1. The linked diagram theorem

Definition 1.1. ***Model problem.*** In perturbation theory, the *model Hamiltonian* is an operator $H_0 \approx H_e$ which approximates the full Hamiltonian and has eigenfunctions spanning the complete n-particle Fock space. An obvious choice in electronic structure is the diagonal one-particle component of H_e, which is diagonal in the determinant basis.

$$H_0\Phi^{a_1\cdots a_k}_{i_1\cdots i_k} = \mathcal{E}^{a_1\cdots a_k}_{i_1\cdots i_k}\Phi^{a_1\cdots a_k}_{i_1\cdots i_k} \qquad H_c = H_0 + V_c \qquad H_0 \equiv f^p_p\tilde{a}^p_p \qquad \mathcal{E}^{a_1\cdots a_k}_{i_1\cdots i_k} \equiv \left(f^{a_1}_{a_1} + \cdots + f^{a_k}_{a_k} - f^{i_1}_{i_1} - \cdots - f^{i_k}_{i_k}\right)$$

where the perurbation is $V_c \equiv f^q_p(1-\delta^q_p)\tilde{a}^p_q + \frac{1}{4}\overline{g}^{rs}_{pq}\tilde{a}^{pq}_{rs}$. In this context, the reference determinant Φ is termed the *model function*. Note that we are playing fast and loose with Einstein summation here: the i and a indices are not summed over, but the p index in H_0 is. The eigenvalue can be determined by noting that $a^p_p\Phi_k = n^k_p\Phi_k$ where n^k_p is the occupation number of ψ_p in Φ_k. Therefore $\tilde{a}^p_p = a^p_p - \tilde{a}^{p^\circ}_{p^\circ} = a^p_p - n_p$ which implies that $\tilde{a}^p_p\Phi_k = (n^k_p - n_p)\Phi_k$. It then follows that $\sum_p f^p_p\tilde{a}^p_p\Phi_k = (\sum_{p\in\Phi_k} f^p_p - \sum_{p\in\Phi} f^p_p)\Phi_k$, which leads to the expression above for $\mathcal{E}^{a_1\cdots a_k}_{i_1\cdots i_k}$.

Definition 1.2. ***Model space projection operators.*** The projection $P = |\Phi\rangle\langle\Phi|$ onto the model function is termed the *model space projection operator*, and its orthogonal complement $Q = 1 - P = \sum_k(\frac{1}{k!})^2\sum_{\substack{a_1\cdots a_k\\ i_1\cdots i_k}}|\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}\rangle\langle\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}|$ is the *orthogonal space projection operator*. Note that $P^2 = Q^2 = 1$ and $PQ = QP = 0$ are necessary consequences of the fact that P and Q are projection operators for orthogonal subspaces, and note that $P + Q = 1$. Assuming *intermediate normalization*, where we set the norm of the wavefunction such that $\langle\Phi|\Psi\rangle = 1$ rather than $\langle\Psi|\Psi\rangle = 1$, the model space projection operator takes the wavefunction into our model function, $P\Psi = \Phi\langle\Phi|\Psi\rangle = \Phi$.

Definition 1.3. ***Resolvent.*** Let R_0 be minus[1] the inverse of H_0 in the orthogonal space, so that $-R_0H_0 = Q$. The operator R_0 is termed the *resolvent*. Explicitly, we can apply resolution of the identity in the orthogonal space to get

$$R_0 = (-H_0)^{-1}Q = \sum_k\left(\frac{1}{k!}\right)^2\sum_{\substack{a_1\cdots a_k\\ i_1\cdots i_k}}(-H_0)^{-1}|\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}\rangle\langle\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}| = \sum_k\left(\frac{1}{k!}\right)^2\sum_{\substack{a_1\cdots a_k\\ i_1\cdots i_k}}\frac{|\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}\rangle\langle\Phi^{a_1\cdots a_k}_{i_1\cdots i_k}|}{\mathcal{D}^{a_1\cdots a_k}_{i_1\cdots i_k}} \qquad \mathcal{D}^{a_1\cdots a_k}_{i_1\cdots i_k} \equiv -\mathcal{E}^{a_1\cdots a_k}_{i_1\cdots i_k}$$

where we recognize that H_0^{-1} does not exist outside of the model space because $H_0\Phi = 0 \implies H_0P = 0$. Note that R_0 simply acts as the null operator outside of the orthogonal space, so that $R_0Q = R_0$ and $R_0P = 0$.

Definition 1.4. ***Rayleigh-Schrödinger perturbation theory.*** Rearranging the Schrödinger equation to the form $H_0\Psi = (E_c - V_c)\Psi$ and operating R_0 on both sides, recognizing that $R_0H_0 = -Q$ and $Q\Psi = (1-P)\Psi = \Psi - \Phi$, we find

$$R_0H_0\Psi = -Q\Psi = -\Psi + \Phi = R_0(E_c - V_c)\Psi \implies \Psi = \Phi - R_0(E_c - V_c)\Psi = \Phi + R_0(V_c - E_c)\Psi$$

which gives a recursive equation for Ψ. Straightforward induction gives $\Psi = \sum_{k=0}^n(R_0(V_c - E_c))^k\Phi + (R_0(V_c - E_c))^{n+1}\Psi$. Noting that $H_0\Phi = 0$ and $\langle\Phi|\Psi\rangle = 1$, projecting the Schrödinger equation by Φ gives an expression for the correlation energy: $E_c = \langle\Phi|V_c|\Psi\rangle$. Assuming the recursive definition for Ψ converges, we find

$$\Psi = \sum_{k=0}^\infty(R_0(V_c - E_c))^k\Phi \qquad\qquad E_c = \sum_{k=0}^\infty\langle\Phi|V_c|\Psi^{(k)}\rangle = \sum_{k=0}^\infty\langle\Phi|V_c(R_0(V_c - E_c))^k|\Phi\rangle \tag{1.1}$$

which can be solved iteratively in orders of perturbation theory. Introducing a perturbation parameter $V_c \mapsto \lambda V_c$ that acts as a switch to turn the perturbation on, $\lambda = 1$, or off, $\lambda = 0$, the wavefunction and correlation energy are given by

$$\Psi(\lambda) = \sum_k\frac{1}{k!}\lambda^k\left(\frac{\partial^k\Psi}{\partial\lambda^k}\right)_{\lambda=0} \equiv \sum_k\lambda^k\Psi^{(k)} \qquad\qquad E_c(\lambda) = \sum_k\frac{1}{k!}\lambda^k\left(\frac{\partial^k E_c}{\partial\lambda^k}\right)_{\lambda=0} \equiv \sum_k\lambda^k E_c^{(k)}$$

and we can separate eq (1.1) in powers of λ. The first-order energy contribution vanishes $\lambda E_c^{(1)} = \lambda\langle\Phi|V_c|\Phi\rangle = 0$ since V_c is composed of Φ-normal operators. The first order wavefunction contribution is $\lambda\Psi^{(1)} = \lambda R_0(V_c - E_c^{(1)})\Phi = \lambda R_0V_c\Phi$,

[1]The annoying sign factor is required for consistency with the standard definition $R_0 \equiv (E_0 - H_0)^{-1}Q$. Since we have already subtracted off E_0, we have $R_0 = (-H_0)^{-1}Q$. This also results in a more convenient sign rule for the bracketing theorem.

which can be directly evaluated using Wick's theorem and Φ normal ordering

$$\begin{aligned}
\Psi^{(1)} = R_0 V_c \Phi &= \sum_k \left(\frac{1}{k!}\right)^2 \sum_{\substack{a_1\cdots a_k \\ i_1\cdots i_k}} |\Phi_{i_1\cdots i_k}^{a_1\cdots a_k}\rangle \frac{\langle\Phi|\tilde{a}_{a_1\cdots a_k}^{i_1\cdots i_k} V_c|\Phi\rangle}{\mathcal{D}_{i_1\cdots i_k}^{a_1\cdots a_k}} \\
&= \sum_{ia} |\Phi_i^a\rangle \frac{\sum_{pq} f_p^q (1-\delta_p^q)\langle\Phi|\colon\!\tilde{a}_{a^\bullet}^{i^\circ}\tilde{a}_{q^\circ}^{p^\bullet}\!\colon|\Phi\rangle}{f_i^i - f_a^a} + \frac{1}{4}\sum_{ijab} |\Phi_{ij}^{ab}\rangle \frac{\frac{1}{4}\sum_{pqrs}\overline{g}_{pq}^{rs} P_{(r/s)}^{(p/q)}\langle\Phi|\colon\!\tilde{a}_{a^\bullet b^\bullet}^{i^\circ j^{\circ\circ}}\tilde{a}_{r^\circ s^{\circ\circ}}^{p^\bullet q^{\bullet\bullet}}\!\colon|\Phi\rangle}{f_i^i + f_j^j - f_a^a - f_b^b} \\
&= \sum_{ia} |\Phi_i^a\rangle \frac{f_a^i}{f_i^i - f_a^a} + \frac{1}{4}\sum_{ijab} |\Phi_{ij}^{ab}\rangle \frac{\overline{g}_{ab}^{ij}}{f_i^i + f_j^j - f_a^a - f_b^b}
\end{aligned}$$

where we have recognized that only singly and doubly excited determinants can fully contract V_c. The second-order energy contribution, $\lambda^2 E_c^{(2)} = \lambda^2\langle\Phi|V_c|\Psi^{(1)}\rangle$, can be evaluated from our expression for $\Psi^{(1)}$.

$$E^{(2)} = \sum_{ia}\langle\Phi|V_c\tilde{a}_i^a|\Phi\rangle\frac{f_a^i}{f_i^i - f_a^a} + \frac{1}{4}\sum_{ijab}\langle\Phi|V_c\tilde{a}_{ij}^{ab}|\Phi\rangle\frac{\overline{g}_{ab}^{ij}}{f_i^i + f_j^j - f_a^a - f_b^b} = \sum_{ia}\frac{f_i^a f_a^i}{f_i^i - f_a^a} + \frac{1}{4}\sum_{ijab}\frac{\overline{g}_{ij}^{ab}\overline{g}_{ab}^{ij}}{f_i^i + f_j^j - f_a^a - f_b^b}$$

Note that the one-particle contributions involving f_i^a are present only for non-Hartree-Fock references. In both canonical and non-canonical Hartree-Fock $f_i^a = 0$. The second order wavefunction contribution is $\lambda^2\Psi^{(2)} = -\lambda^2 E_c^{(2)} R_0\Phi + \lambda^2 R_0(V_c - E_c^{(1)})R_0(V_c - E_c^{(1)})\Phi = \lambda^2 R_0 V_c R_0 V_c \Phi$ since $R_0\Phi = 0$ and $E_c^{(1)} = 0$. The third order energy can be then obtained from $\Psi^{(2)}$ as $\lambda^3 E_c^{(3)} = \lambda^3\langle\Phi|V_c|\Psi^{(2)}\rangle$. In this manner, one can in principle solve the Schrödinger equation recursively by alternately evaluating the wavefunction and energy contributions at increasing orders in the perturbation parameter.

Derivation 1.1. Writing the RSPT wavefunction equation as $\Psi = \sum_{k=0}^{\infty}(R_0V_c - R_0E_c)^k\Phi$, note that if R_0 and V_c were to commute we could to an ordinary binomial expansion of $(R_0V_c - R_0E_c)^k$ to give $\sum_{p=0}^{k}\binom{k}{p}(-)^p(R_0V_c)^{k-p}(R_0E_c)^p$. Since they don't commute, we can write the binomial expansion in the following slightly modified form

$$(R_0E_c - R_0V_c)^k = \sum_{p=0}^{k}(-)^p\{R_0E_c\}^p\text{insert}\{R_0V_c\}^{k-p}$$

where $\{B_1,\ldots,B_p\}\text{insert}\{A\}^{k-p}$ denotes the sum over all $\binom{k}{p}$ possible ways of inserting $k-p$ copies of A into the product $B_1\cdots B_p$. For example, $\{B_1,B_2\}\text{insert}\{A\}^2$ evaluates to $AAB_1B_2 + AB_1AB_2 + AB_1B_2A + B_1AAB_2 + B_1AB_2A + B_1B_2AA$. This allows the wavefunction expansion to be easily grouped by orders

$$\begin{aligned}
\Psi &= \sum_{k=0}^{\infty}\sum_{p=0}^{k}(-)^p\{R_0E_c\}^p\text{insert}\{R_0V_c\}^{k-p}\Phi \\
&= \sum_{n=0}^{\infty}\sum_{(n_1,n_2)}^{\mathcal{C}_2(n)\cup\{(0,n)\}}\sum_{(r_1,\ldots,r_m)}^{\mathcal{C}(n_1)}(-)^m\{R_0E_c^{(r_1)},\ldots,R_0E_c^{(r_m)}\}\text{insert}\{R_0V_c\}^{n_2}\Phi = \sum_{n=0}^{\infty}\Psi^{(n)}
\end{aligned}$$

where $\mathcal{C}(n)$ denotes the set of integer compositions of n, i.e. all ordered tuples $(r_1,\ldots,r_m)$ of strictly positive integers that add up to n. $\mathcal{C}_k(n) \subset \mathcal{C}(n)$ is the set of k-tuple integer compositions of n, i.e. all $(r_1,\ldots,r_k)$ of fixed length k such that $r_1 + \cdots + r_k = n$. The rearrangement follows from the fact that all possible terms of the form $(-)^k\{R_0E_c^{(n_1)},\ldots,R_0E_c^{(n_k)}\}\text{insert}\{R_0V_c\}^{n_{k+1}}\Phi$ contribute to the sum, and the composition sums group these into all possible terms of this form that are of a given order n in the perturbation parameter λ. Note that we have appended the tuple $(0,n)$ to our sum over $\mathcal{C}_2(n)$ but not $(n,0)$ since R_0 acting directly on Φ gives 0. These results are summarized in lem 1.1.

Lemma 1.1. ***The Energy Substitution Lemma.*** *The n^{th}-order contribution to the wavefunction is given by*

$$\Psi^{(n)} = (R_0V_c)^n\Phi + \sum_{(n_1,n_2)}^{\mathcal{C}_2(n)}\sum_{(r_1,\ldots,r_m)}^{\mathcal{C}(n_1)}(-)^m\{R_0E_c^{(r_1)},\ldots,R_0E_c^{(r_m)}\}\text{insert}\{R_0V_c\}^{n_2}\Phi$$

which can be evaluated as the sum of a principal term, $(R_0V_c)^n\Phi$, *plus all possible m-tuple substitutions of adjacent factors $(R_0V_c)^{r_k}$ in the principal term by $R_0E_c^{(r_k)}$ times a sign factor $(-)^m$.*

Example 1.1. Using the energy substitution lemma, we can directly write down the first few wavefunction contributions

$$\begin{aligned}
\Psi^{(1)} &= R_0 V_c \Phi \\
\Psi^{(2)} &= R_0 V_c R_0 V_c \Phi - R_0 E_c^{(1)} R_0 V_c \Phi - R_0 V_c R_0 E_c^{(1)} \Phi \\
\Psi^{(3)} &= R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 E_c^{(2)} R_0 V_c \Phi - R_0 V_c R_0 E_c^{(2)} \Phi + R_0 E_c^{(1)} R_0 E_c^{(1)} R_0 V_c \Phi + R_0 E_c^{(1)} R_0 V_c R_0 E_c^{(1)} \Phi \\
&\quad + R_0 V_c R_0 E_c^{(1)} R_0 E_c^{(1)} \Phi - R_0 E_c^{(1)} R_0 V_c R_0 V_c \Phi - R_0 V_c R_0 E_c^{(1)} R_0 V_c \Phi - R_0 V_c R_0 V_c R_0 E_c^{(1)} \Phi
\end{aligned}$$

where we have directly evaluated the formula of lem 1.1 without simplifying. These expressions can be simplified by recognizing that $E_c^{(1)} = 0$ and that any term with an energy factor next to Φ vanishes since $R_0\Phi = 0$. Omitting these terms, the wavefunction contributions can be simplified as follows.

$$\begin{aligned}
\Psi^{(1)} &= R_0 V_c \Phi \\
\Psi^{(2)} &= R_0 V_c R_0 V_c \Phi \\
\Psi^{(3)} &= R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 E_c^{(2)} R_0 V_c \Phi \\
\Psi^{(4)} &= R_0 V_c R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 E_c^{(3)} R_0 V_c \Phi - R_0 E_c^{(2)} R_0 V_c R_0 V_c \Phi - R_0 V_c R_0 E_c^{(2)} R_0 V_c \Phi \\
\Psi^{(5)} &= R_0 V_c R_0 V_c R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 E_c^{(4)} R_0 V_c \Phi + R_0 E_c^{(2)} R_0 E_c^{(2)} R_0 V_c \Phi - R_0 E_c^{(3)} R_0 V_c R_0 V_c \Phi \\
&\quad - R_0 V_c R_0 E_c^{(3)} R_0 V_c \Phi - R_0 E_c^{(2)} R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 V_c R_0 E_c^{(2)} R_0 V_c R_0 V_c \Phi - R_0 V_c R_0 V_c R_0 E_c^{(2)} R_0 V_c \Phi
\end{aligned}$$

Projecting these equations by $\langle\Phi|V_c$ then yields $E_c^{(2)}$, $E_c^{(3)}$, $E_c^{(4)}$, $E_c^{(5)}$, and $E_c^{(6)}$.

Theorem 1.1. ***The Bracketing Theorem.*** *The n^{th}-order contribution to the wavefunction consists of a principal term $(R_0V_c)^n\Phi = R_0V_c\cdots R_0V_c\Phi$ plus the sum over all possible ways of inserting one or more pairs of brackets $\langle\cdots\rangle \equiv \langle\Phi|\cdots|\Phi\rangle$ into the principal term, $R_0V_c\cdots R_0\langle V_c\cdots R_0V_c\rangle\cdots R_0V_c\Phi$, allowing nested brackets. Each of these terms gets a phase factor $(-)^k$ where k is the total number of brackets.*

Proof: This obviously holds for $\Psi^{(1)}$ since $\Psi^{(1)} = R_0V_c\Phi$ and there are no possible bracketings. Assume it holds up to $n-1$ and consider n. By the substitution lemma, $\Psi^{(n)}$ equals a principal term $R_0V_c\cdots R_0V_c\Phi$ plus all unique substitutions of factors $(R_0V_c)^{r_1},\ldots,(R_0V_c)^{r_m}$ in the principal term with energy factors $R_0E_c^{(r_1)},\ldots,R_0E_c^{(r_m)}$, weighted by a sign $(-)^m$. But, by our inductive assumption, the substituted energies $E_c^{(r_k)} = \langle\Phi|V_c|\Psi^{(r_k)}\rangle$ are sums of a principal term $\langle V_cR_0V_c\cdots R_0V_c\rangle$ plus all possible bracketings, with the appropriate sign factor, which shows that $\Psi^{(n)}$ is the sum over all nested bracketings and completes the proof.

Example 1.2. Noting that bracketings of the form $R_0\langle V_c\rangle$ vanish because $\langle V\rangle_c = E_c^{(1)} = 0$, and that any bracketing including the last factor vanish because $R_0\langle V_c\cdots R_0V_c\rangle\Phi = \langle V_c\cdots R_0V_c\rangle R_0\Phi = 0$, we can write down the bracketing theorem expansion for the first few contributions to the wavefunction as follows.

$$\begin{aligned}
\Psi^{(1)} &= R_0 V_c \Phi \\
\Psi^{(2)} &= R_0 V_c R_0 V_c \Phi \\
\Psi^{(3)} &= R_0 V_c R_0 V_c R_0 V_c \Phi - R_0\langle V_c R_0 V_c\rangle R_0 V_c \Phi \\
\Psi^{(4)} &= R_0 V_c R_0 V_c R_0 V_c R_0 V_c \Phi - R_0\langle V_c R_0 V_c\rangle R_0 V_c R_0 V_c \Phi - R_0 V_c R_0\langle V_c R_0 V_c\rangle R_0 V_c \Phi - R_0\langle V_c R_0 V_c R_0 V_c\rangle R_0 V_c \Phi \\
\Psi^{(5)} &= R_0 V_c R_0 V_c R_0 V_c R_0 V_c R_0 V_c \Phi - R_0\langle V_c R_0 V_c\rangle R_0 V_c R_0 V_c R_0 V_c \Phi - R_0 V_c R_0\langle V_c R_0 V_c\rangle R_0 V_c R_0 V_c \Phi \\
&\quad - R_0 V_c R_0 V_c R_0\langle V_c R_0 V_c\rangle R_0 V_c \Phi + R_0\langle V_c R_0 V_c\rangle R_0\langle V_c R_0 V_c\rangle R_0 V_c \Phi - R_0\langle V_c R_0 V_c R_0 V_c\rangle R_0 V_c R_0 V_c \Phi \\
&\quad - R_0 V_c R_0\langle V_c R_0 V_c R_0 V_c\rangle R_0 V_c \Phi - R_0\langle V_c R_0 V_c R_0 V_c R_0 V_c\rangle R_0 V_c \Phi + R_0\langle V_c R_0\langle V_c R_0 V_c\rangle R_0 V_c\rangle R_0 V_c \Phi
\end{aligned}$$

The bracketing expansions for the corresponding energies are as follows.

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

Remark 1.1. Individual terms in the perturbation expansion are readily evaluated using Wick's theorem and Φ-normal ordering. Using resolution of the identity in the orthogonal space, the general structure of a principal term is as follows.

$$(R_0V_c)^n|\Phi\rangle = Q(R_0V_c)^n|\Phi\rangle = \sum_k |\Phi_k\rangle\langle\Phi_k|(R_0V_c)^n|\Phi\rangle = \sum_k |\Phi_k\rangle \sum_{k_1\cdots k_n} \frac{\langle\Phi_k|V_c|\Phi_{k_1}\rangle\langle\Phi_{k_1}|V_c|\Phi_{k_2}\rangle\langle\Phi_{k_2}|\cdots|\Phi_{k_n}\rangle\langle\Phi_{k_n}|V_c|\Phi\rangle}{\mathcal{D}_{k_1}\mathcal{D}_{k_2}\cdots\mathcal{D}_{k_n}}$$

Terms with bracketing insertions differ from the principal term by a scalar $\langle\cdots\rangle$ which can be factored out, leaving a squared resolvent at the point of insertion. By orthonormality of the determinant basis, the squared resolvent equals

$$R_0^2 = \sum_{k_1k_2} \frac{|\Phi_{k_1}\rangle\langle\Phi_{k_1}|\Phi_{k_2}\rangle\langle\Phi_{k_2}|}{\mathcal{D}_{k_1}\mathcal{D}_{k_2}} = \sum_{k_1k_2} \frac{|\Phi_{k_1}\rangle\delta_{k_1k_2}\langle\Phi_{k_2}|}{\mathcal{D}_{k_1}\mathcal{D}_{k_2}} = \sum_k \frac{|\Phi_k\rangle\langle\Phi_k|}{\mathcal{D}_k^2}$$

which is of course equal to $(H_0^2)^{-1}$ restricted to the orthogonal space where it is non-singular, $R_0^2H_0^2 = Q$. Consequently, every wavefunction contribution is proportional to a term of the following generic form

$$R_0^{p_1}V_cR_0^{p_2}V_c\cdots R_0^{p_n}V_c|\Phi\rangle = \sum_k |\Phi_k\rangle\langle\Phi|\tilde{a}_k^\dagger R_0^{p_1}V_cR_0^{p_2}V_c\cdots R_0^{p_n}V_c|\Phi\rangle \qquad\qquad R_0^p = \sum_k \frac{|\Phi_k\rangle\langle\Phi_k|}{\mathcal{D}_k^p}$$

which can be evaluated by determining all complete Φ-normal contractions of $\tilde{a}_k^\dagger R_0^{p_1}V_cR_0^{p_2}V_c\cdots R_0^{p_n}V_c$, where $\tilde{a}_k^\dagger$ is a de-excitation operator $\tilde{a}_k^\dagger \in \{\tilde{a}^{i_1\cdots i_n}_{a_1\cdots a_n} \,|\, {}^{i_1<\cdots<i_n}_{a_1<\cdots<a_n}\}$.

Remark 1.2. Note that, when an operator of the form $M_\mathrm{o} = \sum_i a_i|\Phi\rangle m_i\langle\Phi|a^i$ or $M_\mathrm{v} = \sum_a a^a|\Phi\rangle m_a\langle\Phi|a_a$ is contracted on the left and on the right, we can make the following rearrangement

$$\sum_i \overbrace{a^p a_i}|\Phi\rangle m_i\langle\Phi|\overbrace{a^i a_s} = |\Phi\rangle\langle\Phi|m_p\,\overbrace{a^p a_s} \qquad\qquad \sum_a \overbrace{a_q a^a}|\Phi\rangle m_a\langle\Phi|\overbrace{a_a a^r} = |\Phi\rangle\langle\Phi|m_q\,\overbrace{a_q a^r}$$

where the requirement that m_p have a hole index and m_q have a particle index is taken care of by the contractions. In words, contracting one operator to the left side of M_o and another operator to the right side is equivalent to contracting these operators to each other and freezing out the term from M_o that matches the left (or, equivalently, the right) index. This generalizes directly to operators of the form $\sum_{\substack{i_1<\cdots<i_k\\ a_1<\cdots<a_k}} \tilde{a}^{a_1\cdots a_k}_{i_1\cdots i_k}|\Phi\rangle M^{a_1\cdots a_k}_{i_1\cdots i_k}\langle\Phi|\tilde{a}^{i_1\cdots i_k}_{a_1\cdots a_k}$ and can be used to simplify the contractions of an operator product with an intervening resolvent, QR_0^nQ':

$$\colonarrow{\overbrace{QR_0^nQ'}} = \sum_k \frac{\colonarrow{\overbrace{Q\tilde{a}_k}}|\Phi\rangle\langle\Phi|\colonarrow{\overbrace{\tilde{a}_k^\dagger Q'}}}{\mathcal{D}_k^n} = |\Phi\rangle\langle\Phi|\sum_k \frac{\colonarrow{\overbrace{Q\tilde{a}_k}}\colonarrow{\overbrace{\tilde{a}_k^\dagger Q'}}}{\mathcal{D}_k^n} = |\Phi\rangle\langle\Phi|\colonarrow{\overbrace{Q\overset{R_0^n}{\vdots}Q'}}.$$

Here, we have introduced the notion of a *resolvent line* $\overset{R_0^n}{\vdots}$. Complete contractions through a resolvent line are defined as

$$\colonarrow{a^{p_1}\cdots a^{p_k}\overbrace{a_{q_1}\cdots a_{q_k}\overset{R_0^n}{\vdots}a^{r_1}\cdots a^{r_k}}a_{s_1}\cdots a_{s_k}} \equiv \frac{\colonarrow{a^{p_1}\cdots a^{p_k}\overbrace{a_{q_1}\cdots a_{q_k}a^{r_1}\cdots a^{r_k}}a_{s_1}\cdots a_{s_k}}}{(\mathcal{D}^{q_1\cdots q_k}_{p_1\cdots p_k})^n}.$$

That is, each hole contraction $\overbrace{a^p a_s}$ through the resolvent line $\overset{R_0^n}{\vdots}$ fixes a hole index in the denominator $(\mathcal{D}_{\cdots p\cdots})^n$ and each particle contraction $\overbrace{a_q a^r}$ fixes a a particle index in the denominator $(\mathcal{D}^{\cdots q\cdots})^n$. This result further generalizes to completely contracted products with multiple resolvents, and is codified in the next proposition.

Proposition 1.1. ***Reduced Wick theorem for expectation values with resolvents.***

$$\langle\Phi|QR_0^{p_1}Q_1R_0^{p_2}Q_2\cdots R_0^{p_n}Q_n|\Phi\rangle = \colonarrow{\overbrace{Q\overset{R_0^{p_1}}{\vdots}Q_1\overset{R_0^{p_2}}{\vdots}Q_2\cdots\overset{R_0^{p_n}}{\vdots}Q_n}}$$

Example 1.3. The reduced Wick theorem of prop 1.1 can be used to evaluate the following

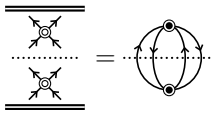
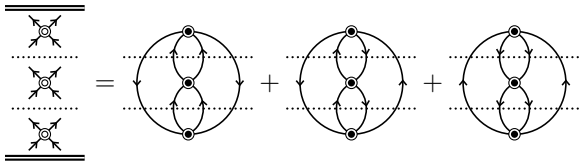
$$\begin{aligned}
\colonarrow{\overbrace{\tilde{a}^{p_1q_1}_{r_1s_1}\overset{R_0}{\vdots}\tilde{a}^{p_2q_2}_{r_2s_2}}} &= P^{(p_2/q_2)}_{(r_2/s_2)}\colonarrow{\tilde{a}^{p_1^\circ q_1^{\circ\circ}}_{r_1^\bullet s_1^{\bullet\bullet}}\overset{R_0}{\vdots}\tilde{a}^{p_2^\bullet q_2^{\bullet\bullet}}_{r_2^\circ s_2^{\circ\circ}}} \\
\colonarrow{\overbrace{\tilde{a}^{p_1q_1}_{r_1s_1}\overset{R_0}{\vdots}\tilde{a}^{p_2q_2}_{r_2s_2}\overset{R_0}{\vdots}\tilde{a}^{p_3q_3}_{r_3s_3}}} &= P^{(p_1/q_1|p_3/q_3)}_{(r_1/s_1|r_3/s_3)}\colonarrow{\tilde{a}^{p_1^\circ q_1^{\circ 2}}_{r_1^\bullet s_1^{\bullet 2}}\overset{R_0}{\vdots}\tilde{a}^{p_2^\bullet q_2^{\bullet 2}}_{r_2^{\bullet 3} s_2^{\bullet 4}}\overset{R_0}{\vdots}\tilde{a}^{p_3^{\bullet 3} q_3^{\bullet 4}}_{r_3^{\circ 1} s_3^{\circ 2}}} + P^{(p_1/q_1|p_2/q_2|p_3/q_3)}_{(r_1/s_1|r_2/s_2|r_3/s_3)}\colonarrow{\tilde{a}^{p_1^{\circ 3} q_1^{\circ 1}}_{r_1^{\bullet 3} s_1^{\bullet 1}}\overset{R_0}{\vdots}\tilde{a}^{p_2^\bullet q_2^{\bullet 2}}_{r_2^{\circ 1} s_2^{\bullet 2}}\overset{R_0}{\vdots}\tilde{a}^{p_3^\bullet q_3^{\bullet 3}}_{r_3^{\circ 2} s_3^{\circ 3}}} \\
&\quad + P^{(p_1/q_1|p_3/q_3)}_{(r_1/s_1|r_3/s_3)}\colonarrow{\tilde{a}^{p_1^{\circ 3} q_1^{\circ 4}}_{r_1^{\bullet 1} s_1^{\bullet 2}}\overset{R_0}{\vdots}\tilde{a}^{p_2^{\circ 1} q_2^{\circ 2}}_{r_2^{\circ 3} s_2^{\circ 4}}\overset{R_0}{\vdots}\tilde{a}^{p_3^{\bullet 1} q_3^{\bullet 2}}_{r_3^{\circ 1} s_3^{\circ 2}}}
\end{aligned}$$

in order to derive the second- and third-order energy contributions

$$E_c^{(2)} = \langle V_c R_0 V_c \rangle = \colon \overbrace{\overline{V_c \vdots \overline{V_c}}}^{R_0} \colon = \left(\tfrac{1}{4}\right)^2 \overline{g}^{r_1 s_1}_{p_1 q_1} \overline{g}^{r_2 s_2}_{p_2 q_2} \colon \overbrace{\overline{\tilde{a}^{p_1 q_1}_{r_1 s_1} \vdots \tilde{a}^{p_2 q_2}_{r_2 s_2}}}^{R_0} \colon = \frac{1}{4} \frac{\overline{g}^{ab}_{ij} \overline{g}^{ij}_{ab}}{\mathcal{D}^{ab}_{ij}}$$

$$E_c^{(3)} = \langle V_c R_0 V_c R_0 V_c \rangle = \colon \overbrace{\overline{V_c \vdots \overline{V_c} \vdots \overline{V_c}}}^{R_0 \quad R_0} \colon = \left(\tfrac{1}{4}\right)^3 \overline{g}^{r_1 s_1}_{p_1 q_1} \overline{g}^{r_2 s_2}_{p_2 q_2} \overline{g}^{r_3 s_3}_{p_3 q_3} \colon \overbrace{\overline{\tilde{a}^{p_1 q_1}_{r_1 s_1} \vdots \tilde{a}^{p_2 q_2}_{r_2 s_2} \vdots \tilde{a}^{p_3 q_3}_{r_3 s_3}}}^{R_0 \quad R_0} \colon = \frac{1}{4} \frac{\overline{g}^{ab}_{ij} \overline{g}^{cd}_{ab} \overline{g}^{ij}_{cd}}{\mathcal{D}^{ab}_{ij} \mathcal{D}^{cd}_{ij}} + \frac{\overline{g}^{ab}_{ij} \overline{g}^{jc}_{bk} \overline{g}^{ki}_{ca}}{\mathcal{D}^{ab}_{ij} \mathcal{D}^{ca}_{ki}} + \frac{1}{4} \frac{\overline{g}^{ab}_{ij} \overline{g}^{ij}_{kl} \overline{g}^{kl}_{ab}}{\mathcal{D}^{ab}_{ij} \mathcal{D}^{ab}_{kl}}$$

where we have used implicit summation (over all indices) to keep the expressions relatively compact. Here, we have assumed a canonical Hartree-Fock (RHF or UHF) reference so that the one-particle perturbation vanishes $f^q_p(1-\delta^q_p) = 0$ and $V_c = \frac{1}{4}\overline{g}^{rs}_{pq}\tilde{a}^{pq}_{rs}$. Non-canonical Hartree-Fock (such as ROHF) has the same second-order contribution, but introduces two additional terms at third order. In Hugenholtz diagram notation, this looks as follows.

$E_c^{(2)} =$  $E_c^{(3)} =$ 

Example 1.4. Contributions to the wavefunction can be separated into singles, doubles, triples, etc. contributions by a resolution of the identity in the orthogonal space

$$\Psi^{(n)} = Q\Psi^{(n)} = \sum_k \left(\tfrac{1}{k!}\right)^2 \sum_{\substack{a_1 \cdots a_k \\ i_1 \cdots i_k}} \Phi^{a_1 \cdots a_k}_{i_1 \cdots i_k} \, {}^{(n)}c^{i_1 \cdots i_k}_{a_1 \cdots a_k} \qquad {}^{(n)}c^{i_1 \cdots i_k}_{a_1 \cdots a_k} \equiv \langle \Phi | a^{i_1 \cdots i_k}_{a_1 \cdots a_k} | \Psi^{(n)} \rangle$$

which turns the problem into one of identitfying contributions to the CI coefficients. At second and third order, only doubles contributions are non-vanishing.

$${}^{(2)}c^i_a = \langle \tilde{a}^i_a R_0 V_c \rangle = \colon \overbrace{\overline{\tilde{a}^i_a \vdots V_c}}^{R_0} \colon = 0$$