

## 5 Traditional coupled-cluster theory

**Definition 5.1. Traditional coupled-cluster theory.** A wave operator maps a determinant into a correlated wavefunction,  $\Psi = \Omega\Phi$ . The *coupled-cluster Ansatz* is characterized by an exponential parametrization of the wave operator.

$$H_c\Psi_{CC} = E_c\Psi_{CC} \quad \Psi_{CC} \equiv \exp(T)\Phi \quad T \equiv T_1 + T_2 + \cdots + T_n \quad T_k \equiv \left(\frac{1}{k!}\right)^2 t_{a_1 \dots a_k}^{i_1 \dots i_k} \tilde{a}_{i_1 \dots i_k}^{a_1 \dots a_k} \quad (5.1)$$

The coupled-cluster Schrödinger equation can be projected onto the determinant basis to arrive at a series of equations

$$\langle \Phi | H_c | \Psi_{CC} \rangle = E_c \quad \langle \Phi_{ij \dots}^{ab \dots} | H_c | \Psi_{CC} \rangle = E_c t_{ab \dots}^{ij \dots} \quad (5.2)$$

which specify the coupled-cluster energy and the *amplitudes*,  $t_{ab \dots}^{ij \dots}$ . A different approach, known as *traditional coupled-cluster (TCC) theory*, first multiplies the Schrödinger equation on the left by the inverse of the wave operator

$$\bar{H}_c \Phi = E_c \Phi \quad \bar{H}_c \equiv \exp(-T) H_c \exp(T) \quad (5.3)$$

to define an *effective Hamiltonian*,  $\bar{H}_c$ . The eigenvalue of this similarity-transformed<sup>1</sup> Hamiltonian is the exact correlation energy,  $E_c$ , but its eigenstate is the reference determinant,  $\Phi$ , rather than the correlated wavefunction. Note that, unlike the true Hamiltonian,  $\bar{H}_c$  is non-Hermitian. Projection onto the determinant basis yields energy and amplitude equations

$$\langle \Phi | \bar{H}_c | \Phi \rangle = E_c \quad \langle \Phi_{ij \dots}^{ab \dots} | \bar{H}_c | \Phi \rangle = 0 \quad (5.4)$$

which look similar to eq 5.2, except that the right-hand side of the amplitude equations is now zero. The next few results show that the TCC similarity transformation removes disconnected terms in eq 5.2, of which  $E_c t_{ab \dots}^{ij \dots}$  is an example.

**Theorem 5.1. The Hausdorff Expansion.**  $e^{-X} Y e^X = \sum_{n=0}^{\infty} \frac{1}{n!} [\cdot, X]^n(Y)$ <sup>2</sup>

Proof: This follows from  $\frac{\partial^n}{\partial \lambda^n} e^{-\lambda X} Y e^{\lambda X} = [\cdot, X]^n(e^{-\lambda X} Y e^{\lambda X})$ , which we will prove by induction. This is trivially true for  $n = 0$ . Assuming it holds for  $n$ , the following shows that it also holds for  $n + 1$ , completing the induction.

$$\frac{\partial^{n+1}}{\partial \lambda^{n+1}} e^{-\lambda X} Y e^{\lambda X} = [\cdot, X]^n \left( \frac{\partial}{\partial \lambda} e^{-\lambda X} Y e^{\lambda X} \right) = [\cdot, X]^n (e^{-\lambda X} Y e^{\lambda X} X - X e^{-\lambda X} Y e^{\lambda X}) = [\cdot, X]^{n+1} (e^{-\lambda X} Y e^{\lambda X})$$

Substituting this result into a Taylor expansion of  $e^{-\lambda X} Y e^{\lambda X}$  about  $\lambda = 0$  evaluated at  $\lambda = 1$  completes the proof.

**Example 5.1.** The Hausdorff expansion can be used to express the TCC effective Hamiltonian in powers of  $T$ .

$$\bar{H}_c = \exp(-T) H_c \exp(T) = H_c + [H_c, T] + \frac{1}{2!} [[H_c, T], T] + \frac{1}{3!} [[[H_c, T], T], T] + \frac{1}{4!} [[[[H_c, T], T], T], T] + \cdots$$

This expansion can be further simplified by analyzing the commutators with  $T$  using Wick's theorem.

**Proposition 5.1.** If  $Q$  and  $Q'$  are normal ordered and one of them has an even operator count,  $[Q, Q'] = : \overline{Q} Q' : - : \overline{Q'} Q :$ .

Proof: By Wick's theorem,  $QQ' - Q'Q = :QQ': + : \overline{Q} Q' : - : Q' Q : - : \overline{Q'} Q :$ . The proposition follows from the fact that  $:QQ': = :Q'Q:$  when one of the strings contains an even number of operators.

**Corollary 5.1.** TCC similarity-transformed operators,  $\bar{W} \equiv \exp(-T) W \exp(T)$ , can be evaluated as  $\bar{W} = (W \exp(T))_C$ , where the subscript C denotes a restriction to connected diagrams.

Proof: Prop 5.1 implies  $[W, T] = : \overline{WT} :$  and, by straightforward induction,  $[\cdot, T]^n(W) = : \overline{WTT \cdots T} : = (WT^n)_C$ , since  $T$  has no contractions with operators to its right.<sup>3</sup> Applying thm 5.1 to  $\bar{W}$  and using this result completes the proof.

**Remark 5.1.** Applying corollary 5.1 to the coupled-cluster effective Hamiltonian gives the following expansion

$$\bar{H}_c = (H_c \exp(T))_C = (H_c + H_c T + \frac{1}{2!} H_c T^2 + \frac{1}{3!} H_c T^3 + \frac{1}{4!} H_c T^4)_C$$

which ends at the fourth power because  $H_c$  is a linear combination of one- and two-particle operators, which can contract at most two and four  $T$ 's, respectively. Using this result, the energy and amplitude equations are often written as

$$\langle \Phi | H_c \exp(T) | \Phi \rangle_C = E_c \quad \langle \Phi_{ij \dots}^{ab \dots} | H_c \exp(T) | \Phi \rangle_C = 0 \quad (5.5)$$

where the subscript C on the expectation value ket is shorthand for  $\langle \Phi_{ij \dots}^{ab \dots} | (H_c \exp(T))_C | \Phi \rangle$ .

<sup>1</sup>See [https://en.wikipedia.org/wiki/Matrix\\_similarity](https://en.wikipedia.org/wiki/Matrix_similarity).

<sup>2</sup> $[\cdot, X]^n(Y)$  denotes a nested commutator,  $[\cdots [[Y, X], X] \cdots, X]$ . For  $n = 0$ , we define  $[\cdot, X]^0(Y) \equiv Y$ .

<sup>3</sup>This is easily seen from the diagram. It comes from the fact that  $T$  is composed entirely of quasi-particle creation operators.

**Notation 5.1.** The following is suggested notation for the diagonal and off-diagonal contributions to the Fock operator.

$$\begin{aligned} \otimes \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} &= \ominus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} & \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} &\equiv H_0 & \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} &\equiv f_p^q(1 - \delta_p^q)\tilde{a}_q^p \end{aligned} \quad (5.6)$$

so that  $H = E_{\text{ref}} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \sim \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array}$  is the full electronic Hamiltonian and  $V_c = \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \sim \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array}$ . Note that

$$\begin{aligned} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} &= \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \\ \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} &= \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \end{aligned}$$

where the excitation level  $\pm 1$  contributions to  $H_0$  have been omitted because its interaction tensor is diagonal.

**Remark 5.2.** It can be shown that the determinant basis forms an eigenbasis for the diagonal part of the Fock operator.<sup>4</sup>

$$H_0 \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} = \mathcal{E}_{i_1 \dots i_k}^{a_1 \dots a_k} \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} \quad H_0 \equiv f_p^p \tilde{a}_p^p \quad \mathcal{E}_{q_1 \dots q_k}^{p_1 \dots p_k} \equiv \sum_{r=1}^k f_{p_r}^{p_r} - \sum_{r=1}^k f_{q_r}^{q_r} \quad (5.7)$$

Noting that  $H_0$  is Hermitian, this implies  $\langle \Phi_{ij \dots}^{ab \dots} | H_0 \exp(T) | \Phi \rangle = \mathcal{E}_{ij \dots}^{ab \dots} \langle \Phi_{ij \dots}^{ab \dots} | \exp(T) | \Phi \rangle = \mathcal{E}_{ij \dots}^{ab \dots} t_{ab \dots}^{ij \dots}$ . This can be used to rearrange the amplitude equation in (5.5) as follows, which defines the working equations used to iteratively solve TCC.

$$t_{ab \dots}^{ij \dots} = (\mathcal{E}_{ab \dots}^{ij \dots})^{-1} \langle \Phi_{ab \dots}^{ij \dots} | V_c \exp(T) | \Phi \rangle_C \quad V_c \equiv H_c - H_0 = f_p^q(1 - \delta_p^q)\tilde{a}_q^p + \frac{1}{4}\tilde{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} \quad (5.8)$$

In Møller-Plesset perturbation theory,  $H_0$  is known the *zeroth order Hamiltonian* and  $V_c$  is the *perturbation*. These operators are also known as the *model Hamiltonian* and *fluctuation potential*, respectively.

**Definition 5.2. Excitation level.** The *excitation level* of a graph equals the net number of particles or quasi-particles it creates, divided by two. For example, the quasi-particle excitation levels of the  $T_1$ ,  $T_2$  and  $T_3$  operators are 1, 2, and 3, respectively, and that of  $\tilde{a}_{abcd}^{ijkl}$  is  $-4$ . A convenient rule for evaluating reference expectation values is that the total excitation level of a closed graph must balance out to zero.

**Example 5.2.** The excitation levels in the quasi-particle expansions of one- and two-particle operators are as follows.

$$\begin{aligned} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} &= \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \\ &\quad (0) \quad (0) \quad (+1) \quad (-1) \quad (0) \\ \\ \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} &= \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \oplus \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \\ &\quad (0) \quad (0) \quad (+1) \quad (-1) \quad (+2) \quad (0) \quad (-2) \quad (+1) \quad (-1) \quad (0) \end{aligned}$$

**Example 5.3. The CCSDTQ equations.** Truncating the cluster operator at quadruples,  $T \approx T_1 + T_2 + T_3 + T_4$ , gives the CCSDTQ approximation. The resulting singles, doubles, triples, and quadruples amplitude equations are given by

$$\begin{aligned} t_a^i &= (\mathcal{E}_a^i)^{-1} \langle \Phi_a^i | V_c (1 + T_1 + T_2 + T_3 + \frac{1}{2}T_1^2 + T_1T_2 + \frac{1}{3!}T_1^3) | \Phi \rangle_C \\ t_{ab}^{ij} &= (\mathcal{E}_{ab}^{ij})^{-1} \langle \Phi_{ab}^{ij} | V_c (1 + T_1 + T_2 + T_3 + T_4 + \frac{1}{2}T_1^2 + T_1T_2 + T_1T_3 + \frac{1}{2}T_2^2 + \frac{1}{3!}T_1^3 + \frac{1}{2}T_1^2T_2 + \frac{1}{4!}T_1^4) | \Phi \rangle_C \\ t_{abc}^{ijk} &= (\mathcal{E}_{abc}^{ijk})^{-1} \langle \Phi_{abc}^{ijk} | V_c (T_2 + T_3 + T_4 + T_1T_2 + T_1T_3 + \frac{1}{2}T_2^2 + T_1T_4 + T_2T_3 + \frac{1}{2}T_1^2T_2 + \frac{1}{2}T_1^2T_3 + \frac{1}{2}T_1T_2^2 + \frac{1}{3!}T_1^3T_2) | \Phi \rangle_C \\ t_{abcd}^{ijkl} &= (\mathcal{E}_{abcd}^{ijkl})^{-1} \langle \Phi_{abcd}^{ijkl} | V_c (T_3 + T_4 + T_1T_3 + \frac{1}{2}T_2^2 + T_1T_4 + T_2T_3 + T_2T_4 + \frac{1}{2}T_3^2 + \frac{1}{2}T_1^2T_3 + \frac{1}{2}T_1T_2^2 + \frac{1}{2}T_1^2T_4 \\ &\quad + T_1T_2T_3 + \frac{1}{3!}T_2^3 + \frac{1}{3!}T_1^3T_3 + \frac{1}{2!2!}T_1^2T_2^2) | \Phi \rangle_C \end{aligned}$$

where several contributions to  $\exp(T_1 + T_2 + T_3 + T_4)$  have been omitted either because the excitation levels do not balance or because they require one of the cluster operators to be disconnected from the Hamiltonian.

<sup>4</sup>The proof is as follows. First, note that  $a_p^p \Phi_\sigma = n_p^\sigma \Phi_\sigma$ , where  $n_p^\sigma$  is the occupation of  $\psi_p$  in  $\Phi_\sigma$ . By Wick's theorem,  $a_p^p = \tilde{a}_p^p + n_p^{\text{ref}}$ , where  $n_p^{\text{ref}}$  denotes the occupation of  $\psi_p$  in  $\Phi$ . Therefore,  $\tilde{a}_p^p \Phi_\sigma = (n_p^\sigma - n_p^{\text{ref}}) \Phi_\sigma$  and  $H_0 \Phi_\sigma = \left( \sum_{p \in \Phi_\sigma} f_p^p - \sum_{p \in \Phi} f_p^p \right) \Phi_\sigma$ .

**Definition 5.3. Isomorphism.** For any invertible map  $S : \bar{V} \rightarrow V$ , we can express operators and vectors on  $V$  as

$$A = S\bar{A}S^{-1} \quad |v\rangle = S|\bar{v}\rangle \quad \langle v| = \langle \bar{v}|S^{-1} \quad (5.9)$$

in terms of operators and vectors on  $\bar{V}$ . Note that the transformed bra and ket,  $\langle \bar{v}|$  and  $|\bar{v}\rangle$ , corresponding to  $v$  are not adjoints unless the transformation is unitary,  $S^{-1} = S^\dagger$ . The similarity-transformed operator  $\bar{A}$  retains all of the basis-independent properties of  $A$ , such as its trace, determinant, and eigenvalue spectrum, and its matrix elements satisfy  $\langle \bar{v}|\bar{A}|\bar{v}'\rangle = \langle v|A|v'\rangle$ . More broadly, the invertibility of  $S$  implies an *isomorphism* between  $V$  and  $\bar{V}$ , such that all statements about  $V$  are in one-to-one correspondence with statements about  $\bar{V}$  under this transformation.

**Remark 5.3.** Since exponential operators are automatically invertible, the TCC wave operator defines a similarity transformation of Fock space into itself. The image of the Schrödinger equation under this transformation is as follows

$$\begin{aligned} \bar{H}|\bar{\Psi}_k\rangle &= E_k|\bar{\Psi}_k\rangle & \langle \bar{\Psi}_k|\bar{H} &= \langle \bar{\Psi}_k|E_k & \bar{H} &= \exp(-T)H\exp(T) \\ & & & & |\bar{\Psi}_k\rangle &= \exp(-T)|\Psi_k\rangle \\ & & & & \langle \bar{\Psi}_k| &= \langle \Psi_k|\exp(T) \end{aligned} \quad (5.10)$$

where the  $k^{\text{th}}$  left and right eigenstates are not adjoints because  $\exp(T)$  is inherently non-unitary. In TCC,  $T$  is determined by the requirement that the ground-state right eigenvector of  $\bar{H}$  be the reference determinant,  $|\bar{\Psi}_0\rangle \stackrel{!}{=} |\Phi\rangle$ .

**Definition 5.4. Equation-of-motion coupled-cluster theory.** Expanding the left and right eigenstates of  $\bar{H}$  in the determinant basis leads to the *equation-of-motion (EOM) coupled-cluster equations*

$$\begin{aligned} \bar{H}^k R|\Phi\rangle &= E_k^k R|\Phi\rangle & R &= R_0 + R_1 + \cdots + R_n & \langle \Phi|^k L^l R|\Phi\rangle &\stackrel{!}{=} \delta_{kl} \\ \langle \Phi|^k L \bar{H} &= \langle \Phi|^k L E_k & L &= L_0 + L_1 + \cdots + L_n \end{aligned} \quad (5.11)$$

which are analogous to the configuration interaction eigenvalue equation,  $^k R$  and  $^k L$  being linear excitation and de-excitation operators analogous to  $C$  and  $C^\dagger$ . The condition on the right indicates that left and right eigenstates are chosen to form a *biorthonormal system* by normalizing the overlap of the  $k^{\text{th}}$  left and right eigenfunctions to equal one. Observable expectation values are given by  $\langle \Psi_k|W|\Psi_k\rangle = \langle \Phi|^k L \bar{W}^k R|\Phi\rangle$  in terms of left and right EOM coefficients. Transition matrix elements are given by  $\langle \Psi_k|W|\Psi_l\rangle = \langle \Phi|^k L \bar{W}^l R|\Phi\rangle$ .

**Definition 5.5. The coupled-cluster Lagrangian.** The ground-state TCC equations are equivalent to requiring  $^0 R = 1$ , which implies  $^0 L_0 = 1$  from the biorthonormality condition. Therefore, the ground-state left eigenvector has the form

$$^0 L = 1 + \Lambda \quad \Lambda = \Lambda_1 + \cdots + \Lambda_n \quad \Lambda_k \equiv \left(\frac{1}{k!}\right)^2 \lambda_{i_1 \dots i_k}^{a_1 \dots a_k} \tilde{a}_{a_1 \dots a_k}^{i_1 \dots i_k} \quad (5.12)$$

and the ground-state energy can be written as follows, in an expression known as the *coupled-cluster Lagrangian*.

$$\langle \Psi_0|H|\Psi_0\rangle = \langle \Phi|(1 + \Lambda)\bar{H}|\Phi\rangle \equiv \mathcal{L}(\mathbf{t}, \boldsymbol{\lambda}) \quad (5.13)$$

To see why this constitutes a Lagrangian, note that setting its gradient with respect to  $\lambda_{i_1 \dots i_k}^{a_1 \dots a_k}$  equal to zero yields the TCC amplitude equations of eq 5.4. If these are satisfied, the  $\lambda$ -dependent part of the equation vanishes and the Lagrangian returns the coupled-cluster energy:  $\langle \Phi|\bar{H}|\Phi\rangle = E$ . Therefore, the  $\lambda$  coefficients can be viewed as Lagrange multipliers enforcing the TCC amplitude equations as a constraint.

**Definition 5.6. The coupled-cluster lambda equations.** Setting the gradient of  $\mathcal{L}$  with respect to  $t_{a_1 \dots a_k}^{i_1 \dots i_k}$  equal to zero gives the *coupled-cluster lambda equations*, which determine the Lagrange multipliers.

$$\langle \Phi|(1 + \Lambda)H_c \exp(T)|\Phi_{i_1 \dots i_k}^{a_1 \dots a_k}\rangle_C \stackrel{!}{=} 0 \quad (5.14)$$

The subscript C now denotes that  $H_c$  is connected both to the ket and to the  $T$  operators. This can be rearranged as<sup>5</sup>

$$\lambda_{i_1 \dots i_k}^{a_1 \dots a_k} = (\mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k})^{-1} \langle \Phi|(1 + \Lambda)V_c \exp(T)|\Phi_{i_1 \dots i_k}^{a_1 \dots a_k}\rangle_C \quad (5.15)$$

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.

<sup>5</sup>Note that  $\langle \Phi|\Lambda H_0 T^p|\Phi_{i_1 \dots i_k}^{a_1 \dots a_k}\rangle_C = 0$  for  $p \geq 1$ , since the model Hamiltonian can only connect to one operator on either side.

**Example 5.4. The CCSD lambda equations.** Truncating the wave operator at doubles,  $T \approx T_1 + T_2$ , gives the CCSD approximation. The resulting singles and doubles lambda equations are given by the following

$$\begin{aligned}\lambda_i^a &= (\mathcal{E}_a^i)^{-1} \langle \Phi | V_c (1 + T_1) + \Lambda_1 V_c (1 + T_1 + T_2 + \frac{1}{2} T_1^2) + \Lambda_2 V_c (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2) | \Phi_i^a \rangle_C \\ \lambda_{ij}^{ab} &= (\mathcal{E}_{ab}^{ij})^{-1} \langle \Phi | V_c + \Lambda_1 V_c (1 + T_1) + \Lambda_2 V_c (1 + T_1 + T_2 + \frac{1}{2} T_1^2) | \Phi_{ij}^{ab} \rangle_C\end{aligned}$$

where we have omitted any contributions to  $\exp(T_1 + T_2)$  that vanish.

**Example 5.5.** Assuming Brillouin's theorem holds, the CCD lambda equations are as follows.

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

**Remark 5.4. The Hellmann-Feynman theorem.** If the Hamiltonian depends on a parameter  $\xi$ , such as a nuclear coordinate or an electric field strength, we can express the Schrödinger equation as a function of that parameter

$$H(\xi)\Psi(\xi) = E(\xi)\Psi(\xi) \qquad \langle \Psi(\xi) | \Psi(\xi) \rangle \stackrel{!}{=} 1 \quad (5.16)$$

Then the total derivative of the energy  $E(\xi) = \langle \Psi(\xi) | H(\xi) | \Psi(\xi) \rangle$  with respect to  $\xi$  is given by the following.

$$\frac{dE(\xi)}{d\xi} = \langle \Psi(\xi) | \frac{\partial H(\xi)}{\partial \xi} | \Psi(\xi) \rangle + \cancel{\langle \frac{\partial \Psi(\xi)}{\partial \xi} | H(\xi) | \Psi(\xi) \rangle} + \cancel{\langle \Psi(\xi) | H(\xi) | \frac{\partial \Psi(\xi)}{\partial \xi} \rangle} \quad (5.17)$$

The second and third terms cancel by the *Hellmann-Feynman theorem*, which one can prove by substituting the Schrödinger equation into both terms and employing the derivative of the normalization condition with respect to  $\xi$ . In words, it says that the first derivative of the energy does not depend on the “response” of the wavefunction. More generally, for approximate methods, the wavefunction may be parametrized by a set of coefficients  $\mathbf{c}$  which are *stationary* in the sense that their energy gradient equals zero. Denoting the remaining non-stationary coordinates by  $\mathbf{p}$ , we have

$$\frac{dE(\xi)}{d\xi} = \frac{\partial E(\xi)}{\partial \xi} + \cancel{\frac{\partial E}{\partial \mathbf{c}} \cdot \frac{d\mathbf{c}}{d\xi}} + \frac{\partial E}{\partial \mathbf{p}} \cdot \frac{d\mathbf{p}}{d\xi} \qquad \frac{\partial E}{\partial \xi} = \langle \Psi(\mathbf{c}, \mathbf{p}) | \frac{\partial H(\xi)}{\partial \xi} | \Psi(\mathbf{c}, \mathbf{p}) \rangle \quad (5.18)$$

which applies to configuration interaction and other variational methods. For most methods  $\mathbf{p}$  will include parameters which determine the molecular orbital coefficients, since the shape of the Hartree-Fock orbitals depends on  $\xi$ . When  $\xi$  is a nuclear coordinate, the atomic-orbital basis functions themselves change<sup>6</sup> and we must include parameters to account for this as well. The Hellmann-Feynman theorem does not apply to TCC energy, which is not stationary in any of its parameters. However, it does apply to the coupled-cluster Lagrangian as follows.

$$\frac{d\mathcal{L}(\xi)}{d\xi} = \frac{\partial \mathcal{L}(\xi)}{\partial \xi} + \cancel{\frac{\partial \mathcal{L}}{\partial \mathbf{t}} \cdot \frac{d\mathbf{t}}{d\xi}} + \cancel{\frac{\partial \mathcal{L}}{\partial \boldsymbol{\lambda}} \cdot \frac{d\boldsymbol{\lambda}}{d\xi}} + \frac{\partial \mathcal{L}}{\partial \mathbf{p}} \cdot \frac{d\mathbf{p}}{d\xi} \qquad \frac{\partial \mathcal{L}(\xi)}{\partial \xi} = \langle \Phi(\mathbf{p}) | (1 + \Lambda) \frac{\partial H(\xi)}{\partial \xi} \exp(T) | \Phi(\mathbf{p}) \rangle_C \quad (5.19)$$

This is known as the *generalized Hellmann-Feynman theorem* for coupled-cluster theory. Note that one must solve both the amplitude equations and the lambda equations in order to evaluate the equation on the right.

<sup>6</sup>The parameters defining the basis functions are constant, but their centers of origin move with the nuclei.