

# MANY-BODY PERTURBATION THEORY

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Having solved for the Hartree-Fock ground-state wave function, it is known that we are missing out on electron correlation. Expanding our wave function fully as a linear combination of all Slater determinants would recover the missing electron correlation; however, it is intractable. Here, we use perturbation theory to try and recover this missing correlation. The main approach of perturbation theory is to expand our solutions and energies in a power series about some perturbation. Right now, it is not obvious what perturbation we should add to our system, or what our reference Hamiltonian will be. Instead, lets focus on the fundamentals of time-independent perturbation theory and then move on to its application to molecular systems.

## 1. TIME-INDEPENDENT PERTURBATION THEORY: RAYLEIGH-SCHRÖDINGER (RS) PERTURBATION THEORY

For some, this may be a review, for others, this may be the first time you have seen perturbation theory. This approximation scheme is useful whenever we know to solutions to the eigenvalue problem of some reference Hamiltonian,  $\hat{H}^{(0)}$ , but want to find the solution to  $\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)}$  where  $\hat{H}^{(1)}$  is our perturbation to the system. In a more physical sense, one can think of  $\hat{H}^{(0)}$  as the regular hydrogen Coulomb potential (which we have analytical solutions), and  $\hat{H}^{(1)}$  is some external electric field that we apply to our system. Lets make these ideas a bit more concrete.

**Definition 1.** We call  $\hat{H}^{(0)}$  our reference, or **unperturbed Hamiltonian** and  $\hat{H}^{(1)}$  as our **perturbing Hamiltonian** or **perturbation**.

Now, let us assume we have all of the energy eigenstates of  $\hat{H}^{(0)}$ . That is,

$$\hat{H}^{(0)}|n^{(0)}\rangle = \mathcal{E}_n^{(0)}|n^{(0)}\rangle \quad (1)$$

Now, we assume that for every eigenket  $|n^{(0)}\rangle$ , there is a corresponding eigenket  $|n\rangle$  of  $\hat{H}$  with eigenvalue  $E_n$ . Our assumption that the perturbation is small is such that if we slowly vary  $\lambda$ , the states  $|n^{(0)}\rangle$  transform continuously to  $|n\rangle$  (Fig. 1). Then, we assume that the eigenkets and eigenvalues of  $\hat{H}$  can be expanded in a perturbation series

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

$$\mathcal{E}_n = \mathcal{E}_n^{(0)} + \lambda\mathcal{E}_n^{(1)} + \lambda^2\mathcal{E}_n^{(2)} + \dots \quad (3)$$

The superscripts denote the  $k$ -th order term of the expansion. This is analogous to saying that the true eigenstates are approximately close to the unperturbed states, and we can model them as Taylor expansions around the unperturbed states.

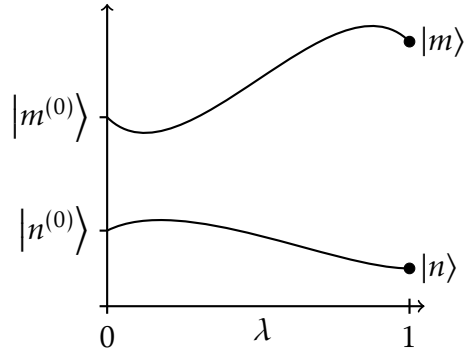


FIGURE 1. For non-degenerate perturbation theory, we assume that there is a continuous path from the initial states  $|n^{(0)}\rangle$  and  $|m^{(0)}\rangle$  to final states  $|n\rangle$  and  $|m\rangle$  as a function of  $\lambda$ .

Now, to find the expansion terms, we start with

$$\hat{H}|n\rangle = \mathcal{E}_n|n\rangle \quad (4)$$

Substituting the expressions above we have that

$$(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \dots) = (\mathcal{E}_n^{(0)} + \lambda\mathcal{E}_n^{(1)} + \dots)(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \dots) \quad (5)$$

Now, what we will do is collect terms on each side with the same exponent of  $\lambda$ . Lets see what the means. The left-hand side can be written as

$$\begin{aligned} (\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \dots) = & \hat{H}^{(0)}|n^{(0)}\rangle \\ & + \lambda(\hat{H}^{(0)}|n^{(1)}\rangle + \hat{H}^{(1)}|n^{(0)}\rangle) \\ & + \lambda^2(\hat{H}^{(0)}|n^{(2)}\rangle + \hat{H}^{(1)}|n^{(1)}\rangle) \\ & + \dots \end{aligned} \quad (6)$$

In general, the  $k$ -term is given by

$$\hat{H}^{(0)}|n^{(k)}\rangle + \hat{H}^{(1)}|n^{(k-1)}\rangle \quad (7)$$

Lets now approach the right-hand side. A similar procedure yields

$$\begin{aligned} (\mathcal{E}_n^{(0)} + \lambda\mathcal{E}_n^{(1)} + \dots)(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \dots) = & \mathcal{E}_n^{(0)}|n^{(0)}\rangle \\ & + \lambda(\mathcal{E}_n^{(1)}|n^{(0)}\rangle + \mathcal{E}_n^{(0)}|n^{(1)}\rangle) \\ & + \lambda^2(\mathcal{E}_n^{(2)}|n^{(0)}\rangle + \mathcal{E}_n^{(1)}|n^{(1)}\rangle + \mathcal{E}_n^{(0)}|n^{(2)}\rangle) \\ & + \dots \end{aligned} \quad (8)$$

Again, the general  $k$ -term is given by

$$\sum_{i=0}^k \mathcal{E}_n^{(i)}|n^{(k-i)}\rangle \quad (9)$$

Now, for Eq. (5) to be correct, we must have each term in the power of  $\lambda$  be the same on both sides! This is because we are freely able to vary  $\lambda$  from 0 to 1 say and the equation must hold at every value. Thus, we can get the zero-, first-, second-, and  $k$ th-order perturbation equations by equating terms as

$$\hat{H}^{(0)}|n^{(k)}\rangle + \hat{H}^{(1)}|n^{(k-1)}\rangle = \sum_{i=0}^k \mathcal{E}_n^{(i)}|n^{(k-i)}\rangle \quad (10)$$

The zero-order equation is just the Schrödinger equation for the unperturbed problem

$$\hat{H}^{(0)}|n^{(0)}\rangle = \mathcal{E}_n^{(0)}|n^{(0)}\rangle \quad (11)$$

The first-order term is given by

$$\hat{H}^{(0)}|n^{(1)}\rangle + \hat{H}^{(1)}|n^{(0)}\rangle = \mathcal{E}_n^{(1)}|n^{(0)}\rangle + \mathcal{E}_n^{(0)}|n^{(1)}\rangle \quad (12)$$

We can get the first order energy correction by dotting both sides with  $\langle n^{(0)}|$  to find that

$$\mathcal{E}_n^{(1)} = \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \quad (13)$$

If we dot both sides with  $\langle m^{(0)}|$  ( $m \neq n$ ), we have that

$$\langle m^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle + \langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle = \mathcal{E}_n^{(1)}\langle m^{(0)}|n^{(0)}\rangle + \mathcal{E}_n^{(0)}\langle m^{(0)}|n^{(1)}\rangle \quad (14)$$

Using the fact that  $|n^{(0)}\rangle$  are eigenstates of  $\hat{H}^{(0)}$ , and thus orthonormal, we can simplify to

$$\langle m^{(0)}|n^{(1)}\rangle = \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{\mathcal{E}_n^{(0)} - \mathcal{E}_m^{(0)}} \quad (15)$$

Since  $m \neq n$ , this equation determines all the components of  $|n^{(1)}\rangle$  in the eigenbasis of  $\hat{H}^{(0)}$ , except for the component parallel to  $|n^{(0)}\rangle$ , call it  $|n_{\parallel}^{(1)}\rangle$ . We determine it by the **intermediate normalization** requirement that  $|n\rangle$  be normalized to the given order. That is,

$$1 = \langle n|n\rangle = \left( \langle n^{(0)}| + \lambda \langle n_{\perp}^{(1)}| + \lambda \langle n_{\parallel}^{(1)}| \right) \left( |n^{(0)}\rangle + \lambda |n_{\perp}^{(1)}\rangle + \lambda |n_{\parallel}^{(1)}\rangle \right) \quad (16)$$

Hence, in general we have that

$$1 = \langle n^{(0)}|n^{(0)}\rangle + \lambda \left( \langle n_{\parallel}^{(1)}|n^{(0)}\rangle + \langle n^{(0)}|n_{\parallel}^{(1)}\rangle \right) + \text{higher order} \quad (17)$$

Or the requirement that

$$0 = \langle n_{\parallel}^{(1)}|n^{(0)}\rangle + \langle n^{(0)}|n_{\parallel}^{(1)}\rangle + \text{higher order} \quad (18)$$

To first order, this means that

$$\langle n^{(0)}|n_{\parallel}^{(1)}\rangle = i\alpha, \text{ with } \alpha \in \mathbf{R} \quad (19)$$

We are essentially free to choose this  $\alpha$ , but it makes sense to just set it equal to zero for us. At the end of the day, though (ie removing any issues with phases etc.), we can write the first order wave function is

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \langle m^{(0)} | n^{(1)} \rangle \\ &= |n^{(0)}\rangle + \sum_{m \neq n} \frac{|m^{(0)}\rangle \langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle}{\mathcal{E}_n^{(0)} - \mathcal{E}_m^{(0)}} \end{aligned} \quad (20)$$

Note that  $|n^{(1)}\rangle$  is orthogonal to  $|n^{(0)}\rangle$  and proportional to the first power of  $\hat{H}^{(1)}$ , which is to be anticipated based off of the expansion. We want our expanding wave functions to only contribute in directions other than  $|n^{(0)}\rangle$ , otherwise there is a redundancy. Now, we are in position to get the second-order energy. Starting from the second-order part

$$\hat{H}^{(0)} |n^{(2)}\rangle + \hat{H}^{(1)} |n^{(1)}\rangle = \mathcal{E}_n^{(0)} |n^{(2)}\rangle + \mathcal{E}_n^{(1)} |n^{(1)}\rangle + \mathcal{E}_n^{(2)} |n^{(0)}\rangle \quad (21)$$

We again dot with  $\langle n^{(0)} |$  and use the result for  $|n^{(1)}\rangle$  to find that

$$\begin{aligned} \mathcal{E}_n^{(2)} &= \langle n^{(0)} | \hat{H}^{(1)} | n^{(1)} \rangle \\ &= \sum_{m \neq n} \frac{\langle n^{(0)} | \hat{H}^{(1)} | m^{(0)} \rangle \langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle}{\mathcal{E}_n^{(0)} - \mathcal{E}_m^{(0)}} \\ &= \sum_{m \neq n} \frac{|\langle n^{(0)} | \hat{H}^{(1)} | m^{(0)} \rangle|^2}{\mathcal{E}_n^{(0)} - \mathcal{E}_m^{(0)}} \end{aligned} \quad (22)$$

Here, we stop, but one can keep repeating this procedure to go to higher and higher terms. In general, to get the  $k$ th energy correction, the  $k - 1$ th wave function is needed. Let stop though and examine some features. Note that if we had degenerate states, that is  $E_m^{(0)} = E_n^{(0)}$ , the correction terms will blow up since we will be dividing by zero. Additionally, these power series expansions are only valid within some radius  $R$ , that is only for  $|\lambda| < R$ . The radius is determined by the smallest value of  $\lambda$  where another state becomes degenerate with the ground state; that is, the series is convergent only if there are no excited states that become degenerate with the ground state within the circle in the complex plane corresponding to  $|\lambda| = 1$ . We will revisit this aspect once we discuss its application to HF theory.

**1.1. Degenerate Perturbation Theory.** In the case of a degenerate state  $|m^{(0)}\rangle$  such that  $\mathcal{E}_m^{(0)} = \mathcal{E}_n^{(0)}$ , our expansion will have singularities which must be remedied. We can consider this breakdown in an alternative, yet more physical way.

Returning to the non-degenerate case for both  $\hat{H}^{(0)}$  and  $\hat{H}^{(1)}$ . Then scaling  $\lambda$ , we can continuously go from  $|n^{(0)}\rangle$  to  $|n\rangle$ , or the eigenbasis changes continuously. Thus, it is possible to find  $|n\rangle$  starting from  $|n^{(0)}\rangle$ , it is uniquely determined. Now consider the case where  $\hat{H}^{(0)}$  has a degenerate subspace, but  $\hat{H}^{(0)} + \lambda\hat{H}^{(1)}$  is nondegenerate in that subspace ( $\lambda > 0$ ). If we were in the state  $|n\rangle$  and then we slowly turned off the potential,

we will end up in some basis  $|\bar{n}^{(0)}\rangle$  of  $\hat{H}^{(0)}$ . Turning the perturbation back on, we could retrace our steps to  $|n\rangle$ . But since  $\hat{H}^{(0)}$  is degenerate, we could have started in a different, random basis  $|n^{(0)}\rangle$ . The problem is that starting in any basis *other than*  $|\bar{n}^{(0)}\rangle$  and have  $\lambda$  be infinitesimally small, the change in basis would not be infinitesimal! This is the nonanalytic behaviour given by the divergence in the perturbation series. All of this is to say, we must start with the right basis in the degenerate space.

It turns out that the right basis will be that which diagonalizes  $\hat{H}^{(1)}$  in the degenerate subspace. This makes sense from the analogy above, but also because the series will not blowup. Instead, we will have 0/0 terms in our summation and these terms would have to be dealt with individually.

## 2. MØLLER-PLESSET PERTURBATION THEORY

Our discussion so far has been very general. Now, we aim to apply it to our Hartree-Fock calculation to recover the missing electron correlation. The first question becomes, what should our reference Hamiltonian be? Well, our MOs are eigenfunctions of the Fock operator, so lets take the many-body Fock operator to be our reference Hamiltonian.

$$\hat{H}^{(0)} = \sum_i^N \hat{f}(i) \quad (23)$$

where  $\hat{f}(i)$  is the Fock operator acting on the  $i$ th electron.

$$\hat{f} = \hat{h} + \sum_b^N \hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b \quad (24)$$

Here, we are using  $\sum_b$  to indicate a summation only over the occupied spin orbitals. This form of perturbation theory is known as **Møller-Plesset perturbation theory** (MP). If we go to  $M$ th order, we call the energy the MPM energy. Lets now take  $\hat{H}^{(1)}$  to be the difference between  $\hat{H}^{(0)}$  and the real electronic Hamiltonian.

$$\hat{H}^{(1)} = \hat{H}^{\text{el}} - \sum_i^N \hat{f}(i) \quad (25)$$

This can be simplified to be just a term that depends on the two-electron integrals as

$$\frac{1}{2} \sum_{ij} \hat{f}_{ij}^{-1} - \sum_b \hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b \quad (26)$$

This difference is also known as the **fluctuation potential**.

Lets have  $|\Psi^{(0)}\rangle$  be our Hartree-Fock wave function. Now, we can evaluate  $\mathcal{E}^{(0)}$  which is just

$$\mathcal{E}^{(0)} = \langle \Psi^{(0)} | \sum_i^N \hat{f}(i) | \Psi^{(0)} \rangle = \sum_a \epsilon_a \quad (27)$$

That is, our reference energy is just the sum of occupied Hartree-Fock orbital energies. We can also evaluate the first-order energy correction to find that

$$\mathcal{E}^{(1)} = \langle \Psi^{(0)} | \frac{1}{2} \sum_{ij} \hat{r}_{ij}^{-1} - \sum_b \hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b | \Psi^{(0)} \rangle \quad (28)$$

Recall that

$$\frac{1}{2} \sum_{ij} \langle \Psi^{(0)} | \hat{r}_{ij}^{-1} | \Psi^{(0)} \rangle = \frac{1}{2} \langle \Psi^{(0)} | \sum_b \hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b | \Psi^{(0)} \rangle \quad (29)$$

Or another way of noticing this, is that the Hartree-Fock has twice the amount of two-electron terms. The first-order correction is thus removing these two-electron terms as

$$\mathcal{E}^{(1)} = -\frac{1}{2} \sum_{ab} \mathcal{J}_{ab} - \mathcal{K}_{ab} \quad (30)$$

where again we are summing over *spin orbitals*. If we had a restricted HF calculation, we could instead write this over spatial orbitals as

$$\mathcal{E}^{(1)} = -\frac{1}{2} \sum_{ab} (2 \mathcal{J}_{ab} - \mathcal{K}_{ab}) \quad (31)$$

What we can see then is that the Hartree-Fock energy is just the sum of  $\mathcal{E}^{(0)}$  and  $\mathcal{E}^{(1)}$ .

$$\mathcal{E}^{\text{HF}} = \mathcal{E}^{(0)} + \mathcal{E}^{(1)} = \sum_a \varepsilon_a - \frac{1}{2} \sum_{ab} \mathcal{J}_{ab} - \mathcal{K}_{ab} \quad (32)$$

Or in other words, MP0 is the sum of Hartree-Fock orbital energies and MP1 is the Hartree-Fock energy. What we see is that we must at least go to second-order perturbation theory to get any dynamical correlation.

Recall that the second-order energy correction is given by

$$\mathcal{E}^{(2)} = \sum_{m \neq \Psi^{(0)}} \frac{|\langle \Psi^{(0)} | \hat{H}^{(1)} | m^{(0)} \rangle|^2}{E^{(0)} - E_m^{(0)}} \quad (33)$$

But the question is, what should our choice of  $|m^{(0)}\rangle$  be? We know that  $|m^{(0)}\rangle$  cannot be single excitations from the ground-state,  $|\Psi^{(0)}\rangle$  as

$$\langle \Psi^{(0)} | \hat{H}^{(1)} | \Psi_a^r \rangle = \langle \Psi^{(0)} | \hat{H}^{\text{el}} | \Psi_a^r \rangle - f_{ar} = 0 \quad (34)$$

The first term vanishes by *Brillouin's theorem* and the second term vanishes because the spin functions are eigenstates of the Fock operator. Furthermore, we know they cannot be triple or higher excitations since our perturbation only has 2-electron operators. Lets have  $|\Psi_{ab}^{rs}\rangle$  the set of all possible double excitations from the HF wave function. Note that

$$\hat{H}^{(0)} |\Psi_{ab}^{rs}\rangle = E^{(0)} - (\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s) |\Psi_{ab}^{rs}\rangle \quad (35)$$

This allows us to see that the denominator term is just given by

$$E^{(0)} - E_m^{(0)} = \varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s \quad (36)$$

Furthermore, the numerator term we must evaluate

$$\langle \Psi^{(0)} | \hat{H}^{\text{el}} | \Psi_a^r \rangle - \langle \Psi^{(0)} | \sum_i \hat{f} | \Psi_{ab}^{rs} \rangle \quad (37)$$

Note that since  $\hat{f}$  are just one-electron operators, by the *Slater-Condon rules*, the second term must be zero. Another way of seeing this is that both  $|\Psi^{(0)}\rangle$  and  $|\Psi_{ab}^{rs}\rangle$  are eigenstates of  $\sum_i \hat{f}$  but with different eigenvalues. Hence, the term must be zero. Finally, we must just deal with the electronic matrix element between the HF state and a double excitation. But again, using the Slater-Condon rules,

$$\langle \Psi^{(0)} | \hat{H}^{\text{el}} | \Psi_{ab}^{rs} \rangle = g_{arbs} - g_{asbr} \quad (38)$$

Where I have defined  $g_{pqrs}$  to be the general 2-electron integral as

$$g_{pqrs} = \langle pr | qs \rangle = \int \frac{\chi_p^*(1) \chi_r^*(2) \chi_q(1) \chi_s(2)}{r_{12}} = (pq | rs) \quad (39)$$

All of this allows us to write that

$$\mathcal{E}^{(2)} = \frac{1}{4} \sum_{abrs} \frac{(g_{arbs} - g_{asbr})^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \quad (40)$$

In a similar way, one can derive the third-order energy correction as

$$\begin{aligned} \mathcal{E}^{(3)} = & \frac{1}{8} \sum_{abcdrs} \frac{(g_{arbs} - g_{asbr})(g_{cadb} - g_{cbda})(g_{rcsd} - g_{rdsc})}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_c + \varepsilon_d - \varepsilon_r - \varepsilon_s)} \\ & + \frac{1}{8} \sum_{abrstu} \frac{(g_{arbs} - g_{asbr})(g_{rtsu} - g_{rust})(g_{taub} - g_{tbua})}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_b - \varepsilon_t - \varepsilon_u)} \\ & + \sum_{abcrst} \frac{(g_{arbs} - g_{asbr})(g_{ctsb} - g_{cbst})(g_{ratc} - g_{rcta})}{(\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s)(\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_t)} \end{aligned} \quad (41)$$

As can be seen, the MP2 energy requires just a simple calculation from the 2-electron integrals which generally scales as  $N_{\text{basis}}^4$ . However, typically one has to go from AO to MO basis and this transformation is on the order of  $N_{\text{basis}}^5$ . In practical calculations, this means that the MP2 energy for systems with a few hundred basis functions can be calculated at a cost similar to, or less than, what is required for calculating the HF energy. Additionally, MP2 accounts for typically 80-90% of the correlation energy and can be pretty economical.

Going to higher-order perturbation theories, ie MP3, MP4, increases the overall cost. Additionally, we might think that as one goes to higher and higher orders, the energy should begin to converge to the correct value. Unfortunately, this is not necessarily the case as briefly discussed in the prior section. The series only converges if it is well-defined within some circle of the complex plane  $|\lambda| = 1$ . It is possible that for certain  $\lambda$ , which may be negative and correspond to unphysical solutions,  $\mathcal{E}_n^{(0)} - \mathcal{E}_m^{(0)}$  is zero. This is equivalent to the orbital energies being degenerate. In such case, we have **intruder states**. In practice, it is hard to perform a complete search for intruder states within the complex plane corresponding to  $|\lambda| = 1$ , but it is something to be concerned about.