7 Perturbative analysis

Remark 7.1. ***Perturbative analysis of the configuration interaction (CI) equations.*** The CI eigenvalue equation can be expressed as $\mathbf{H}_\mathrm{c}\,\mathbf{c} = E_\mathrm{c}\,\mathbf{c}$ in terms of the reference-shifted Hamiltonian matrix $(\mathbf{H}_\mathrm{c})_{\sigma\tau} \equiv \langle\Phi_\sigma|H_\mathrm{c}|\Phi_\tau\rangle$.[1] Separating this matrix into model-Hamiltonian and fluctuation-potential contributions gives an equivalent matrix equation

$$(-\mathbf{H}_0 + E_\mathrm{c}\mathbf{1})\,\mathbf{c} = \mathbf{V}_\mathrm{c}\,\mathbf{c} \qquad \begin{aligned}(\mathbf{H}_0)_{\sigma\tau} &\equiv \langle\Phi_\sigma|H_0|\Phi_\tau\rangle \\ (\mathbf{V}_\mathrm{c})_{\sigma\tau} &\equiv \langle\Phi_\sigma|V_\mathrm{c}|\Phi_\tau\rangle\end{aligned} \tag{7.1}$$

which provides a good starting point for a perturbative analysis of CI and for comparison to the coupled-cluster equations. The matrix elements of the model Hamiltonian are given by $\mathcal{E}_\sigma\delta_{\sigma\tau}$, so the matrix on the left is diagonal with eigenvalues of the form $\mathcal{E}^{i_1\cdots i_k}_{a_1\cdots a_k} + E_\mathrm{c}$. The first five rows of this equation can be written in terms of CI operators as follows[2]

$$\underset{(0^+)}{c_0}\ \underset{(2^+)}{E_\mathrm{c}} = \langle\Phi|\underset{(1)}{V_\mathrm{c}}(\ \underset{(1^+)}{C_1} + \underset{(1^+)}{C_2}\ )|\Phi\rangle \tag{7.2}$$

$$\underset{(1^+)}{c^i_a}\ (\underset{(0)}{\mathcal{E}^i_a} + \underset{(2^+)}{E_\mathrm{c}}) = \langle\Phi^a_i|\underset{(1)}{V_\mathrm{c}}(\ \underset{(0^+)}{C_0} + \underset{(1^+)}{C_1} + \underset{(1^+)}{C_2} + \underset{(2^+)}{C_3}\ )|\Phi\rangle \tag{7.3}$$

$$\underset{(1^+)}{c^{ij}_{ab}}\,(\underset{(0)}{\mathcal{E}^{ij}_{ab}} + \underset{(2^+)}{E_\mathrm{c}}) = \langle\Phi^{ab}_{ij}|\underset{(1)}{V_\mathrm{c}}(\ \underset{(0^+)}{C_0} + \underset{(1^+)}{C_1} + \underset{(1^+)}{C_2} + \underset{(2^+)}{C_3} + \underset{(3^+)}{C_4}\ )|\Phi\rangle \tag{7.4}$$

$$\underset{(2^+)}{c^{ijk}_{abc}}(\underset{(0)}{\mathcal{E}^{ijk}_{abc}} + \underset{(2^+)}{E_\mathrm{c}}) = \langle\Phi^{abc}_{ijk}|\underset{(1)}{V_\mathrm{c}}(\ \underset{(1^+)}{C_1} + \underset{(1^+)}{C_2} + \underset{(2^+)}{C_3} + \underset{(2^+)}{C_4} + \underset{(3^+)}{C_5}\ )|\Phi\rangle \tag{7.5}$$

$$\underset{(2^+)}{c^{ijkl}_{abcd}}(\underset{(0)}{\mathcal{E}^{ijkl}_{abcd}} + \underset{(2^+)}{E_\mathrm{c}}) = \langle\Phi^{abcd}_{ijkl}|\underset{(1)}{V_\mathrm{c}}(\ \underset{(1^+)}{C_2} + \underset{(2^+)}{C_3} + \underset{(2^+)}{C_4} + \underset{(3^+)}{C_5} + \underset{(3^+)}{C_6}\ )|\Phi\rangle \tag{7.6}$$

where the numbers in parentheses denote orders in perturbation theory. The notation (p^+) denotes that a term involves contributions of order p and higher. 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, which implies that the lowest-order contributions to C_k appear at order $\lceil \frac{k}{2} \rceil$. If Brillouin's theorem holds, the C_0 term in equation 7.3 vanishes and the order of C_1 is 2^+. In general, the coefficient equation for doubles look as follows.

$$\underset{(\lceil k/2\rceil^+)}{c^{i_1\cdots i_k}_{a_1\cdots a_k}}\,(\underset{(0)}{\mathcal{E}^{i_1\cdots i_k}_{a_1\cdots a_k}} + \underset{(2^+)}{E_\mathrm{c}}) = \langle\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}|\underset{(1)}{V_\mathrm{c}}(\ \underset{(\lceil k/2\rceil^+-1)}{C_{k-2}} + \underset{(\lceil k/2-1/2\rceil^+)}{C_{k-1}} + \underset{(\lceil k/2\rceil^+-1)}{C_k} + \underset{(\lceil k/2+1/2\rceil^+)}{C_{k+1}} + \underset{(\lceil k/2\rceil^+ + 1)}{C_{k+2}}\ )|\Phi\rangle \quad k \geq 2 \tag{7.7}$$

Definition 7.1. ***Complete orders in perturbation theory.*** We say that approximations to a quantity X are *complete to p^{th}-order in perturbation theory* when they contain all contributions to $X^{(1)}, \ldots, X^{(p)}$. The quantity may also contain higher-order contributions in perturbation theory, but the polynomial dependence of its error is $\mathcal{O}(V_\mathrm{c}^{p+1})$ or better.

Definition 7.2. ***The Davidson correction.*** Truncating the CI wave operator at doubles yields

$$c_0 E_\mathrm{c} = \langle\Phi|V_\mathrm{c}(C_1 + C_2)|\Phi\rangle \qquad c^i_a(\mathcal{E}^i_a + E_\mathrm{c}) = \langle\Phi^a_i|V_\mathrm{c}(C_1 + C_2)|\Phi\rangle \qquad c^{ij}_{ab}(\mathcal{E}^{ij}_{ab} + E_\mathrm{c}) = \langle\Phi^{ab}_{ij}|V_\mathrm{c}(C_0 + C_1 + C_2)|\Phi\rangle \tag{7.8}$$

which are the *CI singles and doubles* (*CISD*) *equations*. Comparison to equations 7.2–7.4 the CISD singles and doubles are complete to second order in perturbation theory and the CISD correlation energy is complete to third order.

$$-\mathbf{H}_0\,\mathbf{t} = \langle\mathbf{\Phi}|V_\mathrm{c}\exp(T(\mathbf{t}))|\Phi\rangle_\mathrm{C} \qquad \mathbf{\Phi} = \begin{bmatrix}\Phi \\ \mathbf{s}_1 \\ \mathbf{s}_2 \\ \vdots \\ \mathbf{s}_n\end{bmatrix} \tag{7.9}$$

Remark 7.2. From PT, we know that the lowest order contributions to T_1, T_2, and T_3 (or C_1 and C_2) occur at first and second order in perturbation theory.

$$t^i_a\mathcal{E}^i_a = \langle\Phi^a_i|\underset{(1)}{V_\mathrm{c}}(\ \underset{(0)}{1} + \underset{(1^+)}{T_2} + \underset{(2^+)}{T_1} + T_1T_2 + \tfrac{1}{2}T_1^2 + \tfrac{1}{3!}T_1^3 + T_3)|\Phi\rangle_\mathrm{C} \tag{7.10}$$

$$t^{ij}_{ab}\mathcal{E}^{ij}_{ab} = \langle\Phi^{ab}_{ij}|V_\mathrm{c}(1 + T_2 + \tfrac{1}{2}T_2^2 + T_1 + T_1T_2 + \tfrac{1}{2}T_1^2 + \tfrac{1}{2}T_1^2T_2 + \tfrac{1}{3!}T_1^3 + \tfrac{1}{4!}T_1^4 + T_3 + T_1T_3 + T_4)|\Phi\rangle_\mathrm{C} \tag{7.11}$$

$$t^{ijk}_{abc}\mathcal{E}^{ijk}_{abc} = \langle\Phi^{abc}_{ijk}|V_\mathrm{c}(T_2 + T_3 + \tfrac{1}{2}T_2^2 + T_1T_2 + T_2T_3 + T_1T_3 + \tfrac{1}{2}T_1^2T_2 + \tfrac{1}{2}T_1T_2^2 + \tfrac{1}{2}T_1^2T_3 + \tfrac{1}{3!}T_1^3T_2)|\Phi\rangle_\mathrm{C} \tag{7.12}$$

[1] By "reference-shifted Hamiltonian matrix" we mean that $\mathbf{H}_\mathrm{c}$ equals $\mathbf{H}_e - E_\mathrm{ref}\mathbf{1}$, which has elements $\langle\Phi_\sigma|H_e|\Phi_\tau\rangle - E_\mathrm{ref}\delta_{\sigma\tau}$.

[2] The C_0 operator simply is simply c_0 times the identity. Under intermediate normalization $C_0 = 1$.

Now, just to be confusing, redefine some shit.

$$\mathbf{1}_\mathrm{i} \equiv \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix} \qquad \mathbf{1}_\mathrm{e} \equiv \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{bmatrix} \qquad \mathbf{H}_\mathrm{xy} \equiv \mathbf{1}_\mathrm{x}\,\mathbf{H}\,\mathbf{1}_\mathrm{y} \qquad \mathbf{c}_\mathrm{x} \equiv \mathbf{1}_\mathrm{x}\,\mathbf{c} \tag{7.13}$$

$$\mathbf{H} = \mathbf{H}_\mathrm{ii} + \mathbf{H}_\mathrm{ie} + \mathbf{H}_\mathrm{ei} + \mathbf{H}_\mathrm{ee} \tag{7.14}$$

$$\mathbf{R}_\mathrm{ee} \equiv (E - \mathbf{H})^{-1}\big|_\mathrm{e} \qquad \mathbf{R}_\mathrm{ee}(E - \mathbf{H})\mathbf{1}_\mathrm{e} = \mathbf{1}_\mathrm{e} \qquad \begin{aligned} \mathbf{R}_\mathrm{ee}\,(E - \mathbf{H}) &= -\mathbf{R}_\mathrm{ee}\,\mathbf{H}_\mathrm{ei} + \mathbf{1}_\mathrm{e} \\ (E - \mathbf{H})\,\mathbf{R}_\mathrm{ee} &= -\mathbf{H}_\mathrm{ie}\,\mathbf{R}_\mathrm{ee} + \mathbf{1}_\mathrm{e} \end{aligned} \tag{7.15}$$

Operating the upper equation on $\mathbf{c}$ gives zero due to the Schrödinger equation, which implies $\mathbf{c}_\mathrm{e} = \mathbf{R}_\mathrm{ee}\mathbf{H}_\mathrm{ei}\mathbf{c}_\mathrm{i}$. Projecting the Schrödinger equation by $\mathbf{1}_\mathrm{i}$ and substituting in this result leads to the following.

$$(\mathbf{H}_\mathrm{ii} + \mathbf{V}_\mathrm{ii})\mathbf{c}_\mathrm{i} = E\mathbf{c}_\mathrm{i} \qquad \mathbf{V}_\mathrm{ii} \equiv \mathbf{H}_\mathrm{ie}\mathbf{R}_\mathrm{ee}\mathbf{H}_\mathrm{ei} \tag{7.16}$$

$$E = \frac{\mathbf{c}_\mathrm{i}^\dagger(\mathbf{H}_\mathrm{ii} + \mathbf{V}_\mathrm{ii})\mathbf{c}_\mathrm{i}}{\mathbf{c}_\mathrm{i} \cdot \mathbf{c}_\mathrm{i}} \tag{7.17}$$

$$E = \langle\Phi|(1 + \Lambda)\overline{H}|\Phi\rangle + \langle\Phi|\Lambda\overline{H}|\mathbf{e}\rangle\langle\mathbf{e}|E - \overline{H}|\mathbf{e}\rangle^{-1}\langle\mathbf{e}|\overline{H}|\Phi\rangle$$

$$\delta E = \langle\Phi|\Lambda\overline{H}|\mathbf{e}\rangle\langle\mathbf{e}|E - \overline{H}|\mathbf{e}\rangle^{-1}\langle\mathbf{e}|\overline{H}|\Phi\rangle \approx \langle\Phi|\Lambda\overline{H}^{(1)}|\mathbf{e}\rangle\langle\mathbf{e}|E^{(0)} - \overline{H}^{(0)}|\mathbf{e}\rangle^{-1}\langle\mathbf{e}|\overline{H}^{(m)}|\Phi\rangle$$

$$\overline{H} = E_\mathrm{ref} + H_0 + (H_0 T + V_\mathrm{c}\exp(T))_\mathrm{C} \tag{7.18}$$

$$\overline{H}^{(0)} = E_\mathrm{ref} + H_0 \qquad \overline{H}^{(1)} = (H_0 T^{(1)})_\mathrm{C} + V_\mathrm{c} \qquad \overline{H}^{(2)} = (H_0 T^{(2)} + V_\mathrm{c}\,T^{(1)})_\mathrm{C} \tag{7.19}$$

(7.20)

$$\overline{H}\mathcal{R}_k|\Phi\rangle = E_k\mathcal{R}_k|\Phi\rangle \quad \langle\Phi|\mathcal{L}_k\overline{H} = \langle\Phi|\mathcal{L}_k\omega_k \quad \langle\Phi|\mathcal{L}_k\mathcal{R}_l\Phi = \delta_{kl} \quad \overline{H} = \exp(-T)H\exp(T) = E_{\rm ref} + \overline{H}_{\rm c} \tag{7.21}$$

Note to self: Go back and change E_0 to $E_{\rm ref}$ throughout to avoid problems like this (E_0 should refer to the ground state energy).

Note to self: Go back and change H_e to H for simplicity.

$$\mathcal{R}_0 = 1 \qquad \mathcal{L}_0 = 1 + \Lambda \qquad \Lambda = \sum_{h=1}^{n}\Lambda_h \qquad \Lambda_h \equiv (\tfrac{1}{h!})^2\,\lambda^{a_1\cdots a_h}_{i_1\cdots i_h}\tilde{a}^{i_1\cdots i_h}_{a_1\cdots a_h} \tag{7.22}$$

Note to self: Go back and change k to h for summations over excitation levels.

$$E_{\rm c} \equiv \langle\Phi|\mathcal{L}_0\overline{H}\mathcal{R}_0\Phi - E_{\rm ref} = \langle\Phi|(1+\Lambda)\overline{H}_{\rm c}|\Phi\rangle$$

Structure of matrix

$$\overline{\mathbf{H}}_{\rm c} = \begin{bmatrix} E_{\rm c} & \langle\Phi|\overline{H}_{\rm c}|\,\mathbf{i}\,\rangle & \langle\Phi|\overline{H}_{\rm c}|\,\mathbf{e}\,\rangle \\ \mathbf{0} & \langle\,\mathbf{i}\,|\overline{H}_{\rm c}|\,\mathbf{i}\,\rangle & \langle\,\mathbf{i}\,|\overline{H}_{\rm c}|\,\mathbf{e}\,\rangle \\ \langle\,\mathbf{e}\,|\overline{H}_{\rm c}|\Phi\rangle & \langle\,\mathbf{e}\,|\overline{H}_{\rm c}|\,\mathbf{i}\,\rangle & \langle\,\mathbf{e}\,|\overline{H}_{\rm c}|\,\mathbf{e}\,\rangle \end{bmatrix} \quad \mathbf{i} \equiv \begin{bmatrix}\mathbf{s}_1 & \cdots & \mathbf{s}_m\end{bmatrix} \quad \mathbf{e} \equiv \begin{bmatrix}\mathbf{s}_{m-1} & \cdots & \mathbf{s}_n\end{bmatrix} \quad \mathbf{s}_h \equiv \begin{bmatrix}\cdots & \Phi^{a_1\cdots a_h}_{i_1\cdots i_h} & \cdots\end{bmatrix}$$

Theorem 7.1. ***Fa di Bruno's formula.***

$$\frac{\partial^n}{\partial x_1\cdots\partial x_n}f(g(\boldsymbol{x})) = \sum_{k=1}^{n}\sum_{(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_k)}^{\mathcal{P}_k(\boldsymbol{x})} f^{(k)}(g(\boldsymbol{x}))\prod_{i=1}^{k}\frac{\partial^{|\boldsymbol{x}_i|}g(\boldsymbol{x})}{\partial x_{i,1}\cdots\partial x_{i,|\boldsymbol{x}_i|}} \tag{7.23}$$