Lecture 5: Perturbation Theory II

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In perturbation theory, we split our Hamiltonian into parts $H = H_0 + V$, and our ground state wavefunction $|\Psi_0\rangle$ and energy E_0 are expressed as an infinite series, where the first term is the unperturbed quantity of some simpler model system described by H_0, and the rest of the terms are corrections at various "orders" n:

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{n=1}^{\infty} |\Phi_0^{(n)}\rangle$$

$$E_0 = E_0^{(0)} + \sum_{n=1}^{\infty} E_0^{(n)}$$

As we saw in the previous set of notes, the expression for each wavefunction and energy correction needs to be derived from a system of equations. This way of doing things is very inefficient at high orders, so in this set of notes we will use a new scheme, which was primarily popularized and championed by Per-Olav Löwdin in his highly influential series of papers *Studies in Perturbation Theory* in the 1960s. The majority of the content in these notes can be found in the 9th (IX) paper in the series. This new methodology will allow you to derive each order of PT using the same exact procedure. Though the higher order wavefunctions and energy expressions get more and more complex, the procedure for deriving them does not change at higher orders. This methodology also beautifully translates into clean diagrams, which we will see later on.

1 The Wave Operator

Suppose there was some magical operator Ω which acts on the unperturbed state $|\Phi_0\rangle$ (an eigenstate of H_0) and transforms it into the exact state $|\Psi_0\rangle$ described by $H_0 + V$

$$|\Psi_0\rangle = \Omega |\Phi_0\rangle$$

We will call Ω the *wave operator*. For now, we have no idea what it is, but we do know what it does. Suppose further that we are using an intermediate normalized Ψ_0 and normalized Φ_0 such that

$$\langle\Phi_0|\Phi_0\rangle = 1$$

$$\langle\Phi_0|\Psi_0\rangle = \langle\Phi_0|\Omega|\Phi_0\rangle = 1$$

Under the above conditions, we will now see what happens to the Schrödinger equation,

$$(H_0 + V)|\Psi_0\rangle = E_0 |\Psi_0\rangle$$

Projecting both sides of this equation by $\langle\Phi_0|$ gives

$$\langle\Phi_0|H_0|\Psi_0\rangle + \langle\Phi_0|V|\Psi_0\rangle = E_0 \langle\Phi_0|\Psi_0\rangle$$

The first term reduces to $E_0^{(0)}$ by acting H_0 to the left. The second term can be re-expressed in terms of Ω, and we obtain an expression for the perturbed eigenvalue E_0 in terms of a *shift* from the unperturbed eigenvalue $E_0^{(0)}$.

$$E_0 = E_0^{(0)} + \langle\Phi_0|V\Omega|\Phi_0\rangle$$

If we were to know what Ω is, at this point the eigenstates and eigenvalues would be completely determined. Löwdin derived that such an Ω can be constructed from an operator called a *resolvent*, and under this definition, Ω yields the same perturbation expansion for E_0 and $|\Psi_0\rangle$.

2 Resolvents

A resolvent is a mathematical structure which is used to study the eigenspectrum of operators, among other things. The concept of a *reduced resolvent* arises when one considers an eigenvalue problem

$$A\phi = a\phi$$

Suppose the eigenfunctions ϕ can be expanded in an orthonormal basis $(f_1, f_2, f_3,...)$ such that $\sum_i c_i f_i$ and let $\mathbf{A}_{ij} = \langle f_i|A|f_j \rangle$ be the matrix representation of the operator A in this basis. Suppose we divide the basis f into two partitions p and q. If the p partition is just a single basis function ($p : f_1$) (which we will just denote by the number 1) and the q partition is all other basis functions ($q : f_2, f_3, ...$), one finds with some manipulation that the eigenvalues are defined by the relation

$$a = A_{11} + \mathbf{A}_{1q}(a \cdot \mathbf{1}_{qq} - \mathbf{A}_{qq})^{-1}\mathbf{A}_{q1}$$

The above is the "reduced" characteristic equation, and it can be used for finding the eigenvalues. It arises in the particular case of our partitioning of our basis in this manner. The above equation can be thought of as an alternative to the standard characteristic equation $\det(\mathbf{A} - a\mathbf{1}) = 0$.

If we replace the eigenvalues a in the expression above with some continuous, variable parameter κ, we obtain the following:

$$f(\kappa) = A_{11} + \mathbf{A}_{1q}(\kappa \cdot \mathbf{1}_{qq} - \mathbf{A}_{qq})^{-1}\mathbf{A}_{q1}$$

Now, whenever this function is such that $f(\kappa) = \kappa$, we have found an eigenvalue $a = \kappa$. If we vary this κ until $f(\kappa) - \kappa = 0$, we pull out a discrete eigenvalue which is a solution to the eigenvalue problem.

The key quantity above

$$\mathcal{R}_\kappa(A) = (\kappa \cdot \mathbf{1}_{qq} - \mathbf{A}_{qq})^{-1}$$

is the **reduced resolvent** operator of $\mathbf{A}$ for a particular κ. [1] In words, the reduced resolvent is an operator that is assigned to another operator $\mathbf{A}$. It is only defined in q-space part of the operator, and different values of κ give different reduced resolvents. As abstract as that is, it is tremendously useful, as we will see later.

Notice how the resolvent is dependent on just the matrix elements of the operator $\mathbf{A}$ which correspond to the q partition; it lives in the q-space partition of our basis. Expressed pictorially as a matrix representation divided into pp, pq, qp, qq blocks,

$$\mathcal{R}_\kappa(A) = \begin{pmatrix} 0 & \mathbf{0} \\ \hline \mathbf{0} & (\kappa\mathbf{1}_{qq} - A_{qq})^{-1} \end{pmatrix}$$

3 Löwdin's big idea: using reduced resolvents to define perturbation theory and solve the Schrödinger equation

Back to the world of quantum chemistry and the Schrödinger equation, we can define two projection operators P and Q which partition our n-electron Hilbert space into two parts (note: if that sounds like gobbledygook to you, see the Appendix for details). It is this partitioning which birthed the idea of a reduced resolvent above.

P is the "model space projection operator", which can act on a state and project it onto some reference determinant Φ_0.

$$P = |\Phi_0\rangle \langle \Phi_0|$$

Q is the *orthogonal complement* of P, which projects out every determinant other than the reference Φ_0

$$Q = 1 - P = \sum_{n \neq 0} |\Phi_n\rangle \langle \Phi_n|$$

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[1] Here, $\mathbf{1}_{qq}$ is the identity matrix of size $q \times q$ and $\mathbf{A}_{qq}$ is the matrix representation of the operator in just the q-space, (over just q basis functions)

P and Q basically just split our basis into two parts, and the sum of P and Q yield the resolution of the identity, $P + Q = 1$. In terms of operators, the definition of the reduced resolvent for some operator H is

$$\mathcal{R}_\kappa = (\kappa - H)^{-1} Q$$

This is the operator analogue of the matrix representation form of $\mathcal{R}_\kappa(A)$ we defined earlier. Instead of only explicitly including matrix elements in the q space, we use our newly defined operator Q to project the negative inverse of H into the Q space.

Löwdin's idea, in short, was to generalize the Schrödinger equation to a continous spectrum in κ, and use the κ-dependent reduced resolvent in the definition of a trial wavefunction to solve for the eigenvalues. Read that last sentence a few more times. Hopefully, it will soon become clear what I mean by this. Starting from the re-arranged Schrödinger equation,

$$(E_0 - H) |\Psi_0\rangle = 0$$

suppose we choose a form for the wavefunction which has a continuous dependence on some parameter κ:

$$(\kappa - H) |\Psi_\kappa\rangle = ...$$

The above equation *becomes* the Schrodinger equation whenever the right side is 0. If this is the case, κ happens to be equal to a true eigenvalue E_0. For this reason, we refer to it as a *generalization* of the Schrödinger equation.

Löwdin derived that a **trial wavefunction** $|\Psi_\kappa\rangle$ which is of the form $|\Psi_\kappa\rangle = \Omega_\kappa |\Phi_0\rangle$ can be expressed in terms of the reduced resolvent.

$$|\Psi_\kappa\rangle = \Omega_\kappa |\Phi_0\rangle$$

$$\Omega_\kappa = P + \mathcal{R}_\kappa H P$$

$$|\Psi_\kappa\rangle = |\Phi_0\rangle + \mathcal{R}_\kappa H |\Phi_0\rangle$$

What happens when we apply $(\kappa - H)$ to our trial wavefunction $|\Psi_\kappa\rangle$? as in the above expression $(\kappa - H) |\Psi_\kappa\rangle = ...$? Applying the resolution of the identity $P + Q = 1$, we find

$$(\kappa - H) |\Psi_\kappa\rangle = P(\kappa - H) |\Psi_\kappa\rangle + Q(\kappa - H) |\Psi_\kappa\rangle$$

Looking at just the Q term, we find that

$$
\begin{aligned}
Q(\kappa - H) |\Psi_\kappa\rangle &= Q(\kappa - H) |\Phi_0\rangle + Q(\kappa - H)\mathcal{R}_\kappa H |\Phi_0\rangle \\
&= \kappa Q |\Phi_0\rangle - QH |\Phi_0\rangle + QH |\Phi_0\rangle \\
&= \kappa Q |\Phi_0\rangle \\
&= 0
\end{aligned}
$$

Above we have used the fact that $Q(\kappa - H)\mathcal{R}_\kappa = Q$, which follows clearly from the definition of the reduced resolvent, and that Q acting on $|\Phi_0\rangle$ is 0, since $|\Phi_0\rangle$ lives in the P space. We conclude the Q term is 0, so we are left with:

$$(\kappa - H) |\Psi_\kappa\rangle = P(\kappa - H) |\Psi_\kappa\rangle$$

Using the definition of $P = |\Phi_0\rangle \langle\Phi_0|$, and noting that we can always ensure $|\Psi_\kappa\rangle$ is intermediately normalized, we obtain

$$
\begin{aligned}
(\kappa - H) |\Psi_\kappa\rangle &= |\Phi_0\rangle \langle\Phi_0| (\kappa - H) |\Psi_\kappa\rangle \\
&= \kappa |\Phi_0\rangle \langle\Phi_0|\Psi_\kappa\rangle - |\Phi_0\rangle \langle\Phi_0|H|\Psi_\kappa\rangle \\
&= (\kappa - \langle\Phi_0|H|\Psi_\kappa\rangle) |\Phi_0\rangle \\
&= (\kappa - \langle\Phi_0|H\Omega_\kappa|\Phi_0\rangle) |\Phi_0\rangle \\
&= (\kappa - \langle\Phi_0|H + H\mathcal{R}_\kappa H|\Phi_0\rangle) |\Phi_0\rangle \\
&= (\kappa - f(\kappa)) |\Phi_0\rangle
\end{aligned}
$$

where we have defined the function of κ, denoted $f(\kappa)$ as

$$f(\kappa) = \langle \Phi_0 | H | \Psi_\kappa \rangle = \langle \Phi_0 | H + H\mathcal{R}_\kappa H | \Phi_0 \rangle$$

Löwdin calls this the *bracketing function*, since it enables one to obtain both lower and upper bounds to true eigenvalues. Restating the above in one compact expression, we have

$$(\kappa - H) | \Psi_\kappa \rangle = (\kappa - f(\kappa)) | \Phi_0 \rangle$$

$$(\kappa - H)\Omega_\kappa | \Phi_0 \rangle = (\kappa - f(\kappa)) | \Phi_0 \rangle$$

This is a monumental result. **When κ is equal to $f(\kappa)$, the right side above goes to zero. If this occurs, we conclude that our trial function $|\Psi_\kappa\rangle$ is a solution to the Schrödinger equation, and the eigenvalue κ is the corresponding energy eigenvalue.** Thus, our chosen trial function (derived by Löwdin) gives us access to the solutions of the Schrodinger equation, by looking for zeros of $F(\kappa) = f(\kappa) - \kappa$.

To summarize, our discrete eigenvalue problem (the Schrödinger equation) was modified into a continuous form, which was enabled by the κ dependence of the reduced resolvent $\mathcal{R}_\kappa$, which Lowdin realized can be used to construct our magical wave operator Ω_κ, which transforms our reference determinant into some function Ψ_κ by $|\Psi_\kappa\rangle = \Omega_\kappa |\Phi_0\rangle$. When κ happens to be equal to an eigenvalue of the Schrödinger equation, we will know it, since $\kappa - f(\kappa) = 0$, and we will have found an eigenstate and eigenvalue (solved the Schrödinger equation).

3.1 Löwdin's Rayleigh-Schrödinger Perturbation Theory

We can now take our generalized Schrödinger equation from above

$$(\kappa - H)\Omega_\kappa | \Phi_0 \rangle = (\kappa - f(\kappa)) | \Phi_0 \rangle$$

and consider how it behaves when our Hamiltonian is split into two parts $H = H_0 + V$.

The Wave Operator   Our wave operator becomes

$$\Omega_\kappa = P + \mathcal{R}_\kappa H_0 P + \mathcal{R}_\kappa V P$$

$$\Omega_\kappa = P + \mathcal{R}_\kappa H_0 | \Phi_0 \rangle \langle \Phi_0 | + \mathcal{R}_\kappa V P$$

$$\Omega_\kappa = P + E_0 \mathcal{R}_\kappa P + \mathcal{R}_\kappa V P$$

$$\Omega_\kappa = P + \mathcal{R}_\kappa V P$$

where the reduced resolvent acting on P is zero, since the resolvent entirely resides in the Q space, which is orthogonal to P.

The Bracketing Function   After a few manipulations which are left as an exercise, the bracketing function $f(\kappa) = \langle \Phi_0 | H\Omega_\kappa | \Phi_0 \rangle$ becomes

$$f(\kappa) = E_0^{(0)} + \langle \Phi_0 | V\Omega_\kappa | \Phi_0 \rangle$$

The Reduced Resolvent   We have one last quantity to fully define: the reduced resolvent. How does the resolvent behave for our Hamiltonian $H = H_0 + V$?

$$\mathcal{R}_\kappa = (\kappa - H)^{-1} Q$$

We are about to do a lot of tricky manipulations, but in doing so, we will arrive at perhaps the most important result in this set of notes. Let's do it. First we will expand H and add $0 = E_0^{(0)} - E_0^{(0)}$

$$\mathcal{R}_\kappa = (\kappa - E_0^{(0)} + E_0^{(0)} - H_0 - V)^{-1} Q$$

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Rearranging and letting $V' = V - (\kappa - E_0^{(0)})$:

$$\mathcal{R}_\kappa = (E_0^{(0)} - H_0 - V')^{-1}Q$$

To move further, we use of the following identity for two operators A and B,

$$(A - B)^{-1} = A^{-1} + A^{-1}B(A - B)^{-1}$$

If we let $A = (E_0^{(0)} - H_0)$ and $B = V'$, we have

$$\mathcal{R}_\kappa = \left[(E_0^{(0)} - H_0)^{-1} + (E_0^{(0)} - H_0)^{-1}V'(E_0^{(0)} - H_0 - V')^{-1}\right]Q$$

$$\mathcal{R}_\kappa = (E_0^{(0)} - H_0)^{-1}Q + (E_0^{(0)} - H_0)^{-1}V'(E_0^{(0)} - H_0 - V')^{-1}Q$$

Since $Q^2 = Q$ and Q is Hermitian we can insert a Q in the second term:

$$\mathcal{R}_\kappa = (E_0^{(0)} - H_0)^{-1}Q + (E_0^{(0)} - H_0)^{-1}QV'(E_0^{(0)} - H_0 - V')^{-1}Q$$

Expanding the definition of V' in the parentheses we obtain

$$\mathcal{R}_\kappa = (E_0^{(0)} - H_0)^{-1}Q + (E_0^{(0)} - H_0)^{-1}QV'(\kappa - H)^{-1}Q$$

Now, we define the quantity $\mathcal{R}_0 = (E_0^{(0)} - H_0)^{-1}Q$, the **unperturbed reduced resolvent**, which is the resolvent defined for $\kappa = E_0^{(0)}$ and unperturbed Hamiltonian H_0.

$$\mathcal{R}_\kappa = \mathcal{R}_0 + \mathcal{R}_0 V'(\kappa - H)^{-1}Q$$

Noting the last part of the second term is just our original reduced resolvent $\mathcal{R}_\kappa = (\kappa - H)^{-1}Q$, we finally arrive at our result:

$$\mathcal{R}_\kappa = \mathcal{R}_0 + \mathcal{R}_0 V' \mathcal{R}_\kappa$$

The resolvent is dependent on itself. Because of this, we can iteratively construct an expansion of the resolvent. This will ultimately be the source of our perturbation expansion. In an exercise, you will explicitly iterate the resolvent, and show that it generalizes to the following

$$\mathcal{R}_\kappa = \sum_{n=0}^{\infty} (\mathcal{R}_0 V')^n \mathcal{R}_0$$

Up to this point, we have defined everything with the subscript κ. From here on, we will focus on just finding solutions for which κ is our ground state energy $\kappa = E_0$, so we will drop the κ subscripts. Since the only part of the resolvent above which depends on κ is $V' = V - (\kappa - E_0^{(0)})$, we will now have

$$V' = V - (E_0 - E_0^{(0)})$$

$$\mathcal{R} = \sum_{n=0}^{\infty} (\mathcal{R}_0 V')^n \mathcal{R}_0$$

We will likewise drop the κ from our definition of the wave operator and the wave function

$$\Omega = P + \sum_{n=0}^{\infty} (\mathcal{R}_0 V')^n \mathcal{R}_0 V P$$

$$|\Psi_0\rangle = \Omega |\Phi_0\rangle$$

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{n=0}^{\infty} (\mathcal{R}_0 V')^n \mathcal{R}_0 V |\Phi_0\rangle$$

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This is our perturbation expansion for the wavefunction. From section 1, "The Wave Operator", we derived our energy expression to be,

$$E_0 = E_0^{(0)} + \langle \Phi_0 | V\Omega | \Phi_0 \rangle$$

Our energy expansion is therefore,

$$E_0 = E_0^{(0)} + \langle \Phi_0 | V | \Phi_0 \rangle + \sum_{n=0}^{\infty} \langle \Phi_0 | V(\mathcal{R}_0 V')^n \mathcal{R}_0 V | \Phi_0 \rangle$$

This is our perturbation expansion for the energy.

The operator V' introduces some complexity that is worth discussing. It contains E_0, which is the exact energy, so it involves a sum over all orders of energy corrections.

$$V' = V - (E_0 - E_0^{(0)})$$

$$V' = V - \sum_{m=1} E_0^{(m)}$$

$$V' = V - E_0^{(1)} - E_0^{(2)} - E_0^{(3)} - \cdots$$

To conclude, we have obtained expressions for the nth order wavefunction and energy corrections in perturbation theory. Looking at the expression for $|\Psi_0\rangle$, each order wavefunction correction at higher orders is just a string of operators $(\mathcal{R}_0, V, V')$ acting on our reference determinant. Each energy is just an expectation value of a string of operators $(\mathcal{R}_0, V, V')$. Using these expansions in practice can be a bit tricky, as we will see in the next section.

4 Deriving Perturbation Theory Orders

Before we get started, we need to know how to identify the "order" of a term in our wavefunction expansion. The reason is that if we want the mth order wavefunction correction, we need to pull out all mth order terms in $|\Psi_0\rangle = |\Phi_0\rangle + \sum_{n=0}^{\infty} (\mathcal{R}_0 V')^n \mathcal{R}_0 V |\Phi_0\rangle$.

How to identify the order of a term? Some tips for finding the order of a given term:

- Each V contributes an order of 1

- Each $E_0^{(m)}$ contributes an order of m

- Instead of counting orders from V and $E_0^{(m)}$, you can instead count the number of resolvents $\mathcal{R}_0$. Before doing so, you must convert all $E_0^{(m)}$ to the corresponding analytic expression.

As an example of the above rules, when determining the order of the term

$$\mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V |\Phi_0\rangle$$

which appears in the third-order wavefunction, we could reason that V and $E_0^{(2)}$ is $1 + 2 = 3 \implies$ third order. Alternatively, we could recognize that $E_0^{(2)} = \langle \Phi_0 | V \mathcal{R}_0 V | \Phi_0 \rangle$ (for now, just accept that this is true, we will derive it later), so therefore our expression is

$$\mathcal{R}_0 \langle \Phi_0 | V \mathcal{R}_0 V | \Phi_0 \rangle \mathcal{R}_0 V |\Phi_0\rangle$$

The above expression has 3 resolvents, so we conclude it is third order. OR, we could count that the above expression has 3 V's, and conclude it is third order. Everything checks out. Let's derive some perturbation theory orders.

Zero order   The 0th order wavefunction correction is just the first term of the respective perturbation expansion fro above, which is of course just our reference determinant $|\Phi_0\rangle$. The 0th order energy is just $E_0^{(0)}$.

First order

$$|\Phi_0^{(1)}\rangle = \mathcal{R}_0 V |\Phi_0\rangle$$

$$E_0^{(1)} = \langle\Phi_0|V|\Phi_0\rangle$$

Second order   We read off from the expansion for $n = 1$,

$$|\Phi_0^{(2)}\rangle = \mathcal{R}_0 V' \mathcal{R}_0 V |\Phi_0\rangle$$

Here is the only tricky thing with this formalism: V' contains higher order contributions to the energy

$$V' = V - E_0^{(1)} - E_0^{(2)} - E_0^{(3)} - \cdots$$

Since we are building the second order wavefunction, it must be composed of only second order pieces. The prefactor $\mathcal{R}_0 V' \mathcal{R}_0 V$ above should therefore only be second order. The V is first order, so multiplying by V' should only increase the order by 1. This means only terms in the V' expansion which are first order contribute to the second order wavefunction. This means our V' in this case is truncated to just $V + E_0^{(1)}$, so we have,

$$|\Phi_0^{(2)}\rangle = \mathcal{R}_0 (V - E_0^{(1)}) \mathcal{R}_0 V |\Phi_0\rangle$$

$$|\Phi_0^{(2)}\rangle = \mathcal{R}_0 V \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V |\Phi_0\rangle$$

That's it! The energy correction is,

$$E_0^{(2)} = \langle\Phi_0|V\mathcal{R}_0 V|\Phi_0\rangle$$

Third order   Here we have track of the orders of various terms more carefully. To remind you, our wavefunction perturbation expansion is

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{n=0}^{\infty} (\mathcal{R}_0 V')^n \mathcal{R}_0 V |\Phi_0\rangle$$

At $n = 2$, we have a V and two V' in our term. To make the term third order overall (this is our target for constructing $|\Phi_0^{(3)}\rangle$), we require that each V' is 1st order, so we only take out the first order energy and V in our V' expansion $V' = V - E_0^{(1)}$. Let's now write this $n = 2$ term down before moving on,

$$|\Phi_0^{(3)}\rangle = (\mathcal{R}_0 (V - E_0^{(1)}))^2 \mathcal{R}_0 V |\Phi_0\rangle + (...\text{more})$$

There is also a third-order term which appears when $n = 1$, $(\mathcal{R}_0 V')^1 \mathcal{R}_0 V |\Phi_0\rangle$. That V' has a second order contribution from $E_0^{(2)}$, therefore we set $V' = -E_0^{(2)}$ and pick up an additional term $\mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V |\Phi_0\rangle$ for $|\Phi_0^{(3)}\rangle$

$$|\Phi_0^{(3)}\rangle = (\mathcal{R}_0 (V - E_0^{(1)}))^2 \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V |\Phi_0\rangle$$

Expanding this and simplifying yields

$$|\Phi_0^{(3)}\rangle = \mathcal{R}_0 V \mathcal{R}_0 V \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 V \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V |\Phi_0\rangle + \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V |\Phi_0\rangle$$

Our energy expansion is

$$E_0 = E_0^{(0)} + \langle\Phi_0|V|\Phi_0\rangle + \sum_{n=0}^{\infty} \langle\Phi_0|V(\mathcal{R}_0 V')^n \mathcal{R}_0 V|\Phi_0\rangle$$

The third order contribution to the energy expression occurs for $n = 1$ and is

$$E_0^{(3)} = \langle \Phi_0 | V(\mathcal{R}_0(V - E_0^{(1)}))\mathcal{R}_0 V|\Phi_0\rangle$$

Alternatively, we could have also found the above by noting that generally the $(m + 1)$ order energy is found by the mth order wavefunction,

$$E_0^{(m+1)} = \langle \Phi_0|V|\Phi_0^{(m)}\rangle$$

$$E_0^{(3)} = \langle \Phi_0|V|\Phi_0^{(2)}\rangle$$

and just plug in our derived $|\Phi_0^{(2)}\rangle$.

5   The Energy Substitution Theorem

There is a pattern for finding equations for $\Phi_0^{(m)}$, so you don't have to go through the tedious process of analyzing where to get terms of a certain order for different values of n in the expansion, or plucking out the proper terms from V' (but you should know how to do this anyway).

Energy Substitution Theorem $|\Phi_0^{(m)}\rangle$ is equal to the sum of a "principal term" $(\mathcal{R}_0 V)^m |\Phi_0\rangle$ plus all unique substitutions of adjacent factors $(\mathcal{R}_0 V)^r$ with $(\mathcal{R}_0 E_0^{(r)})$. Each term in the sum is waited by a sign factor $(-1)^k$ where k is the number of substitutions. The pair of operators $\mathcal{R}_0 V$ closest to the ket $|\Phi_0\rangle$ is not considered for substitutions.

We will not prove this, but hopefully by looking at the expressions for $|\Phi_0^{(2)}\rangle$ and $|\Phi_0^{(3)}\rangle$ that we just derived will convince you:

$$|\Phi_0^{(2)}\rangle = \mathcal{R}_0 V \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V |\Phi_0\rangle$$

$$|\Phi_0^{(3)}\rangle = \mathcal{R}_0 V \mathcal{R}_0 V \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 V \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V |\Phi_0\rangle + \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 E_0^{(1)} \mathcal{R}_0 V |\Phi_0\rangle - \mathcal{R}_0 E_0^{(2)} \mathcal{R}_0 V |\Phi_0\rangle$$

Now we barely even need to think when we write down our perturbative wavefunction corrections. Keeping in mind the energy corrections follow form

$$E^{(m+1)} = \langle \Phi_0|V|\Phi_0^{(m)}\rangle$$

our wavefunction correction expressions determine our energy expression corrections.

6   Concluding Remarks

I should note that we have not actually translated the energy corrections into programmable expressions. To do this, we would have to actually evaluate the expectation values, and it would be a lot of work. Later on in the course, after learning diagrams, we will revisit PT and learn how to diagrammatically derive programmable expressions for the various energy orders. When we do this, we will cleverly choose H_0 and V such that $E_0^{(0)} = E_0^{(1)} = 0$, which simplifies things a good bit, and also makes it so that each energy correction is purely a correlation energy contribution. For a sneak peak, you can look at handout 6 from the 2017 edition of this course.

That was a long and arduous mathematical climb. But we have finally reached the summit, and now hopefully you can see that all of perturbation theory is obtainable by just smacking your reference state $|\Phi_0\rangle$ with operator strings consisting of resolvents $\mathcal{R}_0$ and the perturbed part of the Hamiltonian V. Compare this to how we derived MP2 in the previous set of notes; we had to do a bunch of algebraic manipulations to get to the end result. As you can imagine, deriving MP3 and MP4 under that framework only gets worse. In Löwdin's resolvent formalism, we can just read off the result, and then evaluate it to an algebraic expression using diagrams.

7 Appendix

7.1 Hilbert Space

Recall that many of the objects we have been talking about (spin orbitals, Slater determinants, wavefunctions) "live" in some Hilbert space. This means many things, but for our purposes, we just need to know there is some "space" of *abstract vectors* which have a defined inner product with a certain set of properties. Every abstract vector in the space can be described in terms of the orthonormal basis which makes up the space.

- The set of all spin orbitals form a basis for what you might call the one-electron Hilbert space $\mathcal{H}$

- n tensor products of $\mathcal{H}$ with itself forms an n-electron Hilbert space $\mathcal{H}^n$. A member of the basis of such a space is a product of spin orbitals (Hartree products)

- Denote the *antisymmetric subspace* of $\mathcal{H}^n$ as $\mathscr{H}^n$. The basis of this space is the set of n-electron Slater determinants. All possible Slater determinants for an n-electron system live in $\mathscr{H}^n$ The full CI wavefunction for an n-electron system can be constructed from a linear combination of basis vectors in $\mathscr{H}^n$

7.2 Partitioning

Consider the following *partition* of this n-electron antisymmetric Hilbert space $\mathscr{H}^n$ into a "P" space and a "Q" space.

$$\mathscr{H}^n = \mathscr{H}^n_P \oplus \mathscr{H}^n_Q$$

where P is the *projection operator* onto some reference determinant

$$P = |\Phi_0\rangle \langle\Phi_0|$$

and Q is the *orthogonal complement* of P, which projects onto every determinant other than the reference Φ_0

$$Q = 1 - P = \sum_{n\neq 0} |\Phi_n\rangle \langle\Phi_n|$$

You can think of this as just dividing your Slater determinant basis into two parts, P and Q. The sum $P + Q$ is equal to unity. This can be most easily seen by thinking of P and Q as two distinct chunks of the resolution of the identity.