

6 Perturbation theory

Definition 6.1. Model Hamiltonian. The electronic Hamiltonian¹ 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.

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

In general the model Hamiltonian is chosen to make the matrix representation of H_c in the model eigenbasis diagonally dominant.² 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* λ that smoothly toggles between the model Hamiltonian at $\lambda = 0$ to the exact one at $\lambda = 1$. The m^{th} -order contribution to a quantity X is then defined as the m^{th} coefficient in its Taylor series about $\lambda = 0$, denoted $X^{(m)}$. In particular, the wavefunction and correlation energy can be expanded as follows.

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

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 Φ 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^{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 Φ -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*.³

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

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

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

Due to intermediate normalization, we also have that $P\Psi = \Phi$ and $Q\Psi = \Psi - \Phi$.

Definition 6.4. Resolvent. The *resolvent*, $R_0 \equiv (-H_0)^{-1}Q$, is the negative⁴ inverse of H_0 in the orthogonal space.⁵

$$R_0 \Phi = 0 \Phi \quad R_0 \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} = (\mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k})^{-1} \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} \quad R_0 = \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1 \dots a_k \\ i_1 \dots i_k}} \frac{|\Phi_{i_1 \dots i_k}^{a_1 \dots a_k}\rangle \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k}|}{\mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k}} \quad (6.7)$$

The equation on the right is the spectral decomposition of the resolvent.⁶ 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.

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

²See https://en.wikipedia.org/wiki/Diagonally_dominant_matrix.

³ $1_n \equiv 1|_{\mathcal{F}_n}$ is the identity on \mathcal{F}_n , which is equivalent to a projection onto this subspace. For our purposes, this is the identity.

⁴The 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.

⁵Note that this implies $R_0 P = 0$ and $R_0 Q = R_0$.

⁶This follows from the eigenvalue equations, but you can derive it explicitly by substituting equation 6.5 into $R_0 = (-H_0)^{-1}Q$.

Remark 6.2. A recursive solution to the Schrödinger equation. Operating R_0 on $H(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda)$ gives⁷

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

which provides a recursive equation for $\Psi(\lambda)$ that can be used to solve for wavefunction contributions order by order.

Example 6.1. The first two derivatives of equation 6.8 are given by

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

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

$$\Psi^{(1)} = \left. \frac{\partial \Psi(\lambda)}{\partial \lambda} \right|_{\lambda=0} = R_0 V_c \Phi \quad \Psi^{(2)} = \left. \frac{1}{2} \frac{\partial^2 \Psi(\lambda)}{\partial \lambda^2} \right|_{\lambda=0} = R_0 V_c \Psi^{(1)} = R_0 V_c R_0 V_c \Phi \quad (6.9)$$

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

Example 6.2. Plugging in the spectral decomposition for R_0 allows us to expand $\Psi^{(1)}$ in the determinant basis.

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

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.

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

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.

Definition 6.5. Resolvent line. We can generalize our previous definition of the *resolvent line* as follows

$$\vdots Y \equiv \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1 \dots a_k \\ i_1 \dots i_k}} \frac{y_{a_1 \dots a_k}^{i_1 \dots i_k}}{\mathcal{E}_{a_1 \dots a_k}^{i_1 \dots i_k}} \tilde{a}_{i_1 \dots i_k}^{a_1 \dots a_k} \quad Y = Y_{n \rightarrow n} + Y_{n \not\rightarrow n} \quad Y_{n \rightarrow n} = y_0 + \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{p_1 \dots p_k \\ q_1 \dots q_k}} y_{p_1 \dots p_k}^{q_1 \dots q_k} \tilde{a}_{q_1 \dots q_k}^{p_1 \dots p_k} \quad (6.11)$$

where Y is an arbitrary operator. The last equation is the Wick expansion of $Y_{n \rightarrow n}$, which denotes the purely particle-number-conserving part⁸ of Y . This definition immediately implies $\vdots |\Psi\rangle = R_0 |\Psi\rangle$ for all Ψ .⁹ Other expressions are defined by giving resolvent lines priority in the order of operations, with maximum priority given to the rightmost resolvent.

$$Y_1 \vdots Y_2 \dots \vdots Y_n \equiv Y_1 (\vdots Y_2 (\dots (\vdots Y_n) \dots)) \quad \vdots Y_1 \vdots Y_2 \dots \vdots Y_n \equiv \vdots Y_1 (\vdots Y_2 (\dots (\vdots Y_n) \dots)) \vdots \quad (6.12)$$

This definition also specifies the interpretation rule for a graphs with resolvent lines, which are formally defined below.

Corollary 6.1. Wick's theorem for perturbation theory. $Y R_0 Y_1 \dots R_0 Y_m |\Phi\rangle = (\vdots Y \vdots Y_1 \dots \vdots Y_m \vdots + \vdots Y \vdots Y_1 \dots \vdots Y_m \vdots) |\Phi\rangle$

Proof: This follows directly from Wick's theorem and definition 6.5.

Definition 6.6. Resolvent graph. A *resolvent graph* represents a normal-ordered product of operators and resolvents. Graphs with disconnected parts that don't share any resolvent lines are considered products of separate resolvent graphs. Vertical spaces between resolvent lines in a resolvent graph are termed *levels*, which are numbered from bottom with zero indexing. Therefore, an operator lies in the k^{th} level if there are k resolvent lines below it. Formally, then, an *m-level resolvent graph* $G(\rho, m) \equiv (G, \rho, m)$ associates each operator o in G with a specific level $\rho(o) = \rho_o$ in $\mathbb{Z}_m = \{0, 1, \dots, m-1\}$ through the *level map* ρ .¹⁰ Therefore, each line l in G crosses resolvents $\min(\rho_{h(l)}, \rho_{t(l)}) + 1$ through $\max(\rho_{h(l)}, \rho_{t(l)})$.

⁷This follows from $R_0 H_0 \Psi = -Q\Psi = -\Psi + \Phi$.

⁸The component that maps $\mathcal{F}_n \rightarrow \mathcal{F}_n$ for all n , which can always be written as a linear combination of excitation operators.

⁹Since any $|\Psi\rangle$ can be written as $Y|\Phi\rangle$, this follows from applying eq 6.7 to each term in the Wick expansion of Y in $R_0 Y|\Phi\rangle$.

¹⁰Note that an m -level resolvent graph contains $m-1$ resolvents.

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

$$\Psi^{(1)} = \begin{array}{c} \text{Diagram 1: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it.} \\ \text{Diagram 2: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \end{array} + \begin{array}{c} \text{Diagram 3: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 4: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \end{array} \quad E_c^{(2)} = \begin{array}{c} \text{Diagram 5: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 6: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \end{array} \quad (6.13)$$

Example 6.5. The expansion for $\Psi^{(2)}$ can be evaluated using corollary 6.1. Assuming Brillouin's theorem for simplicity,

$$\Psi^{(2)} = R_0 V_c R_0 V_c |\Phi\rangle = \begin{array}{c} \text{Diagram 1: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 2: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 3: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 4: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 5: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \end{array} + \begin{array}{c} \text{Diagram 6: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 7: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 8: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 9: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \end{array} \quad (6.14)$$

$$= \frac{1}{2} \sum_{\substack{abc \\ ij}} \Phi_i^a \frac{\bar{g}_{aj}^{bc} \bar{g}_{bc}^{ij}}{\mathcal{E}_a^i \mathcal{E}_{bc}^{ij}} - \frac{1}{2} \sum_{\substack{ab \\ ijk}} \Phi_i^a \frac{\bar{g}_{jk}^{ib} \bar{g}_{ab}^{jk}}{\mathcal{E}_a^i \mathcal{E}_{ab}^{jk}} + \frac{1}{2^3} \sum_{\substack{abcd \\ ij}} \Phi_{ij}^{ab} \frac{\bar{g}_{ab}^{cd} \bar{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{ij}} + \frac{1}{2^3} \sum_{\substack{ab \\ ijk}} \Phi_{ij}^{ab} \frac{\bar{g}_{kl}^{ij} \bar{g}_{ab}^{kl}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{kl}^{ij}} \\ + \sum_{\substack{abc \\ ijk}} \Phi_{ij}^{ab} \frac{\bar{g}_{ac}^{ik} \bar{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ac}^{ik}} + \frac{1}{2^2} \sum_{\substack{abcd \\ ijk}} \Phi_{ijk}^{abc} \frac{\bar{g}_{ad}^{ij} \bar{g}_{bc}^{dk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ad}^{ij}} - \frac{1}{2^2} \sum_{\substack{abc \\ ijk}} \Phi_{ijk}^{abc} \frac{\bar{g}_{ab}^{il} \bar{g}_{lc}^{jk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{il}^{jk}} + \frac{1}{2^4} \sum_{\substack{abcd \\ ijk}} \Phi_{ijkl}^{abcd} \frac{\bar{g}_{ab}^{ij} \bar{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} \quad (6.15)$$

where the operators in the final diagram do not form an equivalent pair because they pass through different resolvent lines. The third-order contribution to the correlation energy can be evaluated as the complete contractions of $V_c R_0 V_c R_0 V_c$

$$E_c^{(3)} = \begin{array}{c} \text{Diagram 1: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 2: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \\ \text{Diagram 3: A vertex with two incoming lines from the left and one outgoing line to the right, with a horizontal line below it and a wavy line connecting the two incoming lines.} \end{array} = \frac{1}{2^3} \sum_{\substack{abcd \\ ij}} \frac{\bar{g}_{ij}^{ab} \bar{g}_{ab}^{cd} \bar{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{ij}} + \frac{1}{2^3} \sum_{\substack{ab \\ ijk}} \frac{\bar{g}_{ij}^{ab} \bar{g}_{kl}^{ij} \bar{g}_{ab}^{kl}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{kl}^{ij}} + \sum_{\substack{abc \\ ijk}} \frac{\bar{g}_{ab}^{ij} \bar{g}_{ac}^{ik} \bar{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ac}^{ik}} \quad (6.16)$$

which is equivalent to contracting the doubles contributions to $\Psi^{(2)}$ with $\frac{1}{4} \bar{g}_{ij}^{ab} \bar{a}_{ab}^{ij}$. 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 6.6. 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 6.14 by contracting a bare excitation operator with the top of each diagram. Interpreting these graphs gives the following.

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

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,¹¹ 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.

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

¹¹This is the original name for coupled-cluster doubles.

Lemma 6.1. The Energy Substitution Lemma. $\Psi^{(m)}$ equals the sum of a “principal term” $(R_0 V_c)^m \Phi$ plus all possible substitutions of adjacent factors $(R_0 V_c)^{r_i}$ in the principal term by $R_0 E_c^{(r_i)}$. Each term in the sum is weighted by a sign factor $(-)^k$, where k is the number of substitutions.

Proof: See appendix A.

Example 6.7. Lemma 6.1 is consistent with equation 6.9 because substitution of the rightmost factors in the principal term leaves a resolvent acting on the reference determinant and because the first-order energy contribution equals zero. The first non-trivial examples of the energy substitution lemma begin at third order.

$$\Psi^{(3)} = R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 E_c^{(2)} R_0 V_c \Phi \quad (6.17)$$

$$\Psi^{(4)} = R_0 V_c R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 E_c^{(2)} R_0 V_c R_0 V_c \Phi - R_0 V_c R_0 E_c^{(2)} R_0 V_c \Phi - R_0 E_c^{(3)} R_0 V_c \Phi \quad (6.18)$$

$$\begin{aligned} \Psi^{(5)} = & R_0 V_c R_0 V_c R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 E_c^{(2)} R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 V_c R_0 E_c^{(2)} R_0 V_c R_0 V_c \Phi \\ & - R_0 V_c R_0 V_c R_0 E_c^{(2)} R_0 V_c \Phi + R_0 E_c^{(2)} R_0 E_c^{(2)} R_0 V_c \Phi - R_0 E_c^{(3)} R_0 V_c R_0 V_c \Phi \\ & - R_0 V_c R_0 E_c^{(3)} R_0 V_c \Phi - R_0 E_c^{(4)} R_0 V_c \Phi \end{aligned} \quad (6.19)$$

Theorem 6.1. The Bracketing Theorem. $\Psi^{(m)}$ equals the principal term plus all possible insertions of nested brackets into the principal term. Each term in the sum is weighted by $(-)^k$ where k is the total number of brackets.¹²

Proof: See appendix A.

Example 6.8. Equations 6.17 and 6.18 are clearly consistent with thm 6.1, since $E_c^{(2)} = \langle V_c R_0 V_c \rangle$ and $E_c^{(3)} = \langle V_c R_0 V_c R_0 V_c \rangle$.

$$\Psi^{(3)} = R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 \langle V_c R_0 V_c \rangle R_0 V_c \Phi \quad (6.20)$$

$$\Psi^{(4)} = R_0 V_c R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 \langle V_c R_0 V_c \rangle R_0 V_c R_0 V_c \Phi - R_0 V_c R_0 \langle V_c R_0 V_c \rangle R_0 V_c \Phi - R_0 \langle V_c R_0 V_c R_0 V_c \rangle R_0 V_c \Phi \quad (6.21)$$

The first non-vanishing terms with nested brackets appear at fifth-order

$$\begin{aligned} \Psi^{(5)} = & R_0 V_c R_0 V_c R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 \langle V_c R_0 V_c \rangle R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 V_c R_0 \langle V_c R_0 V_c \rangle R_0 V_c R_0 V_c \Phi \\ & - R_0 V_c R_0 V_c R_0 \langle V_c R_0 V_c \rangle R_0 V_c \Phi + R_0 \langle V_c R_0 V_c \rangle R_0 \langle V_c R_0 V_c \rangle R_0 V_c \Phi - R_0 \langle V_c R_0 V_c R_0 V_c \rangle R_0 V_c R_0 V_c \Phi \\ & - R_0 V_c R_0 \langle V_c R_0 V_c R_0 V_c \rangle R_0 V_c \Phi - R_0 \langle V_c R_0 V_c R_0 V_c R_0 V_c \rangle R_0 V_c \Phi + R_0 \langle V_c R_0 \langle V_c R_0 V_c \rangle R_0 V_c \rangle R_0 V_c \Phi \end{aligned} \quad (6.22)$$

which follows from substituting equation 6.20 into $E^{(4)} = \langle \Phi | V_c | \Psi^{(3)} \rangle$ in the energy substitution expansion of $\Psi^{(5)}$.

Example 6.9. Assuming Brillouin’s theorem, the simplest non-vanishing term with an inserted bracket appears in $\Psi^{(3)}$.

$$R_0 \langle V_c R_0 V_c \rangle R_0 V_c \Phi = \frac{\text{level of the insertion}}{\text{insertion}} \rightarrow \begin{array}{c} \text{1st level} \\ \text{0th level} \\ \text{remainder} \quad \text{insertion} \end{array}$$

Proposition 6.2. Wigner’s $(2n+1)$ rule.

¹²The “brackets” here are reference expectation values: $\langle W \rangle \equiv \langle \Phi | W | \Phi \rangle$.

A Proof of the Linked-Diagram Theorem

Notation A.1. Let “ Y^m choose Z^k ”, denoted ${}^m C_k(Y : Z)$, refer to a sum over the m choose k permutations of $Y^{m-k} Z^k$,¹³ where Y and Z are operators that may or may not commute.¹⁴ This defines a generalization of the binomial theorem.

$$(Y + Z)^m = \sum_{k=0}^m {}^m C_k(Y : Z) \quad (\text{A.1})$$

Furthermore, let ${}^m C(Y : Z_1, \dots, Z_k)$ be a sum over permutations of $Y^{m-k} Z_1 \cdots Z_k$ that preserve the ordering of the Z_i 's.¹⁵ When all of the Z_i 's equal Z , we can write ${}^m C(Y : Z_1, \dots, Z_k) = {}^m C_k(Y : Z)$.

Proposition A.1. $\Psi(\lambda) = \sum_{m=0}^{\infty} (R_0(\lambda V_c - E(\lambda)))^m \Phi$

Proof: This follows by infinite recursion of equation 6.8 with the assumption $\lim_{m \rightarrow \infty} (R_0(\lambda V_c - E(\lambda)))^m \Psi(\lambda) = 0$.

Definition A.1. Integer compositions. The *compositions* of an integer m are the ways of writing m as a sum of positive integers. The full set of integer compositions of m is given by $\mathcal{C}(m) = \mathcal{C}_1(m) \cup \mathcal{C}_2(m) \cup \cdots \cup \mathcal{C}_m(m)$ where $\mathcal{C}_k(m) = \{(r_1, \dots, r_k) \in \mathbb{N}_0^k \mid r_1 + \cdots + r_k = m\}$ are the integer compositions of m into k parts.

Lemma A.1. The Energy Substitution Lemma. $\Psi^{(m)}$ equals the sum of a “principal term” $(R_0 V_c)^m \Phi$ plus all possible substitutions of adjacent factors $(R_0 V_c)^{r_i}$ in the principal term by $R_0 E_c^{(r_i)}$. Each term in the sum is weighted by a sign factor $(-)^k$, where k is the number of substitutions.

Proof: Using equation A.1 and a double sum identity¹⁶ in the infinite recursion formula for $\Psi(\lambda)$ gives the following.

$$\Psi(\lambda) = \sum_{m=0}^{\infty} (R_0(\lambda V_c - E(\lambda)))^m \Phi = \sum_{m=0}^{\infty} \sum_{k=0}^m \lambda^{m-k} (-)^k {}^m C_k(R_0 V_c : R_0 E(\lambda)) \Phi = \sum_{k'=0}^{\infty} \sum_{k=0}^{\infty} \lambda^{k'} (-)^k {}^{k'+k} C_k(R_0 V_c : R_0 E(\lambda)) \Phi$$

The $k' = 0$ term has no operators separating Φ from the resolvent and vanishes. Taylor expansion of the energies gives

$$\begin{aligned} \Psi(\lambda) &= \sum_{k=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p_1=1}^{\infty} \cdots \sum_{p_k=1}^{\infty} \lambda^{k'+p_1+\cdots+p_k} (-)^k {}^{k'+k} C_k(R_0 V_c : R_0 E_c^{(p_1)}, \dots, R_0 E_c^{(p_k)}) \Phi \\ &= \sum_{m=1}^{\infty} \sum_{k=0}^{m-1} \sum_{(r_1, \dots, r_{k+1}) \in \mathcal{C}_{k+1}(m)} \lambda^m (-)^k {}^{k+r_1} C_k(R_0 V_c : R_0 E_c^{(r_2)}, \dots, R_0 E_c^{(r_{k+1})}) \Phi \end{aligned}$$

where we have grouped powers of λ using a multi-sum reduction. Writing the inner sums as a sum over $\mathcal{C}(m)$ we find

$$\Psi^{(m)} = \frac{1}{m!} \frac{\partial^m \Psi(\lambda)}{\partial \lambda^m} \Big|_{\lambda=0} = \sum_{(r_1, \dots, r_{k+1}) \in \mathcal{C}(m)} (-)^k {}^{k+r_1} C_k(R_0 V_c : R_0 E_c^{(r_2)}, \dots, R_0 E_c^{(r_{k+1})}) \Phi \quad (\text{A.2})$$

which, given notation A.1 and definition A.1, is an algebraic statement of the proposition, completing the proof.

Theorem A.1. The Bracketing Theorem. $\Psi^{(m)}$ equals the principal term plus all possible insertions of nested brackets into the principal term. Each term in the sum is weighted by $(-)^k$ where k is the total number of brackets.

Proof: The proposition holds for $m = 1$ because $\Psi^{(1)} = R_0 V_c \Phi$ and there are no possible bracketings. Assume it holds for $m - 1$. Then by the energy substitution lemma it also holds for m because $E_c^{(r_i)}$ equals $\langle \Phi | V_c | \Psi^{(r_i)} \rangle$ which, by our inductive assumption, equals $\langle V_c(R_0 V_c)^{r_i} \rangle$ plus all nested bracketings weighted by appropriate sign factors.

¹³For example, ${}^4 C_2(Y : Z) = Y^2 Z^2 + Y Z Y Z + Y Z^2 Y + Z Y^2 Z + Z Y Z Y + Z^2 Y^2$.

¹⁴If they do commute, then ${}^m C_k(Y : Z) = \binom{m}{k} Y^{m-k} Z^k$.

¹⁵For example, ${}^4 C(Y : Z_1, Z_2) = Y^2 Z_1 Z_2 + Y Z_1 Y Z_2 + Y Z_1 Z_2 Y + Z_1 Y^2 Z_2 + Z_1 Y Z_2 Y + Z_1 Z_2 Y^2$.

¹⁶Reverse double-sum reduction: $\sum_{m=0}^{\infty} \sum_{k=0}^m t_{m-k, k} = \sum_{k'=0}^{\infty} \sum_{k=0}^{\infty} t_{k', k}$. See <http://functions.wolfram.com/GeneralIdentities/12/>.