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 $R_0 H_0\Psi = -Q\Psi = -\Psi + \Phi$.

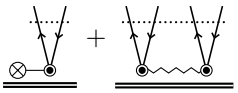
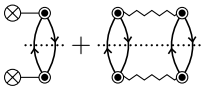
[7] That is, it contains a balanced number of creation and annihilation operators so that $Y|\Phi\rangle \in \mathcal{F}_n$.

[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.

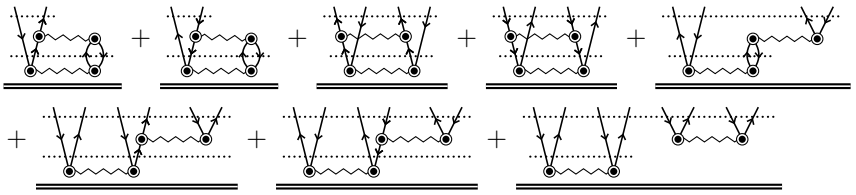
$\Psi^{(1)} =$  $E_{\rm c}^{(2)} =$  (6.11)

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 $+2$.

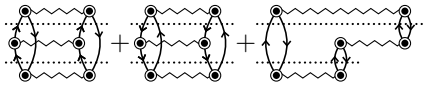
Example 6.6. The expansion for $\Psi^{(2)}$ can be evaluated graphically. Assuming Brillouin's theorem for simplicity,

$\Psi^{(2)} =$  (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.*

Proof: See appendix A.

Example 6.9. Equations 6.15 and 6.16 are trivially consistent with the Bracketing theorem

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

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

since $E_\mathrm{c}^{(2)} = \langle V_\mathrm{c}R_0V_\mathrm{c}\rangle$ and $E_\mathrm{c}^{(3)} = \langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle$. The first non-vanishing terms with nested brackets appear at fifth-order.

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

Definition 6.6. ***Separate graph.*** The parts of a disconnected graph are termed *separate* if they each have their own sets of resolvent lines. Otherwise, they form part of the same *combined* graph.

Definition 6.7. ***Level.*** Each vertical position in a graph containing an interaction line or resolvent line defines a *level*. In other words, two operators share the same level if their interactions lie on the same horizontal line. Levels are numbered from top to bottom, so that the *first level* refers to the topmost operator or resolvent. If two separate parts are drawn so that none of their operators or resolvents occupy the same level, we define the *corresponding combined graph* as the result of extending the resolvent lines across both parts. We can form different combined graphs corresponding to the same separated graph by changing the relative vertical ordering of its parts.

Definition 6.8. ***Insertion graph.*** A separate, unlinked part in a graph is termed an *insertion*. The rest of the graph is termed the *remainder*. In the context of perturbation theory, inserted graphs come from the expectation values in the bracketing expansion. The position of each left angle bracket in the bracketing expansion is referred to as the *level of the insertion*. The *corresponding set* of a graph with an insertion contains corresponding graphs for all relative vertical orderings, keeping the top of the inserted graph at the level of the insertion.

Theorem 6.2. ***The Frantz-Mills Factorization Theorem.*** *A graph with an insertion equals the sum over all corresponding graphs in which the top of the inserted graph .*

Example 6.10. $R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi$

Theorem 6.3. ***The Linked Diagram Theorem.*** *An in*

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 $Y^{m-k}Z^k$,[12] where Y and Z are operators that may or may not commute.[13] 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.[14] 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. ***Infinite Recursion Formula for $\Psi(\lambda)$.*** $\Psi(\lambda) = \sum_{m=0}^{\infty} \left(R_0(\lambda V_c - E(\lambda))\right)^m \Phi$

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[15] in the infinite recursion formula for $\Psi(\lambda)$ gives the following.

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

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.

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

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

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

[15] 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/`.