Algorithms of Quantum Chemistry

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1 Hartree–Fock Method

The Hartree–Fock (HF) method stands as a cornerstone in quantum chemistry, offering a systematic approach to solve the electronic structure problem in molecules. This computational technique strives to determine the optimal wave function for a given molecular system, providing insights into the distribution of electrons and their energies.

1.1 Theoretical Background

Ultimately, we are interested in solving the Schrödinger equation in the form

$$\hat{\mathbf{H}} \left| \Psi \right\rangle = E \left| \Psi \right\rangle, \tag{1.1}$$

where $\hat{H}$ is the molecular Hamiltonian operator, Ψ is the molecular wave function, and E is the total energy of the system. The HF method aims to approximate the wave function Ψ by a single Slater determinant, which we will write in the form

$$\left| \Psi \right\rangle = \left| \chi_1 \chi_2 \cdots \chi_N \right\rangle, \tag{1.2}$$

where χ_i represents a Molecular Spinorbital (MS) and N is the total number of electrons. The HF method seeks to optimize these molecular orbitals to minimize the total energy of the system, providing a reliable estimate of the electronic structure. However, in the Restricted Hartree–Fock (RHF) method, we impose a constraint on the electron spin, and instead of spin orbitals, we work with spatial orbitals, which allows us to write the slater determinant in terms of spatial orbitals in the form

$$\left| \Psi \right\rangle = \left| \Phi_1 \Phi_2 \cdots \Phi_{N/2} \right\rangle, \tag{1.3}$$

where Φ_i represents a molecular spatial orbital. We can see, that for the RHF method, we need to have an even number of electrons in the system. In practical calculations, it is convenient to expand the molecular orbitals (spin or spatial) in terms of basis functions ϕ (usually sums of Gaussian functions) and work with the expansion coefficients. If we assume that the wavefunction is a single Slater determinant, our molecular orbitals are expanded in terms of basis functions and optimize the energy of such determinant, we arrive at the Roothaan equations in the form

$$\mathbf{FC} = \mathbf{SC}\varepsilon, \tag{1.4}$$

where $\mathbf{F}$ is the Fock matrix (defined later), $\mathbf{C}$ is a matrix of orbital coefficients, $\mathbf{S}$ is the overlap matrix (also defined later), and ε represents orbital energies.

1.2 Implementation of the Restricted Hartree–Fock Method

Let's begin by defining the core Hamiltonian, also known as the one-electron Hamiltonian. The core Hamiltonian represents a part of the full Hamiltonian that excludes electron-electron repulsion. In index notation, it is expressed as

$$H_{\mu\nu}^{core} = T_{\mu\nu} + V_{\mu\nu} \tag{1.5}$$

where μ and ν are indices of basis functions, $T_{\mu\nu}$ is a kinetic energy matrix element and $V_{\mu\nu}$ is a potential energy matrix element. These matrix elements are given as

$$T_{\mu\nu} = \langle \phi_\mu | \hat{T} | \phi_\nu \rangle \tag{1.6}$$

$$V_{\mu\nu} = \langle \phi_\mu | \hat{V} | \phi_\nu \rangle \tag{1.7}$$

are usually calculated using analytical expressions. Additionally, using analytical expressions, we can calculate

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle \tag{1.8}$$

and the two-electron Coulomb repulsion integral

$$J_{\mu\nu\kappa\lambda} = \langle \phi_\mu \phi_\mu | \hat{J} | \phi_\kappa \phi_\lambda \rangle \,, \tag{1.9}$$

which play crucial roles in the HF calculation. The HF method revolves around solving the Roothaan equations 1.4 iteratively. The Fock matrix is defined as

$$F_{\mu\nu} = H_{\mu\nu}^{core} + D_{\kappa\lambda}(J_{\mu\nu\kappa\lambda} - \frac{1}{2}J_{\mu\lambda\kappa\nu}) \tag{1.10}$$

depends on the unknown density matrix **D**. This iterative process is carried out through a Self-Consistent Field method. In each iteration, a guess for the density matrix is made, and the Roothaan equations are solved. The density matrix is then updated as

$$D_{\mu\nu} = 2C_{\mu i}C_{\nu i} \tag{1.11}$$

and the total energy of the system

$$E = \frac{1}{2}D_{\mu\nu}(H_{\mu\nu}^{core} + F_{\mu\nu}) + E_{nuc} \tag{1.12}$$

is then calculated using the core Hamiltonian and the Fock matrix. The important thing to note is that the Fock matrix depends on the density matrix, which is updated in each iteration. The initial guess for the density matrix is often set to zero. After the density matrix and the total energy are converged, the Self-Consistent Field procedure is terminated, and the optimized molecular orbitals are obtained. To get the final energy of the system, we need to add the nuclear repulsion energy of the form

$$E_{nuc} = \sum_A \sum_{B<A} \frac{Z_A Z_B}{R_{AB}}, \tag{1.13}$$

where Z_A is the nuclear charge of atom A, and R_{AB} is the distance between atoms A and B.

1.2.1 Gradient of the Restricted Hartree–Fock Method

If we perform the calculation as described above and get the density matrix $\mathbf{D}$ we can evaluate the nuclear energy gradient as

$$\frac{\partial E}{\partial X_{A,i}} = D_{\mu\nu} \frac{\partial H_{\mu\nu}^{core}}{\partial X_{A,i}} + 2D_{\mu\nu}D_{\kappa\lambda} \frac{\partial J_{\mu\nu\kappa\lambda}}{\partial X_{A,i}} - 2W_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial X_{A,i}} \tag{1.14}$$

where i is the index of the coordinate and where $\mathbf{W}$ is energy weighed density matrix defined as

$$W_{\mu\nu} = 2C_{\mu i}C_{\nu i}\varepsilon_i \tag{1.15}$$

1.3 Integral Transforms to the Basis of Molecular Spinorbitals

To perform most of the post-Hartree–Fock (post-HF) calculations, we usually need to transform the integrals to the MS basis. We will describe it here and refer to it in the post-HF methods sections. We will also present the post-HF methods using the integrals in the MS basis (and its antisymmetrized form in case of the Coulomb integrals), since it is more general.

All the integrals defined in the equations 1.5, 1.8, and 1.9 and even the Fock matrix in the equation 1.10 are defined in the basis of atomic orbitals. To transform these integrals to the MS basis, we need to use the coefficient matrix $\mathbf{C}$ obtained from the solution of the Roothaan equations 1.4. The coefficient matrix $\mathbf{C}$, which is obtained from the RHF calculation, is calculated in the spatial molecular orbital basis. The first step is to expand the coefficient matrix $\mathbf{C}$ to the MS basis. This can be done mathematically using the tiling matrix $\mathbf{P}_{n\times 2n}$, defined as

$$\mathbf{P} = \begin{pmatrix} e_1 & e_1 & e_2 & e_2 & \dots & e_n & e_n \end{pmatrix} \tag{1.16}$$

where e_i represents the i-th column of the identity matrix $\mathbf{I}_n$ and the matrices $\mathbf{M}_{n\times 2n}$ and $\mathbf{N}_{n\times 2n}$ with elements given by

$$M_{ij} = 1 - j \bmod 2, N_{ij} = j \bmod 2. \tag{1.17}$$

The coefficient matrix $\mathbf{C}$ in the MS basis can be then expressed as

$$\mathbf{C}^{MS} = \begin{pmatrix} \mathbf{CP} \\ \mathbf{CP} \end{pmatrix} \odot \begin{pmatrix} \mathbf{M} \\ \mathbf{N} \end{pmatrix}, \tag{1.18}$$

where $\odot$ denotes the Hadamard product. This transformed matrix $\mathbf{C}^{MS}$ is then used to transform the Coulomb integrals $\mathbf{J}$ to the MS basis as

$$J_{pqrs}^{MS} = C_{\mu p}^{MS} C_{\nu q}^{MS} (\mathbf{I_2} \otimes_K (\mathbf{I_2} \otimes_K \mathbf{J})^{(4,3,2,1)})_{\mu\nu\kappa\lambda} C_{\kappa r}^{MS} C_{\lambda s}^{MS}, \tag{1.19}$$

where the superscript $(4, 3, 2, 1)$ denotes the axes transposition and $\otimes_K$ is the Kronecker product. This notation accounts for the spin modifications and ensures that the transformations adhere to quantum mechanical principles. We also define the antisymmetrized Coulomb integrals in physicists' notation as

$$\langle pq||rs \rangle = (J_{pqrs}^{MS} - J_{psrq}^{MS})^{(1,3,2,4)}. \tag{1.20}$$

For the transformation of the one-electron integrals such as the core Hamiltonian, the overlap matrix and also the Fock matrix, we use the formula

$$A_{pq}^{MS} = C_{\mu p}^{MS} (\mathbf{I_2} \otimes_K \mathbf{A})_{\mu\nu} C_{\nu q}^{MS}, \tag{1.21}$$

where $\mathbf{A}$ is an arbitrary one-electron integral.

2 Møller–Plesset Perturbation Theory

Møller–Plesset Perturbation Theory (MPPT) is a quantum mechanical method used to improve the accuracy of electronic structure calculations within the framework of HF theory. It involves treating electron-electron correlation effects as a perturbation to the reference HF wave function. The method is named after its developers, physicists C. Møller and M. S. Plesset. By systematically including higher-order corrections, Møller–Plesset Perturbation Pheory provides more accurate predictions of molecular properties compared to the initial HF approximation.

2.1 Theory of the Pertrubative Approach

As for the HF method, we start with the Schrödinger equation in the form

$$\hat{\mathbf{H}} \left| \Psi \right\rangle = E \left| \Psi \right\rangle, \tag{2.1}$$

where $\hat{\mathbf{H}}$ is the molecular Hamiltonian operator, $\left| \Psi \right\rangle$ is the molecular wave function, and E is the total energy of the system. In the Møller–Plesset perturbation theory we write the Hamiltonian operator as

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}^{(0)} + \lambda \hat{\mathbf{H}}', \tag{2.2}$$

where $\hat{\mathbf{H}}^{(0)}$ is the Hamiltonian used in the HF method (the electrons are moving in the mean field), λ is a parameter between 0 and 1, and $\hat{\mathbf{H}}'$ is the perturbation operator representing the missing electron-electron interactions. We can then expand the wavefunction $\left| \Psi \right\rangle$ and total energy E in a power series of λ as

$$\left| \Psi \right\rangle = \left| \Psi^{(0)} \right\rangle + \lambda \left| \Psi^{(1)} \right\rangle + \lambda^2 \left| \Psi^{(2)} \right\rangle + \dots \tag{2.3}$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \tag{2.4}$$

and ask, how how does the total energy change with the included terms. After some algebra, we can show that the first-order correction to the total energy is zero, the second-order correction is given by

$$E_{corr}^{MP2} = \sum_{s>0} \frac{H_{0s}' H_{s0}'}{E_0 - E_s}, \tag{2.5}$$

where s runs over all doubly excited determinants, H_{0s}' is the matrix element of the perturbation operator between the HF determinant and the doubly excited determinant, and E_0 and E_s are the energies of the reference and doubly excited determinants, respectively. We could express

all higher-order corrections in a similar way, using only the matrix elements of the perturbation operator and the energies of the determinants. For practical calculations, we apply Slater-Condon rules to evaluate the matrix elements and use the orbital energies obtained from the HF calculation. The expressions for calculation are summarised below.

2.2 Implementation of 2nd and 3rd Order Corrections

Having the antisymmetrized Coulomb integrals in the MS basis and physicists' notation defined in section 1.3, we can now proceed with the calculation of the correlation energy. We wil use the convention, that the indices i, j, k, and l run over occupied spinorbitals, while the indices a, b, c, and d run over virtual spinorbitals. The 2nd-order and 3rd-order correlation energies are given by the following expressions.

The 2nd-order correlation energy:

$$E_{corr}^{MP2} = \frac{1}{4} \sum_{ijab} \frac{\langle ab||ij \rangle \langle ij||ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{2.6}$$

The 3rd-order correlation energy:

$$E_{corr}^{MP3} = \frac{1}{8} \sum_{ijab} \frac{\langle ab||ij \rangle \langle cd||ab \rangle \langle ij||cd \rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_j - \varepsilon_c - \varepsilon_d)} + \tag{2.7}$$

$$+ \frac{1}{8} \sum_{ijab} \frac{\langle ab||ij \rangle \langle ij||kl \rangle \langle kl||ab \rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_k + \varepsilon_l - \varepsilon_a - \varepsilon_b)} + \tag{2.8}$$

$$+ \sum_{ijab} \frac{\langle ab||ij \rangle \langle cj||kb \rangle \langle ik||ac \rangle}{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_c)} \tag{2.9}$$

To calculate the 4th order correction, we would need to write 39 terms, which is not practical. Higher-order corrections are usually not programmed this way, instead, the diagrammatic approach is used.

3 Configuration Interaction

Configuration Interaction (CI) is a post-HF, utilizing a linear variational approach to address the nonrelativistic Schrödinger equation under the Born–Oppenheimer approximation for multi-electron quantum systems. CI mathematically represents the wave function as a linear combination of Slater determinants. The term "configuration" refers to different ways electrons can occupy orbitals, while "interaction" denotes the mixing of these electronic configurations or states. CI computations, however, are resource-intensive, requiring significant CPU time and memory, limiting their application to smaller molecular systems. While Full Configuration Interaction (FCI) considers all possible electronic configurations, making it computationally prohibitive for larger systems, truncated versions like Configuration Interaction Singles and Doubles (CISD) or Configuration Interaction Singles, Doubles and Triples (CISDT) are more feasible and commonly employed in quantum chemistry studies.

3.1 Theoretical Background of General Configuration Interaction

The idea is quite simple, using the convention, that the indices i, j, k, and l run over occupied spinorbitals and the indices a, b, c, and d run over virtual spinorbitals. The CI wavefunction is written as

$$|\Psi\rangle = c_0 \,|\Psi_0\rangle + \left(\frac{1}{1!}\right)^2 c_i^a \,|\Psi_i^a\rangle + \left(\frac{1}{2!}\right)^2 c_{ij}^{ab} \,|\Psi_{ij}^{ab}\rangle + \left(\frac{1}{3!}\right)^2 c_{ijk}^{abc} \,|\Psi_{ijk}^{abc}\rangle + \dots \qquad (3.1)$$

and we would like to know the coefficients c that minimize the energy. To do that, we simply construct the hamiltonian matrix in the basis of excited determinants and diagonalize it. The CI Hamiltonian matrix $\mathbf{H}^{CI}$ is constructed as

$$\mathbf{H}^{CI} = \begin{bmatrix} \langle\Psi_0|\hat{H}|\Psi_0\rangle & \langle\Psi_0|\hat{H}|\Psi_i^a\rangle & \langle\Psi_0|\hat{H}|\Psi_{ij}^{ab}\rangle & \dots \\ \langle\Psi_i^a|\hat{H}|\Psi_0\rangle & \langle\Psi_i^a|\hat{H}|\Psi_i^a\rangle & \langle\Psi_i^a|\hat{H}|\Psi_{ij}^{ab}\rangle & \dots \\ \langle\Psi_{ia}^{jb}|\hat{H}|\Psi_0\rangle & \langle\Psi_{ia}^{jb}|\hat{H}|\Psi_1\rangle & \langle\Psi_{ia}^{jb}|\hat{H}|\Psi_{ia}^{jb}\rangle & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \qquad (3.2)$$

and solving the eigenvalue problem

$$\mathbf{H}^{CI}\mathbf{C}^{CI} = \mathbf{C}^{CI}\varepsilon^{CI} \qquad (3.3)$$

where $\mathbf{C}^{CI}$ is a matrix of coefficients and ε^{CI} is a diagonal matrix of eigenvalues. The lowest eigenvalue corresponds to the ground state energy, while the eigenvector corresponding to the lowest eigenvalue gives the coefficients that minimize the energy. The matrix elements of the CI Hamiltonian are calculated using the Slater-Condon rules in the form

$$
\mathbf{H}_{ij}^{CI} =
\begin{cases}
\sum\limits_{k} H_{kk}^{core,MS} + \frac{1}{2} \sum\limits_{k} \sum\limits_{l} \langle kl||kl \rangle & D_i = D_j \\[2ex]
H_{pr}^{core,MS} + \sum\limits_{k} \langle pk||lk \rangle & D_i = \{\cdots p \cdots\} \wedge D_j = \{\cdots r \cdots\} \\[2ex]
\langle pq||rs \rangle & D_i = \{\cdots p \cdots q \cdots\} \wedge D_j = \{\cdots r \cdots s \cdots\} \\[2ex]
0 & \text{otherwise,}
\end{cases}
\tag{3.4}
$$

where D_i and D_j are Slater determinants, $\mathbf{H}^{core,MS}$ is the core Hamiltonian in the basis of molecular spinorbitals, and $\langle pk||lk \rangle$ are the antisymmetrized Coulomb repulsion integrals in the basis of molecular spinorbitals and physicists' notation. The sums extend over all spinorbitals common between the two determinants. All the integrals in the MS basis are already explained in section 1.3. Keep in mind, that to apply the Slater-Condon rules, the determinants must be aligned, and the sign of the matrix elements must be adjusted accordingly, based on the number of permutations needed to align the determinants.

The problem with CI is that it is not size-extensive, meaning that the energy does not scale linearly with the number of electrons. This is because the CI wavefunction is not size-consistent, and the energy of a system is not the sum of the energies of its parts. This is a significant drawback of CI, as it limits its application to small systems.

3.2 Full Configuration Interaction Implementation

Let's consider the FCI method, which considers all possible electronic configurations within a given basis set. The FCI method provides the most accurate description of the electronic structure, but its computational cost grows exponentially with the number of electrons and basis functions, making it infeasible for large systems.

The only thing that is needed, besides the general CI equations, are the determinants. For simplicity, we will include singlet and triplet states. The number of these determinants N_D can be for FCI calculated using the binomial coefficients

$$
N_D = \binom{n}{k}
\tag{3.5}
$$

assuming k is the total number of electrons, and n is the total number of spinorbitals. Each determinant is formed by permuting the electrons between spinorbitals. For practical representation, it's useful to describe determinants as arrays of numbers, where each number corresponds to the index of an occupied orbitals. For example, the ground state determinant for a system with 6 electrons and 10 spinorbitals can be represented as $\{0, 1, 2, 3, 4, 5\}$, whereas the determinant $\{0, 1, 2, 3, 4, 6\}$ represents an excited state with one electron excited from orbital 5 to orbital 6. Using the determinants, the CI Hamiltonian matrix 3.2 can be constructed, and the eigenvalue problem 3.3 can be solved to obtain the ground and excited state energies.

4 Coupled Cluster Theory

Coupled Cluster (CC) theory is a post-HF method used in quantum chemistry to achieve highly accurate solutions to the electronic Schrödinger equation, particularly for ground states and certain excited states. It improves upon HF by incorporating electron correlation effects through a systematic inclusion of excitations (singles, doubles, triples, etc.) from a reference wavefunction, usually the HF wavefunction. The method uses an exponential ansatz to account for these excitations, leading to a size-consistent and size-extensive approach, making it one of the most accurate methods available for small to medium-sized molecular systems.

Within CC theory, specific truncations are often applied to manage computational cost. The Coupled Cluster Doubles (CCD) method considers only double excitations, capturing electron correlation more effectively than simpler methods like HF but at a lower computational expense than higher-level methods. Coupled Cluster Singles and Doubles (CCSD) extends this approach by including both single and double excitations, offering greater accuracy, particularly for systems where single excitations play a significant role. CCSD is widely used due to its balance between accuracy and computational feasibility, making it a reliable choice for many chemical systems. In the below equations, we will again use the convention that the indices i, j, k, and l run over occupied spinorbitals, while the indices a, b, c, and d run over virtual spinorbitals.

4.1 Coupled Cluster Formalism

In the CC formalism, we write the total wavefunction in an exponential form as

$$|\Psi\rangle = e^{\hat{\mathbf{T}}} |\Psi_0\rangle \tag{4.1}$$

where $|\Psi_0\rangle$ is the reference wavefunction, usually the HF wavefunction, and $\hat{T}$ is the cluster operator that generates excitations from the reference wavefunction. The cluster operator is defined as

$$\hat{\mathbf{T}} = \hat{\mathbf{T}}_1 + \hat{\mathbf{T}}_2 + \hat{\mathbf{T}}_3 + \ldots \tag{4.2}$$

where $\hat{\mathbf{T}}_1$ generates single excitations, $\hat{\mathbf{T}}_2$ generates double excitations, and so on. For example

$$\hat{\mathbf{T}}_1 |\Psi_0\rangle = \left(\frac{1}{1!}\right)^2 t_i^a |\Psi_i^a\rangle, \tag{4.3}$$

where t_i^a are the single excitation amplitudes. These amplitudes are just expansion coefficients that determine the contribution of each excitation to the total wavefunction. In the context of configuration interaction, we denoted these coefficients as c_i^a. Now that we have the total wavefunction, we want to solve the Schrödinger equation

$$\hat{\mathbf{H}} \ket{\Psi} = E \ket{\Psi} \tag{4.4}$$

where $\hat{H}$ is the molecular Hamiltonian operator, E is the total energy of the system, and $\ket{\Psi}$ is the total wavefunction. In the CC theory, we usually rewrite the Schrödinger equation in the exponential form as

$$e^{-\hat{\mathbf{T}}}\hat{\mathbf{H}}e^{\hat{\mathbf{T}}} \ket{\Psi_0} = E \ket{\Psi_0} \tag{4.5}$$

because we can then express the CC energy as

$$E = \bra{\Psi_0} e^{-\hat{\mathbf{T}}}\hat{\mathbf{H}}e^{\hat{\mathbf{T}}} \ket{\Psi_0}, \tag{4.6}$$

taking advantage of the exponential form of the wavefunction. We could then proceed to express the total energy for various CC methods like CCD and CCSD, but the equations would be quite lengthy. Instead, we will leave the theory here and proceed to the actual calculations. One thing to keep in mind is that the CC equations are nonlinear and require iterative solution methods to obtain the final amplitudes. The initial guess for the amplitudes is often set to zero, and the equations are solved iteratively until convergence is achieved.

4.2 Implementation of CCD and CCSD

The derivation of the equations that are actually used to perform the calculations is quite lengthy and involves a lot of algebra. We will not go into the details here, but we will provide the final expressions for the CCD and CCSD methods. The CCD and CCSD methods are the most commonly used CC methods, and they are often used as benchmarks for other methods. All we need for the evaluation of the expressions below are the Coulomb integrals in the MS basis and physicists' notation, Fock matrix in the MS basis and the orbital energies obtained from the Hartree-Fock calculation. All these transformations are already explained in section 1.3 in the HF section. The expressions for the CCD can be expressed as

$$E_{\text{CCD}} = \frac{1}{4} \braket{ij||ab} t_{ij}^{ab} \tag{4.7}$$

where the double excitation amplitudes t_{ij}^{ab} are determined by solving the CCD amplitude equation. The CCD amplitude equations are given by

$$t_{ij}^{ab} = \braket{ab||ij} + \frac{1}{2}\braket{ab||cd} t_{cd}^{ij} + \frac{1}{2}\braket{kl||ij} t_{ab}^{kl} + \hat{P}_{(a/b)}\hat{P}_{(i/j)} \braket{ak||ic} t_{cb}^{ij} - \tag{4.8}$$

$$- \frac{1}{2}\hat{P}_{(a/b)} \braket{kl||cd} t_{ac}^{ij} t_{bd}^{kl} - \frac{1}{2}\hat{P}_{(i/j)} \braket{kl||cd} t_{ab}^{ik} t_{cd}^{jl} + \tag{4.9}$$

$$+ \frac{1}{4}\braket{kl||cd} t_{cd}^{ij} t_{ab}^{kl} + \hat{P}_{(i/j)} \braket{kl||cd} t_{ac}^{ik} t_{bd}^{jl} \tag{4.10}$$

where $\hat{P}_{(a/b)}$ and $\hat{P}_{(i/j)}$ are permutation operators that ensure the correct antisymmetry of the amplitudes. The CCSD energy expression is given by

$$E_{\text{CCSD}} = F_{ia}^{MS} t_a^i + \frac{1}{4} \langle ij||ab \rangle t_{ij}^{ab} + \frac{1}{2} \langle ij||ab \rangle t_i^a t_b^j \tag{4.11}$$

where the single and double excitation amplitudes t_a^i and t_{ij}^{ab} are determined by solving the CCSD amplitude equations. To simplify the notation a little bit, we define the the $\mathscr{F}$ and $\mathscr{W}$ intermediates as

$$\mathscr{F}_{ae} = (1 - \delta_{ae}) F_{ae} - \frac{1}{2} \sum_m F_{me} t_m^a + \sum_{mf} t_m^f \langle ma||fe \rangle - \frac{1}{2} \sum_{mnf} \tilde{\tau}_{mn}^{af} \langle mn||ef \rangle \tag{4.12}$$

$$\mathscr{F}_{mi} = (1 - \delta_{mi}) F_{mi} + \frac{1}{2} \sum_e F_{me} t_i^e + \sum_{en} t_n^e \langle mn||ie \rangle + \frac{1}{2} \sum_{nef} \tilde{\tau}_{in}^{ef} \langle mn||ef \rangle \tag{4.13}$$

$$\mathscr{F}_{me} = F_{me} + \sum_{nf} t_n^f \langle mn||ef \rangle \tag{4.14}$$

$$\mathscr{W}_{mnij} = \langle mn||ij \rangle + \hat{P}_{(i/j)} \sum_e t_j^e \langle mn||ie \rangle + \frac{1}{4} \sum_{ef} \tau_{ij}^{ef} \langle mn||ef \rangle \tag{4.15}$$

$$\mathscr{W}_{abef} = \langle ab||ef \rangle - \hat{P}_{(a/b)} \sum_e t_m^b \langle am||ef \rangle + \frac{1}{4} \sum_{mn} \tau_{mn}^{ab} \langle mn||ef \rangle \tag{4.16}$$

$$\mathscr{W}_{mbej} = \langle mb||ej \rangle + \sum_f t_j^f \langle mb||ef \rangle - \sum_n t_n^b \langle mn||ej \rangle - \tag{4.17}$$

$$- \sum_{nf} \left(\frac{1}{2} t_{jn}^{fb} + t_j^f t_n^b \right) \langle mn||ef \rangle \tag{4.18}$$

and two-particle excitation operators as

$$\tilde{\tau}_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2} \left(t_i^a t_j^b - t_i^b t_j^a \right) \tag{4.19}$$

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a \tag{4.20}$$

The CCSD single excitations amplitude equations are then given by

$$t_i^a = F_{ai}^{MS} + \sum_e t_i^e \mathscr{F}_{ae} - \sum_m t_m^a \mathscr{F}_{mi} \sum_{me} t_{im}^{ae} \mathscr{F}_{me} - \sum_{nf} t_n^f \langle na||if \rangle - \tag{4.21}$$

$$- \frac{1}{2} \sum_{mef} t_{im}^{ef} \langle ma||ef \rangle - \frac{1}{2} \sum_{men} t_{mn}^{ae} \langle nm||ei \rangle \tag{4.22}$$

and the CCSD double excitations amplitude equations are given by

$$t_{ij}^{ab} = \langle ab||ij\rangle + \hat{P}_{(a/b)} \sum_e t_{ij}^{ae} \left(\mathscr{F}_{be} - \frac{1}{2} \sum_m t_m^b \mathscr{F}_{ae} \right) - \tag{4.23}$$

$$- \hat{P}_{(i/j)} \sum_m t_{im}^{ab} \left(\mathscr{F}_{mi} + \frac{1}{2} \sum_e t_j^e \mathscr{F}_{me} \right) + \frac{1}{2} \sum_{mn} \tau_{mn}^{ab} \mathscr{W}_{mnij} + \tag{4.24}$$

$$+ \frac{1}{2} \sum_{ef} \tau_{ij}^{ef} \mathscr{W}_{abef} + \hat{P}_{(i/j)} \hat{P}_{(a/b)} \sum_{me} (t_{im}^{ae} \mathscr{W}_{mbej} - t_i^e t_m^a \langle mb||ej\rangle) + \tag{4.25}$$

$$+ \hat{P}_{(i/j)} \sum_e t_i^e \langle ab||ej\rangle - \hat{P}_{(a/b)} \sum_m t_m^a \langle mb||ij\rangle \tag{4.26}$$

The CCSD amplitude equations are, again, nonlinear and require iterative solution methods to obtain the final amplitudes. The initial guess for the amplitudes is often set to zero, and the equations are solved iteratively until convergence is achieved.

List of Acronyms

CC Coupled Cluster. 11, 12

CCD Coupled Cluster Doubles. 11, 12

CCSD Coupled Cluster Singles and Doubles. 11–14

CI Configuration Interaction. 9, 10

CISD Configuration Interaction Singles and Doubles. 9

CISDT Configuration Interaction Singles, Doubles and Triples. 9

FCI Full Configuration Interaction. 9, 10

HF Hartree–Fock. 3, 4, 7, 8, 11

MPPT Møller–Plesset Perturbation Theory. 7

MS Molecular Spinorbital. 3, 5

post-HF post-Hartree–Fock. 5, 9, 11

RHF Restricted Hartree–Fock. 3, 5