

## 6 Perturbation theory

**Definition 6.1. Model Hamiltonian.** The electronic Hamiltonian<sup>1</sup> can be expressed as the sum of a *zeroth order* or “*model*” Hamiltonian  $H_0$  and a *perturbation*  $V_c$ , known as the *fluctuation potential*. For well-behaved electronic systems, a common choice for the model Hamiltonian is the diagonal part of the Fock operator.

$$H_0 \equiv f_p^p \tilde{a}_p^p \quad V_c \equiv f_p^q (1 - \delta_p^q) \tilde{a}_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} \tilde{a}_{rs}^{pq} \quad (6.1)$$

This choice of  $H_0$  brings the advantage that its eigenbasis is the standard basis of determinants.

$$H_0 \Phi = 0 \Phi \quad H_0 \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} = \mathcal{E}_{i_1 \dots i_k}^{a_1 \dots a_k} \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} \quad \mathcal{E}_{q_1 \dots q_k}^{p_1 \dots p_k} \equiv \sum_{r=1}^k f_{p_r}^{q_r} - \sum_{r=1}^k f_{q_r}^{p_r} \quad (6.2)$$

In general the model Hamiltonian is chosen to make the matrix representation of  $H_c$  in the model eigenbasis diagonally dominant.<sup>2</sup> Our choice of  $H_0$  is appropriate for *weakly correlated systems*, where the reference determinant can be chosen to satisfy  $\langle \Phi | \Psi \rangle \gg \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | \Psi \rangle$  for all substituted determinants. In this context it is convenient to employ intermediate normalization for the wavefunction, which will be assumed from here on out.

**Definition 6.2. Perturbation theory.** *Perturbation theory* analyzes the polynomial order with which the wavefunction and its observables depend on the fluctuation potential. For this purpose, we define a continuous series of Hamiltonians  $H(\lambda) \equiv H_0 + \lambda V_c$  parametrized by a *strength parameter*  $\lambda$  that smoothly toggles between the model Hamiltonian at  $\lambda = 0$  to the exact one at  $\lambda = 1$ . The  $m^{\text{th}}$ -order contribution to a quantity  $X$  is then defined as the  $m^{\text{th}}$  coefficient in its Taylor series about  $\lambda = 0$ , which is denoted by  $X^{(m)}$ . In particular,  $\Psi$  and  $E_c$  can be expanded as follows.

$$\Psi = \sum_{m=0}^{\infty} \Psi_c^{(m)} \quad E_c = \sum_{n=0}^{\infty} E_c^{(n)} \quad \Psi^{(m)} \equiv \frac{1}{m!} \left. \frac{\partial^m \Psi(\lambda)}{\partial \lambda^m} \right|_{\lambda=0} \quad E_c^{(m)} \equiv \frac{1}{m!} \left. \frac{\partial^m E(\lambda)}{\partial \lambda^m} \right|_{\lambda=0} \quad H(\lambda) \Psi(\lambda) = E(\lambda) \Psi(\lambda) \quad (6.3)$$

The order(s) at which a term contributes to the wavefunction or energy provides one measure of its relative importance.

**Remark 6.1.** Projecting the Schrödinger equation by  $\Phi$  and using eq 6.2, along with intermediate normalization, implies

$$E_c = \langle \Phi | V_c | \Psi \rangle \quad \implies \quad E_c^{(m+1)} = \langle \Phi | V_c | \Psi^{(m)} \rangle \quad (6.4)$$

where the equation on the right follows from generalizing the energy expression to  $E(\lambda) = \langle \Phi | \lambda V_c | \Psi(\lambda) \rangle$ . In words, this says that the  $m^{\text{th}}$ -order wavefunction contribution determines the  $(m+1)^{\text{th}}$ -order energy contribution. This immediately identifies the first-order energy as  $E_c^{(1)} = \langle \Phi | V_c | \Phi \rangle = 0$ , since  $V_c$  consists of  $\Phi$ -normal-ordered operators.

**Definition 6.3. Model space projection operator.** The projection onto the reference determinant,  $P = |\Phi\rangle\langle\Phi|$ , is termed the *model space projection operator*. Its complement is the *orthogonal space projection operator*.

$$Q \equiv 1 - P = \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1 \dots a_k \\ i_1 \dots i_k}} |\Phi_{i_1 \dots i_k}^{a_1 \dots a_k}\rangle \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k}| \quad (6.5)$$

Note that  $P$  and  $Q$  satisfy the following relationships, which are characteristic of complementary projection operators.

$$P + Q = 1 \quad P^2 = P \quad Q^2 = Q \quad PQ = QP = 0 \quad (6.6)$$

Due to intermediate normalization, the model space projection operator also satisfies  $P\Psi = \Phi$  and  $Q\Psi = \Psi - \Phi$ .

**Definition 6.4. Resolvent.** The *resolvent*,  $R_0 \equiv (-H_0)^{-1}Q$ , is the negative<sup>3</sup> inverse of  $H_0$  in the orthogonal space. Expanding the orthogonal space projection operator according to equation 6.5 yields the spectral decomposition for  $R_0$ .<sup>4</sup>

$$R_0 = \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1 \dots a_k \\ i_1 \dots i_k}} \frac{|\Phi_{i_1 \dots i_k}^{a_1 \dots a_k}\rangle \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k}|}{\mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k}} \quad (6.7)$$

Note that the resolvent satisfies  $R_0 P = 0$  and  $R_0 Q = R_0$ . Restriction to the orthogonal space is necessary because  $H_0$  is singular in the model space, which means that  $H_0^{-1}$  does not exist there.

<sup>1</sup>For the sake of brevity I will here refer to  $H_c$  as “the electronic Hamiltonian”. We could also use  $H_e = E_0 + H_c$ , which will simply shift some of the equations by a constant.

<sup>2</sup>See [https://en.wikipedia.org/wiki/Diagonally\\_dominant\\_matrix](https://en.wikipedia.org/wiki/Diagonally_dominant_matrix).

<sup>3</sup>The annoying sign factor is required for consistency with  $R(\zeta) \equiv (\zeta - H_0)^{-1}Q$ , which is a more general definition of the resolvent.

<sup>4</sup>Note that  $(-H_0)^{-1} \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} = (-\mathcal{E}_{i_1 \dots i_k}^{a_1 \dots a_k})^{-1} \Phi_{i_1 \dots i_k}^{a_1 \dots a_k}$  and  $-\mathcal{E}_{i_1 \dots i_k}^{a_1 \dots a_k} = \mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k}$

**Remark 6.2. A recursive solution to the Schrödinger equation.** Operating  $R_0$  on the Schrödinger equation gives<sup>5</sup>

$$\Psi = \Phi + R_0(V_c - E_c)\Psi \quad (6.8)$$

which provides a recursive equation for  $\Psi$ . Applying the same manipulation to equation 6.3 gives

$$\Psi(\lambda) = \Phi + R_0(\lambda V_c - E(\lambda))\Psi(\lambda) \quad (6.9)$$

which can be used solve for wavefunction contributions order by order.

**Example 6.1.** The first two derivatives of equation 6.9 are given by

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

which can be used to determine first- and second-order components of the wavefunction.

$$\Psi^{(1)} = \left. \frac{\partial \Psi(\lambda)}{\partial \lambda} \right|_{\lambda=0} = R_0 V_c \Phi \quad \Psi^{(2)} = \left. \frac{\partial^2 \Psi(\lambda)}{\partial \lambda^2} \right|_{\lambda=0} = R_0 V_c \Psi^{(1)} = R_0 V_c R_0 V_c \Phi$$

Here we have used  $E_c^{(0)} = E_c^{(1)} = 0$  and  $R_0 \Phi = 0$  to simplify the result.

**Example 6.2.** Expanding the resolvent according to eq (6.7) allows us to expand  $\Psi^{(1)}$  in the determinant basis.

$$\Psi^{(1)} = R_0 V_c \Phi = \sum_i \Phi_i^a \frac{\langle \Phi_i^a | V_c | \Phi \rangle}{\mathcal{E}_a^i} + \left( \frac{1}{2!} \right)^2 \sum_{ab} \Phi_{ij}^{ab} \frac{\langle \Phi_{ij}^{ab} | V_c | \Phi \rangle}{\mathcal{E}_{ab}^{ij}} \quad (6.10)$$

The expansion truncates at double excitations because the maximum excitation level of  $V_c$  is +2.

**Example 6.3.** The numerators in example 6.2 are easily evaluated using Slater's rules, which leads to the following.

$$\Psi^{(1)} = \sum_i \Phi_i^a \frac{f_a^i}{\mathcal{E}_a^i} + \left( \frac{1}{2!} \right)^2 \sum_{ab} \Phi_{ij}^{ab} \frac{\bar{g}_{ab}^{ij}}{\mathcal{E}_{ab}^{ij}} \implies E_c^{(2)} = \langle \Phi | V_c | \Psi^{(1)} \rangle = \sum_i \frac{f_a^i f_a^i}{\mathcal{E}_a^i} + \left( \frac{1}{2!} \right)^2 \sum_{ab} \frac{\bar{g}_{ij}^{ab} \bar{g}_{ab}^{ij}}{\mathcal{E}_{ab}^{ij}}$$

Note that the singles contribution vanishes for canonical Hartree-Fock references, since  $f_a^i = 0$ . These extra terms are required for non-canonical orbitals, such as those obtained from restricted open-shell Hartree-Fock (ROHF) theory.

**Example 6.4.** Diagrammatically,  $\Psi^{(1)}$  and  $E_c^{(2)}$  can be expressed as follows.

$$\Psi^{(1)} = \text{diagram 1} + \text{diagram 2} \quad E_c^{(2)} = \text{diagram 3} + \text{diagram 4} \quad (6.11)$$

**Remark 6.3.** Notice that a fully contracted operator of the form  $\sum_i v_i a_i |\Phi\rangle \langle \Phi | a_i^\dagger$  can be simplified as

$$\sum_i v_i \overline{a_p^\dagger a_i} |\Phi\rangle \langle \Phi | \overline{a_i^\dagger a_q} = v_p \overline{a_p^\dagger a_q} |\Phi\rangle \langle \Phi |$$

where  $v_p$  is required to have an occupied index by the hole contraction. A similar argument can be made for completely contracted operators of the form  $\sum_a v_a a_a^\dagger |\Phi\rangle \langle \Phi | a_a$  or in general  $\sum_{abc\dots} v_{abc\dots}^{ijk\dots} a_{abc\dots}^{ijk\dots} |\Phi\rangle \langle \Phi | a_{ijk\dots}^{abc\dots}$ , which leads to<sup>6</sup>

$$\langle \Phi | X R_0 X_1 R_0 X_2 \cdots R_0 X_n | \Phi \rangle = \overline{\text{diagram}} \quad (6.12)$$

for a general series of excitation operators  $X, X_1, \dots, X_n$ . This makes a convenient corollary to Wick's theorem for operator products with resolvents.

<sup>5</sup>This follows from  $R_0 H_c \Psi = R_0 (H_0 + V_c) \Psi = -Q \Psi + R_0 \Psi$  along with  $Q \Psi = \Psi - \Phi$ .

<sup>6</sup>The dotted lines are resolvent lines.

**Example 6.5.** Expanding the resolvent in  $\Psi^{(2)} = R_0 V_c \Psi^{(1)}$  gives an expansion that includes up to quadruples

$$\Psi^{(2)} = \sum_i \Phi_i^a \frac{\langle \Phi_i^a | V_c | \Psi^{(1)} \rangle}{\mathcal{E}_a^i} + \left(\frac{1}{2!}\right)^2 \sum_{ab} \Phi_{ij}^{ab} \frac{\langle \Phi_{ij}^{ab} | V_c | \Psi^{(1)} \rangle}{\mathcal{E}_{ab}^{ij}} + \left(\frac{1}{3!}\right)^2 \sum_{abc} \Phi_{ijk}^{abc} \frac{\langle \Phi_{ijk}^{abc} | V_c | \Psi^{(1)} \rangle}{\mathcal{E}_{abc}^{ijk}} + \left(\frac{1}{4!}\right)^2 \sum_{abcd} \Phi_{ijkl}^{abcd} \frac{\langle \Phi_{ijkl}^{abcd} | V_c | \Psi^{(1)} \rangle}{\mathcal{E}_{abcd}^{ijkl}}$$

since the two-electron part of  $\Psi^{(1)}$  has an excitation level of +2 and the excitation level of  $V_c$  ranges from  $-2$  to  $+2$ .

**Example 6.6.** The expansion for  $\Psi^{(2)}$  can be evaluated graphically. Assuming Brillouin's theorem for simplicity,

$$\Psi^{(2)} = \begin{array}{c} \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4} + \text{Diagram 5} \\ \text{Diagram 6} + \text{Diagram 7} + \text{Diagram 8} + \text{Diagram 9} \end{array} \quad (6.13)$$

$$\begin{aligned} &= \frac{1}{2} \sum_{abc} \Phi_i^a \frac{\bar{g}_{aj}^{bc} \bar{g}_{bc}^{ij}}{\mathcal{E}_a^i \mathcal{E}_{bc}^{ij}} + \frac{1}{2} \sum_{ab} \Phi_i^a \frac{\bar{g}_{ij}^{ab} \bar{g}_{ab}^{ij}}{\mathcal{E}_a^i \mathcal{E}_{ab}^{ij}} + \frac{1}{2^3} \sum_{abcd} \Phi_{ij}^{ab} \frac{\bar{g}_{cd}^{ab} \bar{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{ij}} + \frac{1}{2^3} \sum_{ab} \Phi_{ij}^{ab} \frac{\bar{g}_{kl}^{ij} \bar{g}_{kl}^{ab}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{kl}^{ab}} + \sum_{abc} \Phi_{ij}^{ab} \frac{\bar{g}_{ac}^{ik} \bar{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ac}^{ik}} \\ &+ \frac{1}{2^2} \sum_{abcd} \Phi_{ijk}^{abc} \frac{\bar{g}_{ad}^{ij} \bar{g}_{bc}^{dk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ad}^{ij}} - \frac{1}{2^2} \sum_{abc} \frac{\bar{g}_{ab}^{il} \bar{g}_{lc}^{jk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ab}^{ij}} + \frac{1}{2^4} \sum_{abcd} \Phi_{ijkl}^{abcd} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} \end{aligned} \quad (6.14)$$

where the operators in the final diagram do not form an equivalent pair because they pass through different resolvent lines. This can be used to determine the third-order correlation energy

$$E_c^{(3)} = \langle \Phi | V_c | \Psi^{(2)} \rangle = \begin{array}{c} \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} \end{array} = \frac{1}{2^3} \sum_{abcd} \frac{\bar{g}_{ij}^{ab} \bar{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{ij}} + \frac{1}{2^3} \sum_{ab} \frac{\bar{g}_{ij}^{ab} \bar{g}_{kl}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{kl}^{ab}} + \sum_{abc} \frac{\bar{g}_{ac}^{ab} \bar{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ac}^{ik}} \quad (6.15)$$

which also equals  $\langle \Psi^{(1)} | V_c | \Psi^{(1)} \rangle$ . This is an example of the *Wigner (2n+1) rule*, which says that  $E_c^{(2n+1)} = \langle \Psi^{(n)} | V_c | \Psi^{(n)} \rangle$ . Note that  $E_c^{(m+1)}$  always only depends on the doubles contribution to  $\Psi^{(m)}$ , but that the doubles coefficients themselves may involve triples, quadruples and higher contributions from wavefunction components of order less than  $m$ .

**Example 6.7.** Using  ${}^{(m)}c_{ab\dots}^{ij\dots} = \langle \Phi_{ij\dots}^{ab\dots} | \Psi^{(m)} \rangle$ , the second order CI coefficients can be determined from eq 6.13 by contracting a bare excitation operator with the top of each diagram. Interpreting these graphs gives the following.

$$\begin{aligned} {}^{(2)}c_a^i &= \frac{1}{2} \sum_{bc} \frac{\bar{g}_{aj}^{bc} \bar{g}_{bc}^{ij}}{\mathcal{E}_a^i \mathcal{E}_{bc}^{ij}} + \frac{1}{2} \sum_{jk} \frac{\bar{g}_{jk}^{ab} \bar{g}_{ab}^{ij}}{\mathcal{E}_a^i \mathcal{E}_{jk}^{ab}} \\ {}^{(2)}c_{ab}^{ij} &= \frac{1}{2} \sum_{cd} \frac{\bar{g}_{ab}^{cd} \bar{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{ij}} + \frac{1}{2} \sum_{kl} \frac{\bar{g}_{kl}^{ij} \bar{g}_{kl}^{ab}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{kl}^{ab}} + \hat{P}_{(a/b)} \sum_c \frac{\bar{g}_{ac}^{ik} \bar{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ac}^{ik}} \\ {}^{(2)}c_{abc}^{ijk} &= \hat{P}_{(a/bc)} \sum_d \frac{\bar{g}_{ad}^{ij} \bar{g}_{bc}^{dk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ad}^{ij}} - \hat{P}_{(a/bc)} \sum_l \frac{\bar{g}_{ab}^{il} \bar{g}_{lc}^{jk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ab}^{ij}} \\ {}^{(2)}c_{abcd}^{ijkl} &= \hat{P}_{(ab/cd)} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} \end{aligned}$$

Note that the second order quadruples coefficient is disconnected. Prop. 6.1 shows that the second-order quadruples operator is actually a simple product of first-order doubles operators. This fact was an early motivation for coupled-pair many-electron theory,<sup>7</sup> since it justifies approximating  $\Psi_{\text{CIDQ}} = (1 + C_2 + C_4)\Phi$  by  $\Psi_{\text{CPMET}} = (1 + C_2 + \frac{1}{2}C_2^2)\Phi$ .

**Proposition 6.1.**  ${}^{(2)}C_4 = \frac{1}{2} {}^{(1)}C_2^2$

Proof: This follows from rearranging the resolvent denominator.

$$\frac{1}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} + \frac{1}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{cd}^{kl}} = \frac{\mathcal{E}_{cd}^{kl} + \mathcal{E}_{ab}^{ij}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{kl}} = \frac{1}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{kl}} \implies {}^{(2)}C_4 = \left(\frac{1}{2}\right)^4 \sum_{abcd} \tilde{a}_{abcd}^{ijkl} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} = \frac{1}{2} \cdot \left(\frac{1}{2}\right)^4 \sum_{abcd} \tilde{a}_{abcd}^{ijkl} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{kl}} = \frac{1}{2} {}^{(1)}C_2^2$$

<sup>7</sup>This is the original name for coupled-cluster doubles.