Introduction to perturbation theory and coupled-cluster theory for electron correlation

Julien Toulouse
Laboratoire de Chimie Théorique
Université Pierre et Marie Curie et CNRS, 75005 Paris, France
julien.toulouse@upmc.fr

October 25, 2019

http://www.lct.jussieu.fr/pagesperso/toulouse/enseignement/introduction_pt_cc.pdf

Contents

These notes provide an introduction to perturbation theory and coupled-cluster theory for ground-state electron correlation. For general reference on this subject, see e.g. Refs. [1, 2].

1 Review of the many-body problem

1.1 The Hamiltonian and the many-body wave function

We consider a N-electron system (atom, molecule, solid) in the Born-Oppenheimer and non-relativistic approximations. The electronic Hamiltonian in the position representation is, in atomic units,

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \sum_i^N h(\mathbf{r}_i) + \frac{1}{2} \sum_i^N \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{1}$$

where $h(\mathbf{r}_i) = -(1/2)\nabla^2_{\mathbf{r}_i} + v_{\text{ne}}(\mathbf{r}_i)$ is the one-electron contribution composed of the kinetic-energy operator and of the nuclei-electron interaction $v_{\text{ne}}(\mathbf{r}_i) = -\sum_\alpha Z_\alpha/|\mathbf{r}_i - \mathbf{R}_\alpha|$ (where $\mathbf{R}_\alpha$ and Z_α are the positions and charges of the nuclei). The stationary electronic states are determined by the time-independent Schrödinger equation

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N), \tag{2}$$

where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is a wave function written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i = \uparrow$ or $\downarrow$) which is antisymmetric with respect to the exchange of two coordinates, and E is the associated energy. Using Dirac notations, the Schrödinger equation (2) can be rewritten in a convenient representation-independent formalism nuclei-electron interaction

$$\hat{H}|\Psi\rangle = E|\Psi\rangle. \tag{3}$$

We are interested in calculating an approximation for the wave function Ψ and the associated energy E of a specific state, most often the ground-state wave function Ψ_0 and the ground-state energy E_0.

1.2 The Hartree-Fock approximation

The Hartree-Fock (HF) method[1] consists in approximating the ground-state wave function as a single Slater determinant, $\Psi_0 \approx \Phi_0$,

$$\Phi_0(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}, \tag{4}$$

where $\chi_i(\mathbf{x})$ are orthonormal spin orbitals. The HF total electronic energy, $E_{\text{HF}} = \langle \Phi_0|\hat{H}|\Phi_0\rangle$, can be expressed in terms of integrals over these spin orbitals, using Slater's rules for calculating expectation values over Slater determinants,

$$E_{\text{HF}} = \langle \Phi_0|\hat{H}|\Phi_0\rangle = \sum_a^{\text{occ}} h_{aa} + \frac{1}{2} \sum_{a,b}^{\text{occ}} \langle ab||ab\rangle, \tag{5}$$

---

[1]We present here the *unrestricted* Hartree-Fock (UHF) method, in which the spatial part of the ↑- and ↓-spin orbitals are allowed to be different, which generally leads to the breaking of $\hat{S}^2$ symmetry. By contrast, the *restricted* Hartree-Fock (RHF) method imposes $\hat{S}^2$ symmetry by constraining the spatial part of the ↑- and ↓-spin orbitals to be the same.

where the sums over a and b are over occupied spin orbitals. In this expression, h_{aa} are the one-electron integrals

$$h_{aa} = \int d\mathbf{x}\, \chi_a^*(\mathbf{x})h(\mathbf{r})\chi_a(\mathbf{x}), \tag{6}$$

and $\langle ab||ab\rangle = \langle ab|ab\rangle - \langle ab|ba\rangle$ are the antisymmetrized two-electron integrals (in physicists' notation) where

$$\langle ij|kl\rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2\, \frac{\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|}. \tag{7}$$

The spin orbitals are determined by minimizing the HF energy subject to the normalization constraints

$$\min_{\{\chi_a\}} \left\{ E_{\mathrm{HF}}[\{\chi_a\}] - \sum_a^{\mathrm{occ}} \varepsilon_a \langle \chi_a|\chi_a\rangle \right\}, \tag{8}$$

where ε_a are the orbital energies playing the role of Lagrange multipliers for the normalization constraints. This minimization leads to the HF eigenvalue equations

$$f(\mathbf{x})\chi_i(\mathbf{x}) = \varepsilon_i \chi_i(\mathbf{x}), \tag{9}$$

which determine both the occupied and virtual spin orbitals $\chi_i(\mathbf{x})$ and associated orbital energies ε_i. In these equations, $f(\mathbf{x})$ is the one-electron HF Hamiltonian (or often called simply Fock Hamiltonian)

$$f(\mathbf{x}) = h(\mathbf{r}) + v_{\mathrm{HF}}(\mathbf{x}), \tag{10}$$

where $v_{\mathrm{HF}}(\mathbf{x})$ is the one-electron HF potential operator

$$v_{\mathrm{HF}}(\mathbf{x}) = \sum_a^{\mathrm{occ}} J_a(\mathbf{x}) - K_a(\mathbf{x}), \tag{11}$$

composed of a Coulomb (or Hartree) operator written as

$$J_a(\mathbf{x}_1) = \int d\mathbf{x}_2 \frac{\chi_a^*(\mathbf{x}_2)\chi_a(\mathbf{x}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|}, \tag{12}$$

and an exchange (or Fock) operator whose action on a spin orbital $\chi_i(\mathbf{x}_1)$ is given by

$$K_a(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \int d\mathbf{x}_2 \frac{\chi_a^*(\mathbf{x}_2)\chi_i(\mathbf{x}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|}\chi_a(\mathbf{x}_1). \tag{13}$$

The HF potential $v_{\mathrm{HF}}(\mathbf{x})$ is a one-electron mean-field potential approximating the effect of the two-electron interaction $(1/2)\sum_i^N \sum_{i \neq j}^N 1/|\mathbf{r}_i - \mathbf{r}_j|$. In other words, the HF approximation only accounts for the electron-electron interaction in an averaged, mean-field way. The effect of the electron-electron interaction beyond the HF approximation is called *electron correlation*. The difference between the exact ground-state total energy E_0 and the HF total energy E_{HF} is called the *correlation energy*

$$E_{\mathrm{c}} = E_0 - E_{\mathrm{HF}}. \tag{14}$$

Even though E_{c} is usually a small percentage of the total energy, it very often makes a large and crucial contribution to *energy differences* (such as reaction energies, reaction barrier heights, ...) which are the quantities of chemical interest. It is therefore important to go beyond the HF approximation and calculate the value of the correlation energy, which is the goal of the post-HF methods.

1.3 Straightforward configuration-interaction methods

The most straightforward post-HF method is the *configuration-interaction (CI)* method. In this method, the wave function is expanded in the basis of the HF determinant Φ_0, the single-excited determinants Φ_a^r, the double-excited determinants Φ_{ab}^{rs}, and so on

$$|\Psi_{\text{CI}}\rangle = c_0|\Phi_0\rangle + \sum_a^{\text{occ}}\sum_r^{\text{vir}} c_a^r|\Phi_a^r\rangle + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \cdots. \tag{15}$$

The coefficients $\mathbf{c} = (c_0, c_a^r, c_{ab}^{rs}, ...)$ corresponding to the ground-state wave function are found by minimizing the total CI energy $\langle\Psi_{\text{CI}}|\hat{H}|\Psi_{\text{CI}}\rangle$ with the constraint of the normalization of the wave function

$$\min_{\mathbf{c}} \left\{ \langle\Psi_{\text{CI}}|\hat{H}|\Psi_{\text{CI}}\rangle - E\langle\Psi_{\text{CI}}|\Psi_{\text{CI}}\rangle \right\}, \tag{16}$$

leading to the following eigenvalue equation

$$\begin{pmatrix} \langle\Phi_0|\hat{H}|\Phi_0\rangle & \langle\Phi_0|\hat{H}|\Phi_a^r\rangle & \langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle & \cdots \\ \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_0\rangle & \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_a^r\rangle & \langle\Phi_{a'}^{r'}|\hat{H}|\Phi_{ab}^{rs}\rangle & \cdots \\ \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_0\rangle & \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_a^r\rangle & \langle\Phi_{a'b'}^{r's'}|\hat{H}|\Phi_{ab}^{rs}\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_0 \\ c_a^r \\ c_{ab}^{rs} \\ \vdots \end{pmatrix} = E \begin{pmatrix} c_0 \\ c_a^r \\ c_{ab}^{rs} \\ \vdots \end{pmatrix}. \tag{17}$$

The eigenvector associated to the lowest eigenvalue corresponds to the ground state, whereas the other eigenvectors correspond to excited states. If all levels of excitations are included (i.e., up to N-fold excitations for a N-electron system), then exact wave functions are obtained *within the underlying one-electron basis set used for expanding the orbitals*. This is referred to as the *full configuration-interaction (FCI)* method. In practice, FCI can only be performed for very small systems with small basis sets. For most systems, one has to truncate the CI expansion in Eq. (15) at a given level of excitations for manageable calculations. This is referred to as *truncated CI*. Often, only the single and double excitations are included in the expansion, leading to the configuration-interaction singles doubles (CISD) method.

The truncated CI method has a serious shortcoming. Consider the *size consistency* property that the total energy of a system composed of two non-interacting fragments A and B must be the sum of the total energies of the separate fragments

$$E(A \cdots B) = E(A) + E(B). \tag{18}$$

This property is particularly important in chemistry since it is often concerned with systems composed of fragments (atoms, molecules). It is of course satisfied for the exact total energy, but not necessarily with approximate methods. A method which gives total energies satisfying this property is said to be size-consistent. For example, the unrestricted HF method is size-consistent but the restricted HF method is generally not. The FCI method is size-consistent, but the truncated CI method has the important drawback of being generally *not* size-consistent.

We will now see two other post-HF approaches which have the advantage of being size-consistent: perturbation theory and coupled-cluster theory.

2 Perturbation theory

This section provides a basic introduction to Møller-Plesset perturbation theory. For a historical perspective and recent research developments, see e.g. Ref. [3].

2.1 General Rayleigh–Schrödinger perturbation theory

We start by reviewing the general expressions of Rayleigh–Schrödinger perturbation theory. Consider a Hamiltonian $\hat{H}^\lambda$ depending on a coupling constant λ

$$\hat{H}^\lambda = \hat{H}^{(0)} + \lambda\hat{V}, \tag{19}$$

where $\hat{H}^{(0)}$ is a zeroth-order Hamiltonian operators and $\hat{V}$ is a perturbation operator. These two operators are chosen so that the "physical" Hamiltonian of interest corresponds to $\lambda = 1$, i.e. $\hat{H} = \hat{H}^{\lambda=1} = \hat{H}^{(0)} + \hat{V}$. By varying λ from 0 to 1, we can thus go from the zeroth-order Hamiltonian, $\hat{H}^{\lambda=0} = \hat{H}^{(0)}$, to the physical Hamiltonian $\hat{H}^{\lambda=1} = \hat{H}$. We will be ultimately interested in the value $\lambda = 1$.

The zeroth-order Hamiltonian $\hat{H}^{(0)}$ is chosen such that its eigenstates Φ_n and associated eigenvalues $E_n^{(0)}$ are known. They of course satisfy the eigenvalue equation

$$\hat{H}^{(0)}|\Phi_n\rangle = E_n^{(0)}|\Phi_n\rangle, \tag{20}$$

and the eigenstates are chosen to be orthonormal, i.e. $\langle\Phi_n|\Phi_m\rangle = \delta_{n,m}$. We would like to determine the eigenstates Ψ_n^λ and associated eigenvalues E_n^λ of the Hamiltonian $\hat{H}^\lambda$

$$\hat{H}^\lambda|\Psi_n^\lambda\rangle = E_n^\lambda|\Psi_n^\lambda\rangle. \tag{21}$$

In the following, we will only consider the specific case of the determination of the ground state Ψ_0^λ and its energy E_0^λ. We assume that the energy can be expanded in powers of λ

$$E_0^\lambda = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots, \tag{22}$$

and, similarly, for the wave function Ψ_0^λ

$$|\Psi_0^\lambda\rangle = |\Psi_0^{(0)}\rangle + \lambda|\Psi_0^{(1)}\rangle + \lambda^2|\Psi_0^{(2)}\rangle + \cdots. \tag{23}$$

Note that the zeroth-order wave function is just $\Psi_0^{(0)} = \Phi_0$. We are free to choose the normalization of Ψ_0^λ. A convenient choice is the so-called *intermediate normalization*, i.e. $\langle\Phi_0|\Psi_0^\lambda\rangle = 1$ for all λ. Since the zeroth-order wave function is normalized as $\langle\Phi_0|\Phi_0\rangle = 1$, it implies that $\langle\Phi_0|\Psi_0^{(i)}\rangle = 0$ for all $i \geq 1$, i.e. the wave-function correction at each order is orthogonal to the zeroth-order wave function.

Inserting Eqs. (22) and (23) into Eq. (21) gives

$$\left(\hat{H}^{(0)} + \lambda\hat{V}\right)\left(|\Phi_0\rangle + \lambda|\Psi_0^{(1)}\rangle + \lambda^2|\Psi_0^{(2)}\rangle + \cdots\right)$$
$$= \left(E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots\right)\left(|\Phi_0\rangle + \lambda|\Psi_0^{(1)}\rangle + \lambda^2|\Psi_0^{(2)}\rangle + \cdots\right). \tag{24}$$

Looking at this equation order by order in λ, we obtain at zeroth order

$$\hat{H}^{(0)}|\Phi_0\rangle = E_0^{(0)}|\Phi_0\rangle, \tag{25}$$

which is just Eq. (20) for the ground state.

At first order, we obtain

$$\hat{H}^{(0)}|\Psi_0^{(1)}\rangle + \hat{V}|\Phi_0\rangle = E_0^{(0)}|\Psi_0^{(1)}\rangle + E_0^{(1)}|\Phi_0\rangle. \tag{26}$$

Projecting this equation on the bra state $\langle\Phi_0|$, and using $\langle\Phi_0|\hat{H}^{(0)} = E_0^{(0)}\langle\Phi_0|$ and $\langle\Phi_0|\Psi_0^{(1)}\rangle = 0$, gives the first-order energy correction

$$E_0^{(1)} = \langle\Phi_0|\hat{V}|\Phi_0\rangle. \tag{27}$$

Projecting now Eq. (26) on the bra states $\langle\Phi_n|$ for $n \neq 0$, and using $\langle\Phi_n|\hat{H}^{(0)} = E_n^{(0)}\langle\Phi_n|$ and $\langle\Phi_n|\Phi_0\rangle = 0$, gives

$$E_n^{(0)}\langle\Phi_n|\Psi_0^{(1)}\rangle + \langle\Phi_n|\hat{V}|\Phi_0\rangle = E_0^{(0)}\langle\Phi_n|\Psi_0^{(1)}\rangle, \tag{28}$$

leading to the projection coefficients of the $\Psi_0^{(1)}$ in the basis of Φ_n

$$\langle\Phi_n|\Psi_0^{(1)}\rangle = -\frac{\langle\Phi_n|\hat{V}|\Phi_0\rangle}{E_n^{(0)} - E_0^{(0)}}, \tag{29}$$

and, since $\langle\Phi_0|\Psi_0^{(1)}\rangle = 0$, it leads to the first-order wave-function correction

$$|\Psi_0^{(1)}\rangle = -\sum_{n\neq 0}\frac{\langle\Phi_n|\hat{V}|\Phi_0\rangle}{E_n^{(0)} - E_0^{(0)}}|\Phi_n\rangle. \tag{30}$$

Similarly, at second order, we obtain

$$\hat{H}^{(0)}|\Psi_0^{(2)}\rangle + \hat{V}|\Psi_0^{(1)}\rangle = E_0^{(0)}|\Psi_0^{(2)}\rangle + E_0^{(1)}|\Psi_0^{(1)}\rangle + E_0^{(2)}|\Phi_0\rangle. \tag{31}$$

Projecting this equation on the bra state $\langle\Phi_0|$, and using $\langle\Phi_0|\hat{H}^{(0)} = E_0^{(0)}\langle\Phi_0|$ and $\langle\Phi_0|\Psi_0^{(1)}\rangle = \langle\Phi_0|\Psi_0^{(2)}\rangle = 0$, gives the second-order energy correction

$$E_0^{(2)} = \langle\Phi_0|\hat{V}|\Psi_0^{(1)}\rangle, \tag{32}$$

or, after using Eq. (30),

$$E_0^{(2)} = -\sum_{n\neq 0}\frac{|\langle\Phi_0|\hat{V}|\Phi_n\rangle|^2}{E_n^{(0)} - E_0^{(0)}}. \tag{33}$$

Note that $E_0^{(2)}$ diverges if there is a state Φ_n (with $n \neq 0$) of energy $E_n^{(0)}$ equals to $E_0^{(0)}$, i.e. if the zeroth-order Hamiltonian $\hat{H}^{(0)}$ has a degenerate ground state. In this case, the expansions in Eqs. (22) and (23) are not valid, and one must instead diagonalize the Hamiltonian in the degenerate space before applying perturbation theory, which is known as degenerate perturbation theory.

Exercise 1 : Prove that the third-order energy correction has the following expression

$$\begin{aligned}
E_0^{(3)} &= \langle\Phi_0|\hat{V}|\Psi_0^{(2)}\rangle \\
&= \sum_{n,m\neq 0}\frac{\langle\Phi_0|\hat{V}|\Phi_n\rangle\langle\Phi_n|\hat{V}|\Phi_m\rangle\langle\Phi_m|\hat{V}|\Phi_0\rangle}{(E_n^{(0)} - E_0^{(0)})(E_m^{(0)} - E_0^{(0)})} - E_0^{(1)}\sum_{n\neq 0}\frac{|\langle\Phi_0|\hat{V}|\Phi_n\rangle|^2}{(E_n^{(0)} - E_0^{(0)})^2}.
\end{aligned} \tag{34}$$

2.2 Møller-Plesset perturbation theory

2.2.1 General spin-unrestricted theory in terms of spin orbitals

Møller-Plesset (MP) perturbation theory is a particular case of Rayleigh–Schrödinger perturbation theory for which the zeroth-order Hamiltonian is chosen to be the (many-electron) Hartree-Fock (sometimes also simply called Fock) Hamiltonian

$$\hat{H}^{(0)} = \hat{F}, \tag{35}$$

where the expression of $\hat{F}$ in the position representation is

$$F(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \sum_i^N f(\mathbf{x}_i). \tag{36}$$

The corresponding perturbation operator $\hat{V}$ is thus the difference between the electron-electron Coulomb interaction and the HF potential

$$V(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \frac{1}{2} \sum_i^N \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i^N v_{\mathrm{HF}}(\mathbf{x}_i). \tag{37}$$

Zeroth order
The zeroth-order ground-state wave function is the HF single determinant Φ_0, and the zeroth-order excited-state wave functions are the single, double, ... excited determinants $\Phi_n = \Phi_a^r, \Phi_{ab}^{rs}, ...$ According to Eq. (9), the zeroth-order ground-state energy $E_0^{(0)}$ is given by the sum of occupied orbital energies

$$E_0^{(0)} = \sum_a^{\mathrm{occ}} \varepsilon_a. \tag{38}$$

First order
The first-order energy correction is the expectation value of the HF determinant over the perturbation operator, which is calculated according to Slater's rules,

$$
\begin{aligned}
E_0^{(1)} &= \langle \Phi_0 | \hat{V} | \Phi_0 \rangle \\
&= \frac{1}{2} \sum_{a,b}^{\mathrm{occ}} \langle ab || ab \rangle - \sum_a^{\mathrm{occ}} \langle a | \hat{v}_{\mathrm{HF}} | a \rangle \\
&= -\frac{1}{2} \sum_{a,b}^{\mathrm{occ}} \langle ab || ab \rangle,
\end{aligned} \tag{39}
$$

where, according to the definition of the HF potential in Eq. (11), we have used the fact that $\sum_a^{\mathrm{occ}} \langle a | \hat{v}_{\mathrm{HF}} | a \rangle = \sum_{a,b}^{\mathrm{occ}} \langle ab || ab \rangle$. Therefore, the sum of the zeroth-order energy and first-order

energy correction just gives back the HF energy

$$
\begin{aligned}
E_0^{(0)} + E_0^{(1)} &= \sum_a^{\text{occ}} \varepsilon_a - \frac{1}{2} \sum_{a,b}^{\text{occ}} \langle ab||ab \rangle, \\
&= \sum_a^{\text{occ}} \left(h_{aa} + \sum_b^{\text{occ}} \langle ab||ab \rangle \right) - \frac{1}{2} \sum_{a,b}^{\text{occ}} \langle ab||ab \rangle \\
&= \sum_a^{\text{occ}} h_{aa} + \frac{1}{2} \sum_{a,b}^{\text{occ}} \langle ab||ab \rangle \\
&= E_{\text{HF}},
\end{aligned}
\tag{40}
$$

where we have used the fact that $\varepsilon_a = h_{aa} + \sum_b^{\text{occ}} \langle ab||ab \rangle$.

Second order

The second-order energy correction, which is called in this context the second-order Møller-Plesset (MP2) correlation energy, is

$$
E_0^{(2)} = E_{\text{c}}^{\text{MP2}} = - \sum_{n \neq 0} \frac{|\langle \Phi_0 | \hat{V} | \Phi_n \rangle|^2}{E_n^{(0)} - E_0^{(0)}},
\tag{41}
$$

where Φ_n can be *a priori* single, double, triple, ... excited determinants. In fact, since $\hat{V}$ is a two-body operator, according to Slater's rules, triple and higher excitations with respect to Φ_0 give vanishing matrix elements $\langle \Phi_0 | \hat{V} | \Phi_n \rangle$. In addition, it turns out that single excitations only give a vanishing contribution

$$
\begin{aligned}
\langle \Phi_0 | \hat{V} | \Phi_a^r \rangle &= \sum_b^{\text{occ}} \langle ab||rb \rangle - \langle a | \hat{v}_{\text{HF}} | r \rangle \\
&= \sum_b^{\text{occ}} \langle ab||rb \rangle - \sum_b^{\text{occ}} \langle ab||rb \rangle \\
&= 0.
\end{aligned}
\tag{42}
$$

It thus remains only the double excitations, $\Phi_n = \Phi_{ab}^{rs}$. Only the two-body part of the perturbation operator gives a non-zero matrix element,

$$
\langle \Phi_0 | \hat{V} | \Phi_{ab}^{rs} \rangle = \langle ab||rs \rangle.
\tag{43}
$$

Besides, the zeroth-order energy corresponding to the doubly-excited determinants Φ_{ab}^{rs} is

$$
E_n^{(0)} = E_{ab}^{rs,(0)} = E_0^{(0)} + \varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b.
\tag{44}
$$

Using Eqs. (43) and (44) in Eq. (41), we arrive at the following expression for the MP2 correlation energy

$$
E_{\text{c}}^{\text{MP2}} = - \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} \frac{|\langle ab||rs \rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}.
\tag{45}
$$

Using the antisymmetry property of the integrals, i.e. $\langle ab||rs \rangle = -\langle ab||sr \rangle = -\langle ba||rs \rangle$, and the fact that $\langle ab||rs \rangle = 0$ if $a = b$ or $r = s$, the MP2 correlation energy can also be written without constraints in the sums

$$
E_{\text{c}}^{\text{MP2}} = - \frac{1}{4} \sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \frac{|\langle ab||rs \rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}.
\tag{46}
$$

Note the MP2 correlation energy is always negative. It diverges to $-\infty$ if one energy denominator $\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b$ is zero. This happens for systems with zero HF HOMO-LUMO gap, in which case MP perturbation theory cannot be applied.

The MP2 total energy is simply defined as $E_{\mathrm{MP2}} = E_{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{MP2}}$. Since it is not a variational theory, the MP2 total energy is not necessarily above the exact ground-state total energy. The MP2 method can be considered as the computationally cheapest post-HF method, and is thus widely used.

Third order

Similarly, starting from Eq. (34), it can be shown, after much work, that the third-order Møller-Plesset (MP3) energy correction has the following expression

$$
\begin{aligned}
E_0^{(3)} &= \frac{1}{8} \sum_{a,b,c,d}^{\mathrm{occ}} \sum_{r,s}^{\mathrm{vir}} \frac{\langle ab||rs\rangle \langle rs||cd\rangle \langle cd||ab\rangle}{(\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b)(\varepsilon_r + \varepsilon_s - \varepsilon_c - \varepsilon_d)} \\
&+ \frac{1}{8} \sum_{a,b}^{\mathrm{occ}} \sum_{r,s,t,u}^{\mathrm{vir}} \frac{\langle ab||rs\rangle \langle rs||tu\rangle \langle tu||ab\rangle}{(\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b)(\varepsilon_t + \varepsilon_u - \varepsilon_a - \varepsilon_b)} \\
&+ \sum_{a,b,c}^{\mathrm{occ}} \sum_{r,s,t}^{\mathrm{vir}} \frac{\langle ab||rs\rangle \langle cs||tb\rangle \langle rt||ac\rangle}{(\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b)(\varepsilon_r + \varepsilon_t - \varepsilon_a - \varepsilon_c)}.
\end{aligned}
\tag{47}
$$

The calculation of the third- or higher-order terms is often considered as not worthwhile in comparison with coupled-cluster methods for example.

When starting from an unrestricted HF calculation, MP perturbation theory is correctly size consistent at each order. This is a consequence of the fact that the energy correction at each order cannot be factorized in uncoupled sums. This coupling between all the orbital indices is an expression of the *linked-cluster theorem*.

2.2.2 Spin-restricted theory in terms of spatial orbitals for closed-shell systems

For closed-shell systems, with spin-singlet symmetry, the MP2 correlation energy expression can be simplified by summing over the spin coordinates. One can first rewrite Eq. (46) as

$$
\begin{aligned}
E_{\mathrm{c}}^{\mathrm{MP2}} &= -\frac{1}{4} \sum_{a,b}^{\mathrm{occ}} \sum_{r,s}^{\mathrm{vir}} \frac{|\langle ab|rs\rangle - \langle ab|sr\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} \\
&= -\frac{1}{4} \sum_{a,b}^{\mathrm{occ}} \sum_{r,s}^{\mathrm{vir}} \frac{(\langle ab|rs\rangle - \langle ab|sr\rangle)(\langle rs|ab\rangle - \langle sr|ab\rangle)}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} \\
&= -\frac{1}{2} \sum_{a,b}^{\mathrm{occ}} \sum_{r,s}^{\mathrm{vir}} \frac{\langle ab|rs\rangle \langle rs|ab\rangle - \langle ab|rs\rangle \langle rs|ba\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b},
\end{aligned}
\tag{48}
$$

where the last line has been obtained by expanding, using the permutation symmetry property of the integrals such as $\langle sr|ab\rangle = \langle rs|ba\rangle$, and exchanging the dummy indices such as r and s in the summation. We can now perform the summations over the spin coordinates. After paying

attention to whether the spin integration in the two-electron integrals gives 0 or 1, we arrive at

$$
\begin{aligned}
E_{\mathrm{c}}^{\mathrm{MP2}} &= -\sum_{a,b}^{\text{spt occ}} \sum_{r,s}^{\text{spt vir}} \frac{2\langle ab|rs\rangle\langle rs|ab\rangle - \langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}, \\
&= -\sum_{a,b}^{\text{spt occ}} \sum_{r,s}^{\text{spt vir}} \frac{\langle ab|rs\rangle\left[2\langle rs|ab\rangle - \langle rs|ba\rangle\right]}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b},
\end{aligned} \tag{49}
$$

where a, b and r, s refer now to *spatial* occupied and virtual orbitals, respectively. This last expression is also frequently given using chemists' notation for the two-electron integrals $(ij|kl) = \langle ik|jl\rangle$

$$
E_{\mathrm{c}}^{\mathrm{MP2}} = -\sum_{a,b}^{\text{spt occ}} \sum_{r,s}^{\text{spt vir}} \frac{(ar|bs)\left[2(ra|sb) - (rb|sa)\right]}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}. \tag{50}
$$

Exercise 2 : Write down the MP2 correlation energy expression for the case of the H_2 molecule in a minimal basis (orbitals: $1 = \sigma_{\mathrm{g}}$, $2 = \sigma_{\mathrm{u}}$). What happens in the dissociation limit?

2.2.3 Diagrammatic representation of perturbation theory

The various terms appearing in perturbation theory can be conveniently represented by *Feynman diagrams*, used in many areas of many-body theory. In quantum chemistry, the particular kind of diagrams most often used are called *Goldstone diagrams*.

For example, the spin-orbital expression of the MP2 correlation energy written in Eq. (48) as the sum of a direct and exchange term

$$
E_{\mathrm{c}}^{\mathrm{MP2}} = -\frac{1}{2}\sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \frac{\langle ab|rs\rangle\langle rs|ab\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} + \frac{1}{2}\sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \frac{\langle ab|rs\rangle\langle rs|ba\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}, \tag{51}
$$

is represented by the corresponding two diagrams:

Each diagram is made of only three types of lines:

- a full line with a downward arrow representing a *occupied* spin orbital (a, b, ...), and is called a *hole* line;

- a full line with a upward arrow representing a *virtual* spin orbital (r, s, ...), and is called a *particle* line;

- a horizontal dash line representing the Coulomb interaction between four spin orbitals, and is called an *interaction* line.

Each interaction line has two extremities called *interaction vertices*. Each such interaction vertex is connected with one full line coming *in* and one full line coming *out* of the vertex.

The mathematical expression corresponding to each diagram is obtained by applying the following rules:

1. each interaction line contributes a two-electron integral factor with spin-orbital indices as $\langle orb\text{-}left\text{-}in,\ orb\text{-}right\text{-}in\ |\ orb\text{-}left\text{-}out,\ orb\text{-}right\text{-}out\rangle$;

2. each pair of adjacent interaction lines contributes a factor $-1/(\sum \varepsilon_{\text{particle}} - \sum \varepsilon_{\text{hole}})$ where the sums are over indices of all particle and hole lines crossing an imaginary line separating the two adjacent interaction lines;

3. sum over all particle and hole indices;

4. if the diagram is left/right symmetric, there is an overall factor of $1/2$;

5. the overall sign is given by $(-1)^{h+l}$ where h and l are the number of hole lines and closed full-line loops, respectively.

The diagrams do not only provide a visually appealing representation of the perturbation expansion that one can draw after having derived the mathematical expressions of the perturbation terms. They can also be used to avoid the mathematical derivations. Indeed, one can first draw all possible diagrams at a given perturbation order, and then translate them into mathematical expressions.

In the context of diagrammatic perturbation theory, the linked-cluster theorem can be easily formulated: each diagram contributing to the perturbative expansion of the energy is made of a single connected piece. Unconnected diagrams do not contribute. This ensures the size consistency of the perturbative expansion at each order.

3 Coupled-cluster theory

This section provides a basic introduction to coupled-cluster theory. For more details, its extension for excited-state calculations, and recent developments, see e.g. Ref. [4].

3.1 The exponential ansatz

In *coupled-cluster (CC)* theory, one starts by an exponential ansatz for the CC wave function

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle, \tag{52}$$

where $|\Phi_0\rangle$ is the HF wave function, and $\hat{T}$ is the *cluster operator* which is the sum of cluster operators of different excitation levels

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N. \tag{53}$$

In this expression, $\hat{T}_1$ is the cluster operator for the single excitations, which can be written in a second-quantization formalism as

$$\hat{T}_1 = \sum_a^{\mathrm{occ}} \sum_r^{\mathrm{vir}} t_a^r \, \hat{a}_r^\dagger \hat{a}_a, \tag{54}$$

where t_a^r are the single-excitation cluster amplitudes to be determined, and $\hat{a}_a$ and $\hat{a}_r^\dagger$ are annihilation and creation operators for the spin-orbitals a and r, respectively. When the operator $\hat{a}_r^\dagger \hat{a}_a$ acts on the HF single determinant $|\Phi_0\rangle$, it generates the single-excited determinant $|\Phi_a^r\rangle = \hat{a}_r^\dagger \hat{a}_a|\Phi_0\rangle$. Similarly, $\hat{T}_2$ is the cluster operator for the double excitations, which is written as

$$\hat{T}_2 = \sum_{a<b}^{\mathrm{occ}} \sum_{r<s}^{\mathrm{vir}} t_{ab}^{rs} \, \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a = \frac{1}{4} \sum_{a,b}^{\mathrm{occ}} \sum_{r,s}^{\mathrm{vir}} t_{ab}^{rs} \, \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a, \tag{55}$$

where t_{ab}^{rs} are the double-excitation cluster amplitudes to be determined. When the operator $\hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a$ acts on the HF single determinant $|\Phi_0\rangle$, it generates the double-excited determinant $|\Phi_{ab}^{rs}\rangle = \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_b \hat{a}_a|\Phi_0\rangle$. The second equality in Eq. (55) comes from imposing to the amplitudes t_{ab}^{rs} to be antisymmetric with respect to the exchange of two indices, i.e. $t_{ab}^{rs} = -t_{ba}^{rs} = -t_{ab}^{sr} = t_{ba}^{sr}$, and from the anticommutation property of two annihilation operators, i.e. $\hat{a}_b \hat{a}_a = -\hat{a}_a \hat{a}_b$, or two creation operators, i.e. $\hat{a}_r^\dagger \hat{a}_s^\dagger = -\hat{a}_s^\dagger \hat{a}_r^\dagger$. And so on up to the $\hat{T}_N$ cluster operator for N-fold excitations.

To understand the action of the operator $e^{\hat{T}}$ on the HF wave function $|\Phi_0\rangle$, one can expand the exponential and rearrange the operators in terms of excitation levels

$$
\begin{aligned}
e^{\hat{T}} &= \hat{1} + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots \\
&= \hat{1} + \hat{C}_1 + \hat{C}_2 + \cdots + \hat{C}_N,
\end{aligned}
\tag{56}
$$

where the operator $\hat{C}_1$ generates single excitations, $\hat{C}_2$ generates double excitations, etc. Noting that the cluster operators $\hat{T}_1$, $\hat{T}_2$, ..., $\hat{T}_N$ commute with each other, we find for example for the first four excitation operators

$$\hat{C}_1 = \hat{T}_1, \tag{57}$$

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2, \tag{58}$$

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3, \tag{59}$$

$$\hat{C}_4 = \hat{T}_4 + \hat{T}_1\hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4, \tag{60}$$

and so on. The single excitations are generated only by $\hat{T}_1$. The double excitations can be generated in two ways: by $\hat{T}_2$ describing a "simultaneous" excitations of two electrons, or by $\hat{T}_1^2$ describing two independent single excitations. The triple excitations can be generated in three ways: by $\hat{T}_3$ describing a simultaneous excitations of three electrons, by $\hat{T}_1\hat{T}_2$ describing independent single and double excitation, or by $\hat{T}_1^3$ three independent single excitations. And so on. The CC wave function can thus be written as

$$
\begin{aligned}
|\Psi_{\text{CC}}\rangle &= |\Phi_0\rangle + \sum_a^{\text{occ}}\sum_r^{\text{vir}} c_a^r|\Phi_a^r\rangle + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{vir}} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle \\
&\quad + \sum_{a<b<c}^{\text{occ}}\sum_{r<s<t}^{\text{vir}} c_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \sum_{a<b<c<d}^{\text{occ}}\sum_{r<s<t<u}^{\text{vir}} c_{abcd}^{rstu}|\Phi_{abcd}^{rstu}\rangle + \cdots ,
\end{aligned} \tag{61}
$$

with coefficients related to the cluster amplitudes by

$$c_a^r = t_a^r, \tag{62}$$

$$c_{ab}^{rs} = t_{ab}^{rs} + t_a^r * t_b^s, \tag{63}$$

$$c_{abc}^{rst} = t_{abc}^{rst} + t_a^r * t_{bc}^{st} + t_a^r * t_b^s * t_c^t, \tag{64}$$

$$c_{abcd}^{rstu} = t_{abcd}^{rstu} + t_a^r * t_{bcd}^{stu} + t_{ab}^{rs} * t_{cd}^{tu} + t_a^r * t_b^s * t_{cd}^{tu} + t_a^r * t_b^s * t_c^t * t_d^u, \tag{65}$$

and so on. In these expressions, $*$ means an antisymmetric product making the resulting coefficients properly antisymmetric with respect to any exchange of two occupied spin orbitals or two virtual spin orbitals. For example, we have

$$t_a^r * t_b^s = t_a^r t_b^s - t_b^r t_a^s, \tag{66}$$

$$t_a^r * t_{bc}^{st} = t_a^r t_{bc}^{st} - t_b^r t_{ac}^{st} + t_c^r t_{ab}^{st} - t_a^s t_{bc}^{rt} + t_b^s t_{ac}^{rt} - t_c^s t_{ab}^{rt} + t_a^t t_{bc}^{rs} - t_b^t t_{ac}^{rs} + t_c^t t_{ab}^{rs}, \tag{67}$$

$$t_a^r * t_b^s * t_c^t = t_a^r t_b^s t_c^t - t_a^r t_c^s t_b^t - t_b^r t_a^s t_c^t - t_c^r t_b^s t_a^t + t_c^r t_a^s t_b^t + t_b^r t_c^s t_a^t, \tag{68}$$

etc. These expressions can be obtained by starting from Eqs. (57)-(60), introducing the definitions of the cluster operators $\hat{T}_1$, $\hat{T}_2$, ..., and imposing all the constraints of the type $a < b < c < d$ or $r < s < t < u$ in the sums by using the anticommutation property of the annihilation and creation operators.

Exercise 3 : Check Eqs. (62)-(68), and find the expressions of $t_a^r * t_{bcd}^{stu}$, $t_{ab}^{rs} * t_{cd}^{tu}$, $t_a^r * t_b^s * t_{cd}^{tu}$, and $t_a^r * t_b^s * t_c^t * t_d^u$. Warning: the time required to do this exercise is inversely proportional to your ease with combinatorics.

Thus, the CC wave function contains all excited determinants, just as the FCI wave function. If the cluster operator $\hat{T}$ is not truncated, the CC wave function is just a nonlinear reparametrization of the FCI wave function: optimizing the cluster amplitudes $\mathbf{t} = (t_a^r, t_{ab}^{rs}, t_{abc}^{rst}, ...)$ so as to minimize the total energy would lead to the FCI wave function. The interest of the CC approach only appears when the cluster operator is truncated.

3.2 Truncation of the cluster operator

Let us now consider the truncation of the cluster operator at a given excitation level. For example, it is frequent to keep only $\hat{T}_1$ and $\hat{T}_2$

$$\hat{T} = \hat{T}_1 + \hat{T}_2, \tag{69}$$

which is known as *coupled-cluster singles doubles (CCSD)*. The expansion of $e^{\hat{T}}$ gives

$$e^{\hat{T}} = \hat{1} + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right) + \left(\hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3\right) + \left(\frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{24}\hat{T}_1^4\right) + \cdots. \tag{70}$$

Applying this expansion to the HF wave function $|\Phi_0\rangle$, we see that the CCSD wave function has the same form as in Eq. (61), i.e. it contains *all* excited determinants with coefficients now given by

$$c_a^r = t_a^r, \tag{71}$$

$$c_{ab}^{rs} = t_{ab}^{rs} + t_a^r * t_b^s, \tag{72}$$

$$c_{abc}^{rst} = t_a^r * t_{bc}^{st} + t_a^r * t_b^s * t_c^t, \tag{73}$$

$$c_{abcd}^{rstu} = t_{ab}^{rs} * t_{cd}^{tu} + t_a^r * t_b^s * t_{cd}^{tu} + t_a^r * t_b^s * t_c^t * t_d^u, \tag{74}$$

and so on. In comparison to the untruncated CC case, the coefficients of triple excitations c_{abc}^{rst} are fully determined by only products of single- and double-excitation amplitudes t_a^r and t_{bc}^{st}, and similarly for the coefficients of quadruple excitations c_{abcd}^{rstu}, and all higher-level excitations. Presumably, the triple-excitation amplitudes t_{abc}^{rst}, quadruple-excitation amplitudes t_{abcd}^{rstu}, and higher-level-excitation amplitudes are smaller than the double-excitation amplitude t_{ab}^{rs}, and this is thus a reasonable approximation. The CCSD wave function contains much more excited determinants than the CISD wave function, while keeping the same number of free parameters $\mathbf{t} = (t_a^r, t_{ab}^{rs})$ to optimize.

One big advantage of truncated CC over truncated CI is that truncated CC is size-consistent. This directly stems from the exponential form of the wave function. Consider a system composed of two infinitely separated (and thus non-interacting) fragments A and B. Because the orbitals of each fragments do not overlap, the cluster operator of the system is additively separable, i.e. $\hat{T}^{A\cdots B} = \hat{T}^A + \hat{T}^B$, where $\hat{T}^A$ and $\hat{T}^B$ are the clusters operators of fragments A and B, respectively. Moreover, in the case where the HF calculation is size-consistent, the starting HF wave function is multiplicatively separable $|\Phi_0^{A\cdots B}\rangle = |\Phi_0^A\rangle \otimes |\Phi_0^B\rangle$ (where $\otimes$ is the antisymmetric tensor product). We can then write

$$
\begin{aligned}
|\Psi_{\text{CC}}^{A\cdots B}\rangle &= e^{\hat{T}^{A\cdots B}}|\Phi_0^{A\cdots B}\rangle \\
&= e^{\hat{T}^A + \hat{T}^B}|\Phi_0^A\rangle \otimes |\Phi_0^B\rangle \\
&= e^{\hat{T}^A}|\Phi_0^A\rangle \otimes e^{\hat{T}^B}|\Phi_0^B\rangle \\
&= |\Psi_{\text{CC}}^A\rangle \otimes |\Psi_{\text{CC}}^B\rangle,
\end{aligned} \tag{75}
$$

i.e. the CC wave function is multiplicatively separable. This implies in turn that the CC total energy is additively separable, i.e. the method is size-consistent.

3.3 The coupled-cluster energy and the coupled-cluster equations

Let us consider an arbitrary truncation level of the cluster operator. The most natural way to calculate the cluster amplitude $\mathbf{t}$ would seem to be by using the *variational method*, i.e. minimizing the CC total energy with the normalization constraint, just like in CI,

$$\min_{\mathbf{t}} \left\{ \langle \Psi_{\text{CC}} | \hat{H} | \Psi_{\text{CC}} \rangle - E \langle \Psi_{\text{CC}} | \Psi_{\text{CC}} \rangle \right\}. \tag{76}$$

However, the CC wave function includes all excited determinants up to N-fold excitations which contribute to these expectation values, giving too complex equations to be efficiently solved.

A more convenient approach for obtaining the CC energy and amplitudes is the *projection method.* In this method, we require that the CC wave function satisfies the Schrödinger equation

$$(\hat{H} - E)|\Psi_{\text{CC}}\rangle = 0, \tag{77}$$

projected onto the space spanned by the HF determinant $\langle \Phi_0 |$, and the excited determinants $\langle \Phi_a^r |, \langle \Phi_{ab}^{rs} |, \langle \Phi_{abc}^{rst} |, ...$

$$\langle \Phi_0 | (\hat{H} - E) | \Psi_{\text{CC}} \rangle = 0, \tag{78}$$

$$\langle \Phi_a^r | (\hat{H} - E) | \Psi_{\text{CC}} \rangle = 0, \tag{79}$$

$$\langle \Phi_{ab}^{rs} | (\hat{H} - E) | \Psi_{\text{CC}} \rangle = 0, \tag{80}$$

$$\langle \Phi_{abc}^{rst} | (\hat{H} - E) | \Psi_{\text{CC}} \rangle = 0, \tag{81}$$

and so on. Using the expansion of $|\Psi_{\text{CC}}\rangle$ in terms of determinants giving in Eq. (61), we see that $\langle \Phi_0 | \Psi_{\text{CC}} \rangle = 1$ due to the orthonormality of the determinants, and thus Eq. (78) directly gives the CC total energy

$$
\begin{aligned}
E &= \langle \Phi_0 | \hat{H} | \Psi_{\text{CC}} \rangle \\
&= \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \sum_a^{\text{occ}} \sum_r^{\text{vir}} c_a^r \langle \Phi_0 | \hat{H} | \Phi_a^r \rangle + \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} c_{ab}^{rs} \langle \Phi_0 | \hat{H} | \Phi_{ab}^{rs} \rangle,
\end{aligned}
\tag{82}
$$

in which according to Slater's rules triple and higher excited determinants do not contribute. Since the first term in Eq. (82) is just the HF total energy $E_{\text{HF}} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$, and since the second term vanishes by virtue of Brillouin's theorem $\langle \Phi_0 | \hat{H} | \Phi_a^r \rangle = 0$, we obtain the CC correlation energy $E_{\text{c}} = E - E_{\text{HF}}$

$$
\begin{aligned}
E_{\text{c}} &= \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} c_{ab}^{rs} \langle \Phi_0 | \hat{H} | \Phi_{ab}^{rs} \rangle \\
&= \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} (t_{ab}^{rs} + t_a^r * t_b^s) \langle ab || rs \rangle \\
&= \frac{1}{4} \sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} (t_{ab}^{rs} + 2\, t_a^r t_b^s) \langle ab || rs \rangle,
\end{aligned}
\tag{83}
$$

where the antisymmetry property of the amplitudes and of the integrals has been used. Thus, at any truncation level, the expression of the CC correlation energy obtained with the projection method is quite simple. It only involves matrix elements over double-excited determinants and only single- and double-excitation amplitudes t_a^r and t_{ab}^{rs} enter the expression. Except in the uninteresting case where the cluster operator $\hat{T}$ is not truncated, the total CC energy obtained with the projection method is not identical to the one that would have been obtained with the

15

variation method of Eq. (76). Consequently, the total CC energy is not necessarily above the exact ground-state total energy, just as in perturbation theory.

The other equations (79), (80), (81), ... determine the CC amplitudes. They are often more explicitly written as

$$\langle \Phi_a^r | (\hat{H} - E) e^{\hat{T}} | \Phi_0 \rangle = 0, \tag{84}$$

$$\langle \Phi_{ab}^{rs} | (\hat{H} - E) e^{\hat{T}} | \Phi_0 \rangle = 0, \tag{85}$$

$$\langle \Phi_{abc}^{rst} | (\hat{H} - E) e^{\hat{T}} | \Phi_0 \rangle = 0, \tag{86}$$

and so on, which are known as the *unlinked CC amplitude equations*. They represent a system of coupled nonlinear equations for the amplitudes t_a^r, t_{ab}^{rs}, t_{abc}^{rst}, etc. To have the same number of equations as the number of unknown amplitudes, the projection space must correspond to the truncation level of the cluster operator. For example, for determining the CCSD amplitudes, one needs to consider projection on to single and double-excited determinants only. In practice, it is often more convenient to write the CC amplitude equations is a different way, by first multiplying from the left by the operator $e^{-\hat{T}}$ in the Schrödinger equation (77) before projecting on the excited determinants

$$\langle \Phi_a^r | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0, \tag{87}$$

$$\langle \Phi_{ab}^{rs} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0, \tag{88}$$

$$\langle \Phi_{abc}^{rst} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0, \tag{89}$$

and so on, which are known as the *linked CC amplitude equations*. Although equivalent to the unlinked equations, the linked equations have the advantage of leading to more compact expressions which are manifestly size-consistent and at most quartic in the amplitudes (at any truncation level). This last feature comes from the fact that the Baker-Campbell-Hausdorff (BCH) expansion of $e^{-\hat{T}} \hat{H} e^{\hat{T}}$ exactly terminates at fourth order because $\hat{H}$ contains at most a two-electron operator

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}]. \tag{90}$$

3.4 Example: coupled-cluster doubles

As an example, we now write down the complete equations in the simple case of coupled-cluster doubles (CCD). In this case, the cluster operator only contains double excitations

$$\hat{T} = \hat{T}_2, \tag{91}$$

and the CCD wave function thus contains double-excited determinants, quadruple-excited determinants, ...

$$|\Psi_{\text{CCD}}\rangle = |\Phi_0\rangle + \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} t_{ab}^{rs} |\Phi_{ab}^{rs}\rangle + \sum_{a<b<c<d}^{\text{occ}} \sum_{r<s<t<u}^{\text{vir}} (t_{ab}^{rs} * t_{cd}^{tu}) |\Phi_{abcd}^{rstu}\rangle + \cdots, \tag{92}$$

where the coefficients of the quadruple excitations are given by the antisymmetrized product of the coefficients of the double excitations, and so on. The CCD correlation energy is given by

$$E_{\text{c}}^{\text{CCD}} = \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} t_{ab}^{rs} \langle ab || rs \rangle. \tag{93}$$

The double-excitation amplitudes t_{ab}^{rs} can be determined from the unlinked CC amplitude equations

$$\langle\Phi_{ab}^{rs}|(\hat{H}-E)|\Psi_{\mathrm{CCD}}\rangle = 0, \tag{94}$$

leading to

$$\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_0\rangle + \sum_{c<d}^{\mathrm{occ}}\sum_{t<u}^{\mathrm{vir}}\langle\Phi_{ab}^{rs}|\hat{H}-E|\Phi_{cd}^{tu}\rangle t_{cd}^{tu} + \sum_{c<d}^{\mathrm{occ}}\sum_{t<u}^{\mathrm{vir}}\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_{abcd}^{rstu}\rangle(t_{ab}^{rs}*t_{cd}^{tu}) = 0, \tag{95}$$

where the quadruple-excitation term has been simplified by taking into account that matrix elements of $\hat{H}$ over Slater determinants differing by more than 2 spin orbitals are zero. Using now $\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_0\rangle = \langle rs||ab\rangle$ and $\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_{abcd}^{rstu}\rangle = \langle cd||tu\rangle$, and inserting $E = E_{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{CCD}}$ and replacing $E_{\mathrm{c}}^{\mathrm{CCD}}$ by its expression in Eq. (93) gives

$$\langle rs||ab\rangle + \sum_{c<d}^{\mathrm{occ}}\sum_{t<u}^{\mathrm{vir}}\langle\Phi_{ab}^{rs}|\hat{H}-E_{\mathrm{HF}}|\Phi_{cd}^{tu}\rangle t_{cd}^{tu} + \sum_{c<d}^{\mathrm{occ}}\sum_{t<u}^{\mathrm{vir}}\langle cd||tu\rangle(t_{ab}^{rs}*t_{cd}^{tu} - t_{ab}^{rs}t_{cd}^{tu}) = 0. \tag{96}$$

The remaining matrix element is more complicated to calculate. After considering the different possibilities of equality between the indices a, b and c, d, and between r, s and t, u, it can be found

$$\begin{aligned}
\langle\Phi_{ab}^{rs}|\hat{H}-E_{\mathrm{HF}}|\Phi_{cd}^{tu}\rangle &= (\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b)\delta_{ab,cd}\delta_{rs,tu}\\
&\quad + \langle rs||tu\rangle\delta_{ab,cd} + \langle cd||ab\rangle\delta_{rs,tu}\\
&\quad + \langle ds||ub\rangle\delta_{a,c}\delta_{r,t} - \langle cs||ub\rangle\delta_{a,d}\delta_{r,t}\\
&\quad - \langle ds||tb\rangle\delta_{a,c}\delta_{r,u} + \langle cs||tb\rangle\delta_{a,d}\delta_{r,u}.
\end{aligned} \tag{97}$$

The final CCD amplitude equations are

$$\langle rs||ab\rangle + (\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b)t_{ab}^{rs} + \sum_{t<u}^{\mathrm{vir}}\langle rs||tu\rangle t_{ab}^{tu} + \sum_{c<d}^{\mathrm{occ}}\langle cd||ab\rangle t_{cd}^{rs}$$

$$+ \sum_{d}^{\mathrm{occ}}\sum_{u}^{\mathrm{vir}}\langle ds||ub\rangle t_{ad}^{ru} - \sum_{c}^{\mathrm{occ}}\sum_{u}^{\mathrm{vir}}\langle cs||ub\rangle t_{ca}^{ru} - \sum_{d}^{\mathrm{occ}}\sum_{t}^{\mathrm{vir}}\langle ds||tb\rangle t_{ad}^{tr} + \sum_{c}^{\mathrm{occ}}\sum_{t}^{\mathrm{vir}}\langle cs||tb\rangle t_{ca}^{tr}$$

$$+ \sum_{c<d}^{\mathrm{occ}}\sum_{t<u}^{\mathrm{vir}}\langle cd||tu\rangle(t_{ab}^{rs}*t_{cd}^{tu} - t_{ab}^{rs}t_{cd}^{tu}) = 0, \tag{98}$$

which are quadratic equations to be solved iteratively.

It is interesting to consider the expansion of the amplitudes in powers of the electron-electron interaction: $t_{ab}^{rs} = t_{ab}^{rs,(1)} + t_{ab}^{rs,(2)} + \cdots$. The first-order amplitudes are given by

$$\langle rs||ab\rangle + (\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b)t_{ab}^{rs,(1)} = 0, \tag{99}$$

that is

$$t_{ab}^{rs,(1)} = -\frac{\langle rs||ab\rangle}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}. \tag{100}$$

By inserting this expression of $t_{ab}^{rs,(1)}$ in the expression of the correlation energy in Eq. (93), we then recover the MP2 correlation energy

$$E_{\mathrm{c}}^{\mathrm{MP2}} = \sum_{a<b}^{\mathrm{occ}}\sum_{r<s}^{\mathrm{vir}} t_{ab}^{rs,(1)}\langle ab||rs\rangle = -\sum_{a<b}^{\mathrm{occ}}\sum_{r<s}^{\mathrm{vir}}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}. \tag{101}$$

Thus, CCD correctly reduces to MP2 at second order in the electron-electron interaction.

References

[1] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover, New York, 1996).

[2] T. Helgaker, P. Jørgensen and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 2002).

[3] D. Cremer, WIREs Comput. Mol. Sci. **1**, 509 (2011), doi: 10.1002/wcms.58.

[4] R. J. Bartlett, WIREs Comput. Mol. Sci. **2**, 126 (2012), doi: 10.1002/wcms.76.