

Lecture 5: Perturbation Theory I

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To remind you of the current task at hand, we are trying to find good quality approximations to electronic wavefunctions in order to obtain the electronic energy of a molecular system. That is, we seek to solve the Schrödinger equation in the best way possible.

$$H|\Psi\rangle = E|\Psi\rangle$$

We already learned that HF theory is a decent and cheap approximation, and full-CI is exact but very expensive. Perturbation theory is one of many approaches to finding wavefunctions and energies which are of reasonable cost and reasonable accuracy. Recall, however, that the HF wavefunction Φ gives us a very good starting point, so we are really just interested in solving for the correlation energy, which is obtained by shifting our Hamiltonian by the HF energy.

$$H_c|\Psi\rangle = E_{\text{corr}}|\Psi\rangle$$

where

$$H_c = H - \langle\Phi|H|\Phi\rangle$$

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$$

We will start by discussing Rayleigh-Schrödinger perturbation theory (RSPT), which applies the ideas of PT to the time-independent Schrödinger equation. Next, we will apply the results of RSPT to derive Møller-Plesset methods (MP n) for approximating the electronic correlation energy of molecular systems.

1 Rayleigh-Schrödinger Perturbation Theory

Perturbation theory (PT), in the most general sense, is applicable in nearly every domain of physics. If a problem can be separated into some easily solvable piece A and not-so-easily solvable piece B (“the perturbation”), one can approach the exact solution of the problem in terms of the solution to A plus a series of corrections to account for the influence of perturbation. Rayleigh-Schrödinger Perturbation Theory (RSPT) applies the ideas of PT to the time-independent Schrödinger equation. The Hamiltonian is decomposed into a sum of a simple (easy to solve) problem H_0 and a perturbation V :

$$H = H_0 + V$$

If the perturbation is “small” (i.e., does not wildly shift the solutions of the problem) the energy levels/eigenstates associated with the *perturbed system* described by H can be expressed as sum of the energy levels/eigenstates of the *simple system* (described by H_0) and a series of corrections obtained by considering the influence of the perturbation V on the energy levels/eigenstates of the simple system. Each of these corrections contain eigenvalues of H_0 and matrix elements of the perturbation between the eigenfunctions of H_0 , as we will see. In summary, RSPT is applying age-old ideas of general perturbation theory to the time independent Schrödinger equation.

The eigenvalue problem we wish to solve is the following:

$$H|\Psi_i\rangle = (H_0 + V)|\Psi_i\rangle = E_i|\Psi_i\rangle$$

We are assuming H_0 is a simple, easy-to-solve system, for which we have access to all the eigenstates and eigenvalues.

$$H_0 |\Phi_i^{(0)}\rangle = E_i^{(0)} |\Phi_i^{(0)}\rangle$$

These eigenstates $|\Phi_i^{(0)}\rangle$ and eigenvalues E_i for the simple system are hopefully very close to the exact results $|\Psi_i\rangle$ and E_i , that is, the perturbation V is small. Now, we do something a bit weird. We introduce a parameter λ in front of V , which allows us to toggle the influence of the perturbation on the energy levels and eigenstates. Before saying much else about λ , let's write it down and see what it allows us to do.

$$(H_0 + \lambda V) |\Psi_i\rangle = E_i |\Psi_i\rangle$$

When $\lambda = 0$, our Hamiltonian is just H_0 , and our eigenstates and energy levels become that of the simple system $|\Phi_i^{(0)}\rangle$ and $E_i^{(0)}$. When $\lambda = 1$, our Hamiltonian is the full Hamiltonian H , and our eigenstates and energy levels are the perturbed system $|\Psi_i^{(0)}\rangle$ and E_i . By doing this, *the energy levels and eigenstates of the perturbed system are a function of λ* . To put it another way, our energy levels and eigenstates depend on lambda; we might express this mathematically as $E_i(\lambda)$ and $\Psi_i(\lambda)$. Since these quantities are *functions of λ* , we can write down a Taylor series expansion of the energy levels and eigenstates of H in terms of λ :

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$$

$$|\Psi_i\rangle = \Phi_i^{(0)} + \lambda \Phi_i^{(1)} + \lambda^2 \Phi_i^{(2)} + \dots$$

where each term is,

$$E_i^{(k)} = \frac{1}{k!} \frac{d^k E_i}{d\lambda^k} \Big|_{\lambda=0}$$

$$\Phi_i^{(k)} = \frac{1}{k!} \frac{d^k |\Psi_i\rangle}{d\lambda^k} \Big|_{\lambda=0}$$

We call $E_i^{(0)}$ the 0th order energy, which is the energy of the simple system. Every additional term in the energy expansion is the n^{th} order energy correction, and these are what we must solve for. Likewise terminology is used for the eigenstate corrections $|\Phi_i^{(k)}\rangle$

Many textbooks and other resources simply say λ is a “fictitious dummy parameter” or “book-keeping device” that is used to keep track of the “orders” of the terms when working with the perturbation expansion. This is a bit of an oversimplification. The parameter λ has the utility of turning the perturbation on/off, and motivates the use of a Taylor expansion in the first place. Without λ , you have no Taylor expansion, and no perturbation theory. While it does serve as a useful label for the orders of each term, it's not just a “dummy” parameter. It's the key to all of perturbation theory.

We have a form for the wavefunction and the energy. Plugging these into the time-independent Schrödinger equation, we get

$$(H_0 + \lambda V)(\Phi_i^{(0)} + \lambda \Phi_i^{(1)} + \lambda^2 \Phi_i^{(2)} + \dots) = (E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots)(\Phi_i^{(0)} + \lambda \Phi_i^{(1)} + \lambda^2 \Phi_i^{(2)} + \dots)$$

Subtracting from each side so that the left is 0 and grouping like powers of λ gives

$$\begin{aligned} & \left(H_0 |\Phi_i^{(0)}\rangle - E_i^{(0)} |\Phi_i^{(0)}\rangle \right) \\ & + \lambda \left(H_0 |\Phi_i^{(1)}\rangle + V |\Phi_i^{(0)}\rangle - E_i^{(0)} |\Phi_i^{(1)}\rangle - E_i^{(1)} |\Phi_i^{(0)}\rangle \right) \\ & + \lambda^2 \left(H_0 |\Phi_i^{(2)}\rangle + V |\Phi_i^{(1)}\rangle - E_i^{(0)} |\Phi_i^{(2)}\rangle - E_i^{(1)} |\Phi_i^{(1)}\rangle - E_i^{(2)} |\Phi_i^{(0)}\rangle \right) \\ & + \dots \\ & = 0 \end{aligned}$$

The only way the above equation can be satisfied for any arbitrary value of λ is if the coefficient in parentheses for each power of λ is equal to 0. Therefore, since each term for each power of λ is equal to 0,

this equation is fully separable into an infinite series of simultaneous equations

$$\begin{aligned} H_0 |\Phi_i^{(0)}\rangle &= E_i^{(0)} |\Phi_i^{(0)}\rangle \\ H_0 |\Phi_i^{(1)}\rangle + V |\Phi_i^{(0)}\rangle &= E_i^{(0)} |\Phi_i^{(1)}\rangle + E_i^{(1)} |\Phi_i^{(0)}\rangle \\ H_0 |\Phi_i^{(2)}\rangle + V |\Phi_i^{(1)}\rangle &= E_i^{(0)} |\Phi_i^{(2)}\rangle + E_i^{(1)} |\Phi_i^{(1)}\rangle + E_i^{(2)} |\Phi_i^{(0)}\rangle \\ &\dots \end{aligned}$$

Notice we have now dropped the λ 's since each of the above equations hold whether or not λ^n is applied to each term. You could also interpret this as us setting $\lambda = 1$, and fully "turning on" the perturbation.

We will assume henceforth that our reference state is normalized $\langle \Phi_i^{(0)} | \Phi_i^{(0)} \rangle = 1$ and our exact wavefunction is intermediately normalized $\langle \Phi_i^{(0)} | \Psi_i \rangle = 1$. This yields,

$$\langle \Phi_i^{(0)} | \Psi_i \rangle = 1 = \langle \Phi_i^{(0)} | \Phi_i^{(0)} \rangle + \lambda \langle \Phi_i^{(0)} | \Phi_i^{(1)} \rangle + \lambda^2 \langle \Phi_i^{(0)} | \Phi_i^{(2)} \rangle + \dots$$

In order for the above expression to be true for arbitrary λ , it must be the case that $\langle \Phi_i^{(0)} | \Phi_i^{(k)} \rangle = 0$ for $k = 1, 2, 3, \dots$

We can now project each equation in our system of equations on the left by $\langle \Phi_i^{(0)} |$. We can simplify quite a bit by noting $\langle \Phi_i^{(0)} | \Phi_i^{(k)} \rangle = 0$ for $k = 1, 2, 3, \dots$ and that since H_0 is Hermitian, we can act it act on the left to give $\langle \Phi_i^{(0)} | H_0 | \Phi_i^{(k)} \rangle = E_i^{(0)} \langle \Phi_i^{(0)} | \Phi_i^{(k)} \rangle$.

The final result is:

$$\begin{aligned} E_i^{(0)} &= \langle \Phi_i^{(0)} | H_0 | \Phi_i^{(0)} \rangle \\ E_i^{(1)} &= \langle \Phi_i^{(0)} | V | \Phi_i^{(0)} \rangle \\ E_i^{(2)} &= \langle \Phi_i^{(0)} | V | \Phi_i^{(1)} \rangle \end{aligned}$$

Notice that $E_i^{(1)}$ depends on $\Phi_i^{(0)}$, and $E_i^{(2)}$ depends on $\Phi_i^{(1)}$. This trend continues on for higher order energy corrections: the n^{th} order correction to the wavefunction is required for finding the $(n+1)^{th}$ order energy correction.

1.1 The first-order wavefunction and second-order energy corrections

The third equation above, the second-order energy ($E_i^{(2)}$) correction, requires you to know the 1st order correction to the wavefunction $\Phi_i^{(1)}$. To obtain it, we take the equation containing our 1st-order terms and rearrange:

$$H_0 |\Phi_i^{(1)}\rangle + V |\Phi_i^{(0)}\rangle = E_i^{(0)} |\Phi_i^{(1)}\rangle + E_i^{(1)} |\Phi_i^{(0)}\rangle$$

Projecting by $\langle \Phi_n^{(0)} |$ for some $n \neq i$ gives

$$\langle \Phi_n^{(0)} | H_0 | \Phi_i^{(1)} \rangle + \langle \Phi_n^{(0)} | V | \Phi_i^{(0)} \rangle = E_i^{(0)} \langle \Phi_n^{(0)} | \Phi_i^{(1)} \rangle + E_i^{(1)} \langle \Phi_n^{(0)} | \Phi_i^{(0)} \rangle$$

To simplify, note that $\langle \Phi_n^{(0)} | H_0 = E_n^{(0)} \langle \Phi_n^{(0)} |$, so the first term on the left becomes $E_n^{(0)} \langle \Phi_n^{(0)} | \Phi_i^{(1)} \rangle$. The second term on the right goes to 0 since $\langle \Phi_n^{(0)} | \Phi_i^{(0)} \rangle = 0$ when $n \neq i$. The reason is these are both eigenfunctions of H_0 , which are orthonormal. We are left with

$$E_n^{(0)} \langle \Phi_n^{(0)} | \Phi_i^{(1)} \rangle + \langle \Phi_n^{(0)} | V | \Phi_i^{(0)} \rangle = E_i^{(0)} \langle \Phi_n^{(0)} | \Phi_i^{(1)} \rangle$$

Rearranging we get

$$\langle \Phi_n^{(0)} | \Phi_i^{(1)} \rangle = - \frac{\langle \Phi_n^{(0)} | V | \Phi_i^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}}$$

We want to get $|\Phi_i^{(1)}\rangle$ by itself on the left side. The left side above is the expansion coefficients of $\Phi_i^{(1)}$ in the basis of $\Phi_n^{(0)}$. To see this, project each side by $|\Phi_n^{(0)}\rangle$ and sum over all $n \neq i$

$$\sum_{n \neq i} |\Phi_n^{(0)}\rangle \langle \Phi_n^{(0)} | \Phi_i^{(1)} \rangle = \sum_{n \neq i} -\frac{\langle \Phi_n^{(0)} | V | \Phi_i^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} |\Phi_n^{(0)}\rangle$$

The left side above would be equal to $|\Phi_i^{(1)}\rangle$ if the sum was over all n (resolution of the identity), but if we sum over all n , the energy denominator on the right will be 0 for $n = i$. Fortunately, the expansion coefficient $\langle \Phi_n^{(0)} | \Phi_i^{(1)} \rangle$ for $n = i$ is necessarily 0. Why? Because of intermediate normalization.

$$\langle \Phi_i^{(0)} | \Psi_i \rangle = 1 = \langle \Phi_i^{(0)} | \Phi_i^{(0)} \rangle + \lambda \langle \Phi_i^{(0)} | \Phi_i^{(1)} \rangle + \lambda^2 \langle \Phi_i^{(0)} | \Phi_i^{(2)} \rangle + \dots$$

Since our reference wavefunction is normalized $\langle \Phi_i^{(0)} | \Phi_i^{(0)} \rangle = 1$, in order for this expression to be true for arbitrary λ , it must be the case that $\langle \Phi_i^{(0)} | \Phi_i^{(k)} \rangle = 0$ for $k = 1, 2, 3, \dots$. This implies that when $n = i$, the expansion coefficient is 0. Therefore, we can sum over all n (rather than $n \neq i$) on the left side of our expression for $|\Phi_i^{(1)}\rangle$ without penalty; it is the same as adding zero to both sides:

$$\sum_n |\Phi_n^{(0)}\rangle \langle \Phi_n^{(0)} | \Phi_i^{(1)} \rangle = \sum_{n \neq i} -\frac{\langle \Phi_n^{(0)} | V | \Phi_i^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} |\Phi_n^{(0)}\rangle$$

Noting the left side contains the resolution of the identity, we can just remove it:

$$|\Phi_i^{(1)}\rangle = \sum_{n \neq i} -\frac{\langle \Phi_n^{(0)} | V | \Phi_i^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} |\Phi_n^{(0)}\rangle$$

This now enables us to derive an evaluable expression for the second-order energy

$$E_i^{(2)} = \langle \Phi_i^{(0)} | V | \Phi_i^{(1)} \rangle$$

Plugging in the definition for $\Phi_i^{(1)}$ above we obtain

$$E_i^{(2)} = \sum_{n \neq i} -\frac{\langle \Phi_n^{(0)} | V | \Phi_i^{(0)} \rangle \langle \Phi_i^{(0)} | V | \Phi_n^{(0)} \rangle}{E_n^{(0)} - E_i^{(0)}} |\Phi_n^{(0)}\rangle$$

$$E_i^{(2)} = \sum_{n \neq i} \frac{|\langle \Phi_i^{(0)} | V | \Phi_n^{(0)} \rangle|^2}{E_i^{(0)} - E_n^{(0)}}$$

One could keep working through the tedious algebra and derive the expressions for the second order wavefunction, third order wavefunction, etc, and in turn obtain energy corrections $E_i^{(3)}$, $E_i^{(4)}$, etc, but we will stop here. The above results are sufficient for deriving second-order Møller–Plesset perturbation theory.

There does exist a more advanced scheme which generalizes the results of all orders of perturbation theory using a mysterious new thing called “resolvents”. We will touch on this at the end of these notes and continue down that path after learning diagrams.

RSPT, as described above, is a completely general scheme, applicable to any application of the time-independent Schrodinger equation. We will use these ideas to come up with a way to obtain electronic energies with RSPT.

2 Møller–Plesset Perturbation Theory

Møller–Plesset Perturbation Theory (MP n) is the direct application of time-independent RSPT to the problem of finding electronic wavefunctions and energies. In this section, we will derive MP2 by applying the

RSPT equations derived above for a specific partition of our electronic Hamiltonian into H_0 and V . The MP2 energy which is correct up to second-order.

We first must divide our Hamiltonian into two parts, one which has a simple solution H_0 and the perturbation V .

$$H = H_0 + V$$

In MP n methods, the H_0 part of the Hamiltonian is taken to be the Hartree-Fock Hamiltonian,

$$H_0 = F = (h_p^q + \bar{g}_{pi}^{qi})a_q^p = f_p^q a_q^p$$

Note here we are **not** using the Φ -normal ordered Fock operator $f_p^q \tilde{a}_q^p$. The perturbation V will just be everything not included in H_0 .

$$V = H - F$$

$$V = \frac{1}{4} \bar{g}_{pq}^{rs} a_{rs}^{pq} - \bar{g}_{pi}^{qi} a_q^p$$

One could interpret V , the perturbation, as being all of the two-electron interactions, except for the mean-field picture already given by the HF Hamiltonian.

Suppose we seek the energy of the ground state of a system (which we will denote by a subscript 0). The ground state 0th order wavefunction $\Phi_0^{(0)}$ is the Hartree-Fock Slater determinant wavefunction. The ground state 0th order energy is given by $E_0^{(0)} = \langle \Phi_0^{(0)} | H_0 | \Phi_0^{(0)} \rangle$

$$E_0^{(0)} = \langle \Phi_0^{(0)} | H_0 | \Phi_0^{(0)} \rangle$$

$$= \sum_i h_{ii} + \sum_{ij} \langle ij || ij \rangle$$

We note the above expression, from Hartree-Fock theory, is equal to the sum of the occupied orbital energies $\sum_i \varepsilon_i$

$$E_0^{(0)} = \sum_i h_{ii} + \sum_{ij} \langle ij || ij \rangle = \sum_i \varepsilon_i$$

The 1st order energy correction is given by $E_0^{(1)} = \langle \Phi_0^{(0)} | V | \Phi_0^{(0)} \rangle$

$$E_0^{(1)} = \langle \Phi_0^{(0)} | V | \Phi_0^{(0)} \rangle$$

$$= -\frac{1}{2} \sum_{ij} \langle ij || ij \rangle$$

We notice immediately that the sum of the 0th and 1st order energies is the Hartree-Fock energy.

$$E_0^{(0)} + E_0^{(1)} = \sum_i h_{ii} + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle$$

Thus, the first two terms of our energy perturbation expansion is the HF energy.

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \dots$$

$$E_0 = E_{\text{HF}} + E_0^{(2)} + \dots$$

It must be that all higher-order terms constitute *correlation energies*, since in principle the expansion should approach the exact energy so long as the perturbation is small.

The second-order energy correction to the ground state energy is given by

$$E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle \Phi_0^{(0)} | V | \Phi_n^{(0)} \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

What sort of states are $\Phi_n^{(0)}$? They can be any excitation from our ground state reference HF determinant Φ_0 (any determinant in our CI expansion). However, we find that single excitations do not survive:

$$\langle \Phi_0 | V | \Phi_i^a \rangle = \langle \Phi_0 | H - H_0 | \Phi_i^a \rangle = \langle \Phi_0 | H | \Phi_i^a \rangle - \langle \Phi_0 | H_0 | \Phi_i^a \rangle = 0$$

Triple and higher excitations do not survive because you cannot form complete contractions, so $\Phi_n^{(0)}$ can only be the set of unique doubly excited determinants. What about the $E_0^{(0)}$ and $E_n^{(0)}$? Recall $E_0^{(0)}$ is the eigenvalue of H_0 acting on our Hartree-Fock determinant,

$$H_0 |\Phi_0^{(0)}\rangle = E_0^{(0)} |\Phi_0^{(0)}\rangle$$

which is just the sum of the occupied orbital energies $E_0^{(0)} = \sum_k \varepsilon_k$. The same is true for $E_n^{(0)}$, but it has a sum over occupied orbital energies which differs by two spin orbital occupations. Thus,

$$E_0^{(0)} - E_n^{(0)} = \sum_k \varepsilon_k - (\sum_k \varepsilon_k - (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b))$$

$$E_0^{(0)} - E_n^{(0)} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$$

So we finally obtain for the second order energy expression,

$$E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle \Phi_0^{(0)} | V | \Phi_n^{(0)} \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

$$E_0^{(2)} = \sum_{\substack{i < j \\ a < b}} \frac{|\langle \Phi_0 | V | \Phi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

Noting that only the first term of V yields a nonzero result,

$$E_0^{(2)} = \sum_{\substack{i < j \\ a < b}} \frac{|\langle \Phi_0 | \frac{1}{4} \bar{g}_{pq}^{rs} a_{rs}^{pq} | \Phi_{ij}^{ab} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$E_0^{(2)} = \frac{1}{16} \sum_{\substack{i < j \\ a < b}} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$E_0^{(2)} = \frac{1}{4} \sum_{ijab} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$