

## 7 Perturbative analysis

**Definition 7.1. Correct to order  $p$ .** Define  $X^{(p^-)} \equiv X^{(0)} + X^{(1)} + \dots + X^{(p)}$  as well as  $X^{(p^+)} \equiv X^{(p)} + X^{(p+1)} + \dots + X^{(\infty)}$ . Then we say an approximation to  $X$  is *correct to order  $p$*  if it contains all of the contributions in  $X^{(p^-)}$ .

**Definition 7.2. Truncated CI and CC.** Let CISDTQPH7 $\cdots m$  denote truncation of the CI Ansatz at  $m$ -tuples. Similarly, CCS $\cdots m$  means that we omit cluster operators of excitation level  $k > m$ . Note that, unlike  $C_k$ , the cluster operator  $T_k$  in truncated CC describes only *connected  $k$ -tuples*, which are residual correlations that cannot be decomposed into products of smaller clusters. As a result, truncated CC actually contains much higher excitations than CI.

**Notation 7.1.** Let  $\Phi_k$  be a row vector containing all unique  $k$ -fold substitutions of  $\Phi$ ,<sup>1</sup> so that  $\Phi = [\Phi \ \Phi_1 \ \cdots \ \Phi_n]$  spans  $\mathcal{F}_n$ . Using  $\mathbf{c}$  and  $\mathbf{t}$  to denote column vectors of CI coefficients and CC amplitudes leads to the following relationships.<sup>2</sup>

$$\Phi \cdot \mathbf{c} = (C_0 + C_1 + \dots + C_n)\Phi \quad \Phi \cdot \mathbf{t} = (1 + T_1 + \dots + T_n)\Phi \quad (7.1)$$

In Dirac notation the bra  $\langle \Phi |$  is transposed, so that  $\langle \Phi | W | \Phi \rangle = [\langle \Phi_\sigma | W | \Phi_\tau \rangle]$  is the matrix representation of  $W$  in  $\mathcal{F}_n$ . Such matrix representations will be denoted with bolded letters,  $\mathbf{W} \equiv \langle \Phi | W | \Phi \rangle$ .

**Remark 7.1. Perturbative analysis of CI.** Writing the CI eigenvalue equation  $\mathbf{H}_c \mathbf{c} = E_c \mathbf{c}$  in terms of model-Hamiltonian and fluctuation-potential matrices and rearranging yields a new matrix equation

$$(-\mathbf{H}_0 + E_c) \mathbf{c} = \mathbf{V}_c \mathbf{c} \quad (7.2)$$

which provides a convenient starting point for a perturbative analysis and for comparison to the coupled-cluster equations. The matrix elements of the model Hamiltonian are given by  $\langle \Phi_\sigma | H_0 | \Phi_\tau \rangle = \mathcal{E}_\sigma \delta_{\sigma\tau}$ , so the matrix on the left is diagonal with eigenvalues  $-\mathcal{E}_{i_1 \dots i_k}^{a_1 \dots a_k} + E_c$ . The rows of this equation can be written in terms of CI operators as follows<sup>3</sup>

$$\begin{matrix} c_0 & E_c \\ (0^+) & (2^+) \end{matrix} = \begin{matrix} \langle \Phi | V_c ( \\ (1) & ((1^+)) & (1^+) \end{matrix} | \Phi \rangle \quad (7.3)$$

$$\begin{matrix} c_a^i & (\mathcal{E}_a^i + E_c) \\ (1^+) & (0) & (2^+) \end{matrix} = \begin{matrix} \langle \Phi_i^a | V_c ( \\ (1) & ((0^+)) & (1^+) & (1^+) & (2^+) \end{matrix} | \Phi \rangle \quad (7.4)$$

$$\begin{matrix} c_{ab}^{ij} & (\mathcal{E}_{ab}^{ij} + E_c) \\ (1^+) & (0) & (2^+) \end{matrix} = \begin{matrix} \langle \Phi_{ij}^{ab} | V_c ( \\ (1) & (0^+) & (1^+) & (1^+) & (2^+) & (2^+) \end{matrix} | \Phi \rangle \quad (7.5)$$

$$\begin{matrix} c_{abc}^{ijk} & (\mathcal{E}_{abc}^{ijk} + E_c) \\ (2^+) & (0) & (2^+) \end{matrix} = \begin{matrix} \langle \Phi_{ijk}^{abc} | V_c ( \\ (1) & (1^+) & (1^+) & (2^+) & (2^+) & (3^+) \end{matrix} | \Phi \rangle \quad (7.6)$$

$$\begin{matrix} c_{abcd}^{ijkl} & (\mathcal{E}_{abcd}^{ijkl} + E_c) \\ (2^+) & (0) & (2^+) \end{matrix} = \begin{matrix} \langle \Phi_{ijkl}^{abcd} | V_c ( \\ (1) & (1^+) & (2^+) & (2^+) & (3^+) & (3^+) \end{matrix} | \Phi \rangle \quad (7.7)$$

$$\begin{matrix} c_{a_1 \dots a_k}^{i_1 \dots i_k} & (\mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k} + E_c) \\ ([k/2]^+) & (0) & (2^+) \end{matrix} = \begin{matrix} \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | V_c ( \\ (1) & ([k/2]^+ - 1) & ([k/2]^+ - 1) & ([k/2]^+) & ([k/2]^+) & ([k/2]^+ + 1) \end{matrix} | \Phi \rangle \quad (7.8)$$

where the numbers in parentheses denote orders in perturbation theory and the double parentheses denote terms which vanish under Brillouin's theorem. The orders of the CI operators follow from the fact that each order in perturbation theory increases the maximum excitation level of the wavefunction by +2, starting from  $\Psi^{(1)}$  which contains up to doubles. Therefore the leading contributions to  $C_k$  have order  $[k/2]$ . If Brillouin's theorem holds, the first-order contribution to  $C_1$  vanishes and singles contribute at orders  $2^+$  in perturbation theory.

**Example 7.1.** The analysis of remark 7.1 shows that CISD is only correct to first order in the wavefunction, since triples contribute at second order. However,  $C_1$  and  $C_2$  are both correct to second order, since the truncation error in equations 7.4 and 7.5 is  $\mathcal{O}(V_c^3)$ , which makes the CISD correlation energy correct to third order. In order to gain an order in perturbation theory we have to increase the truncation level by at least two, since triples and quadruples contribute at the same order. CISDTQ is correct to second order in the wavefunction and fifth order in the energy.

**Proposition 7.1.** CIS $\cdots m$  is correct to order  $\lfloor m/2 \rfloor$  in the wavefunction and order  $2 \lfloor m/2 \rfloor + 1$  in the energy.

Proof: According to rmk 7.1,  $C_{m+1}$  contributes at order  $\lceil (m+1)/2 \rceil$ , implying that the wavefunction is correct to  $\lceil (m+1)/2 \rceil - 1 = \lfloor m/2 \rfloor$ . Truncation also leaves  $C_m$  and  $C_{m-1}$  correct to  $\lceil (m+1)/2 \rceil = \lfloor m/2 \rfloor + 1$ , and propagating these truncation errors down to  $C_{m-2h}$  and  $C_{m-1-2h}$  makes the latter correct to  $\lfloor m/2 \rfloor + 1 + h$ . One of these operators is  $C_2$  when  $h = \lfloor m/2 \rfloor - 1$ . Since  $C_2$  limits the error in equation 7.3,<sup>4</sup> the energy is correct to  $2 \lfloor m/2 \rfloor + 1$ .

<sup>1</sup>That is,  $\Phi_k = [\Phi_{i_1 \dots i_k}^{a_1 \dots a_k}]$ . Uniqueness can be enforced by requiring  $i_1 < \dots < i_k$  and  $a_1 < \dots < a_k$ .

<sup>2</sup>For the sake of generality we are not assuming intermediate normalization for CI. The  $C_0$  operator scales functions by  $c_0$ .

<sup>3</sup>See [https://en.wikipedia.org/wiki/Floor\\_and\\_ceiling\\_functions](https://en.wikipedia.org/wiki/Floor_and_ceiling_functions) for details floor and ceiling functions,  $\lfloor x \rfloor$  and  $\lceil x \rceil$ .

<sup>4</sup>The error propagation ensures that errors decrease monotonically with excitation level.

**Remark 7.2. Perturbative analysis of CC.** The CC equations can be written as a non-linear matrix equation.

$$E_c \langle \Phi | \Phi \rangle - \mathbf{H}_0 \mathbf{t} = \langle \Phi | V_c \exp(T(\mathbf{t})) | \Phi \rangle_C \quad (7.9)$$

To make the comparison with equation 7.2 more transparent, this can be written as  $(-\mathbf{H}_0 + E_c \langle \Phi | \Phi \rangle) \mathbf{t} = (\mathbf{V}_c \mathbf{t})_C + \mathcal{O}(\mathbf{t}^2)$ . Non-vanishing contributions to the rows of this matrix equation can be expressed in terms of cluster operators as follows

$$E_c = \langle \Phi | V_c ( \underset{(2^+)}{T_1} + \underset{(1) ((1^+))}{T_2} + \underset{(1^+)}{T_2} + \underset{(2^+)}{\frac{1}{2} T_1^2} ) | \Phi \rangle_C \quad (7.10)$$

$$t_{(1^+)(0)}^i \mathcal{E}_a^i = \langle \Phi_i^a | V_c ( \underset{(1)}{1} + \underset{((0))}{T_1} + \underset{(1^+)}{T_2} + \underset{(1^+)}{T_2} + \underset{(2^+)}{T_3} + \underset{(2^+)}{\frac{1}{2} T_1^2} + \underset{(2^+)}{T_1 T_2} + \underset{(3^+)}{\frac{1}{3!} T_1^3} ) | \Phi \rangle_C \quad (7.11)$$

$$t_{(1^+)(0)}^{ij} \mathcal{E}_{ab}^{ij} = \langle \Phi_{ij}^{ab} | V_c ( \underset{(1)}{1} + \underset{(0)}{T_1} + \underset{(1^+)}{T_2} + \underset{(1^+)}{T_2} + \underset{(2^+)}{T_3} + \underset{(3^+)}{T_4} + \underset{(2^+)}{\frac{1}{2} T_1^2} + \underset{(2^+)}{T_1 T_2} + \underset{(3^+)}{T_1 T_3} + \underset{(2^+)}{\frac{1}{2} T_2^2} + \underset{(3^+)}{\frac{1}{3!} T_1^3} + \underset{(3^+)}{\frac{1}{2} T_1^2 T_2} + \underset{(4^+)}{\frac{1}{4!} T_1^4} ) | \Phi \rangle_C \quad (7.12)$$

$$t_{(2^+)(0)}^{ijk} \mathcal{E}_{abc}^{ijk} = \langle \Phi_{ijk}^{abc} | V_c ( \underset{(1)}{T_2} + \underset{(1^+)}{T_3} + \underset{(2^+)}{T_4} + \underset{(3^+)}{T_5} + \underset{(2^+)}{T_1 T_2} + \underset{(3^+)}{T_1 T_3} + \underset{(2^+)}{\frac{1}{2} T_2^2} + \underset{(4^+)}{T_1 T_4} + \underset{(3^+)}{T_2 T_3} + \underset{(3^+)}{\frac{1}{2} T_1^2 T_2} + \underset{(4^+)}{\frac{1}{2} T_1^2 T_3} + \underset{(3^+)}{\frac{1}{2} T_1 T_2^2} + \underset{(4^+)}{\frac{1}{3!} T_1^3 T_2} ) | \Phi \rangle_C \quad (7.13)$$

$$t_{(3^+)(0)}^{ijkl} \mathcal{E}_{abcd}^{ijkl} = \langle \Phi_{ijkl}^{abcd} | V_c ( \underset{(1)}{T_3} + \underset{(2^+)}{T_4} + \underset{(3^+)}{T_5} + \underset{(4^+)}{T_6} + \underset{(5^+)}{T_1 T_3} + \underset{(2^+)}{\frac{1}{2} T_2^2} + \underset{(4^+)}{T_1 T_4} + \underset{(3^+)}{T_2 T_3} + \underset{(5^+)}{T_1 T_5} + \underset{(4^+)}{T_2 T_4} + \underset{(4^+)}{\frac{1}{2} T_3^2} + \underset{(4^+)}{\frac{1}{2} T_1^2 T_3} + \underset{(3^+)}{\frac{1}{2} T_1 T_2^2} + \underset{(5^+)}{\frac{1}{2} T_1^2 T_4} + \underset{(4^+)}{T_1 T_2 T_3} + \underset{(3^+)}{\frac{1}{3!} T_2^3} + \underset{(5^+)}{\frac{1}{3!} T_1^3 T_3} + \underset{(4^+)}{\frac{1}{2!2!} T_1^2 T_2^2} ) | \Phi \rangle_C \quad (7.14)$$

⋮

$$t_{((k-1)^+)(0)}^{i_1 \dots i_k} \mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k} = \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | V_c ( \underset{(1)}{T_{k-1}} + \underset{((k-2)^+)}{T_k} + \underset{((k-1)^+)}{T_{k+1}} + \underset{(k^+)}{T_{k+2}} + \sum_{p=2}^4 \frac{1}{p!} \sum_{h=p-2}^2 \sum_{\mathbf{k}}^{C_p(k+h)} T_{k_1} \dots T_{k_p} ) | \Phi \rangle_C \quad (7.15)$$

where  $C_k(m)$  is the set of  $k$ -tuples integer compositions of  $m$  and  $\phi_{\mathbf{k}}$  is the number of 1's in  $\mathbf{k} = (k_1, \dots, k_p)$ . The orders of the cluster operators follow from straightforward induction on the fact that the lowest order contribution to  $T_k$  always comes from  $(V_c T_{k-1})_C$ , which means that each  $T_k$  contributes at one order above  $T_{k-1}$ , starting from  $k = 2$ . If Brillouin's theorem holds,  $T_1$  has order  $2^+$  and the orders of the disconnected products become  $(k + h - p + 2 \cdot \phi_{\mathbf{k}})^+$ .

**Proposition 7.2.** *CCS  $\dots m$  is correct to order  $m - 1$  in the wavefunction and order  $m + \lfloor m/2 \rfloor$  in the energy.*

Proof: According to rmk 7.2,  $T_{m+1}$  contributes at order  $m$ , implying that the wavefunction is correct to order  $m - 1$ . Truncation also leaves  $T_m$  and  $T_{m-1}$  correct to order  $m$ , and propagating these truncation errors down to  $T_{m-2h}$  and  $T_{m-1-2h}$  makes the latter correct to  $m + h$ . One of these operators is  $T_2$  when  $h = \lfloor m/2 \rfloor - 1$ . Since  $T_2$  limits the error in equation 7.10, the energy is correct to order  $m + \lfloor m/2 \rfloor$ .

**Example 7.2.** Props 7.1 and 7.2 allow us to compare the accuracies of CI and CC in perturbation theory. At double excitations CI and CC are both correct to first order in the wavefunction and third order in the energy. Triples yield no improvement for CI, whereas CC gains an order in both wavefunction and energy. In general, the CC wavefunction and energy improves upon the CI wavefunction and energy by  $m - \lfloor m/2 \rfloor - 1 = \lfloor (m - 1)/2 \rfloor$  orders in perturbation theory.

**Definition 7.3. Order  $p$  truncation.** If  $X$  is a polynomial in  $T_1, T_2, \dots, T_n$ , its *order  $p$  truncation*, denoted  $X^{[p]}$ , retains all terms in the polynomial with leading contributions of order  $p$  or less. This makes  $X^{[p]}$  correct to order  $p$  without isolating specific orders in the cluster operators, which may involve contributions up to infinite order.

**Example 7.3. The [T] correction.** Assuming Brillouin's theorem, we can complete the energy to fourth order using

$$t_{ab}^{ij} = \langle \Phi_{ij}^{ab} | R_0 V_c (1 + T_1 + T_2 + T_3^{[2]} + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{2} T_2^2 + \frac{1}{3!} T_1^3 + \frac{1}{2} T_1^2 T_2 + \frac{1}{4!} T_1^4) | \Phi \rangle_C \quad [2] t_{abc}^{ijk} = \langle \Phi_{ijk}^{abc} | R_0 V_c T_2 | \Phi \rangle_C \quad (7.16)$$

where the resulting energy correction is  $E_e - E_e^{\text{CCSD}} = \langle \Phi | V_c R_0 V_c T_3^{[2]} | \Phi \rangle$ . We can introduce additional infinite order contributions by noting that  $T_2 \Phi = R_0 V_c \Phi + \mathcal{O}(V_c^2)$  and that the additional terms in  $\langle \Phi | T_2^\dagger V_c T_3^{[2]} | \Phi \rangle$  are also valid energy contributions in perturbation theory. There is no risk of double counting since all of these contributions involve connected triples, which are absent in CCSD. With converged CCD or CCSD  $T_2$ -amplitudes, this defines the “brackets T” correction

$$E_{[T]} = \frac{\langle \Phi | T_2^\dagger V_c T_3^{[2]} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \left( \frac{1}{3!} \right)^2 \sum_{\substack{abc \\ ijk}} [2] t_{abc}^{ijk*} \mathcal{E}_{abc}^{ijk} [2] t_{abc}^{ijk} \quad \equiv \quad \text{diagram 1} + \text{diagram 2} + \text{diagram 3} \quad (7.17)$$

corresponding to  $\langle \Phi | T_2^\dagger V_c T_3^{[2]} | \Phi \rangle = -\langle \Phi | T_3^{[2]\dagger} H_0 T_3^{[2]} | \Phi \rangle$ . The dash-dotted line denotes an inverse resolvent line.

**Remark 7.3. CC excited states via equation-of-motion theory.** Similarity transformations preserve operator eigenvalues, so  $\bar{H}_e$  has the same spectrum as the original Hamiltonian,  $H_e$ . The corresponding eigenvalue equations

$$\bar{\mathbf{H}}_e \mathbf{r}_k = E_k \mathbf{r}_k \quad \mathbf{l}_k^\dagger \bar{\mathbf{H}}_e = \mathbf{l}_k^\dagger E_k \quad \mathbf{l}_k^* \cdot \mathbf{r}_l = \delta_{kl} \quad (7.18)$$

involve both right- and left-eigenvectors since  $\bar{\mathbf{H}}_e = \langle \Phi | (H_e \exp(T))_C | \Phi \rangle$  is non-Hermitian. These can also be written as

$$\bar{H}_e \mathcal{R}_k | \Phi \rangle = E_k \mathcal{R}_k | \Phi \rangle \quad \langle \Phi | \bar{H}_e \mathcal{L}_k = \langle \Phi | \mathcal{L}_k E_k \quad \begin{aligned} \mathcal{R}_k | \Phi \rangle &= | \Phi \rangle \cdot \mathbf{r}_k \\ \langle \Phi | \mathcal{L}_k &= \mathbf{l}_k^* \cdot \langle \Phi | \end{aligned} \quad (7.19)$$

in terms of abstract states.  $E_k$  denotes the  $k^{\text{th}}$  excitation energy, which matches the corresponding CI eigenvalue unless we truncate the Ansatz. In general, the expectation value of an observable can be determined as  $\langle \Psi_k | W | \Psi_k \rangle = \langle \Phi | \mathcal{L}_k \bar{W} \mathcal{R}_k | \Phi \rangle$ .

**Definition 7.4. The CC Lagrangian.** Assuming we have solved equation 7.9, the right eigenvector of the ground state is simply a unit vector  $\mathbf{r}_e = \langle \Phi | \Phi \rangle$ . The left ground-state eigenvector is unknown, but the biorthonormality condition in equation 7.18 tells us that its first entry equals 1. Therefore, the left and right ground-state wave operators have the form

$$\mathcal{R}_e = 1 \quad \mathcal{L}_e = 1 + \Lambda \quad \Lambda = \Lambda_1 + \dots + \Lambda_n \quad \Lambda_k \equiv \left(\frac{1}{k!}\right)^2 \lambda_{i_1 \dots i_k}^{a_1 \dots a_k} \tilde{a}_{a_1 \dots a_k}^{i_1 \dots i_k} \quad (7.20)$$

where  $\Lambda$  is a linear de-excitation operator analogous to  $C^\dagger$ . The ground-state expectation value is therefore

$$E_e = \langle \Psi_e | H_e | \Psi_e \rangle = \langle \Phi | (1 + \Lambda) \bar{H}_e | \Phi \rangle \quad (7.21)$$

which is the *coupled-cluster Lagrangian*. To see why this constitutes a Lagrangian, note that setting the  $\lambda$ -gradient equal to zero yields the CC amplitude equations:  $\langle \Phi | \bar{H}_e | \Phi \rangle = 0$ . If these are satisfied, then  $E_e = \langle \Phi | \bar{H}_e | \Phi \rangle$  gives the CC energy. Therefore, we can view the  $\lambda$  as Lagrange multipliers enforcing equation 7.9.

**Definition 7.5. The CC Lambda equations.** Setting the  $\mathbf{t}$ -gradient of the CC Lagrangian equal to zero gives

$$\langle \Phi | (1 + \Lambda) H_c \exp(T) | \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} \rangle_C \stackrel{!}{=} 0 \quad (7.22)$$

which are the CC Lambda equations.<sup>5</sup> Rearranging this equation gives an alternative, more convenient form

$$\lambda_{i_1 \dots i_k}^{a_1 \dots a_k} \mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k} = \langle \Phi | \Lambda H_0 T + (1 + \Lambda) V_c \exp(T) | \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} \rangle_C \quad (7.23)$$

which sets up the iterative procedure for determining  $\lambda_{i_1 \dots i_k}^{a_1 \dots a_k}$  from a given set of amplitudes.

**Example 7.4.** Assuming Brillouin's theorem holds, the CCD lambda equations are as follows.

$$\begin{aligned} \lambda_{ij}^{ab} \mathcal{E}_{ab}^{ij} &= \langle \Phi | V_c + \Lambda_2 V_c + \Lambda_2 V_c T_2 | \Phi_{ij}^{ab} \rangle_C \\ &= \text{[Feynman diagrams]} \\ &= \bar{g}_{ij}^{ab} + \frac{1}{2} \lambda_{ij}^{cd} \bar{g}_{cd}^{ab} + \frac{1}{2} \lambda_{kl}^{ab} \bar{g}_{ij}^{kl} + P_{(i/j)}^{(a/b)} \lambda_{ik}^{ac} \bar{g}_{cj}^{kb} - \frac{1}{2} P_{(i/j)} \lambda_{ik}^{ab} t_{cd}^{kl} \bar{g}_{jl}^{cd} - \frac{1}{2} P^{(a/b)} \lambda_{ij}^{ac} t_{kl}^{bd} \bar{g}_{kl}^{bd} \\ &\quad + \frac{1}{2^2} \lambda_{ij}^{cd} t_{kl}^{ab} \bar{g}_{kl}^{ab} + P_{(i/j)}^{(a/b)} \lambda_{ik}^{ac} t_{cd}^{kl} \bar{g}_{jl}^{bd} + \frac{1}{2^2} \bar{g}_{ij}^{cd} t_{cd}^{kl} \lambda_{kl}^{ab} - \frac{1}{2} P_{(i/j)} \bar{g}_{ik}^{ab} t_{cd}^{kl} \lambda_{jl}^{cd} - \frac{1}{2} P^{(a/b)} \bar{g}_{ij}^{ac} t_{cd}^{kl} \lambda_{kl}^{bd} \end{aligned}$$

**Remark 7.4. The Hellmann-Feynman theorem.** Variational methods satisfy the *Hellmann-Feynman theorem*, which says that the derivative of the energy with respect to a perturbation parameter  $\xi$  is independent of the first-order wavefunction response.<sup>6</sup> This follows from the fact that the parameter gradient vanishes for variational methods.

$$\left. \frac{dE_e(\xi)}{d\xi} \right|_0 = \left. \frac{\partial E_e(\xi)}{\partial \xi} \right|_0 + \cancel{\left. \frac{\partial E_e(\xi)}{\partial \mathbf{c}} \right|_0} \cdot \left. \frac{d\mathbf{c}(\xi)}{d\xi} \right|_0 = \langle \Psi | \left. \frac{\partial H(\xi)}{\partial \xi} \right|_0 | \Psi \rangle \quad (7.24)$$

This is not the case for non-variational methods, but the CC Lagrangian satisfies a *generalized Hellmann-Feynman theorem*

$$\left. \frac{d\mathcal{L}(\xi)}{d\xi} \right|_0 = \left. \frac{\partial \mathcal{L}(\xi)}{\partial \xi} \right|_0 + \cancel{\left. \frac{\partial \mathcal{L}(\xi)}{\partial \mathbf{t}} \right|_0} \cdot \left. \frac{d\mathbf{t}(\xi)}{d\xi} \right|_0 + \cancel{\left. \frac{\partial \mathcal{L}(\xi)}{\partial \boldsymbol{\lambda}} \right|_0} \cdot \left. \frac{d\boldsymbol{\lambda}(\xi)}{d\xi} \right|_0 = \langle \Phi | (1 + \Lambda) \left. \frac{\partial H_e(\xi)}{\partial \xi} \right|_0 \exp(T) | \Phi \rangle_C \quad (7.25)$$

which follows from the fact that  $\mathcal{L}$  is stationary in the amplitudes  $\mathbf{t}$  and their corresponding Lagrangian multipliers,  $\boldsymbol{\lambda}$ .

<sup>5</sup>The subscript C here denotes that  $H_c$  is connected both to the ket and to the  $T$  operators.

<sup>6</sup>By “first-order wavefunction response”, we mean  $\Psi^{(1)} = \left. \frac{d\Psi(\xi)}{d\xi} \right|_0 = \left. \frac{\partial \Psi}{\partial \mathbf{c}} \cdot \frac{d\mathbf{c}(\xi)}{d\xi} \right|_0$ . Note this  $\Psi^{(1)}$  is generally not the first-order correction to the Møller-Plesset set Hamiltonian. Instead, we are usually interested in the energy derivative with respect to a deviation from the full Born-Oppenheimer electronic Hamiltonian,  $H(\xi) = H_e + \sum_{m=1}^{\infty} \xi^m H^{(m)}$ , controlled by a strength parameter  $\xi$ . For example,  $\xi$  might be a geometric parameter or a strength parameter for an electromagnetic field strength.

**Remark 7.5. Löwdin partitioning.** For a given truncation level  $m$ , let us refer to the span of  $\Phi_i = [\Phi \Phi_1 \cdots \Phi_m]$  as the *internal space* and that of  $\Phi_e = [\Phi_{m+1} \cdots \Phi_n]$  as the *external space*, so that  $|\Phi_i\rangle\langle\Phi_i| + |\Phi_e\rangle\langle\Phi_e| = 1_n$ . In the coordinate space over  $\Phi$  this reads  $\mathbf{1}_i + \mathbf{1}_e = \mathbf{1}$ , in terms of the following projection matrices.

$$\mathbf{1}_i \equiv \langle\Phi|\Phi_i\rangle\langle\Phi_i|\Phi\rangle = \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix} \quad \mathbf{1}_e \equiv \langle\Phi|\Phi_e\rangle\langle\Phi_e|\Phi\rangle = \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{bmatrix} \quad (7.26)$$

This allows us to write vector decompositions as  $\mathbf{c} = \mathbf{c}_i + \mathbf{c}_e$  and matrix decompositions as  $\mathbf{H} = \mathbf{H}_{ii} + \mathbf{H}_{ie} + \mathbf{H}_{ei} + \mathbf{H}_{ee}$  in terms of  $\mathbf{c}_x \equiv \mathbf{1}_x \mathbf{c}$  and  $\mathbf{H}_{xy} \equiv \mathbf{1}_x \mathbf{H} \mathbf{1}_y$ .<sup>7</sup> Finally, note that the *external space resolvent*  $\mathbf{R}_{ee} \equiv (E - \mathbf{H})^{-1}|_e$  satisfies

$$\mathbf{R}_{ee}(E - \mathbf{H}) = -\mathbf{R}_{ee}\mathbf{H}_{ei} + \mathbf{1}_e \quad (E - \mathbf{H})\mathbf{R}_{ee} = -\mathbf{H}_{ie}\mathbf{R}_{ee} + \mathbf{1}_e \quad (7.27)$$

and operating the left equation on  $\mathbf{c}$  gives zero due to the Schrödinger equation, implying that  $\mathbf{c}_e = \mathbf{R}_{ee}\mathbf{H}_{ei}\mathbf{c}_i$ . Projecting the Schrödinger equation by  $\mathbf{1}_i$  and substituting in this result then leads to the following.

$$(\mathbf{H}_{ii} + \mathbf{V}_{ii})\mathbf{c}_i = E\mathbf{c}_i \quad \mathbf{V}_{ii} \equiv \mathbf{H}_{ie}\mathbf{R}_{ee}\mathbf{H}_{ei} \quad (7.28)$$

which reduces the Schrödinger equation on  $\mathcal{F}_n$  to an effective Schrödinger equation in the internal space. This gives

$$E = \frac{\mathbf{c}_i^\dagger (\mathbf{H}_{ii} + \mathbf{V}_{ii}) \mathbf{c}_i}{\mathbf{c}_i^* \cdot \mathbf{c}_i} \quad (7.29)$$

as an expression for the exact energy in terms of the internal-space coefficients. Let us refer to this energy expression as the *Löwdin functional*. The Löwdin functional is the central equation the *Löwdin partitioning* method, which can be used to eliminate the leading error incurred by truncating the excitation level.

**Remark 7.6. Löwdin partitioning for CC.** The Löwdin functional readily generalizes to the non-Hermitian CC effective Schrödinger equations as follows. Assuming biorthonormality for the left and right eigenvectors, we have

$$E = \frac{\mathbf{l}_i^\dagger (\overline{\mathbf{H}}_{ii} + \mathbf{V}_{ii}) \mathbf{r}_i}{\mathbf{l}_i^* \cdot \mathbf{r}_i} = \langle\Phi|\mathcal{L}\overline{\mathcal{H}}\mathcal{R}|\Phi\rangle + \langle\Phi|\mathcal{L}\overline{\mathcal{H}}|\Phi_e\rangle\langle\Phi_e|E - \overline{\mathcal{H}}|\Phi_e\rangle^{-1}\langle\Phi_e|\overline{\mathcal{H}}\mathcal{R}|\Phi\rangle \quad (7.30)$$

which leads to the following correction for the ground-state correlation energy

$$E_c - E_c^{\text{CCSD}\cdots m} = \langle\Phi|\Lambda\overline{\mathcal{H}}_c|\Phi_e\rangle\langle\Phi_e|E_c - \overline{\mathcal{H}}_c|\Phi_e\rangle^{-1}\langle\Phi_e|\overline{\mathcal{V}}_c|\Phi\rangle \quad (7.31)$$

where we have substituted in equation 7.20 for the ground-state wave operators and omitted any vanishing contributions. The leftmost factor on the right requires  $\overline{\mathcal{H}}_c$  to have an excitation level of at least  $-1$  in order to form complete contraction between  $\Lambda_m$  and  $\Phi_{m+1}$ , so its lowest-order contribution is  $\overline{\mathcal{H}}_c^{(1)} = V_c$ . The lowest-order contribution to the middle factor enters in zeroth order, which evaluates to  $-\langle\Phi_e|\langle\Phi_e|\overline{\mathcal{H}}_c^{(0)}|\Phi_e\rangle^{-1}\langle\Phi_e| = \langle\Phi_e|\langle\Phi_e|R_0$ . Finally, the rightmost factor requires  $\overline{\mathcal{H}}_c$  to have an excitation level of  $m+1$  in order to fully contract  $\Phi_{m+1}$  on the left. For  $m \geq 2$  the leading contribution of this excitation level will always be  $\overline{\mathcal{V}}_c^{[m]} = (V_c T_m)_C$ . Combining these results leads to

$$E_{(m+1)\Lambda} = \langle\Phi|(\Lambda_{m-1} + \Lambda_m)V_c T_{m+1}^{[m]}|\Phi\rangle \quad \mathbf{t}_{m+1}^{[m]} = \langle\Phi|R_0 V_c T_m|\Phi\rangle_C \quad (7.32)$$

where we have made use of the relation  $\Phi_k \cdot \mathbf{t}_k = T_k \Phi$ . This defines the  $(m+1)_\Lambda$  correction to  $\text{CCSD}\cdots m$ , generates a hierarchy of perturbatively-corrected CC methods:  $\text{CCSD}(T)_\Lambda$ ,  $\text{CCSDT}(Q)_\Lambda$ , etc.

**Example 7.5. The (T) and (Q) corrections.** Given that the leading contributions to  $\Lambda_1$ ,  $\Lambda_2$ , and  $\Lambda_k$  are given by

$$^{(2)}\lambda_i^a = \langle\Phi|\Lambda_2^{(1)}V_c R_0|\Phi_i^a\rangle = ^{(2)}t_a^{i*} \quad ^{(1)}\lambda_{ij}^{ab} = \langle\Phi|V_c R_0|\Phi_{ij}^{ab}\rangle = ^{(1)}t_{ab}^{ij*} \quad ^{(2)}\lambda_{ijk}^{abc} = \langle\Phi|\Lambda_2^{(1)}V_c R_0|\Phi_{ijk}^{abc}\rangle = ^{(2)}\lambda_{abc}^{ijk*} \quad (7.33)$$

the approximation  $\Lambda_k \approx T_k^\dagger$  for  $k < 4$  will capture the leading contributions to equation 7.32 as well as many higher-order ones. The resulting “*parentheses T*” and “*parentheses Q*” corrections have the advantage of being non-iterative.

$$E_{(T)} = \langle\Phi|T_1^\dagger V_c T_3^{[2]}|\Phi\rangle + E_{[T]} \quad E_{(Q)} = \langle\Phi|(T_2^\dagger + T_3^\dagger)V_c T_4^{[3]}|\Phi\rangle \quad (7.34)$$

The new term in the triples correction evaluates as follows.

$$E_{(T)} = E_{[T]} + \text{diagram} \quad \text{diagram} \equiv \text{diagram} = \frac{1}{2^2} \sum_{\substack{abc \\ ijk}} t_a^i \bar{g}_{bc}^{jk} \bar{a}_{ijk}^{abc} \quad (7.35)$$

The CCSD(T) method was originally justified on different grounds, but its truly remarkable performance is difficult to understand with ordinary perturbation theory. Several other fifth-order terms could just as easily be included. Löwdin partitioning shows that  $E_{(T)}$  is the leading correction to the error incurred by truncating the configuration space at doubles.

<sup>7</sup>Note that I am dropping the subscript  $e$  on the Hamiltonian and energy here to avoid confusion with  $e$ .