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.

$$H_\mathrm{c}\Psi_\mathrm{CC} = E_\mathrm{c}\Psi_\mathrm{CC} \qquad \Psi_\mathrm{CC} \equiv \exp(T)\Phi \qquad T \equiv T_1 + T_2 + \cdots + T_n \qquad T_k \equiv (\tfrac{1}{k!})^2 t^{i_1\cdots i_k}_{a_1\cdots a_k}\, \tilde{a}^{a_1\cdots a_k}_{i_1\cdots i_k} \tag{5.1}$$

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

$$\langle\Phi|H_\mathrm{c}|\Psi_\mathrm{CC}\rangle = E_\mathrm{c} \qquad \langle\Phi^{ab\cdots}_{ij\cdots}|H_\mathrm{c}|\Psi_\mathrm{CC}\rangle = E_\mathrm{c}\langle\Phi^{ab\cdots}_{ij\cdots}|\Psi_\mathrm{CC}\rangle \tag{5.2}$$

which specify the coupled-cluster energy and the *amplitudes*, $t^{ij\cdots}_{ab\cdots}$. 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

$$\overline{H}_\mathrm{c}\Phi = E_\mathrm{c}\Phi \qquad \overline{H}_\mathrm{c} \equiv \exp(-T)H_\mathrm{c}\exp(T) \tag{5.3}$$

to define an *effective Hamiltonian*, $\overline{H}_\mathrm{c}$. The eigenvalue of this similarity-transformed[1] Hamiltonian is the exact correlation energy, E_c, but its eigenstate is the reference determinant, Φ, rather than the correlated wavefunction. Note that, unlike the true Hamiltonian, $\overline{H}_\mathrm{c}$ is non-Hermitian. Projection onto the determinant basis yields energy and amplitude equations

$$\langle\Phi|\overline{H}_\mathrm{c}|\Phi\rangle = E_\mathrm{c} \qquad \langle\Phi^{ab\cdots}_{ij\cdots}|\overline{H}_\mathrm{c}|\Phi\rangle = 0 \tag{5.4}$$

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 $E_\mathrm{c}t^{ij\cdots}_{ab\cdots}$ is an example.

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

Proof: This follows from $\frac{\partial^n}{\partial\lambda^n}e^{-\lambda X}Ye^{\lambda X} = [\,\cdot\,,X]^n(e^{-\lambda X}Ye^{\lambda X})$, 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.

$$\tfrac{\partial^{n+1}}{\partial\lambda^{n+1}}e^{-\lambda X}Ye^{\lambda X} = [\,\cdot\,,X]^n(\tfrac{\partial}{\partial\lambda}e^{-\lambda X}Ye^{\lambda X}) = [\,\cdot\,,X]^n(e^{-\lambda X}Ye^{\lambda X}X - Xe^{-\lambda X}Ye^{\lambda X}) = [\,\cdot\,,X]^{n+1}(e^{-\lambda X}Ye^{\lambda X})$$

Substituting this result into a Taylor expansion of $e^{-\lambda X}Ye^{\lambda X}$ 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.

$$\overline{H}_\mathrm{c} = \exp(-T)H_\mathrm{c}\exp(T) = H_\mathrm{c} + [H_\mathrm{c},T] + \tfrac{1}{2!}[[H_\mathrm{c},T],T] + \tfrac{1}{3!}[[[H_\mathrm{c},T],T],T] + \tfrac{1}{4!}[[[[H_\mathrm{c},T],T],T],T] + \cdots$$

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,* $[Q,Q'] = \colon\overbracket{QQ'}\colon - \colon\overbracket{Q'Q}\colon$.

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

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

Proof: Prop 5.1 implies $[W,T] = \colon\overbracket{WT}\colon$ and, by straightforward induction, $[\,\cdot\,,T]^n(W) = \colon\overbracket{W\overbracket{T\overbracket{T\cdots T}}}\colon = (WT^n)_\mathrm{C}$, since T has no contractions with operators to its right.[3] Applying thm 5.1 to $\overline{W}$ and using this result completes the proof.

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

$$\overline{H}_\mathrm{c} = (H_\mathrm{c}\exp(T))_\mathrm{C} = (H_\mathrm{c} + H_\mathrm{c}T + \tfrac{1}{2!}H_\mathrm{c}T^2 + \tfrac{1}{3!}H_\mathrm{c}T^3 + \tfrac{1}{4!}H_\mathrm{c}T^4)_\mathrm{C}$$

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

$$\langle\Phi|H_\mathrm{c}\exp(T)|\Phi\rangle_\mathrm{C} = E_\mathrm{c} \qquad \langle\Phi^{ab\cdots}_{ij\cdots}|H_\mathrm{c}\exp(T)|\Phi\rangle_\mathrm{C} = 0 \tag{5.5}$$

where the subscript C on the expectation value ket is shorthand for $\langle\Phi^{ab\cdots}_{ij\cdots}|(H_\mathrm{c}\exp(T))_\mathrm{C}|\Phi\rangle$.

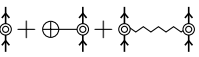
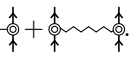
[1] See `https://en.wikipedia.org/wiki/Matrix_similarity`.

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

[3] 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.

(5.6)

so that $H = E_{\text{ref}} +$  is the full electronic Hamiltonian and $V_{\text{c}} =$  . Note that

where the excitation level ± 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.[4]

$$H_0 \Phi^{a_1 \cdots a_k}_{i_1 \cdots i_k} = \mathcal{E}^{a_1 \cdots a_k}_{i_1 \cdots i_k} \Phi^{a_1 \cdots a_k}_{i_1 \cdots i_k} \qquad H_0 \equiv f^p_p \tilde{a}^p_p \qquad \mathcal{E}^{p_1 \cdots p_k}_{q_1 \cdots q_k} \equiv \sum_{r=1}^{k} f^{p_r}_{p_r} - \sum_{r=1}^{k} f^{q_r}_{q_r} \tag{5.7}$$

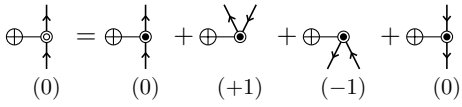
Noting that H_0 is Hermitian, this implies $\langle \Phi^{ab\cdots}_{ij\cdots} | H_0\, T | \Phi \rangle = \mathcal{E}^{ab\cdots}_{ij\cdots} \langle \Phi^{ab\cdots}_{ij\cdots} | T | \Phi \rangle = \mathcal{E}^{ab\cdots}_{ij\cdots} t^{ij\cdots}_{ab\cdots}$. This can be used to rearrange the amplitude equation in (5.5) as follows, which defines the working equations used to iteratively solve TCC.[5]

$$t^{ij\cdots}_{ab\cdots} = (\mathcal{E}^{ij\cdots}_{ab\cdots})^{-1} \langle \Phi^{ij\cdots}_{ab\cdots} | V_{\text{c}} \exp(T) | \Phi \rangle_{\text{C}} \qquad V_{\text{c}} \equiv H_{\text{c}} - H_0 = f^q_p (1 - \delta^q_p) \tilde{a}^p_q + \tfrac{1}{4} \overline{g}^{rs}_{pq} \tilde{a}^{pq}_{rs} \tag{5.8}$$

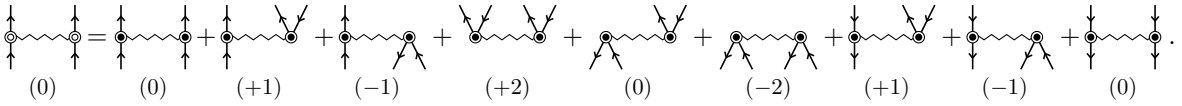
In Møller-Plesset perturbation theory, H_0 is known the *zeroth order Hamiltonian* and V_{c} is the *perturbation*. These operators are also known as the *model Hamiltonian* and *fluctuation potential*, respectively.

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 $\tilde{a}^{ijkl}_{abcd}$ 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.



(0) (0) (+1) (−1) (0)



(0) (0) (+1) (−1) (+2) (0) (−2) (+1) (−1) (0)

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

$$\begin{aligned}
t^i_a &= (\mathcal{E}^i_a)^{-1} \langle \Phi^a_i | V_{\text{c}} (1 + T_1 + T_2 + T_3 + \tfrac{1}{2} T_1^2 + T_1 T_2 + \tfrac{1}{3!} T_1^3) | \Phi \rangle_{\text{C}} \\
t^{ij}_{ab} &= (\mathcal{E}^{ij}_{ab})^{-1} \langle \Phi^{ab}_{ij} | V_{\text{c}} (1 + T_1 + T_2 + T_3 + T_4 + \tfrac{1}{2} T_1^2 + T_1 T_2 + T_1 T_3 + \tfrac{1}{2} T_2^2 + \tfrac{1}{3!} T_1^3 + \tfrac{1}{2} T_1^2 T_2 + \tfrac{1}{4!} T_1^4) | \Phi \rangle_{\text{C}} \\
t^{ijk}_{abc} &= (\mathcal{E}^{ijk}_{abc})^{-1} \langle \Phi^{abc}_{ijk} | V_{\text{c}} (T_2 + T_3 + T_4 + T_1 T_2 + T_1 T_3 + \tfrac{1}{2} T_2^2 + T_1 T_4 + T_2 T_3 + \tfrac{1}{2} T_1^2 T_2 + \tfrac{1}{2} T_1^2 T_3 + \tfrac{1}{2} T_1 T_2^2 + \tfrac{1}{3!} T_1^3 T_2) | \Phi \rangle_{\text{C}} \\
t^{ijkl}_{abcd} &= (\mathcal{E}^{ijkl}_{abcd})^{-1} \langle \Phi^{abcd}_{ijkl} | V_{\text{c}} (T_3 + T_4 + T_1 T_3 + \tfrac{1}{2} T_2^2 + T_1 T_4 + T_2 T_3 + T_2 T_4 + \tfrac{1}{2} T_3^2 + \tfrac{1}{2} T_1^2 T_3 + \tfrac{1}{2} T_1 T_2^2 + \tfrac{1}{2} T_1^2 T_4 \\
&\qquad + T_1 T_2 T_3 + \tfrac{1}{3!} T_2^3 + \tfrac{1}{3!} T_1^3 T_3 + \tfrac{1}{2!2!} T_1^2 T_2^2) | \Phi \rangle_{\text{C}}
\end{aligned}$$

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.

[5] Note that $\langle \Phi^{ab\cdots}_{ij\cdots} | H_0 \exp(T) | \Phi \rangle_{\text{C}} = \langle \Phi^{ab\cdots}_{ij\cdots} | H_0\, T | \Phi \rangle$.

[5] The proof is as follows. First, note that $a^p_p \Phi_\sigma = n^\sigma_p \Phi_\sigma$, where n^σ_p is the occupation of ψ_p in Φ_σ. By Wick's theorem, $a^p_p = \tilde{a}^p_p + n^{\text{ref}}_p$, where n^{ref}_p denotes the occupation of ψ_p in Φ. Therefore, $\tilde{a}^p_p \Phi_\sigma = (n^\sigma_p - n^{\text{ref}}_p) \Phi_\sigma$ 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 $S : \overline{V} \to V$, we can express operators and vectors on V as

$$A = S\overline{A}S^{-1} \qquad |v\rangle = S|\overline{v}\rangle \qquad \langle v| = \langle\overline{v}|S^{-1} \tag{5.9}$$

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

$$\overline{H}|\overline{\Psi}_k\rangle = E_k|\overline{\Psi}_k\rangle \qquad \langle\overline{\Psi}_k|\overline{H} = \langle\overline{\Psi}_k|E_k \qquad \begin{array}{ll} \overline{H} & = \exp(-T)H\exp(T) \\ |\overline{\Psi}_k\rangle & = \exp(-T)|\Psi_k\rangle \\ \langle\overline{\Psi}_k| & = \langle\Psi_k|\exp(T) \end{array} \tag{5.10}$$

where the k^{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 $\overline{H}$ be the reference determinant, $|\overline{\Psi}_0\rangle \stackrel{!}{=} |\Phi\rangle$.

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

$$\begin{array}{ll} \overline{H}\,{}^kR|\Phi\rangle = E_k\,{}^kR|\Phi\rangle & R = R_0 + R_1 + \cdots + R_n \\ \langle\Phi|\,{}^kL\,\overline{H} = \langle\Phi|\,{}^kL\,E_k & L = L_0 + L_1 + \cdots + L_n \end{array} \qquad \langle\Phi|^kL\,{}^lR|\Phi\rangle \stackrel{!}{=} \delta_{kl} \tag{5.11}$$

which are analogous to the configuration interaction eigenvalue equation, ${}^kR$ and ${}^kL$ 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^{th} left and right eigenfunctions to equal one. Observable expectation values are given by $\langle\Psi_k|W|\Psi_k\rangle = \langle\Phi|^kL\,\overline{W}\,{}^kR|\Phi\rangle$ in terms of left and right EOM coefficients. Transition matrix elements are given by $\langle\Psi_k|W|\Psi_l\rangle = \langle\Phi|^kL\,\overline{W}\,{}^lR|\Phi\rangle$.

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

$${}^0L = 1 + \Lambda \qquad \Lambda = \Lambda_1 + \cdots + \Lambda_n \qquad \Lambda_k \equiv (\tfrac{1}{k!})^2\lambda^{a_1\cdots a_k}_{i_1\cdots i_k}\tilde{a}^{i_1\cdots i_k}_{a_1\cdots a_k} \tag{5.12}$$

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

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

To see why this constitutes a Lagrangian, note that setting its gradient with respect to $\lambda^{a_1\cdots a_k}_{i_1\cdots i_k}$ equal to zero yields the TCC amplitude equations of eq 5.4. If these are satisfied, the λ-dependent part of the equation vanishes and the Lagrangian returns the coupled-cluster energy: $\langle\Phi|\overline{H}|\Phi\rangle = E$. Therefore, the λ 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 $t^{i_1\cdots i_k}_{a_1\cdots a_k}$ equal to zero gives the *coupled-cluster lambda equations*, which determine the Lagrange multpliers.

$$\langle\Phi|(1+\Lambda)H_{\text{c}}\exp(T)|\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}\rangle_{\text{C}} \stackrel{!}{=} 0 \tag{5.14}$$

The subscript C now denotes that H_{c} is connected both to the ket and to the T operators. This can be rearranged as[6]

$$\lambda^{a_1\cdots a_k}_{i_1\cdots i_k} = (\mathcal{E}^{i_1\cdots i_k}_{a_1\cdots a_k})^{-1}\langle\Phi|(1+\Lambda)V_{\text{c}}\exp(T)|\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}\rangle_{\text{C}} \tag{5.15}$$

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

[6]Note that $\langle\Phi|\Lambda H_0T^p|\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}\rangle_{\text{C}} = 0$ for $p \geq 1$, since the model Hamiltonian can only connect to one operator on either side.

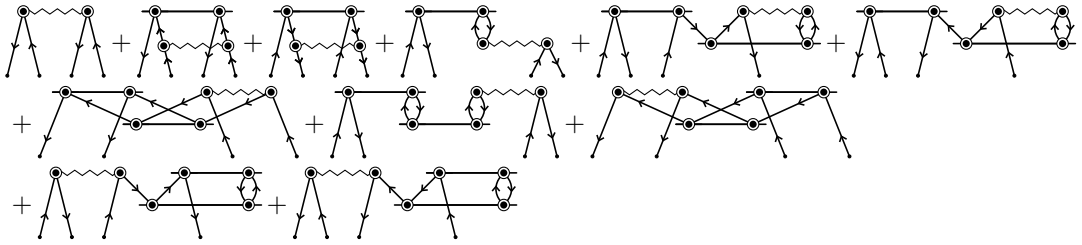
Example 5.4. ***The CCSD lambda equations.*** Truncating the wave operator at doubles, $T \approx T_1 + T_2$, gives the CCSD approximation. The resulting singles and doubles lambda equations are given by the following

$$\lambda_i^a = (\mathcal{E}_a^i)^{-1}\langle\Phi|V_{\rm c}\,(1+T_1) + \Lambda_1 V_{\rm c}\,(1+T_1+T_2+\tfrac{1}{2}T_1^2) + \Lambda_2 V_{\rm c}\,(1+T_1+T_2+\tfrac{1}{2}T_1^2+T_1T_2)|\Phi_i^a\rangle_{\rm C}$$
$$\lambda_{ij}^{ab} = (\mathcal{E}_{ab}^{ij})^{-1}\langle\Phi|V_{\rm c}\, + \Lambda_1 V_{\rm c}\,(1+T_1) + \Lambda_2 V_{\rm c}\,(1+T_1+T_2+\tfrac{1}{2}T_1^2)|\Phi_{ij}^{ab}\rangle_{\rm C}$$

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.

$$\lambda_{ij}^{ab}\mathcal{E}_{ab}^{ij} = \langle\Phi|V_{\rm c} + \Lambda_2 V_{\rm c} + \Lambda_2 V_{\rm c} T_2|\Phi_{ij}^{ab}\rangle_{\rm C}$$



$$= \overline{g}_{ij}^{ab} + \tfrac{1}{2}\lambda_{ij}^{cd}\overline{g}_{cd}^{ab} + \tfrac{1}{2}\lambda_{kl}^{ab}\overline{g}_{ij}^{kl} + P_{(i/j)}^{(a/b)}\lambda_{ik}^{ac}\overline{g}_{cj}^{kb} - \tfrac{1}{2}P_{(i/j)}\lambda_{ik}^{ab}t_{cd}^{kl}\overline{g}_{jl}^{cd} - \tfrac{1}{2}P^{(a/b)}\lambda_{ij}^{ac}t_{cd}^{kl}\overline{g}_{kl}^{bd}$$
$$+ \tfrac{1}{2^2}\lambda_{ij}^{cd}t_{cd}^{kl}\overline{g}_{kl}^{ab} + P_{(i/j)}^{(a/b)}\lambda_{ik}^{ac}t_{cd}^{kl}\overline{g}_{lj}^{db} + \tfrac{1}{2^2}\overline{g}_{ij}^{cd}t_{cd}^{kl}\lambda_{kl}^{ab} - \tfrac{1}{2}P_{(i/j)}\overline{g}_{ik}^{ab}t_{cd}^{kl}\lambda_{jl}^{cd} - \tfrac{1}{2}P^{(a/b)}\overline{g}_{ij}^{ac}t_{cd}^{kl}\lambda_{kl}^{bd}$$

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

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

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

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

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 ξ. 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

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

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 ξ. When ξ is a nuclear coordinate, the atomic-orbital basis functions themselves change[7] 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.

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

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.

[7] The parameters defining the basis functions are constant, but their centers of origin move with the nuclei.