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.

$$H_0 \equiv f_p^p \tilde{a}_p^p \qquad\qquad V_\mathrm{c} \equiv f_p^q(1-\delta_p^q)\tilde{a}_q^p + \tfrac{1}{4}\overline{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} \tag{6.1}$$

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

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

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 $\langle\Phi|\Psi\rangle \gg \langle\Phi_{i_1\cdots i_k}^{a_1\cdots a_k}|\Psi\rangle$ 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 $H(\lambda) \equiv H_0 + \lambda V_\mathrm{c}$ 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.

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

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

$$E_\mathrm{c} = \langle\Phi|V_\mathrm{c}|\Psi\rangle \qquad\Longrightarrow\qquad E_\mathrm{c}^{(m+1)} = \langle\Phi|V_\mathrm{c}|\Psi^{(m)}\rangle \tag{6.4}$$

where the equation on the right follows from generalizing the energy expression to $E(\lambda) = \langle\Phi|\lambda V_\mathrm{c}|\Psi(\lambda)\rangle$. 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 $E_\mathrm{c}^{(1)} = \langle\Phi|V_\mathrm{c}|\Phi\rangle = 0$, 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]

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

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

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

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.[5]

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

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.

[1] For the sake of brevity I will here refer to H_c as "the electronic Hamiltonian". We could also use $H_e = E_0 + H_\mathrm{c}$, which will simply shift some of the equations by a constant.

[2] See `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.

[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] Note that this implies $R_0P = 0$ and $R_0Q = R_0$.

[6] 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[7]

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

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.

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

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.

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

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.

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

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

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

where Y is an arbitrary operator. The last equation is the Wick expansion of $Y_{n\to n}$, which denotes the purely particle-number-conserving part[8] 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.

$$Y_1 \vdots Y_2 \cdots \vdots Y_n \equiv Y_1\left(\vdots Y_2\left(\cdots\left(\vdots Y_n\right)\cdots\right)\right) \qquad\qquad \mathbf{\vdots}\,\overline{Y_1 \vdots Y_2 \cdots \vdots Y_n}\,\mathbf{\vdots} \equiv \mathbf{\vdots}\,\overline{Y_1\left(\vdots Y_2\left(\cdots\left(\vdots Y_n\right)\cdots\right)\right)}\,\mathbf{\vdots} \tag{6.12}$$

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.*** $Y R_0 Y_1 \cdots R_0 Y_m|\Phi\rangle = \left(\mathbf{\vdots}\, Y \vdots Y_1 \cdots \vdots Y_m \,\mathbf{\vdots} + \mathbf{\vdots}\,\overline{Y \vdots Y_1 \cdots \vdots Y_m}\,\mathbf{\vdots}\right)|\Phi\rangle$

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 $\mathbb{Z}_m = \{0, 1, \ldots, m-1\}$ through the *level map* ρ.[10] Therefore, each line l in G crosses resolvents $\min(\rho_{h(l)}, \rho_{t(l)}) + 1$ through $\max(\rho_{h(l)}, \rho_{t(l)})$.

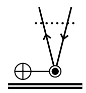
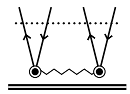
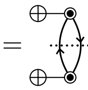
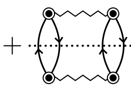
[7] This follows from $R_0 H_0 \Psi = -Q\Psi = -\Psi + \Phi$.

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

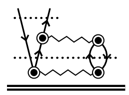
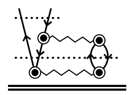
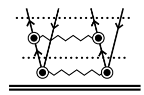
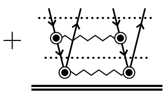
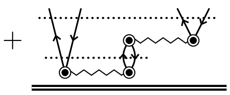
[9] Since any $|\Psi\rangle$ can be written as $Y|\Phi\rangle$, this follows from applying eq 6.7 to each term in the Wick expansion of Y in $R_0 Y|\Phi\rangle$.

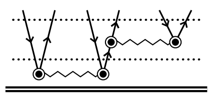
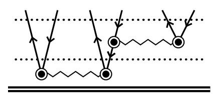
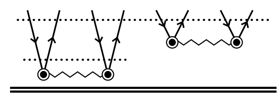
[10] Note that an m-level resolvent graph contains $m-1$ resolvents.

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

$\Psi^{(1)} =$  $+$  $\qquad E_{\mathrm{c}}^{(2)} =$  $+$  (6.13)

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

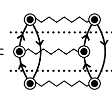
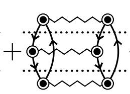
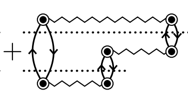
$\Psi^{(2)} = R_0 V_{\mathrm{c}} R_0 V_{\mathrm{c}} |\Phi\rangle =$  $+$  $+$  $+$  $+$ 

$+$  $+$  $+$  (6.14)

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

$$+ \sum_{\substack{abc\\ijk}} \Phi_{ij}^{ab} \frac{\overline{g}_{ac}^{ik}\overline{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij}\mathcal{E}_{ac}^{ik}} + \frac{1}{2^2}\sum_{\substack{abcd\\ijk}} \Phi_{ijk}^{abc} \frac{\overline{g}_{ad}^{ij}\overline{g}_{bc}^{dk}}{\mathcal{E}_{abc}^{ijk}\mathcal{E}_{ad}^{ij}} - \frac{1}{2^2}\sum_{\substack{abc\\ijkl}} \Phi_{ijk}^{abc} \frac{\overline{g}_{ab}^{il}\overline{g}_{lc}^{jk}}{\mathcal{E}_{abc}^{ijk}\mathcal{E}_{ab}^{il}} + \frac{1}{2^4}\sum_{\substack{abcd\\ijkl}} \Phi_{ijkl}^{abcd} \frac{\overline{g}_{ab}^{ij}\overline{g}_{cd}^{kl}}{\mathcal{E}_{abcd}^{ijkl}\mathcal{E}_{ab}^{ij}} \tag{6.15}$$

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 $V_{\mathrm{c}} R_0 V_{\mathrm{c}} R_0 V_{\mathrm{c}}$

$E_{\mathrm{c}}^{(3)} =$  $+$  $+$ 

$$= \frac{1}{2^3}\sum_{\substack{abcd\\ij}} \frac{\overline{g}_{ij}^{ab}\overline{g}_{ab}^{cd}\overline{g}_{cd}^{ij}}{\mathcal{E}_{ab}^{ij}\mathcal{E}_{cd}^{ij}} + \frac{1}{2^3}\sum_{\substack{ab\\ijkl}} \frac{\overline{g}_{ij}^{ab}\overline{g}_{kl}^{ij}\overline{g}_{ab}^{kl}}{\mathcal{E}_{ab}^{ij}\mathcal{E}_{ab}^{kl}} + \sum_{\substack{abc\\ijk}} \frac{\overline{g}_{ij}^{ab}\overline{g}_{ac}^{ik}\overline{g}_{kb}^{cj}}{\mathcal{E}_{ab}^{ij}\mathcal{E}_{ac}^{ik}} \tag{6.16}$$

which is equivalent to contracting the doubles contributions to $\Psi^{(2)}$ with $\frac{1}{4}\overline{g}_{ij}^{ab}\tilde{a}_{ab}^{ij}$. Note that $E_{\mathrm{c}}^{(m+1)}$ 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 ${}^{(m)}c_{ab\cdots}^{ij\cdots} = \langle \Phi_{ij\cdots}^{ab\cdots} | \Psi^{(m)} \rangle$, 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.

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

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

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

Proof: This follows from rearranging the resolvent denominator.

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

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

Lemma 6.1. ***The Energy Substitution Lemma.*** *$\Psi^{(m)}$ equals the sum of a "principal term" $(R_0V_\mathrm{c})^m\Phi$ 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 6.7. 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.

$$\Psi^{(3)} = R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}\Phi \tag{6.17}$$

$$\Psi^{(4)} = R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0V_\mathrm{c}R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(3)}R_0V_\mathrm{c}\Phi \tag{6.18}$$

$$\begin{aligned}\Psi^{(5)} = {} & R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0V_\mathrm{c}R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi \\ & - R_0V_\mathrm{c}R_0V_\mathrm{c}R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}\Phi + R_0E_\mathrm{c}^{(2)}R_0E_\mathrm{c}^{(2)}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(3)}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi \\ & - R_0V_\mathrm{c}R_0E_\mathrm{c}^{(3)}R_0V_\mathrm{c}\Phi - R_0E_\mathrm{c}^{(4)}R_0V_\mathrm{c}\Phi\end{aligned} \tag{6.19}$$

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 $E_\mathrm{c}^{(2)} = \langle V_\mathrm{c}R_0V_\mathrm{c}\rangle$ and $E_\mathrm{c}^{(3)} = \langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle$.

$$\Psi^{(3)} = R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi \tag{6.20}$$

$$\Psi^{(4)} = R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi \tag{6.21}$$

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

$$\begin{aligned}\Psi^{(5)} = {} & R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi - R_0V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi \\ & - R_0V_\mathrm{c}R_0V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi + R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}R_0V_\mathrm{c}\Phi \\ & - R_0V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi - R_0\langle V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi + R_0\langle V_\mathrm{c}R_0\langle V_\mathrm{c}R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\rangle R_0V_\mathrm{c}\Phi\end{aligned} \tag{6.22}$$

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

Definition 6.7. A product of graphs $G = (L, O, h, t)$ and $G' = (L', O', h', t')$ is itself a graph, which is formally given by

$$GG' = (L \cup L', O \cup O', h \oplus h', t \oplus t') \qquad \begin{array}{lll} (h\oplus h')(l) \equiv h(l) & (t\oplus t')(l) \equiv t(l) & \text{for } l \in L \\ (h\oplus h')(l') \equiv h'(l') & (t\oplus t')(l') \equiv t'(l') & \text{for } l' \in L' \end{array} \tag{6.23}$$

in terms of the lines, operators, and head/tail functions of G and G'. According to definition 6.6, however, a product of resolvent graphs is not a resolvent graph. There are several ...
The *combination graphs* of $G(\rho, m)$ and $G'(\rho', m')$ have the form $GG'(\rho_{\pi,\sigma}^{k,k'}, m + m' - 1)$

$$\rho_{\pi,\sigma}^{k,k'}(o) = \begin{cases} \pi(\rho(o)) & \rho(o) < k \\ k + k' & \rho(o) = k \\ \sigma(\rho(o) + k') & \rho(o) > k \end{cases} \qquad o \in O$$

$$\rho_{\pi,\sigma}^{k,k'}(o') = \begin{cases} \pi(\rho'(o') + k) & \rho(o') < k' \\ k + k' & \rho(o') = k' \\ \sigma(\rho'(o') + m - 1) & \rho(o') > k' \end{cases} \qquad \begin{array}{l} o' \in O' \\ \pi \in \mathrm{L}_{k,k'} \\ \sigma \in \mathrm{U}_{k,k'}^{m,m'} \end{array}$$

where $\mathrm{L}_{k,k'} \equiv \mathrm{S}_{\mathbb{Z}_{k+k'}}^{(k,k')}$ and $\mathrm{U}_{k,k'}^{m,m'} \equiv \mathrm{S}_{\mathbb{Z}_{m'+m'-k-k'-2}+k+k'+1}^{(m-k-1,m'-k'-1)}$ are interleavings of the levels below and above level k and k' in the respective graphs.

Theorem 6.2. ***Frantz-Mills Factorization Theorem.***

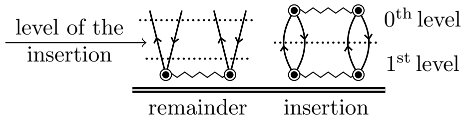
$$G(\rho, m)G'(\rho', m') = \sum_{\pi}^{\mathrm{L}_{k,k'}} GG'(\rho_{\pi,\sigma}^{k,k'}, m + m' - 1) \qquad \begin{array}{l} 0 \le k < m \\ 0 \le k' < m' \end{array} \quad \sigma \in \mathrm{U}_{k,k'}^{m,m'} \tag{6.24}$$

[12]The "brackets" here are reference expectation values: $\langle W\rangle \equiv \langle\Phi|W|\Phi\rangle$.

Definition 6.8. ***Insertion graph.***

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

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



Proposition 6.2. ***Wigner's (2n+1) rule.***

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

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

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

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

Lemma A.1. ***The Energy Substitution Lemma.*** *$\Psi^{(m)}$ 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: Using equation A.1 and a double sum identity[16] in the infinite recursion formula for $\Psi(\lambda)$ gives the following.

$$\Psi(\lambda) = \sum_{m=0}^{\infty}(R_0(\lambda V_\mathrm{c} - E(\lambda)))^m\Phi = \sum_{m=0}^{\infty}\sum_{k=0}^{m}\lambda^{m-k}(-)^k\; {}^mC_k(R_0V_\mathrm{c}:R_0E(\lambda))\Phi = \sum_{k'=0}^{\infty}\sum_{k=0}^{\infty}\lambda^{k'}(-)^k\; {}^{k'+k}C_k(R_0V_\mathrm{c}:R_0E(\lambda))\Phi$$

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

$$\begin{aligned}\Psi(\lambda) &= \sum_{k=0}^{\infty}\sum_{k'=1}^{\infty}\sum_{p_1=1}^{\infty}\cdots\sum_{p_k=1}^{\infty}\lambda^{k'+p_1+\cdots+p_k}(-)^k\; {}^{k'+k}C(R_0V_\mathrm{c}:R_0E_\mathrm{c}^{(p_1)},\dots,R_0E_\mathrm{c}^{(p_k)})\Phi \\ &= \sum_{m=1}^{\infty}\sum_{k=0}^{m-1}\sum_{(r_1,\dots,r_{k+1})}^{\mathcal{C}_{k+1}(m)}\lambda^m(-)^k\; {}^{k+r_1}C(R_0V_\mathrm{c}:R_0E_\mathrm{c}^{(r_2)},\dots,R_0E_\mathrm{c}^{(r_{k+1})})\Phi\end{aligned}$$

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

$$\Psi^{(m)} = \frac{1}{m!}\frac{\partial^m\Psi(\lambda)}{\partial\lambda^m}\bigg|_{\lambda=0} = \sum_{(r_1,\dots,r_{k+1})}^{\mathcal{C}(m)}(-)^k\; {}^{k+r_1}C(R_0V_\mathrm{c}:R_0E_\mathrm{c}^{(r_2)},\dots,R_0E_\mathrm{c}^{(r_{k+1})})\Phi \tag{A.2}$$

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 $\Psi^{(1)} = R_0V_\mathrm{c}\Phi$ and there are no possible bracketings. Assume it holds for $m-1$. Then by the energy substitution lemma it also holds for m because $E_\mathrm{c}^{(r_i)}$ equals $\langle\Phi|V_\mathrm{c}|\Psi^{(r_i)}\rangle$ which, by our inductive assumption, equals $\langle V_\mathrm{c}(R_0V_\mathrm{c})^{r_i}\rangle$ plus all nested bracketings weighted by appropriate sign factors.

[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/`.