{\bar l}|\widehat{H}a^\dagger_{\bar t}a_t a_{\bar j}) &= \mathbf{F}_{\bar j\bar l}\delta_{\bar b\bar t}\delta_{ut} - \mathbf{F}_{\bar j u}\delta_{\bar t\bar b}\delta_{\bar l t} - \mathbf{F}_{t\bar l}\delta_{\bar j u}\delta_{\bar t\bar b} + \mathbf{F}_{tu}\delta_{\bar b\bar t}\delta_{\bar l\bar j} + \mathbf{F}_{\bar b\bar t}[-\delta_{tu}\delta_{\bar l\bar j} + \delta_{\bar l t}\delta_{u\bar j}] \\ &\quad + \langle t\bar j\|\bar l u\rangle\delta_{\bar t\bar b} + \langle\bar b\bar j\|\bar t\bar l\rangle\delta_{ut} - \langle\bar b t\|\bar t\bar l\rangle\delta_{u\bar j} - \langle\bar b\bar j\|\bar t u\rangle\delta_{\bar l t} + \langle t\bar b\|u\bar t\rangle\delta_{\bar l\bar j} \\ &= -\mathbf{F}_{\bar b\bar t}\delta_{tu}\delta_{\bar l\bar j} + \langle\bar b\bar j\|\bar t\bar l\rangle\delta_{ut} + \langle t\bar b\|u\bar t\rangle\delta_{\bar l\bar j}\end{aligned} \tag{C.43}$$

$$\begin{aligned}(a^\dagger_{\bar u}a_v a_{\bar l}|\widehat{H}a^\dagger_{\bar t}a_t a_{\bar j}) &= \mathbf{F}_{\bar j\bar l}\delta_{\bar u\bar t}\delta_{vt} - \mathbf{F}_{\bar j v}\delta_{\bar t\bar u}\delta_{\bar l t} - \mathbf{F}_{t\bar l}\delta_{\bar j v}\delta_{\bar t\bar u} + \mathbf{F}_{tv}\delta_{\bar u\bar t}\delta_{\bar l\bar j} + \mathbf{F}_{\bar u\bar t}[-\delta_{tv}\delta_{\bar l\bar j} + \delta_{\bar l t}\delta_{v\bar j}] \\ &\quad + \langle t\bar j\|\bar l v\rangle\delta_{\bar t\bar u} + \langle\bar u\bar j\|\bar t\bar l\rangle\delta_{vt} - \langle\bar u t\|\bar t\bar l\rangle\delta_{v\bar j} - \langle\bar u\bar j\|\bar t v\rangle\delta_{\bar l t} + \langle t\bar u\|v\bar t\rangle\delta_{\bar l\bar j} \\ &= \mathbf{F}_{\bar j\bar l}\delta_{\bar u\bar t}\delta_{vt} + \mathbf{F}_{tv}\delta_{\bar u\bar t}\delta_{\bar l\bar j} - \mathbf{F}_{\bar u\bar t}\delta_{tv}\delta_{\bar l\bar j} + \langle t\bar j\|\bar l v\rangle\delta_{\bar t\bar u} + \langle\bar u\bar j\|\bar t\bar l\rangle\delta_{vt} + \langle t\bar u\|v\bar t\rangle\delta_{\bar l\bar j}\end{aligned} \tag{C.44}$$

C.6 $(F_5|\widehat{H}F_3)$ Terms

C.6.1 $a^\dagger_{\bar b}a^\dagger_{\bar u}a_u a_{\bar l}a_{\bar k}$

$$\begin{aligned}&(a^\dagger_{\bar b}a^\dagger_{\bar u}a_u a_{\bar l}a_{\bar k}|Ha^\dagger_{\bar s}a_s a_{\bar i}) \\ &\qquad = + \delta_{\bar b\bar s}[(\bar u\bar k||\bar i q)\delta_{su} - (\bar u\bar k||s\bar l)\delta_{\bar i u} - (\bar u\bar l||\bar i\bar k)\delta_{su} \\ &\qquad\quad + (\bar u\bar l||s\bar k)\delta_{\bar i u} - (\bar u u||\bar i\bar l)\delta_{s\bar k} + (\bar u u||s\bar l)\delta_{\bar i\bar k}] \\ &\qquad\quad - \delta_{\bar u\bar s}[(\bar u\bar k||\bar i\bar l)\delta_{su} - (\bar u\bar k||s\bar l)\delta_{\bar i u} - (\bar u\bar l||\bar i\bar k)\delta_{su} \\ &\qquad\quad + (\bar u\bar l||s\bar k)\delta_{\bar i u} - (\bar u u||\bar i\bar l)\delta_{s\bar k} + (\bar u u||s\bar l)\delta_{\bar i\bar k}] \\ &\qquad\quad + (\bar u\bar k||\bar b\bar s)[\delta_{s\bar l}\delta_{\bar i u} - \delta_{su}\delta_{\bar i\bar l}] \\ &\qquad\quad + (\bar u\bar l||\bar b\bar s)[\delta_{su}\delta_{\bar i\bar k} - \delta_{s\bar k}\delta_{\bar i u}] \\ &\qquad\quad + (\bar u u||\bar b\bar s)[\delta_{s\bar k}\delta_{\bar i\bar l} - \delta_{s\bar l}\delta_{\bar i\bar k}] \\ &\qquad\quad = -\delta_{\bar u\bar s}[(\bar u\bar k||\bar i\bar l)\delta_{su} - (\bar u\bar l||\bar i\bar k)\delta_{su} + (\bar u u||s\bar l)\delta_{\bar i\bar k}] \\ &\qquad\quad - (\bar u\bar k||\bar b\bar s)\delta_{su}\delta_{\bar i\bar l} + (\bar u\bar l||\bar b\bar s)\delta_{su}\delta_{\bar i\bar k}\end{aligned} \tag{C.45}$$

C.6.2 $a_b^\dagger a_{\bar{u}}^\dagger a_u a_{\bar{l}} a_k$

$$
\begin{aligned}
&(a_b^\dagger a_{\bar{u}}^\dagger a_u a_{\bar{l}} a_k | H a_{\bar{s}}^\dagger a_s a_{\bar{i}}) \\
&\quad = + \delta_{b\bar{s}}[(\bar{u}k||\bar{i}q)\delta_{su} - (\bar{u}k||s\bar{l})\delta_{\bar{i}u} - (\bar{u}\bar{l}||\bar{i}k)\delta_{su} \\
&\qquad + (\bar{u}\bar{l}||sk)\delta_{\bar{i}u} - (\bar{u}u||\bar{i}\bar{l})\delta_{sk} + (\bar{u}u||s\bar{l})\delta_{\bar{i}k}] \\
&\qquad - \delta_{\bar{u}\bar{s}}[(\bar{u}k||\bar{i}\bar{l})\delta_{su} - (\bar{u}k||s\bar{l})\delta_{\bar{i}u} - (\bar{u}\bar{l}||\bar{i}k)\delta_{su} \\
&\qquad + (\bar{u}\bar{l}||sk)\delta_{\bar{i}u} - (\bar{u}u||\bar{i}\bar{l})\delta_{sk} + (\bar{u}u||s\bar{l})\delta_{\bar{i}k}] \\
&\qquad + (\bar{u}k||b\bar{s})[\delta_{s\bar{l}}\delta_{\bar{i}u} - \delta_{su}\delta_{\bar{i}\bar{l}}] \\
&\qquad + (\bar{u}\bar{l}||b\bar{s})[\delta_{su}\delta_{\bar{i}k} - \delta_{sk}\delta_{\bar{i}u}] \\
&\qquad + (\bar{u}u||b\bar{s})[\delta_{sk}\delta_{\bar{i}\bar{l}} - \delta_{s\bar{l}}\delta_{\bar{i}k}] \\
&\qquad = -\delta_{\bar{u}\bar{s}}[(\bar{u}k||\bar{i}\bar{l})\delta_{su} - (\bar{u}\bar{l}||\bar{i}k)\delta_{su} + (\bar{u}\bar{l}||sk)\delta_{\bar{i}u}] \\
&\qquad - (\bar{u}k||b\bar{s})\delta_{su}\delta_{\bar{i}\bar{l}} + (\bar{u}u||b\bar{s})\delta_{sk}\delta_{\bar{i}\bar{l}}
\end{aligned}
\tag{C.46}
$$

C.6.3 $a_b^\dagger a_{\bar{v}}^\dagger a_u a_v a_{\bar{k}}$

$$
\begin{aligned}
&(a_b^\dagger a_{\bar{v}}^\dagger a_u a_v a_{\bar{k}} | H a_{\bar{s}}^\dagger a_s a_{\bar{i}}) \\
&\quad = + \delta_{b\bar{s}}[(\bar{v}\bar{k}||\bar{i}q)\delta_{su} - (\bar{v}\bar{k}||sv)\delta_{\bar{i}u} - (\bar{v}v||\bar{i}\bar{k})\delta_{su} \\
&\qquad + (\bar{v}v||s\bar{k})\delta_{\bar{i}u} - (\bar{v}u||\bar{i}v)\delta_{s\bar{k}} + (\bar{v}u||sv)\delta_{\bar{i}\bar{k}}] \\
&\qquad - \delta_{\bar{v}\bar{s}}[(\bar{v}\bar{k}||\bar{i}v)\delta_{su} - (\bar{v}\bar{k}||sv)\delta_{\bar{i}u} - (\bar{v}v||\bar{i}\bar{k})\delta_{su} \\
&\qquad + (\bar{v}v||s\bar{k})\delta_{\bar{i}u} - (\bar{v}u||\bar{i}v)\delta_{s\bar{k}} + (\bar{v}u||sv)\delta_{\bar{i}\bar{k}}] \\
&\qquad + (\bar{v}\bar{k}||b\bar{s})[\delta_{sv}\delta_{\bar{i}u} - \delta_{su}\delta_{\bar{i}v}] \\
&\qquad + (\bar{v}v||b\bar{s})[\delta_{su}\delta_{\bar{i}\bar{k}} - \delta_{s\bar{k}}\delta_{\bar{i}u}] \\
&\qquad + (\bar{v}u||b\bar{s})[\delta_{s\bar{k}}\delta_{\bar{i}v} - \delta_{sv}\delta_{\bar{i}\bar{k}}] \\
&\qquad = -\delta_{\bar{v}\bar{s}}[(\bar{v}\bar{k}||\bar{i}v)\delta_{su} - (\bar{v}v||\bar{i}\bar{k})\delta_{su} + (\bar{v}u||sv)\delta_{\bar{i}\bar{k}}] \\
&\qquad + (\bar{v}v||b\bar{s})\delta_{su}\delta_{\bar{i}\bar{k}} - (\bar{v}u||b\bar{s})\delta_{sv}\delta_{\bar{i}\bar{k}}
\end{aligned}
\tag{C.47}
$$

C.6.4 $a^{\dagger}_{\bar{u}}a^{\dagger}_{\bar{v}}a_{v}a_{\bar{l}}a_{\bar{k}}$

$$\begin{aligned}
&(a^{\dagger}_{\bar{u}}a^{\dagger}_{\bar{v}}a_{v}a_{\bar{l}}a_{\bar{k}}|Ha^{\dagger}_{\bar{s}}a_{s}a_{\bar{i}}) \\
&\qquad = + \delta_{\bar{u}\bar{s}}[(\bar{v}\bar{k}||\bar{i}q)\delta_{sv} - (\bar{v}\bar{k}||s\bar{l})\delta_{\bar{i}v} - (\bar{v}\bar{l}||\bar{i}\bar{k})\delta_{sv} \\
&\qquad\quad + (\bar{v}\bar{l}||s\bar{k})\delta_{\bar{i}v} - (\bar{v}v||\bar{i}\bar{l})\delta_{s\bar{k}} + (\bar{v}v||s\bar{l})\delta_{\bar{i}\bar{k}}] \\
&\qquad\quad - \delta_{\bar{v}\bar{s}}[(\bar{v}\bar{k}||\bar{i}\bar{l})\delta_{sv} - (\bar{v}\bar{k}||s\bar{l})\delta_{\bar{i}v} - (\bar{v}\bar{l}||\bar{i}\bar{k})\delta_{sv} \\
&\qquad\quad + (\bar{v}\bar{l}||s\bar{k})\delta_{\bar{i}v} - (\bar{v}v||\bar{i}\bar{l})\delta_{s\bar{k}} + (\bar{v}v||s\bar{l})\delta_{\bar{i}\bar{k}}] \\
&\qquad\quad + (\bar{v}\bar{k}||\bar{u}\bar{s})[\delta_{s\bar{l}}\delta_{\bar{i}v} - \delta_{sv}\delta_{\bar{i}\bar{l}}] \\
&\qquad\quad + (\bar{v}\bar{l}||\bar{u}\bar{s})[\delta_{sv}\delta_{\bar{i}\bar{k}} - \delta_{s\bar{k}}\delta_{\bar{i}v}] \\
&\qquad\quad + (\bar{v}v||\bar{u}\bar{s})[\delta_{s\bar{k}}\delta_{\bar{i}\bar{l}} - \delta_{s\bar{l}}\delta_{\bar{i}\bar{k}}] \\
&\qquad\quad = \delta_{\bar{u}\bar{s}}[(\bar{v}\bar{k}||\bar{i}q)\delta_{sv} - (\bar{v}\bar{l}||\bar{i}\bar{k})\delta_{sv} + (\bar{v}v||s\bar{l})\delta_{\bar{i}\bar{k}}] \\
&\qquad\quad - \delta_{\bar{v}\bar{s}}[(\bar{v}\bar{k}||\bar{i}\bar{l})\delta_{sv} - (\bar{v}\bar{l}||\bar{i}\bar{k})\delta_{sv} + (\bar{v}v||s\bar{l})\delta_{\bar{i}\bar{k}}] \\
&\qquad\quad - (\bar{v}\bar{k}||\bar{u}\bar{s})\delta_{sv}\delta_{\bar{i}\bar{l}} + (\bar{v}\bar{l}||\bar{u}\bar{s})\delta_{sv}\delta_{\bar{i}\bar{k}}
\end{aligned} \tag{C.48}$$

C.7 $(F_3|\widehat{H}F_5)$ Terms

C.7.1 $a^{\dagger}_{\bar{a}}a^{\dagger}_{\bar{s}}a_{s}a_{\bar{j}}a_{\bar{i}}$

$$\begin{aligned}
(a^{\dagger}_{\bar{u}}a_{u}a_{\bar{k}}|Ha^{\dagger}_{\bar{a}}a^{\dagger}_{\bar{s}}a_{s}a_{\bar{j}}a_{\bar{i}}) &= [\delta_{su}(\bar{j}\bar{k}||\bar{i}\bar{s}) - \delta_{s\bar{k}}(\bar{j}u||\bar{i}\bar{s}) - \delta_{\bar{i}u}(\bar{j}\bar{k}||s\bar{s}) \\
&+ \delta_{\bar{i}\bar{k}}(\bar{j}u||s\bar{s}) - \delta_{\bar{j}u}(s\bar{k}||\bar{i}\bar{s}) + \delta_{\bar{j}\bar{k}}(su||\bar{i}\bar{s})]\delta_{\bar{a}\bar{u}} \\
&+ [-\delta_{su}(\bar{j}\bar{k}||\bar{i}\bar{a}) + \delta_{s\bar{k}}(\bar{j}u||\bar{i}\bar{a}) + \delta_{\bar{i}u}(\bar{j}\bar{k}||s\bar{a}) \\
&- \delta_{\bar{i}\bar{k}}(\bar{j}u||s\bar{a}) + \delta_{\bar{j}u}(s\bar{k}||\bar{i}\bar{a}) - \delta_{\bar{j}\bar{k}}(su||\bar{i}\bar{a})]\delta_{\bar{s}\bar{u}} \\
&+ (\bar{u}\bar{a}||\bar{i}\bar{s})(\delta_{u\bar{j}}\delta_{\bar{k}s} - \delta_{us}\delta_{\bar{k}\bar{j}}) \\
&- (\bar{u}\bar{a}||\bar{j}\bar{s})(\delta_{u\bar{i}}\delta_{\bar{k}s} - \delta_{us}\delta_{\bar{k}\bar{i}}) \\
&- (\bar{u}\bar{a}||s\bar{s})(\delta_{u\bar{j}}\delta_{\bar{k}\bar{i}} - \delta_{u\bar{i}}\delta_{\bar{k}\bar{j}}) \\
&= +[-\delta_{su}(\bar{j}\bar{k}||\bar{i}\bar{a}) - \delta_{\bar{i}\bar{k}}(\bar{j}u||s\bar{a}) - \delta_{\bar{j}\bar{k}}(su||\bar{i}\bar{a})]\delta_{\bar{s}\bar{u}} \\
&- (\bar{u}\bar{a}||\bar{i}\bar{s})\delta_{us}\delta_{\bar{k}\bar{j}} + (\bar{u}\bar{a}||\bar{j}\bar{s})\delta_{us}\delta_{\bar{k}\bar{i}}
\end{aligned} \tag{C.49}$$

C.7.2 $a_a^\dagger a_{\bar{s}}^\dagger a_s a_{\bar{j}} a_i$

$$\begin{aligned}(a_{\bar{u}}^\dagger a_u a_{\bar{k}}|Ha_a^\dagger a_{\bar{s}}^\dagger a_s a_{\bar{j}} a_i) &= [\delta_{su}(\bar{j}\bar{k}||i\bar{s}) - \delta_{s\bar{k}}(\bar{j}u||i\bar{s}) - \delta_{iu}(\bar{j}\bar{k}||s\bar{s}) \\ &+ \delta_{i\bar{k}}(\bar{j}u||s\bar{s}) - \delta_{\bar{j}u}(s\bar{k}||i\bar{s}) + \delta_{\bar{j}\bar{k}}(su||i\bar{s})]\delta_{a\bar{u}} \\ &+ [-\delta_{su}(\bar{j}\bar{k}||ia) + \delta_{s\bar{k}}(\bar{j}u||ia) + \delta_{iu}(\bar{j}\bar{k}||sa) \\ &- \delta_{i\bar{k}}(\bar{j}u||sa) + \delta_{\bar{j}u}(s\bar{k}||ia) - \delta_{\bar{j}\bar{k}}(su||ia)]\delta_{\bar{s}\bar{u}} \\ &+ (\bar{u}a||i\bar{s})(\delta_{u\bar{j}}\delta_{\bar{k}s} - \delta_{us}\delta_{\bar{k}\bar{j}}) \\ &- (\bar{u}a||\bar{j}\bar{s})(\delta_{ui}\delta_{\bar{k}s} - \delta_{us}\delta_{\bar{k}i}) \\ &- (\bar{u}a||s\bar{s})(\delta_{u\bar{j}}\delta_{\bar{k}i} - \delta_{ui}\delta_{\bar{k}\bar{j}}) \\ &= +[-\delta_{su}(\bar{j}\bar{k}||ia) - \delta_{\bar{j}\bar{k}}(su||ia)]\delta_{\bar{s}\bar{u}} \\ &- (\bar{u}a||i\bar{s})\delta_{us}\delta_{\bar{k}\bar{j}} + (\bar{u}a||s\bar{s})\delta_{ui}\delta_{\bar{k}\bar{j}}\end{aligned} \tag{C.50}$$

C.7.3 $a_a^\dagger a_{\bar{t}}^\dagger a_s a_t a_{\bar{i}}$

$$\begin{aligned}(a_{\bar{u}}^\dagger a_u a_{\bar{k}}|Ha_a^\dagger a_{\bar{t}}^\dagger a_s a_t a_{\bar{i}}) &= [\delta_{su}(t\bar{k}||\bar{i}\bar{t}) - \delta_{s\bar{k}}(tu||\bar{i}\bar{t}) - \delta_{\bar{i}u}(t\bar{k}||s\bar{t}) \\ &+ \delta_{\bar{i}\bar{k}}(tu||s\bar{t}) - \delta_{tu}(s\bar{k}||\bar{i}\bar{t}) + \delta_{t\bar{k}}(su||\bar{i}\bar{t})]\delta_{a\bar{u}} \\ &+ [-\delta_{su}(t\bar{k}||\bar{i}a) + \delta_{s\bar{k}}(tu||\bar{i}a) + \delta_{\bar{i}u}(t\bar{k}||sa) \\ &- \delta_{\bar{i}\bar{k}}(tu||sa) + \delta_{tu}(s\bar{k}||\bar{i}a) - \delta_{t\bar{k}}(su||\bar{i}a)]\delta_{\bar{t}\bar{u}} \\ &+ (\bar{u}a||\bar{i}\bar{t})(\delta_{ut}\delta_{\bar{k}s} - \delta_{us}\delta_{\bar{k}t}) \\ &- (\bar{u}a||t\bar{t})(\delta_{u\bar{i}}\delta_{\bar{k}s} - \delta_{us}\delta_{\bar{k}\bar{i}}) \\ &- (\bar{u}a||s\bar{t})(\delta_{ut}\delta_{\bar{k}\bar{i}} - \delta_{u\bar{i}}\delta_{\bar{k}t}) \\ &= +[-\delta_{su}(t\bar{k}||\bar{i}a) - \delta_{\bar{i}\bar{k}}(tu||sa) + \delta_{tu}(s\bar{k}||\bar{i}a)]\delta_{\bar{t}\bar{u}} \\ &+ (\bar{u}a||t\bar{t})\delta_{us}\delta_{\bar{k}\bar{i}} - (\bar{u}a||s\bar{t})\delta_{ut}\delta_{\bar{k}\bar{i}}\end{aligned} \tag{C.51}$$

C.7.4 $a^\dagger_{\bar{s}} a^\dagger_{\bar{t}} a_t a_{\bar{j}} a_{\bar{i}}$

$$
\begin{aligned}
(a^\dagger_{\bar{u}} a_u a_{\bar{k}} | H a^\dagger_{\bar{s}} a^\dagger_{\bar{t}} a_t a_{\bar{j}} a_{\bar{i}}) &= [\delta_{tu}(\bar{j}\bar{k}||\bar{i}\bar{t}) - \delta_{t\bar{k}}(\bar{j}u||\bar{i}\bar{t}) - \delta_{\bar{i}u}(\bar{j}\bar{k}||t\bar{t}) \\
&+ \delta_{\bar{i}\bar{k}}(\bar{j}u||t\bar{t}) - \delta_{\bar{j}u}(t\bar{k}||\bar{i}\bar{t}) + \delta_{\bar{j}\bar{k}}(tu||\bar{i}\bar{t})]\delta_{\bar{s}\bar{u}} \\
&+ [-\delta_{tu}(\bar{j}\bar{k}||\bar{i}\bar{s}) + \delta_{t\bar{k}}(\bar{j}u||\bar{i}\bar{s}) + \delta_{\bar{i}u}(\bar{j}\bar{k}||t\bar{s}) \\
&- \delta_{\bar{i}\bar{k}}(\bar{j}u||t\bar{s}) + \delta_{\bar{j}u}(t\bar{k}||\bar{i}\bar{s}) - \delta_{\bar{j}\bar{k}}(tu||\bar{i}\bar{s})]\delta_{\bar{t}\bar{u}} \\
&+ (\bar{u}\bar{s}||\bar{i}\bar{t})(\delta_{u\bar{j}}\delta_{\bar{k}t} - \delta_{ut}\delta_{\bar{k}\bar{j}}) \\
&- (\bar{u}\bar{s}||\bar{j}\bar{t})(\delta_{u\bar{i}}\delta_{\bar{k}t} - \delta_{ut}\delta_{\bar{k}\bar{i}}) \\
&- (\bar{u}\bar{s}||t\bar{t})(\delta_{u\bar{j}}\delta_{\bar{k}\bar{i}} - \delta_{u\bar{i}}\delta_{\bar{k}\bar{j}}) \\
&= [\delta_{tu}(\bar{j}\bar{k}||\bar{i}\bar{t}) + \delta_{\bar{i}\bar{k}}(\bar{j}u||t\bar{t}) + \delta_{\bar{j}\bar{k}}(tu||\bar{i}\bar{t})]\delta_{\bar{s}\bar{u}} \\
&+ [-\delta_{tu}(\bar{j}\bar{k}||\bar{i}\bar{s}) - \delta_{\bar{i}\bar{k}}(\bar{j}u||t\bar{s}) - \delta_{\bar{j}\bar{k}}(tu||\bar{i}\bar{s})]\delta_{\bar{t}\bar{u}} \\
&- (\bar{u}\bar{s}||\bar{i}\bar{t})\delta_{ut}\delta_{\bar{k}\bar{j}} + (\bar{u}\bar{s}||\bar{j}\bar{t})\delta_{ut}\delta_{\bar{k}\bar{i}}
\end{aligned}
\tag{C.52}
$$

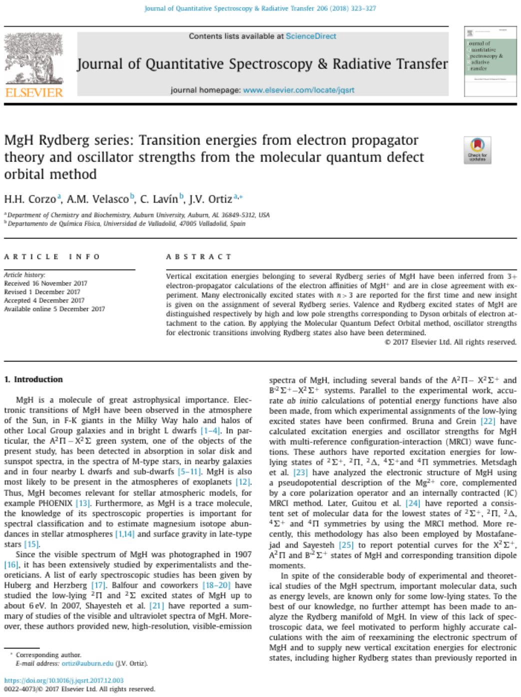
D

List of Publications as graduate student

During the author's academic studies, several papers in diverse topics have published as a result of his research in electron–propagator methods and computational chemistry. A brief summary of his most significant publications is presented below.

D.1 MgH Rydberg Series: Transition Energies from Electron Propagator Theory and Oscillator Strengths from the Molecular Quantum Defect Orbital Method

In this publication vertical excitation energies belonging to several Rydberg series of MgH were inferred from 3+ electron–propagator calculations of the electron affinities of MgH+. Many electronically excited states with $n > 3$ are reported for the first time and new insight is given on the assignment of several Rydberg series. The results obtained in this study are in close agreement with experiment.



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MgH Rydberg series: Transition energies from electron propagator theory and oscillator strengths from the molecular quantum defect orbital method

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A B S T R A C T

Vertical excitation energies belonging to several Rydberg series of MgH have been inferred from 3+ electron-propagator calculations of the electron affinities of MgH^+ and are in close agreement with experiment. Many electronically excited states with $n > 3$ are reported for the first time and new insight is given on the assignment of several Rydberg series. Valence and Rydberg excited states of MgH are distinguished respectively by high and low pole strengths corresponding to Dyson orbitals of electron attachment to the cation. By applying the Molecular Quantum Defect Orbital method, oscillator strengths for electronic transitions involving Rydberg states also have been determined.

1. Introduction

MgH is a molecule of great astrophysical importance. Electronic transitions of MgH have been observed in the atmosphere of the Sun, in F-K giants in the Milky Way halo and halos of other Local Group galaxies and in bright L dwarfs [1–4]. In particular, the $A^2\Pi - X^2\Sigma$ green system, one of the objects of the present study, has been detected in absorption in solar disk and sunspot spectra, in the spectra of M-type stars, in nearby galaxies and in four nearby L dwarfs and sub-dwarfs [5–11]. MgH is also most likely to be present in the atmospheres of exoplanets [12]. Thus, MgH becomes relevant for stellar atmospheric models, for example PHOENIX [13]. Furthermore, as MgH is a trace molecule, the knowledge of its spectroscopic properties is important for spectral classification and to estimate magnesium isotope abundances in stellar atmospheres [1,14] and surface gravity in late-type stars [15].

Since the visible spectrum of MgH was photographed in 1907 [16], it has been extensively studied by experimentalists and theoreticians. A list of early spectroscopic studies has been given by Huberg and Herzberg [17]. Balfour and coworkers [18–20] have studied the low-lying $^2\Pi$ and $^2\Sigma$ excited states of MgH up to about 6 eV. In 2007, Shayesteh et al. [21] have reported a summary of studies of the visible and ultraviolet spectra of MgH. Moreover, these authors provided new, high-resolution, visible-emission spectra of MgH, including several bands of the $A^2\Pi - X^2\Sigma^+$ and $B'^2\Sigma^+ - X^2\Sigma^+$ systems. Parallel to the experimental work, accurate *ab initio* calculations of potential energy functions have also been made, from which experimental assignments of the low-lying excited states have been confirmed. Bruna and Grein [22] have calculated excitation energies and oscillator strengths for MgH with multi-reference configuration-interaction (MRCI) wave functions. These authors have reported excitation energies for low-lying states of $^2\Sigma^+$, $^2\Pi$, $^2\Delta$, $^4\Sigma^+$and $^4\Pi$ symmetries. Metsdagh et al. [23] have analyzed the electronic structure of MgH using a pseudopotential description of the Mg^{2+} core, complemented by a core polarization operator and an internally contracted (IC) MRCI method. Later, Guitou et al. [24] have reported a consistent set of molecular data for the lowest states of $^2\Sigma^+$, $^2\Pi$, $^2\Delta$, $^4\Sigma^+$ and $^4\Pi$ symmetries by using the MRCI method. More recently, this methodology has also been employed by Mostafanejad and Sayesteh [25] to report potential curves for the $X^2\Sigma^+$, $A^2\Pi$ and $B'^2\Sigma^+$ states of MgH and corresponding transition dipole moments.

In spite of the considerable body of experimental and theoretical studies of the MgH spectrum, important molecular data, such as energy levels, are known only for some low-lying states. To the best of our knowledge, no further attempt has been made to analyze the Rydberg manifold of MgH. In view of this lack of spectroscopic data, we feel motivated to perform highly accurate calculations with the aim of reexamining the electronic spectrum of MgH and to supply new vertical excitation energies for electronic states, including higher Rydberg states than previously reported in

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D.2 Numerical test of SAC-CI methods for calculating vertical ionization energies

Valence, vertical ionization energies of closed–shell molecules were calculated with the symmetry–adapted–cluster, configuration–interaction (SAC–CI) method using ten basis sets for its level 1 and level 2 operator inclusion criteria, whereas for its more stringent level 3 scheme, 15 basis sets were used. For SAC-CI level 3, fortuitously better results may be obtained when smaller basis sets are used. Anomalous behavior with respect to the basis set size may occur when the level 1 and level 2 options are employed.

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REGULAR ARTICLE

Numerical test of SAC-CI methods for calculating vertical ionization energies

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Abstract Valence, vertical ionization energies of a representative set of closed-shell molecules were calculated with the symmetry-adapted-cluster, configuration-interaction (SAC-CI) method using ten basis sets for its level 1 and level 2 operator inclusion criteria, whereas for its more stringent level 3 scheme, 15 basis sets were used. SAC-CI level 3 is capable of producing mean unsigned errors of approximately 0.2 eV with quadruple ζ correlation-consistent basis sets. Fortuitously better results may be obtained when smaller basis sets are used. Anomalous behavior with respect to the basis set size may occur when the level 1 and level 2 options are employed.

Keywords SAC-CI · Ionization energies · Vertical detachment energy

1 Introduction

Electron binding energies of molecules are among their most important properties. Molecular ionization energies (IEs) provide qualitative insight into the decay of electron densities at large distance from nuclei [1, 2]. IEs are benchmarks that establish limits on spectra and reactivity associated with electronegativity and charge transfer [3, 4] and provide guidance in the optimization of nanostructures and detection techniques [5–7]. Indices of reactivity, such as hardness and softness, that emerge from qualitative density functional theory depend on IEs [2, 8–11].

IEs are pertinent to the many familiar and emerging varieties of electron spectroscopy [12–14]. Among these techniques for accurately measuring IEs are X-ray spectroscopy [12, 14, 15], photoelectron spectroscopy [13–21], zero-electron-kinetic-energy spectroscopy [22], time-resolved photoionization mass spectrometry [23, 24] and photoion–photoelectron coincidence spectroscopy [25].

Vertical IEs (VIEs) are defined as the energy change that corresponds to removal of an electron from a molecule at its equilibrium geometry. (Geometrical relaxation in the cation and differences in zero-point energies are not pertinent to the evaluation of VIEs.) These transition energies therefore are indices of molecular structure that chiefly characterize electronic degrees of freedom and therefore provide a standard of comparison with one-electron concepts that typically focus on orbitals and their energies. To provide a comprehensive understanding of a molecule's electronic structure, the calculation of several VIEs is desirable. Because photoelectron experiments with ultraviolet or X-ray radiation often exhibit peaks that correspond to more than one electronic state of the cation [15, 20, 25, 26], calculations of VIEs can be an aid to spectral assignments.

Symmetry-adapted-cluster, configuration-interaction [27–32] (SAC-CI) is an *ab-initio* method that employs an exponential Ansatz for a molecule and then applies a linear combination of ionization operators to this reference state to obtain cationic wavefunctions and energies. Practical implementations of the equation-of-motion, coupled-cluster (EOM-CC) method [33–36] and SAC-CI [27–32, 37] may reflect differences in the symmetry adaptation of

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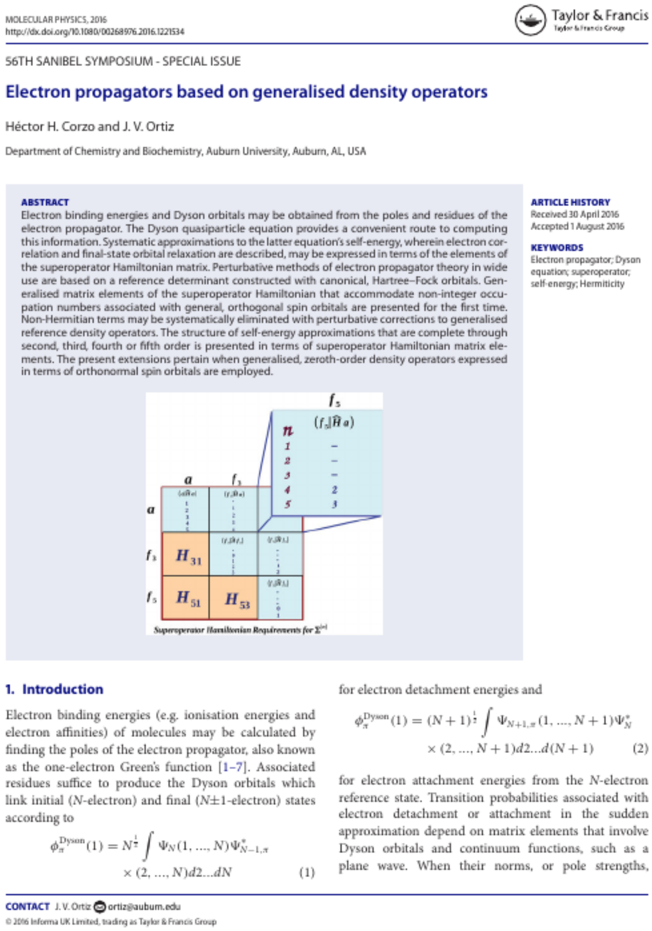
D.3 Electron propagators based on generalised density operators

Generalized matrix elements of the superoperator Hamiltonian that accommodate non–integer occupation numbers associated with general, orthogonal spin orbitals are presented for the first time. Non–Hermitian terms may be systematically eliminated with perturbative corrections to generalized reference density operators. The structure of self–energy approximations that are complete through second, third, fourth or fifth order is presented in terms of superoperator Hamiltonian matrix elements. The present extensions pertain when generalized, zeroth–order density operators expressed in terms of orthonormal spin orbitals are employed.



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Electron propagators based on generalised density operators

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ABSTRACT
Electron binding energies and Dyson orbitals may be obtained from the poles and residues of the electron propagator. The Dyson quasiparticle equation provides a convenient route to computing this information. Systematic approximations to the latter equation's self-energy, wherein electron correlation and final-state orbital relaxation are described, may be expressed in terms of the elements of the superoperator Hamiltonian matrix. Perturbative methods of electron propagator theory in wide use are based on a reference determinant constructed with canonical, Hartree–Fock orbitals. Generalised matrix elements of the superoperator Hamiltonian that accommodate non-integer occupation numbers associated with general, orthogonal spin orbitals are presented for the first time. Non-Hermitian terms may be systematically eliminated with perturbative corrections to generalised reference density operators. The structure of self-energy approximations that are complete through second, third, fourth or fifth order is presented in terms of superoperator Hamiltonian matrix elements. The present extensions pertain when generalised, zeroth-order density operators expressed in terms of orthonormal spin orbitals are employed.

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KEYWORDS
Electron propagator; Dyson equation; superoperator; self-energy; Hermiticity

Superoperator Hamiltonian Requirements for $\Sigma^{(n)}$

1. Introduction

Electron binding energies (e.g. ionisation energies and electron affinities) of molecules may be calculated by finding the poles of the electron propagator, also known as the one-electron Green's function [1–7]. Associated residues suffice to produce the Dyson orbitals which link initial (N-electron) and final ($N\pm1$-electron) states according to

$$\phi_\pi^{\text{Dyson}}(1) = N^{\frac{1}{2}} \int \Psi_N(1, \ldots, N)\Psi^*_{N-1,\pi} \times (2, \ldots, N)d2\ldots dN \tag{1}$$

for electron detachment energies and

$$\phi_\pi^{\text{Dyson}}(1) = (N+1)^{\frac{1}{2}} \int \Psi_{N+1,\pi}(1, \ldots, N+1)\Psi^*_N \times (2, \ldots, N+1)d2\ldots d(N+1) \tag{2}$$

for electron attachment energies from the N-electron reference state. Transition probabilities associated with electron detachment or attachment in the sudden approximation depend on matrix elements that involve Dyson orbitals and continuum functions, such as a plane wave. When their norms, or pole strengths,

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D.4 Electron Propagator Theory: Foundations and Predictions

After a brief discussion of the physical meaning of the poles and residues of the electron propagator, the Dyson quasiparticle equation is derived. Practical approximations of the self-energy operator in common use are defined in terms of the elements of the Hermitian superoperator Hamiltonian matrix.

CHAPTER THIRTEEN

Electron Propagator Theory: Foundations and Predictions

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Contents

Abstract

Electron propagator theory is an efficient means to accurately calculating electron binding energies and associated Dyson orbitals that is systematically improvable and easily interpreted in terms of familiar concepts of valence theory. After a brief discussion of the physical meaning of the poles and residues of the electron propagator, the Dyson quasiparticle equation is derived. Practical approximations of the self-energy operator in common use are defined in terms of the elements of the Hermitian superoperator Hamiltonian matrix. Methods that retain select self-energy terms in all orders of the fluctuation potential include the two-particle-one-hole Tamm–Dancoff approximation, the renormalized third-order method, the third-order algebraic diagrammatic construction, and the renormalized, nondiagonal second-order approximation. Methods based on diagonal second-order and third-order elements of the self-energy matrix, such as the diagonal second-order, diagonal third-order, outer valence Green's function, partial third-order, and renormalized partial third-order approximations, provide efficient alternatives. Recent numerical tests on valence, vertical ionization energies of representative, small molecules, and a comparison of arithmetic and memory requirements provide guidance to users of electron propagator software. A survey of recent applications and extensions illustrates the versatility and interpretive power of electron propagator methodology.

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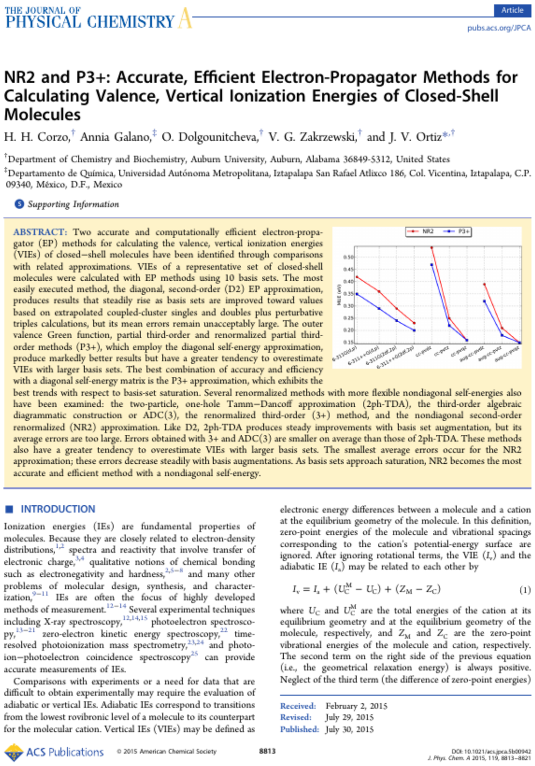
D.5 NR2 And P3+: Accurate, Efficient Electron–Propagator Methods For Calculating Valence, Vertical Ionization Energies Of Closed–Shell Molecules

The renormalized partial third–order method (P3+) and the nondiagonal second–order renormalized (NR2) methods have been identified as accurate and computationally efficient electron–propagator methods for calculating the valence, vertical ionization energies (VIEs) of closed-shell molecules through comparisons with related approximations.



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NR2 and P3+: Accurate, Efficient Electron-Propagator Methods for Calculating Valence, Vertical Ionization Energies of Closed-Shell Molecules

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Ⓢ *Supporting Information*

ABSTRACT: Two accurate and computationally efficient electron-propagator (EP) methods for calculating the valence, vertical ionization energies (VIEs) of closed−shell molecules have been identified through comparisons with related approximations. VIEs of a representative set of closed-shell molecules were calculated with EP methods using 10 basis sets. The most easily executed method, the diagonal, second-order (D2) EP approximation, produces results that steadily rise as basis sets are improved toward values based on extrapolated coupled-cluster singles and doubles plus perturbative triples calculations, but its mean errors remain unacceptably large. The outer valence Green function, partial third-order and renormalized partial third-order methods (P3+), which employ the diagonal self-energy approximation, produce markedly better results but have a greater tendency to overestimate VIEs with larger basis sets. The best combination of accuracy and efficiency with a diagonal self-energy matrix is the P3+ approximation, which exhibits the best trends with respect to basis-set saturation. Several renormalized methods with more flexible nondiagonal self-energies also have been examined: the two-particle, one-hole Tamm−Dancoff approximation (2ph-TDA), the third-order algebraic diagrammatic construction or ADC(3), the renormalized third-order (3+) method, and the nondiagonal second-order renormalized (NR2) approximation. Like D2, 2ph-TDA produces steady improvements with basis set augmentation, but its average errors are too large. Errors obtained with 3+ and ADC(3) are smaller on average than those of 2ph-TDA. These methods also have a greater tendency to overestimate VIEs with larger basis sets. The smallest average errors occur for the NR2 approximation; these errors decrease steadily with basis augmentations. As basis sets approach saturation, NR2 becomes the most accurate and efficient method with a nondiagonal self-energy.

INTRODUCTION

Ionization energies (IEs) are fundamental properties of molecules. Because they are closely related to electron-density distributions,[1,2] spectra and reactivity that involve transfer of electronic charge,[3,4] qualitative notions of chemical bonding such as electronegativity and hardness,[2,5−8] and many other problems of molecular design, synthesis, and characterization,[9−11] IEs are often the focus of highly developed methods of measurement.[12−14] Several experimental techniques including X-ray spectroscopy,[12,14,15] photoelectron spectroscopy,[13−21] zero-electron kinetic energy spectroscopy,[22] time-resolved photoionization mass spectrometry,[23,24] and photoion−photoelectron coincidence spectroscopy[25] can provide accurate measurements of IEs.

Comparisons with experiments or a need for data that are difficult to obtain experimentally may require the evaluation of adiabatic or vertical IEs. Adiabatic IEs correspond to transitions from the lowest rovibronic level of a molecule to its counterpart for the molecular cation. Vertical IEs (VIEs) may be defined as electronic energy differences between a molecule and a cation at the equilibrium geometry of the molecule. In this definition, zero-point energies of the molecule and vibrational spacings corresponding to the cation's potential-energy surface are ignored. After ignoring rotational terms, the VIE (I_v) and the adiabatic IE (I_a) may be related to each other by

$$I_v = I_a + (U_C^M - U_C) + (Z_M - Z_C) \qquad (1)$$

where U_C and U_C^M are the total energies of the cation at its equilibrium geometry and at the equilibrium geometry of the molecule, respectively, and Z_M and Z_C are the zero-point vibrational energies of the molecule and cation, respectively. The second term on the right side of the previous equation (i.e., the geometrical relaxation energy) is always positive. Neglect of the third term (the difference of zero-point energies)

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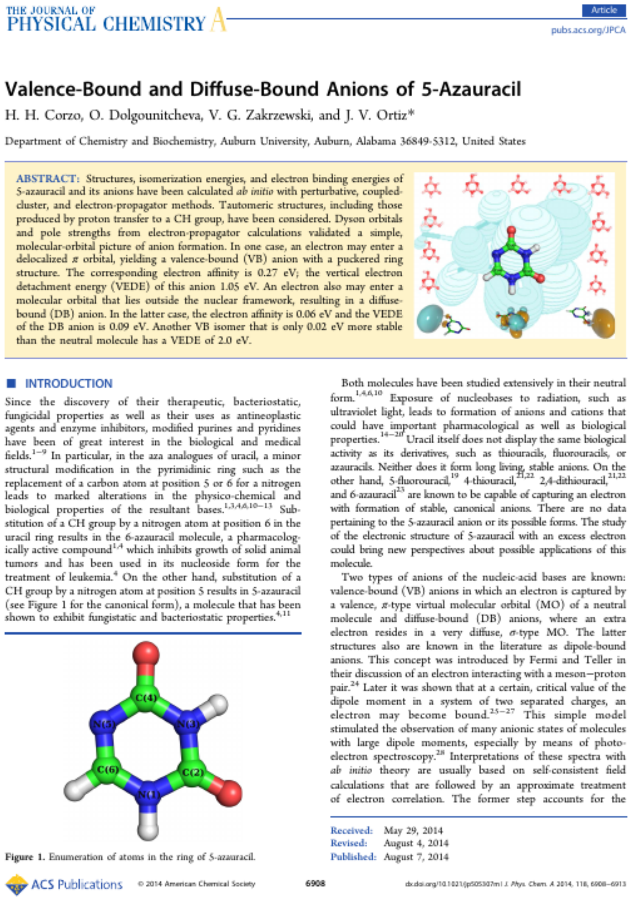
D.6 Valence-Bound and Diffuse-Bound Anions of 5-Azauracil

Structures (including those produced by proton transfer), isomerization energies, and electron binding energies of 5-azauracil and its anions have been calculated ab initio with perturbative, coupled-cluster, and electron-propagator methods.



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Valence-Bound and Diffuse-Bound Anions of 5-Azauracil

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ABSTRACT: Structures, isomerization energies, and electron binding energies of 5-azauracil and its anions have been calculated *ab initio* with perturbative, coupled-cluster, and electron-propagator methods. Tautomeric structures, including those produced by proton transfer to a CH group, have been considered. Dyson orbitals and pole strengths from electron-propagator calculations validated a simple, molecular-orbital picture of anion formation. In one case, an electron may enter a delocalized π orbital, yielding a valence-bound (VB) anion with a puckered ring structure. The corresponding electron affinity is 0.27 eV; the vertical electron detachment energy (VEDE) of this anion 1.05 eV. An electron also may enter a molecular orbital that lies outside the nuclear framework, resulting in a diffuse-bound (DB) anion. In the latter case, the electron affinity is 0.06 eV and the VEDE of the DB anion is 0.09 eV. Another VB isomer that is only 0.02 eV more stable than the neutral molecule has a VEDE of 2.0 eV.

INTRODUCTION

Since the discovery of their therapeutic, bacteriostatic, fungicidal properties as well as their uses as antineoplastic agents and enzyme inhibitors, modified purines and pyridines have been of great interest in the biological and medical fields.[1−9] In particular, in the aza analogues of uracil, a minor structural modification in the pyrimidinic ring such as the replacement of a carbon atom at position 5 or 6 for a nitrogen leads to marked alterations in the physico-chemical and biological properties of the resultant bases.[1,3,4,6,10−13] Substitution of a CH group by a nitrogen atom at position 6 in the uracil ring results in the 6-azauracil molecule, a pharmacologically active compound[1,4] which inhibits growth of solid animal tumors and has been used in its nucleoside form for the treatment of leukemia.[4] On the other hand, substitution of a CH group by a nitrogen atom at position 5 results in 5-azauracil (see Figure 1 for the canonical form), a molecule that has been shown to exhibit fungistatic and bacteriostatic properties.[4,11]

Figure 1. Enumeration of atoms in the ring of 5-azauracil.

Both molecules have been studied extensively in their neutral form.[1,4,6,10] Exposure of nucleobases to radiation, such as ultraviolet light, leads to formation of anions and cations that could have important pharmacological as well as biological properties.[14−20] Uracil itself does not display the same biological activity as its derivatives, such as thiouracils, fluorouracils, or azauracils. Neither does it form long living, stable anions. On the other hand, 5-fluorouracil,[19] 4-thiouracil,[21,22] 2,4-dithiouracil,[21,22] and 6-azauracil[23] are known to be capable of capturing an electron with formation of stable, canonical anions. There are no data pertaining to the 5-azauracil anion or its possible forms. The study of the electronic structure of 5-azauracil with an excess electron could bring new perspectives about possible applications of this molecule.

Two types of anions of the nucleic-acid bases are known: valence-bound (VB) anions in which an electron is captured by a valence, π-type virtual molecular orbital (MO) of a neutral molecule and diffuse-bound (DB) anions, where an extra electron resides in a very diffuse, σ-type MO. The latter structures also are known in the literature as dipole-bound anions. This concept was introduced by Fermi and Teller in their discussion of an electron interacting with a meson−proton pair.[24] Later it was shown that at a certain, critical value of the dipole moment in a system of two separated charges, an electron may become bound.[25−27] This simple model stimulated the observation of many anionic states of molecules with large dipole moments, especially by means of photoelectron spectroscopy.[28] Interpretations of these spectra with *ab initio* theory are usually based on self-consistent field calculations that are followed by an approximate treatment of electron correlation. The former step accounts for the

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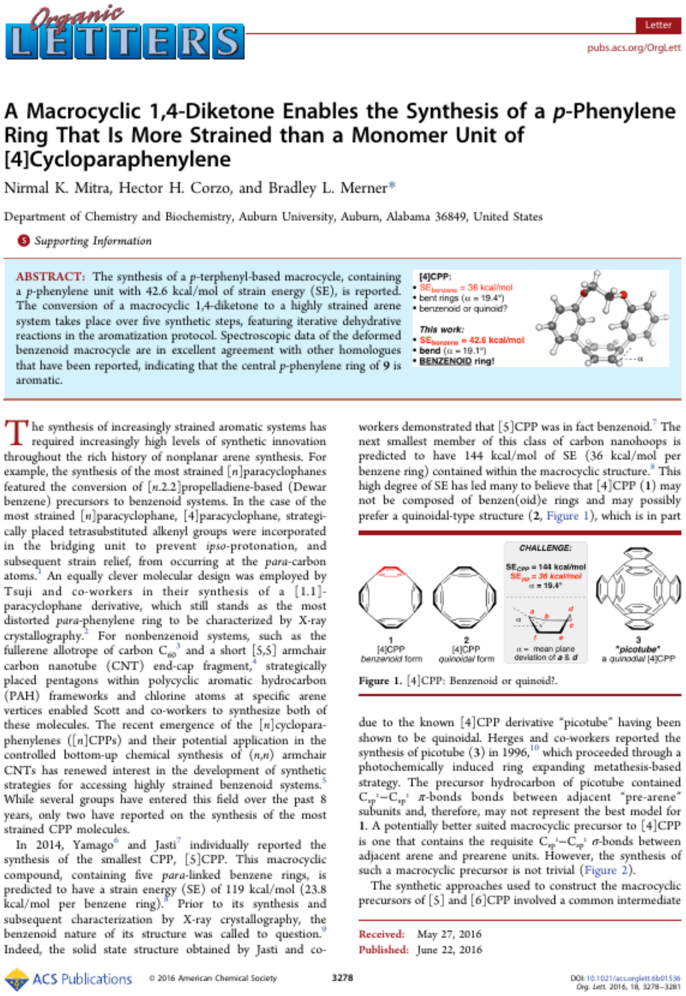
D.7 A Macrocyclic 1,4-Diketone Enables the Synthesis of a p-Phenylene Ring That Is More Strained than a Monomer Unit of [4]Cycloparaphenylene

The synthesis of a p–terphenyl–based macrocycle, containing a p–phenylene unit with 42.6 kcal/mol of strain energy (SE), is reported. The conversion of a macrocyclic 1,4-diketone to a highly strained arene system takes place over five synthetic steps, featuring iterative dehydrative reactions in the aromatization protocol.



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A Macrocyclic 1,4-Diketone Enables the Synthesis of a *p*-Phenylene Ring That Is More Strained than a Monomer Unit of [4]Cycloparaphenylene

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Supporting Information

ABSTRACT: The synthesis of a *p*-terphenyl-based macrocycle, containing a *p*-phenylene unit with 42.6 kcal/mol of strain energy (SE), is reported. The conversion of a macrocyclic 1,4-diketone to a highly strained arene system takes place over five synthetic steps, featuring iterative dehydrative reactions in the aromatization protocol. Spectroscopic data of the deformed benzenoid macrocycle are in excellent agreement with other homologues that have been reported, indicating that the central *p*-phenylene ring of **9** is aromatic.

The synthesis of increasingly strained aromatic systems has required increasingly high levels of synthetic innovation throughout the rich history of nonplanar arene synthesis. For example, the synthesis of the most strained [*n*]paracyclophanes featured the conversion of [*n*.2.2]propelladiene-based (Dewar benzene) precursors to benzenoid systems. In the case of the most strained [*n*]paracyclophane, [4]paracyclophane, strategically placed tetrasubstituted alkenyl groups were incorporated in the bridging unit to prevent *ipso*-protonation, and subsequent strain relief, from occurring at the *para*-carbon atoms.[1] An equally clever molecular design was employed by Tsuji and co-workers in their synthesis of a [1.1]-paracyclophane derivative, which still stands as the most distorted *para*-phenylene ring to be characterized by X-ray crystallography.[2] For nonbenzenoid systems, such as the fullerene allotrope of carbon C_{60}[3] and a short [5,5] armchair carbon nanotube (CNT) end-cap fragment,[4] strategically placed pentagons within polycyclic aromatic hydrocarbon (PAH) frameworks and chlorine atoms at specific arene vertices enabled Scott and co-workers to synthesize both of these molecules. The recent emergence of the [*n*]cycloparaphenylenes ([*n*]CPPs) and their potential application in the controlled bottom-up chemical synthesis of (*n*,*n*) armchair CNTs has renewed interest in the development of synthetic strategies for accessing highly strained benzenoid systems.[5] While several groups have entered this field over the past 8 years, only two have reported on the synthesis of the most strained CPP molecules.

In 2014, Yamago[6] and Jasti[7] individually reported the synthesis of the smallest CPP, [5]CPP. This macrocyclic compound, containing five *para*-linked benzene rings, is predicted to have a strain energy (SE) of 119 kcal/mol (23.8 kcal/mol per benzene ring).[8] Prior to its synthesis and subsequent characterization by X-ray crystallography, the benzenoid nature of its structure was called to question.[9] Indeed, the solid state structure obtained by Jasti and co-workers demonstrated that [5]CPP was in fact benzenoid.[7] The next smallest member of this class of carbon nanohoops is predicted to have 144 kcal/mol of SE (36 kcal/mol per benzene ring) contained within the macrocyclic structure.[8] This high degree of SE has led many to believe that [4]CPP (**1**) may not be composed of benzen(oid)e rings and may possibly prefer a quinoidal-type structure (**2**, Figure 1), which is in part due to the known [4]CPP derivative "picotube" having been shown to be quinoidal. Herges and co-workers reported the synthesis of picotube (**3**) in 1996,[10] which proceeded through a photochemically induced ring expanding metathesis-based strategy. The precursor hydrocarbon of picotube contained $C_{sp^2}–C_{sp^2}$ π-bonds bonds between adjacent "pre-arene" subunits and, therefore, may not represent the best model for **1**. A potentially better suited macrocyclic precursor to [4]CPP is one that contains the requisite $C_{sp^2}–C_{sp^2}$ σ-bonds between adjacent arene and prearene units. However, the synthesis of such a macrocyclic precursor is not trivial (Figure 2).

Figure 1. [4]CPP: Benzenoid or quinoid?.

The synthetic approaches used to construct the macrocyclic precursors of [5] and [6]CPP involved a common intermediate

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D.8 Overcoming Strain-Induced Rearrangement Reactions: A Mild Dehydrative Aromatization Protocol for the Synthesis of Highly Distorted para -Phenylenes

A series of p–terphenyl–based macrocycles, containing highly distorted p–phenylene units, have been synthesized. A streamlined synthetic protocol for the synthesis of 1,4-diketo macrocycles has been developed, using only 2.5 mol % of the Hoveyda–Grubbs second–generation catalyst in both metathesis and transfer hydrogenation reactions.

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Overcoming Strain-Induced Rearrangement Reactions: A Mild Dehydrative Aromatization Protocol for Synthesis of Highly Distorted *p*-Phenylenes

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Supporting Information

ABSTRACT: A series of *p*-terphenyl-based macrocycles, containing highly distorted *p*-phenylene units, have been synthesized. Biaryl bonds of the nonplanar *p*-terphenyl nuclei were constructed in the absence of Pd-catalyzed or Ni-mediated cross-coupling reactions, using 1,4-diketones as surrogates to strained arene units. A streamlined synthetic protocol for the synthesis of 1,4-diketo macrocycles has been developed, using only 2.5 mol % of the Hoveyda–Grubbs second-generation catalyst in both metathesis and transfer hydrogenation reactions. Under protic acid-mediated dehydrative aromatization conditions, the central and most strained benzene ring of the *p*-terphenyl systems was susceptible to rearrangement reactions. To overcome this, a dehydrative aromatization protocol using the Burgess reagent was developed. Under these conditions, no strain-induced rearrangement reactions occur, delivering *p*-phenylene units with up to 28.4 kcal/mol strain energy and deformation angles that sum up to 40°.

INTRODUCTION

Formation of biaryl bonds via transition metal-catalyzed, or mediated, cross-coupling reaction is a venerable transformation in organic synthesis.[1] A plethora of conditions, modifications, and optimizations have been reported over the past 30 years,[1a] and the presence of biaryl systems in natural products,[2] important pharmaceuticals,[3] axially chiral molecules,[4] and designed molecules relevant to materials science[5] has instigated a tireless interest in this area of synthetic method development.[6] Thus, it is surprising to find that such methods have not enjoyed widespread applicability in the synthesis of macrocyclic systems that contain arene-bridged units, as they have in the synthesis of acyclic (linear) arene–arene or polyaryl systems. In fact, biaryl bond formation that results in construction of strained macrocyclic compounds has proven to be a significant challenge for chemical synthesis.[7] One of the main problems posed by the synthesis of macrocyclic arene-bridged systems is the buildup of strain in carbon–carbon (C–C) bond-forming reactions that furnish the intended targets. In particular, if the desired cross-coupling reaction requires bending the arene unit or multiple arene units, then low-yielding reactions result (mode 1, Figure 1a).[7] Furthermore, if arene–arene bond formation requires stretching or elongating C–C bonds within an alkyl chain upon macrocycle formation, the corresponding macrocyclization can be energetically prohibitive (mode 2, Figure 1a). Recently, arylation reactions that avoid cross-coupling reaction partners have emerged as powerful tools for assembling strained macrocyclic systems.[8]

The synthesis of distorted benzene rings has been ongoing for over 65 years,[9] and the quest to synthesize the most perturbed cyclic 6π system culminated with kinetically stabilized [4]paracyclophane derivatives in 2003.[10] However, this field of chemical synthesis has remained quite vigorous over the past decade. The discovery of natural products containing highly strained *p*-phenylene subunits, particularly the haouamine alkaloids,[11] and the notion that macrocyclic benzenoid hydrocarbons may serve as templates in the bottom-up chemical synthesis of carbon nanotubes (CNTs)[12] has kept the level of interest in new synthetic method development high. It is noteworthy that, in both of the aforementioned examples, the bent *p*-phenylene units are part of biaryl macrocyclic systems. The most distorted benzene rings to be characterized by X-ray crystallography belong to the paracyclophanes. In the case of [6]paracylophane derivative **1** of Tobe et al.[13] and [1.1]paracyclophane **2** of Tsuji and co-workers,[14] the highly distorted π-systems were obtained upon valence isomerization of Dewar benzene precursors (Figure 2). For a long time, valence isomerization reactions were viewed as the ultimate method for synthesizing severely distorted aromatic systems. In the case of Dewar benzenes, rupture of the central C–C bond in the bicyclo[2.2.0]hexa-2,5-diene system brought about a release of strain energy (SE) upon destruction of the bicyclic intermediate, and a gain in aromatic stabilization energy (ASE) upon formation of the arene system. Until 2014, no bent *p*-

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D.9 Publications related to Numerical methods

A new numerical method for the calculation of Bessel function integrals is proposed. This method utilizes the integral representation of the Bessel function to recast the problem as a double integral; one of which is calculated with Gauss–Chebyshev quadrature while the other uses a parameter–dependent Gauss–Laguerre quadrature in the complex plane.

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Numerical evaluation of Bessel function integrals for functions with exponential dependence

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A numerical method for the calculation of Bessel function integrals is proposed for trial functions with exponential type behavior and evaluated for functions with and without explicit exponential dependence. This method utilizes the integral representation of the Bessel function to recast the problem as a double integral; one of which is calculated with Gauss-Chebyshev quadrature while the other uses a parameter-dependent Gauss-Laguerre quadrature in the complex plane. Accurate results can be obtained with relatively small orders of quadratures for the studied classes of functions.

Keywords: Bessel function integrals; Gaussian quadrature; Hankel transform; Gauss-Laguerre; Gauss-Chebyshev

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1. Introduction

Bessel function integrals involving a function $f(x)$,

$$I(\rho,\nu)=\int_0^\infty f(x)J_\nu(\rho x)\mathrm{d}x, \tag{1}$$

occur in many areas of science and engineering. Their numerical evaluation continues to be of interest especially for functions which decay slowly since care must be taken for larger values of the argument, ρ, as the integrand begins to oscillate rapidly [1–13]. The particular case when $f(x)$ possesses exponential behavior arises in many contexts.

One avenue of numerical approximation lies in recasting this integral as a double integral using the integral representation of the ν-order Bessel function of the first kind, [9]

$$J_\nu(x)=\frac{x^\nu}{\Gamma(\nu+\frac{1}{2})\sqrt{\pi}2^{\nu-1}}\int_0^1(1-t^2)^{\nu-1/2} \times\cos(xt)\mathrm{d}t,\quad Re\ \nu>\frac{1}{2}. \tag{2}$$

Substituting this integral representation into Eq. (1) and changing the order of integration yields

$$I(\rho,\nu)=\frac{\rho^\nu}{\Gamma(\nu+\frac{1}{2})\sqrt{\pi}2^{\nu-1}}\int_0^1(1-t^2)^{\nu-1/2}F(t)\mathrm{d}t \tag{3}$$

where

$$F(t)=\int_0^\infty x^\nu f(x)\cos(\rho xt)\mathrm{d}x. \tag{4}$$

We take a fresh approach for the calculation of the second integral or cosine transform. It is based on the introduction of a parameter, α, and transformation into the complex plane and has been previously employed to calculate sine transforms of functions with explicit exponential dependence [14]. The introduction of the parameter is used to model the exponential behavior of the function. We emphasize that the applicability of this method for the transform of functions without explicit exponential dependence has not been explored (as we will do here).

Using Euler's identity, $F(t)$ may be re-written as

$$F(t)=Re\left[\int_0^\infty x^\nu e^{\alpha x}f(x)e^{-(\alpha-\imath\rho t)x}\mathrm{d}x\right]. \tag{5}$$

Transforming into the complex plane by setting $z=(\alpha-\imath\rho t)x$ in Eq. (5), yields

$$F(t)=Re\left[\frac{1}{(\alpha-\imath\rho t)^{\nu+1}} \times\int_0^\infty z^\nu e^{\frac{\alpha z}{\alpha-\imath\rho t}}f\left(\frac{z}{\alpha-\imath\rho t}\right)e^{-z}\mathrm{d}z\right]. \tag{6}$$

The factor e^{-z} is the weight function for Gauss-Laguerre quadrature. Thus Eq. (6) can be approximated by

$$F(t)\approx Re\left[\frac{1}{(\alpha-\imath\rho t)^{\nu+1}} \times\sum_{j=1}^N z_j^\nu e^{\frac{\alpha z_j}{\alpha-\imath\rho t}}f\left(\frac{z_j}{\alpha-\imath\rho t}\right)w_j\right] \tag{7}$$

where z_j and w_j are the abscissae and weights of the N-order Gauss-Laguerre quadrature. This methodology is expected to perform well when the function $f(x)$ possesses an exponential-type behavior [14].

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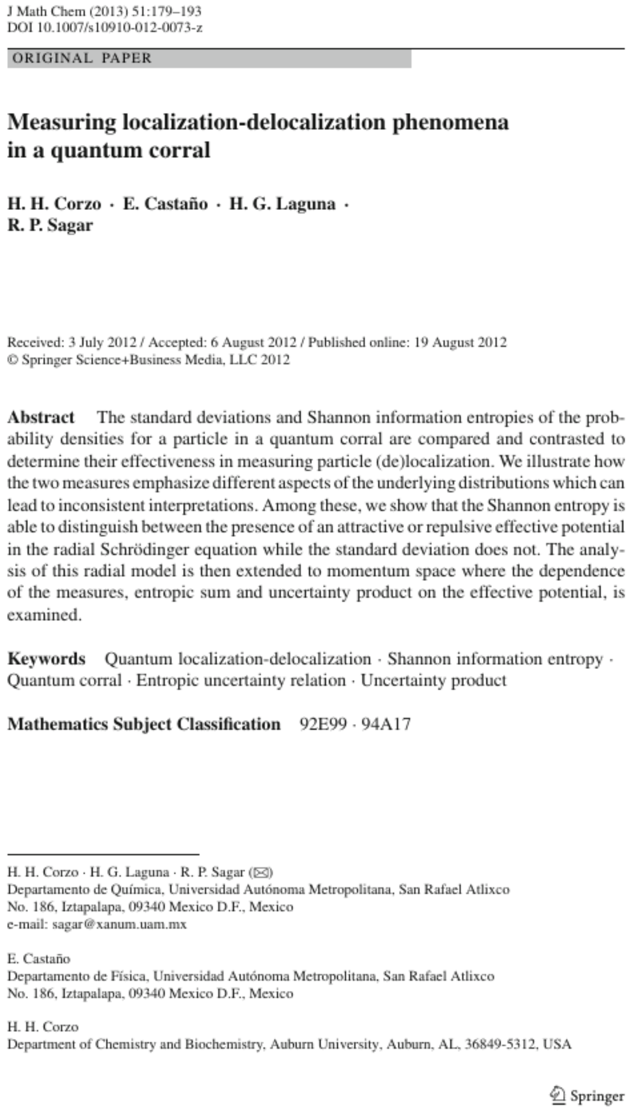
D.10 Measuring localization-delocalization phenomena in a quantum corral

The standard deviations and Shannon information entropies of the probability densities for a particle in a quantum corral are compared and contrasted. Illustrating how these two measures emphasize different aspects of the underlying distributions which can lead to inconsistent interpretations.



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ORIGINAL PAPER

Measuring localization-delocalization phenomena in a quantum corral

H. H. Corzo · E. Castaño · H. G. Laguna · R. P. Sagar

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Abstract The standard deviations and Shannon information entropies of the probability densities for a particle in a quantum corral are compared and contrasted to determine their effectiveness in measuring particle (de)localization. We illustrate how the two measures emphasize different aspects of the underlying distributions which can lead to inconsistent interpretations. Among these, we show that the Shannon entropy is able to distinguish between the presence of an attractive or repulsive effective potential in the radial Schrödinger equation while the standard deviation does not. The analysis of this radial model is then extended to momentum space where the dependence of the measures, entropic sum and uncertainty product on the effective potential, is examined.

Keywords Quantum localization-delocalization · Shannon information entropy · Quantum corral · Entropic uncertainty relation · Uncertainty product

Mathematics Subject Classification 92E99 · 94A17

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