6 Perturbation theory

Definition 6.1. ***Model Hamiltonian.*** The electronic Hamiltonian[1] 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.

$$H_0 \equiv f^p_p \tilde{a}^p_p \qquad\qquad V_c \equiv f^q_p(1-\delta^q_p)\tilde{a}^p_q + \tfrac{1}{4}\overline{g}^{rs}_{pq}\tilde{a}^{pq}_{rs} \tag{6.1}$$

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

$$H_0\Phi = 0\,\Phi \qquad\qquad H_0\Phi^{a_1\cdots a_k}_{i_1\cdots i_k} = \mathcal{E}^{a_1\cdots a_k}_{i_1\cdots i_k}\Phi^{a_1\cdots a_k}_{i_1\cdots i_k} \qquad\qquad \mathcal{E}^{p_1\cdots p_k}_{q_1\cdots q_k} \equiv \sum_{r=1}^{k} f^{p_r}_{p_r} - \sum_{r=1}^{k} f^{q_r}_{q_r} \tag{6.2}$$

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 $\langle\Phi|\Psi\rangle \gg \langle\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}|\Psi\rangle$ 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.

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

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

$$E_c = \langle\Phi|V_c|\Psi\rangle \qquad \Longrightarrow \qquad E_c^{(m+1)} = \langle\Phi|V_c|\Psi^{(m)}\rangle \tag{6.4}$$

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]

$$Q \equiv 1 - P = \sum_k \left(\tfrac{1}{k!}\right)^2 \sum_{\substack{a_1\cdots a_k \\ i_1\cdots i_k}} |\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}\rangle\langle\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}| \tag{6.5}$$

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

$$P + Q = 1 \qquad\qquad P^2 = P \qquad\qquad Q^2 = Q \qquad\qquad PQ = QP = 0 \tag{6.6}$$

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 negative[4] inverse of H_0 in the orthogonal space.

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

The equation on the right is the spectral decomposition of the resolvent.[5] 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.

[1] 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.

[2] See `https://en.wikipedia.org/wiki/Diagonally_dominant_matrix`.

[3] Note that these definitions are implicitly restricted to $\mathcal{F}_n$ rather than the full Fock space.

[4] 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.

[5] This 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 $H(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda)$ gives[6]

$$\Psi(\lambda) = \Phi + R_0(\lambda V_\mathrm{c} - E(\lambda))\Psi(\lambda) \tag{6.8}$$

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

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

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

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

$$\Psi^{(1)} = \left.\frac{\partial\Psi(\lambda)}{\partial\lambda}\right|_{\lambda=0} = R_0 V_\mathrm{c}\Phi \qquad\qquad \Psi^{(2)} = \frac{1}{2}\left.\frac{\partial^2\Psi(\lambda)}{\partial\lambda^2}\right|_{\lambda=0} = R_0 V_\mathrm{c}\Psi^{(1)} = R_0 V_\mathrm{c} R_0 V_\mathrm{c}\Phi \tag{6.9}$$

Here we have used $E_\mathrm{c}^{(0)} = E_\mathrm{c}^{(1)} = 0$ 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.

$$\Psi^{(1)} = R_0 V_\mathrm{c}\Phi = \sum_{\substack{a\\i}} \Phi_i^a \frac{\langle\Phi_i^a|V_\mathrm{c}|\Phi\rangle}{\mathcal{E}_a^i} + (\tfrac{1}{2!})^2 \sum_{\substack{ab\\ij}} \Phi_{ij}^{ab} \frac{\langle\Phi_{ij}^{ab}|V_\mathrm{c}|\Phi\rangle}{\mathcal{E}_{ab}^{ij}} \tag{6.10}$$

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.

$$\Psi^{(1)} = \sum_{\substack{a\\i}} \Phi_i^a \frac{f_a^i}{\mathcal{E}_a^i} + (\tfrac{1}{2!})^2 \sum_{\substack{ab\\ij}} \Phi_{ij}^{ab} \frac{\overline{g}_{ab}^{ij}}{\mathcal{E}_{ab}^{ij}} \qquad\Longrightarrow\qquad E_\mathrm{c}^{(2)} = \langle\Phi|V_\mathrm{c}|\Psi^{(1)}\rangle = \sum_{\substack{a\\i}} \frac{f_i^a f_a^i}{\mathcal{E}_a^i} + (\tfrac{1}{2!})^2 \sum_{\substack{ab\\ij}} \frac{\overline{g}_{ij}^{ab}\overline{g}_{ab}^{ij}}{\mathcal{E}_{ab}^{ij}}$$

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 (extended definition).*** Let Y be a particle-number conserving operator string[7] and compare $R_0 Y|\Phi\rangle$ with $Y|\Phi\rangle$ by expanding this operator string using Wick's theorem. We can turn the second expansion into the first by setting each term to zero unless the contracted Y has the form $\tilde{a}_{j_1\cdots j_m}^{b_1\cdots b_m} \times \mathrm{const}$,[8] in which case we scale it by $(\mathcal{E}_{b_1\cdots b_m}^{j_1\cdots j_m})^{-1}$.[9] Multiplying these expansions by Y' and applying Wick's theorem gives the following

$$Y'Y|\Phi\rangle = \left(\colon Y'Y\colon + \colon\overline{Y'Y}\colon\right)|\Phi\rangle \qquad\qquad Y'R_0Y|\Phi\rangle = \left(\colon Y'\vdots\, Y\colon + \colon\overline{Y'\vdots\, Y}\colon\right)|\Phi\rangle$$

where the dotted lines indicate that wherever the internal contractions on Y leave a remainder of the form $\tilde{a}_{j_1\cdots j_m}^{b_1\cdots b_m} \times$const we scale the term by $(\mathcal{E}_{b_1\cdots b_m}^{j_1\cdots j_m})^{-1}$. All other terms are omitted. This builds upon our earlier concept of a *resolvent line*, which was limited to a particular case: $\langle\Phi|Y'R_0Y|\Phi\rangle = \colon\overline{Y'\vdots\, Y}\colon$ with $Y' = \tilde{a}_{a_1\cdots a_k}^{i_1\cdots i_k}$ and $Y = \tilde{a}_{j_1\cdots j_k}^{b_1\cdots b_k}$. The extended definition implies $\vdots\,|\Phi_{i_1\cdots i_k}^{a_1\cdots a_k}\rangle = (\mathcal{E}_{a_1\cdots a_k}^{i_1\cdots i_k})^{-1}|\Phi_{i_1\cdots i_k}^{a_1\cdots a_k}\rangle$ and $\vdots\,|\Phi\rangle = 0$, which makes an uncontracted resolvent line interchangeable with R_0.[10] This definition of has a simple graphical interpretation: A graph with hole lines $i_1,\ldots,i_h$ and particle lines $a_1,\ldots,a_k$ passing through a resolvent line is scaled by $(\mathcal{E}_{a_1\cdots a_k}^{i_1\cdots i_k})^{-1}$ when $h = k$ and vanishes when $h \neq k$. A graph with no operators separating a resolvent line from the bra or ket of the reference state equals zero.

Corollary 6.1. ***Wick's theorem for perturbation theory.*** $Y R_0 Y_1 \cdots R_0 Y_m|\Phi\rangle = \left(\colon Y\vdots\, Y_1\cdots\vdots\, Y_m\colon + \colon\overline{Y\vdots\, Y_1\cdots\vdots\, Y_m}\colon\right)|\Phi\rangle$

Proof: This follows directly from Wick's theorem and the definition of a resolvent line.

[6] This follows from $R_0 H_0\Psi = -Q\Psi = -\Psi + \Phi$.

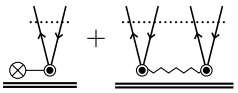
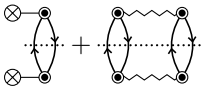
[7] That is, it contains a balanced number of creation and annihilation operators so that $Y|\Phi\rangle \in \mathcal{F}_n$.

[8] Since $R_0\colon X\colon|\Phi\rangle = 0$ unless $\colon X\colon$ can fully contract one of the bras $\langle\Phi_{i_1\cdots i_k}^{a_1\cdots a_k}|$ in the resolvent.

[9] Since $R_0\tilde{a}_{j_1\cdots j_m}^{b_1\cdots b_m}|\Phi\rangle = (\mathcal{E}_{b_1\cdots b_m}^{j_1\cdots j_m})^{-1}\tilde{a}_{j_1\cdots j_m}^{b_1\cdots b_m}|\Phi\rangle$.

[10] The difference between resolvents and resolvent lines is that we haven't defined a "contraction through R_0" operation.

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

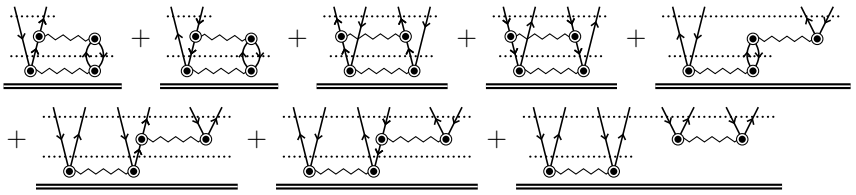
$\Psi^{(1)} =$  $E_{\rm c}^{(2)} =$  (6.11)

Example 6.5. Using the spectral decomposition of R_0 in $\Psi^{(2)} = R_0 V_{\rm c} \Psi^{(1)}$ gives an expansion that truncates at quadruples

$$\Psi^{(2)} = \sum_{\substack{a\\ i}} \Phi_i^a \frac{\langle \Phi_i^a | V_{\rm c} | \Psi^{(1)} \rangle}{\mathcal{E}_a^i} + (\tfrac{1}{2!})^2 \sum_{\substack{ab\\ ij}} \Phi_{ij}^{ab} \frac{\langle \Phi_{ij}^{ab} | V_{\rm c} | \Psi^{(1)} \rangle}{\mathcal{E}_{ab}^{ij}} + (\tfrac{1}{3!})^2 \sum_{\substack{abc\\ ijk}} \Phi_{ijk}^{abc} \frac{\langle \Phi_{ijk}^{abc} | V_{\rm c} | \Psi^{(1)} \rangle}{\mathcal{E}_{abc}^{ijk}} + (\tfrac{1}{4!})^2 \sum_{\substack{abcd\\ ijkl}} \Phi_{ijkl}^{abcd} \frac{\langle \Phi_{ijkl}^{abcd} | V_{\rm c} | \Psi^{(1)} \rangle}{\mathcal{E}_{abcd}^{ijkl}}$$

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

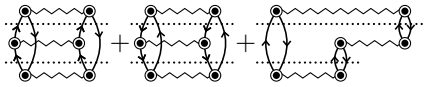
Example 6.6. The expansion for $\Psi^{(2)}$ can be evaluated graphically. Assuming Brillouin's theorem for simplicity,

$\Psi^{(2)} =$  (6.12)

$$= \tfrac{1}{2} \sum_{\substack{abc\\ ij}} \Phi_i^a \frac{\overline{g}_{aj}^{bc} \overline{g}_{bc}^{ij}}{\mathcal{E}_a^i \mathcal{E}_{bc}^{ij}} + \tfrac{1}{2} \sum_{\substack{ab\\ ijk}} \Phi_i^a \frac{\overline{g}_{jk}^{ib} \overline{g}_{ab}^{jk}}{\mathcal{E}_a^i \mathcal{E}_{ab}^{jk}} + \tfrac{1}{2^3} \sum_{\substack{abcd\\ ij}} \Phi_{ij}^{ab} \frac{\overline{g}_{ab}^{cd} \overline{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{ij}} + \tfrac{1}{2^3} \sum_{\substack{ab\\ ijkl}} \Phi_{ij}^{ab} \frac{\overline{g}_{kl}^{ij} \overline{g}_{ab}^{kl}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ab}^{kl}} + \sum_{\substack{abc\\ ijk}} \Phi_{ij}^{ab} \frac{\overline{g}_{ac}^{ik} \overline{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ac}^{ik}}$$

$$+ \tfrac{1}{2^2} \sum_{\substack{abcd\\ ijk}} \Phi_{ijk}^{abc} \frac{\overline{g}_{ad}^{ij} \overline{g}_{bc}^{dk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ad}^{ij}} - \tfrac{1}{2^2} \sum_{\substack{abc\\ ijkl}} \frac{\overline{g}_{ab}^{il} \overline{g}_{lc}^{jk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ab}^{il}} + \tfrac{1}{2^4} \sum_{\substack{abcd\\ ijkl}} \Phi_{ijkl}^{abcd} \frac{\overline{g}_{ab}^{ij} \overline{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}} \tag{6.13}$$

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

$E_{\rm c}^{(3)} = \langle \Phi | V_{\rm c} | \Psi^{(2)} \rangle =$  $= \tfrac{1}{2^3} \sum_{\substack{abcd\\ ij}} \frac{\overline{g}_{ij}^{ab} \overline{g}_{ab}^{cd} \overline{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{ij}} + \tfrac{1}{2^3} \sum_{\substack{ab\\ ijkl}} \frac{\overline{g}_{ij}^{ab} \overline{g}_{kl}^{ij} \overline{g}_{ab}^{kl}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ab}^{kl}} + \sum_{\substack{abc\\ ijk}} \frac{\overline{g}_{ij}^{ab} \overline{g}_{ac}^{ik} \overline{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ac}^{ik}}$ (6.14)

which also equals $\langle \Psi^{(1)} | V_{\rm c} | \Psi^{(1)} \rangle$. This is an example of the *Wigner* $(2n+1)$ *rule*, which says that $E_{\rm c}^{(2n+1)} = \langle \Psi^{(n)} | V_{\rm c} | \Psi^{(n)} \rangle$. Note that $E_{\rm c}^{(m+1)}$ 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 ${}^{(m)}c_{ab\cdots}^{ij\cdots} = \langle \Phi_{ij\cdots}^{ab\cdots} | \Psi^{(m)} \rangle$, the second order CI coefficients can be determined from eq 6.12 by contracting a bare excitation operator with the top of each diagram. Interpreting these graphs gives the following.

$$ {}^{(2)}c_a^i = \tfrac{1}{2} \sum_{\substack{bc\\ j}} \frac{\overline{g}_{aj}^{bc} \overline{g}_{bc}^{ij}}{\mathcal{E}_a^i \mathcal{E}_{bc}^{ij}} + \tfrac{1}{2} \sum_{\substack{b\\ jk}} \frac{\overline{g}_{jk}^{ib} \overline{g}_{ab}^{jk}}{\mathcal{E}_a^i \mathcal{E}_{ab}^{jk}}$$

$$ {}^{(2)}c_{ab}^{ij} = \tfrac{1}{2} \sum_{cd} \frac{\overline{g}_{ab}^{cd} \overline{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{cd}^{ij}} + \tfrac{1}{2} \sum_{kl} \frac{\overline{g}_{kl}^{ij} \overline{g}_{ab}^{kl}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ab}^{kl}} + \hat{P}_{(a/b)}^{(i/j)} \sum_{\substack{c\\ k}} \frac{\overline{g}_{ac}^{ik} \overline{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij} \mathcal{E}_{ac}^{ik}}$$

$$ {}^{(2)}c_{abc}^{ijk} = \hat{P}_{(a/bc)}^{(ij/k)} \sum_{d} \Phi_{ijk}^{abc} \frac{\overline{g}_{ad}^{ij} \overline{g}_{bc}^{dk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ad}^{ij}} - \hat{P}_{(a/bc)}^{(i/jk)} \sum_{l} \frac{\overline{g}_{ab}^{il} \overline{g}_{lc}^{jk}}{\mathcal{E}_{abc}^{ijk} \mathcal{E}_{ab}^{il}}$$

$$ {}^{(2)}c_{abcd}^{ijkl} = \hat{P}_{(ab/cd)}^{(ij/kl)} \frac{\overline{g}_{ab}^{ij} \overline{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl} \mathcal{E}_{ab}^{ij}}$$

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 $\Psi_{\rm CIDQ} = (1 + C_2 + C_4)\Phi$ by $\Psi_{\rm CPMET} = (1 + C_2 + \frac{1}{2}C_2^2)\Phi$.

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

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

Proof: This follows from rearranging the resolvent denominator.

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

Lemma 6.1. ***The Energy Substitution Lemma.*** *$\Psi^{(m)}$ equals the sum of a "principal term" $(R_0V_\mathrm{c})^m\Phi$ plus all possible substitutions of adjacent factors $(R_0V_\mathrm{c})^{r_i}$ in the principal term by $R_0E_\mathrm{c}^{(r_i)}$. Each term in the sum is weighted by a sign factor $(-)^k$, where k is the number of substitutions.*

Proof: See appendix A.

Example 6.8. 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.

$$\Psi^{(3)} = R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}\Phi \tag{6.15}$$

$$\Psi^{(4)} = R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0V_\mathrm{c}R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(3)}R_0V_\mathrm{c}\Phi \tag{6.16}$$

$$\begin{aligned}\Psi^{(5)} = {} & R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0V_\mathrm{c}R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi \\ & - R_0V_\mathrm{c}R_0V_\mathrm{c}R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}\Phi + R_0E_\mathrm{c}^{(2)}R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(3)}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi \\ & - R_0V_\mathrm{c}R_0E_\mathrm{c}^{(3)}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(4)}R_0V_\mathrm{c}\Phi\end{aligned} \tag{6.17}$$

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 6.9. Equations 6.15 and 6.16 are clearly consistent with thm 6.1, since $E_\mathrm{c}^{(2)} = \langle V_\mathrm{c}R_0V_\mathrm{c}\rangle$ and $E_\mathrm{c}^{(3)} = \langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle$.

$$\Psi^{(3)} = R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi \tag{6.18}$$

$$\Psi^{(4)} = R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi \tag{6.19}$$

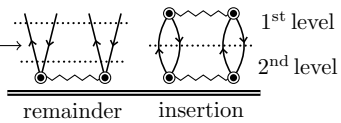
The first non-vanishing terms with nested brackets appear at fifth-order

$$\begin{aligned}\Psi^{(5)} = {} & R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi \\ & - R_0V_\mathrm{c}R_0V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi + R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi \\ & - R_0V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi + R_0\langle V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi\end{aligned} \tag{6.20}$$

which follows from substituting equation 6.18 into $E^{(4)} = \langle\Phi|V_\mathrm{c}|\Psi^{(3)}\rangle$ in the energy substitution expansion of $\Psi^{(5)}$.

Definition 6.6. ***Insertion graph.*** The graphs encountered in perturbation theory contain operators separated by resolvents. Two disconnected parts are termed *separate* if no resolvent line crosses both. Vertical spaces between resolvent lines are termed *levels*, which we number from top to bottom for each separate part. A pair of resolvents with no intervening operators encloses an *empty level*. Inserted brackets in the bracketing expansion produce separate and unlinked *insertion graphs*. The empty level in the *remainder* created by the insertion is the *level of the insertion*.

Example 6.10. Assuming Brillouin's theorem, the simplest non-vanishing term with an inserted bracket appears in $\Psi^{(3)}$.

$R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi =$ 

[12] The "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 ${}^mC_k(Y:Z)$, 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.

$$(Y+Z)^m = \sum_{k=0}^{m} {}^mC_k(Y:Z) \tag{A.1}$$

Furthermore, let ${}^mC(Y:Z_1,\ldots,Z_k)$ 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 ${}^mC(Y:Z_1,\ldots,Z_k) = {}^mC_k(Y:Z)$.

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

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

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 $\mathcal{C}_k(m) = \{(r_1,\ldots,r_k) \in \mathbb{N}_0^k \,|\, r_1+\cdots+r_k = m\}$ are the integer compositions of m into k parts.

Lemma A.1. ***The Energy Substitution Lemma.***

Proof: Using equation A.1 and a double sum identity[16] in the infinite recursion formula for $\Psi(\lambda)$ gives the following.

$$\Psi(\lambda) = \sum_{m=0}^{\infty} (R_0(\lambda V_c - E(\lambda)))^m \Phi = \sum_{m=0}^{\infty}\sum_{k=0}^{m} \lambda^{m-k}(-)^{k\ m} C_k(R_0V_c : R_0E(\lambda))\Phi = \sum_{k'=0}^{\infty}\sum_{k=0}^{\infty} \lambda^{k'}(-)^{k\ k'+k} C_k(R_0V_c : R_0E(\lambda))\Phi$$

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

$$\begin{aligned}\Psi(\lambda) &= \sum_{k=0}^{\infty}\sum_{k'=1}^{\infty}\sum_{p_1=1}^{\infty}\cdots\sum_{p_k=1}^{\infty} \lambda^{k'+p_1+\cdots+p_k}(-)^{k\ k'+k} C(R_0V_c : R_0E_c^{(p_1)},\ldots,R_0E_c^{(p_k)})\Phi \\ &= \sum_{m=1}^{\infty}\sum_{k=0}^{m-1}\sum_{(r_1,\ldots,r_{k+1})}^{\mathcal{C}_{k+1}(m)} \lambda^m(-)^{k\ k+r_{k+1}} C(R_0V_c : R_0E_c^{(r_1)},\ldots,R_0E_c^{(r_k)})\Phi\end{aligned}$$

where we have used a multi-sum reduction to group constant powers of λ. Writing the two inner sums as a single sum over $\mathcal{C}(m)$ and differentiating with respect to λ completes the proof.

$$\Psi^{(m)} = \frac{1}{m!}\frac{\partial^m \Psi(\lambda)}{\partial \lambda^m}\bigg|_{\lambda=0} = \sum_{(r_1,\ldots,r_{k+1})}^{\mathcal{C}(m)} (-)^{k\ k+r_{k+1}} C(R_0V_c : R_0E_c^{(r_1)},\ldots,R_0E_c^{(r_k)})\Phi \tag{A.2}$$

Theorem A.1. ***The Bracketing Theorem.***

Proof: The proposition holds for $m=1$ because $\Psi^{(1)} = R_0V_c\Phi$ 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 $\langle V_c(R_0V_c)^{r_i}\rangle$ plus all nested bracketings.

[13] For example, ${}^4C_2(Y:Z) = Y^2Z^2 + YZYZ + YZ^2Y + ZY^2Z + ZYZY + Z^2Y^2$.

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

[15] For example, ${}^4C(Y:Z_1,Z_2) = Y^2Z_1Z_2 + YZ_1YZ_2 + YZ_1Z_2Y + Z_1Y^2Z_2 + Z_1YZ_2Y + Z_1Z_2Y^2$.

[16] Reverse 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/`.