

1. Derive the recursive equation for the wavefunction, starting from the λ -dependent Schrödinger equation.

$$\Psi(\lambda) = \Phi + R_0(\lambda V_c - E(\lambda))\Psi(\lambda) \quad (1)$$

Assume intermediate normalization and note that $R_0 H_0 = -Q$ follows** from the definition of R_0 .

Answer: Operating R_0 on both sides of $0 = (H(\lambda) - E(\lambda))\Psi(\lambda) = (H_0 + \lambda V_c - E(\lambda))\Psi(\lambda)$ gives

$$\begin{aligned} 0 &= R_0 H_0 \Psi(\lambda) + R_0(\lambda V_c - E(\lambda))\Psi(\lambda) \\ &= -Q\Psi(\lambda) + R_0(\lambda V_c - E(\lambda))\Psi(\lambda) \\ &= -\Psi(\lambda) + \Phi + R_0(\lambda V_c - E(\lambda))\Psi(\lambda) \end{aligned}$$

where the last step follows from $Q = 1_n - P$ and intermediate normalization: $\langle \Phi | \Psi(\lambda) \rangle = 1 \implies P\Psi(\lambda) = \Phi$. Adding $\Psi(\lambda)$ to both sides gives equation 1.

****Extra Credit:** Define “resolvent” and explain why this follows from your definition.

Answer: The resolvent is the negative inverse of H_0 in the orthogonal space, $R_0 = -H_0^{-1}|_o$, which implies that $R_0 H_0 = -1|_o$. Resolution of the identity in the orthogonal space gives Q .

$$1|_o = \sum_{k=1}^n \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1 \cdots a_k \\ i_1 \cdots i_k}} |\Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k}\rangle \langle \Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k}| = Q$$

2. Determine the first- and second-order components of Ψ by differentiating equation 1. You do not need to fully evaluate and simplify your answer,¹ but you should eliminate all terms that vanish and explain why each one evaluates to zero.²

Answer: The λ -dependent first and second derivatives are as follows

$$\begin{aligned}\frac{\partial \Psi(\lambda)}{\partial \lambda} &= R_0 \left(V_c - \frac{\partial E(\lambda)}{\partial \lambda} \right) \Psi(\lambda) + R_0(\lambda V_c - E(\lambda)) \frac{\partial \Psi(\lambda)}{\partial \lambda} \\ \frac{\partial^2 \Psi(\lambda)}{\partial \lambda^2} &= -R_0 \frac{\partial^2 E(\lambda)}{\partial \lambda^2} \Psi(\lambda) + 2R_0 \left(V_c - \frac{\partial E(\lambda)}{\partial \lambda} \right) \frac{\partial \Psi(\lambda)}{\partial \lambda} + R_0(\lambda V_c - E(\lambda)) \frac{\partial^2 \Psi(\lambda)}{\partial \lambda^2}\end{aligned}$$

where we have used the product rule: if $f = gh$, then $f' = g'h + gh'$ and $f'' = g''h + 2g'h' + gh''$. Evaluating these derivatives at $\lambda = 0$ after dividing the second equation by 2 gives the following

$$\begin{aligned}\Psi^{(1)} &= R_0 V_c \Phi - E^{(1)} R_0 \Phi - R_0 E^{(0)} \Psi^{(1)} \\ \Psi^{(2)} &= -E_c^{(2)} R_0 \Phi + R_0 V_c \Psi^{(1)} - E_c^{(1)} R_0 \Psi^{(1)} - R_0 E_c^{(0)} \Psi^{(2)}\end{aligned}$$

since $\Psi^{(0)}$ is the ground-state eigenvector of H_0 , which is Φ . It follows that $E_c^{(0)} = \langle \Phi | H_0 | \Phi \rangle = 0$. Furthermore, using the relation in footnote 2 we have that $E_c^{(1)} = \langle \Phi | V_c | \Phi \rangle = 0$. Since R_0 is only acts on the orthogonal space we have $R_0 = R_0 Q$, which implies $R_0 \Phi = R_0 Q \Phi = 0$. Therefore,

$$\begin{aligned}\Psi^{(1)} &= R_0 V_c \Phi \\ \Psi^{(2)} &= R_0 V_c \Psi^{(1)}\end{aligned}$$

are the non-vanishing contributions to $\Psi^{(1)}$ and $\Psi^{(2)}$.

¹That is, your final answer may contain R_0 's and V_c 's.

²You may take $E_c^{(m+1)} = \langle \Phi | V_c | \Psi^{(m)} \rangle$ as given.

3. Evaluate the following contributions to the CI doubles and quadruples coefficients.

$$^{(1)}c_{ab}^{ij} = \langle \Phi_{ij}^{ab} | R_0 V_c | \Phi \rangle \qquad ^{(2)}c_{abcd}^{ijkl} = \langle \Phi_{ijkl}^{abcd} | R_0 V_c R_0 V_c | \Phi \rangle \quad (2)$$

Use your answer to show that $^{(2)}C_4 = \frac{1}{2} ^{(1)}C_2^2$.

Answer: Only the +2 fluctuation potential contributions can fully contract the products, so there is only one unique graph contraction for each one. Note that the off-diagonal Fock operator has no excitation level +2 component, so the results are the same whether or not we assume Brillouin's theorem.

$$\begin{aligned} ^{(1)}c_{ab}^{ij} &= \text{Diagram 1} = \text{Diagram 2} = \frac{\bar{g}_{ab}^{ij}}{\mathcal{E}_{ab}^{ij}} \\ ^{(2)}c_{abcd}^{ijkl} &= \text{Diagram 3} = \text{Diagram 4} = P_{(ab/cd)}^{(ij/kl)} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} \end{aligned}$$

The corresponding operators are

$$\begin{aligned} ^{(1)}C_2 &= \text{Diagram 5} = \frac{1}{2^2} \sum_{ab, ij} \frac{\bar{g}_{ab}^{ij}}{\mathcal{E}_{ab}^{ij}} \tilde{a}_{ij}^{ab} \\ ^{(2)}C_4 &= \text{Diagram 6} = \frac{1}{2^4} \sum_{abcd, ijkl} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} \tilde{a}_{ijkl}^{abcd} \end{aligned}$$

and by duplicating and reindexing the quadruples operator we get the following.

$$\begin{aligned} ^{(2)}C_4 &= \frac{1}{2^4} \sum_{abcd, ijkl} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} \tilde{a}_{ijkl}^{abcd} = \frac{1}{2} \left(\frac{1}{2^4} \sum_{abcd, ijkl} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} \tilde{a}_{ijkl}^{abcd} + \frac{1}{2^4} \sum_{cdab, klij} \frac{\bar{g}_{cd}^{kl} \bar{g}_{ab}^{ij}}{\mathcal{E}_{cdab}^{klij} \mathcal{E}_{cd}^{kl}} \tilde{a}_{klij}^{cdab} \right) \\ &= \frac{1}{2} \cdot \frac{1}{2^4} \sum_{abcd, ijkl} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl} (\mathcal{E}_{cd}^{kl} + \mathcal{E}_{ab}^{ij})}{\cancel{\mathcal{E}_{abcd}^{ijkl}} \mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{kl}} \tilde{a}_{ijkl}^{abcd} \\ &= \frac{1}{2} \left(\frac{1}{2^4} \sum_{ab, ij} \frac{\bar{g}_{ab}^{ij}}{\mathcal{E}_{ab}^{ij}} \tilde{a}_{ij}^{ab} \right) \left(\frac{1}{2^4} \sum_{cd, kl} \frac{\bar{g}_{cd}^{kl}}{\mathcal{E}_{cd}^{kl}} \tilde{a}_{kl}^{cd} \right) \\ &= \frac{1}{2} ^{(1)}C_2^2 \end{aligned}$$