1. Rayleigh-Schrödinger perturbation theory

Definition 1.1. *Model problem.* In perturbation theory, the *model Hamiltonian* is an operator $H_0 \approx H_e$ which approximates the full Hamiltonian and has eigenfunctions spanning the complete n-particle Fock space. An obvious choice in electronic structure is the diagonal one-particle component of H_e, which is diagonal in the determinant basis.

$$H_0 \Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k} = \mathcal{E}_{i_1 \cdots i_k}^{a_1 \cdots a_k} \Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k} \qquad H_c = H_0 + V_c \qquad H_0 \equiv f_p^p \tilde{a}_p^p \qquad \mathcal{E}_{i_1 \cdots i_k}^{a_1 \cdots a_k} \equiv \left(f_{a_1}^{a_1} + \cdots + f_{a_k}^{a_k} - f_{i_1}^{i_1} - \cdots - f_{i_k}^{i_k} \right)$$

where the perurbation is $V_c \equiv f_p^q (1 - \delta_p^q) \tilde{a}_q^p + \frac{1}{4} \overline{g}_{pq}^{rs} \tilde{a}_{rs}^{pq}$. In this context, the reference determinant Φ is termed the *model function*. Note that we are playing fast and loose with Einstein summation here: the i and a indices are not summed over, but the p index in H_0 is. The eigenvalue can be determined by noting that $a_p^p \Phi_k = n_p^k \Phi_k$ where n_p^k is the occupation number of ψ_p in Φ_k. Therefore $\tilde{a}_p^p = a_p^p - \tilde{a}_{p^\circ}^{p^\circ} = a_p^p - n_p$ which implies that $\tilde{a}_p^p \Phi_k = (n_p^k - n_p) \Phi_k$. It then follows that $\sum_p f_p^p \tilde{a}_p^p \Phi_k = (\sum_{p \in \Phi_k} f_p^p - \sum_{p \in \Phi} f_p^p) \Phi_k$, which leads to the expression above for $\mathcal{E}_{i_1 \cdots i_k}^{a_1 \cdots a_k}$.

Definition 1.2. *Model space projection operators.* The projection $P = |\Phi\rangle\langle\Phi|$ onto the model function is termed the *model space projection operator*, and its orthogonal complement $Q = 1 - P = \sum_k (\frac{1}{k!})^2 \sum_{\substack{a_1 \cdots a_k \\ i_1 \cdots i_k}} |\Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k}\rangle\langle\Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k}|$ is the *orthogonal space projection operator*. Note that $P^2 = Q^2 = 1$ and $PQ = QP = 0$ are necessary consequences of the fact that P and Q are projection operators for orthogonal subspaces, and note that $P + Q = 1$. Assuming *intermediate normalization*, where we set the norm of the wavefunction such that $\langle\Phi|\Psi\rangle = 1$ rather than $\langle\Psi|\Psi\rangle = 1$, the model space projection operator takes the wavefunction into our model function, $P\Psi = \Phi\langle\Phi|\Psi\rangle = \Phi$.

Definition 1.3. *Resolvent.* Let R_0 be minus[1] the inverse of H_0 in the orthogonal complement of Φ, so that $-R_0 H_0 = Q$. The operator R_0 is termed the *resolvent*. Explicitly, we can apply resolution of the identity in the orthogonal space to get

$$R_0 = (-H_0)^{-1} Q = \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1 \cdots a_k \\ i_1 \cdots i_k}} (-H_0)^{-1} |\Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k}\rangle\langle\Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k}| = \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1 \cdots a_k \\ i_1 \cdots i_k}} \frac{|\Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k}\rangle\langle\Phi_{i_1 \cdots i_k}^{a_1 \cdots a_k}|}{\mathcal{D}_{i_1 \cdots i_k}^{a_1 \cdots a_k}} \qquad \mathcal{D}_{i_1 \cdots i_k}^{a_1 \cdots a_k} \equiv -\mathcal{E}_{i_1 \cdots i_k}^{a_1 \cdots a_k}$$

where we recognize that H_0^{-1} does not exist outside of the model space because $H_0 \Phi = 0 \implies H_0 P = 0$. Note that R_0 simply acts as the null operator outside of the orthogonal space, so that $R_0 Q = R_0$ and $R_0 P = 0$.

Definition 1.4. *Rayleigh-Schrödinger perturbation theory.* Rearranging the Schrödinger equation to the form $H_0 \Psi = (E_c - V_c)\Psi$ and operating the R_0 on both sides, recognizing that $R_0 H_0 = Q$ and $Q\Psi = (1-P)\Psi = \Psi - \Phi$, we find

$$R_0 H_0 \Psi = -Q\Psi = -\Psi + \Phi = R_0 (E_c - V_c)\Psi \implies \Psi = \Phi - R_0 (E_c - V_c)\Psi = \Phi + R_0 (V_c - E_c)\Psi$$

which gives a recursive equation for Ψ. Straightforward induction gives $\Psi = \sum_{k=0}^n (R_0 (V_c - E_c))^k \Phi + (R_0 (V_c - E_c))^{n+1} \Psi$. Noting that $H_0 \Phi = 0$ and $\langle\Phi|\Psi\rangle = 1$, projecting the Schrödinger equation by Φ gives an expression for the correlation energy: $E_c = \langle\Phi|V_c|\Psi\rangle$. Assuming the recursive definition for Ψ converges, we find

$$\Psi = \sum_{k=0}^\infty (R_0 (V_c - E_c))^k \Phi \qquad\qquad E_c = \sum_{k=0}^\infty \langle\Phi|V_c|\Psi^{(k)}\rangle = \sum_{k=0}^\infty \langle\Phi|V_c (R_0 (V_c - E_c))^k|\Phi\rangle \qquad (1.1)$$

which can be solved iteratively in orders of perturbation theory. Introducing a perturbation parameter $V_c \mapsto \lambda V_c$ that acts as a switch to turn the perturbation on, $\lambda = 1$, or off, $\lambda = 0$, the wavefunction and correlation energy are given by

$$\Psi(\lambda) = \sum_k \frac{1}{k!} \lambda^k \left(\frac{\partial^k \Psi}{\partial \lambda^k}\right)_{\lambda=0} \equiv \sum_k \lambda^k \Psi^{(k)} \qquad\qquad E_c(\lambda) = \sum_k \frac{1}{k!} \lambda^k \left(\frac{\partial^k E_c}{\partial \lambda^k}\right)_{\lambda=0} \equiv \sum_k \lambda^k E_c^{(k)}$$

and we can separate eq (1.1) in powers of λ. The first-order energy contribution vanishes $\lambda E_c^{(1)} = \lambda\langle\Phi|V_c|\Phi\rangle = 0$ since V_c is composed of Φ-normal operators. The first order wavefunction contribution is $\lambda\Psi^{(1)} = \lambda R_0 (V_c - E_c^{(1)})\Phi = \lambda R_0 V_c \Phi$,

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[1] The annoying sign factor is required for consistency with the standard definition $R_0 \equiv (E_0 - H_0)^{-1} Q$. Since we have already subtracted off E_0, we have $R_0 = (-H_0)^{-1} Q$. This also results in a more convenient sign rule for the bracketing theorem.

which can be directly evaluated using Wick's theorem and Φ normal ordering

$$\Psi^{(1)} = R_0 V_c \Phi = \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1\cdots a_k \\ i_1\cdots i_k}} |\Phi_{i_1\cdots i_k}^{a_1\cdots a_k}\rangle \frac{\langle\Phi|\tilde{a}_{a_1\cdots a_k}^{i_1\cdots i_k} V_c|\Phi\rangle}{\mathcal{D}_{i_1\cdots i_k}^{a_1\cdots a_k}}$$

$$= \sum_{ia} |\Phi_i^a\rangle \frac{\sum_{pq} f_p^q(1-\delta_p^q)\langle\Phi|\!:\!\tilde{a}_{a\bullet}^{i\circ}\tilde{a}_{q\circ}^{p\bullet}\!:\!|\Phi\rangle}{f_i^i - f_a^a} - \frac{1}{4}\sum_{ijab}|\Phi_{ij}^{ab}\rangle\frac{\frac{1}{4}\sum_{pqrs}\overline{g}_{pq}^{rs}P_{(r/s)}^{(p/q)}\langle\Phi|\!:\!\tilde{a}_{a\bullet b\bullet\bullet}^{i\circ j\circ\circ}\tilde{a}_{r\circ s\circ\circ}^{p\bullet q\bullet\bullet}\!:\!|\Phi\rangle}{f_i^i + f_j^j - f_a^a - f_b^b}$$

$$= -\sum_{ia}|\Phi_i^a\rangle\frac{f_a^i}{f_i^i - f_a^a} - \frac{1}{4}\sum_{ijab}|\Phi_{ij}^{ab}\rangle\frac{\overline{g}_{ab}^{rij}}{f_i^i + f_j^j - f_a^a - f_b^b}$$

where we have recognized that only singly and doubly excited determinants can fully contract V_c. The second-order energy contribution, $\lambda^2 E_c^{(2)} = \lambda^2\langle\Phi|V_c R_0(V_c - E_c^{(1)})|\Phi\rangle = \lambda^2\langle\Phi|V_c|\Psi^{(1)}\rangle$, can be evaluated from our expression for $\Psi^{(1)}$.

$$E^{(2)} = \sum_{ia}\langle\Phi|V_c\tilde{a}_i^a|\Phi\rangle\frac{f_a^i}{f_i^i - f_a^a} - \frac{1}{4}\sum_{ijab}\langle\Phi|V_c\tilde{a}_{ij}^{ab}|\Phi\rangle\frac{\overline{g}_{ab}^{ij}}{f_i^i + f_j^j - f_a^a - f_b^b} = \sum_{ia}\frac{f_i^a f_a^i}{f_i^i - f_a^a} - \frac{1}{4}\sum_{ijab}\frac{\overline{g}_{ij}^{ab}\overline{g}_{ab}^{ij}}{f_i^i + f_j^j - f_a^a - f_b^b}$$

The second order wavefunction contribution is $\lambda^2\Psi^{(2)} = -\lambda^2 E_c^{(2)}R_0\Phi + \lambda^2 R_0(V_c - E_c^{(1)})R_0(V_c - E_c^{(1)})\Phi = \lambda^2 R_0 V_c R_0 V_c \Phi$ since $R_0\Phi = 0$ and $E_c^{(1)} = 0$. The third order energy can be then obtained from $\Psi^{(2)}$ as $\lambda^3 E_c^{(3)} = \lambda^3\langle\Phi|V_c|\Psi^{(2)}\rangle$. In this manner, one can in principle solve the Schrödinger equation recursively by alternately evaluating the wavefunction and energy contributions at increasing orders in the perturbation parameter.

Derivation 1.1. Writing the RSPT wavefunction equation as $\Psi = \sum_{k=0}^{\infty}(R_0 V_c - R_0 E_c)^k\Phi$, note that if R_0 and V_c were to commute we could to an ordinary binomial expansion of $(R_0 V_c - R_0 E_c)^k$ to give $\sum_{p=0}^{k}\binom{k}{p}(-)^p(R_0 V_c)^{k-p}(R_0 E_c)^p$. Since they don't commute, we can write the binomial expansion in the following slightly modified form

$$(R_0 E_c - R_0 V_c)^k = \sum_{p=0}^{k}(-)^p\{\underbrace{R_0 E_c,\ldots,R_0 E_c}_{p\text{ times}}\}\text{insert}\{R_0 V_c\}^{p-k}$$

where $\{B_1,\ldots,B_p\}\text{insert}\{A\}^{k-p}$ denotes the sum over all $\binom{k}{p}$ possible ways of inserting $k-p$ copies of A into the product $B_1\cdots B_p$. For example, $\{B_1, B_2\}\text{insert}\{A\}^2$ evaluates to $AAB_1B_2 + AB_1AB_2 + AB_1B_2A + B_1AAB_2 + B_1AB_2A + B_1B_2AA$. This allows the wavefunction expansion to be easily grouped by orders

$$\Psi = \sum_{k=0}^{\infty}\sum_{p=0}^{k}(-)^p\{\underbrace{R_0 E_c,\ldots,R_0 E_c}_{p\text{ times}}\}\text{insert}\{R_0 V_c\}^{p-k}\Phi$$

$$= \sum_{n=0}^{\infty}\sum_{(n_1,n_2)}^{\mathcal{C}_2(n)\cup\{(0,n)\}}\sum_{(r_1,\ldots,r_m)}^{\mathcal{C}(n_1)}(-)^m\{R_0 E_c^{(r_1)},\ldots,R_0 E_c^{(r_m)}\}\text{insert}\{R_0 V_c\}^{n_2}\Phi = \sum_{n=0}^{\infty}\Psi^{(n)}$$

where $\mathcal{C}(n)$ denotes the set of integer compositions of n, i.e. all ordered tuples $(r_1,\ldots,r_m)$ of strictly positive integers that add up to n. $\mathcal{C}_k(n)\subset\mathcal{C}(n)$ is the set of k-tuple integer compositions of n, i.e. all $(r_1,\ldots,r_k)$ of fixed length k such that $r_1 + \cdots + r_k = n$. The rearrangement follows from the fact that all possible terms of the form $(-)^k\{R_0 E_c^{(n_1)},\ldots,R_0 E_c^{(n_k)}\}\text{insert}\{R_0 V_c\}^{n_{k+1}}\Phi$ contribute to the sum, and the composition sums group these into all possible terms of this form that are of a given order n in the perturbation parameter λ. Note that we have appended the tuple $(0,n)$ to our sum over $\mathcal{C}_2(n)$ but not $(n,0)$ since R_0 acting directly on Φ gives 0.

Lemma 1.1. *The Energy Substitution Lemma.* *The nth-order contribution to the wavefunction is given by*

$$\Psi^{(n)} = (R_0 V_c)^n\Phi + \sum_{(n_1,n_2)}^{\mathcal{C}_2(n)}\sum_{(r_1,\ldots,r_m)}^{\mathcal{C}(n_1)}(-)^m\{R_0 E_c^{(r_1)},\ldots,R_0 E_c^{(r_m)}\}\text{insert}\{R_0 V_c\}^{n_2}\Phi$$

which can be evaluated as the sum of a principal term, $(R_0 V_c)^n\Phi$, *plus all possible m-tuple substitutions of adjacent factors $(R_0 V_c)^{r_k}$ in the principal term by $R_0 E_c^{(r_k)}$ times a sign factor $(-)^m$.*

Theorem 1.1. *The Bracketing Theorem.* *The*