Post Hartree-Fock: B. MPn perturbation theory

While the configuration interaction (CI) method is clearly a rigorous way to add correlation energy to the Hartree-Fock results, the method is computationally highly demanding because of the large number of excited Slater determinants that need - at least in principle - to be included. Another commonly used estimate of the correlation energy is based on perturbation theory rather than variational calculations and is often referred to as Möller-Plesset perturbation theory, MPn, where n stands for the order of the perturbation included in the calculations. It is not clear how to reach the exact result with this approach. In fact, the perturbation expansion has been shown to diverge as n increases in some cases. Still, MP2 and MP4 corresponding to second and fourth order perturbation, resp., are commonly used approximations. Before discussing the application of perturbation theory to the electronic structure problem, a review of the basic methodology is given and simple examples taken to illustrate the approach.

Review of Perturbation Theory

When the task is to estimate properties of a system that cannot be solved easily but is similar to a systems for which a solution is known, such as the harmonic oscillator, the method of choice is often perturbation theory rather than variational calculations. The discussion here is limited to stationary states i.e. the bound state solutions to the time independent Schrödinger equation. Perturbation theory can also be applied to scattering states and then gives the so-called Born expansion.

Assume H_0 is a simple time independent Hamiltonian that can be solved and let $|u_k>$ denote the corresponding stationary states

$$H_0|u_k>= E_k|u_k>$$

Let

$$H \equiv H_0 + H'$$

be the full time independent Hamiltonian where the H' term makes the problem too complicated to be solved exactly. Imagine turning H' on gradually:

$$H = H_0 + \lambda H'$$

where

$$\lambda \ \in \ [0,1].$$

In the end we will let $\lambda \to 1$.

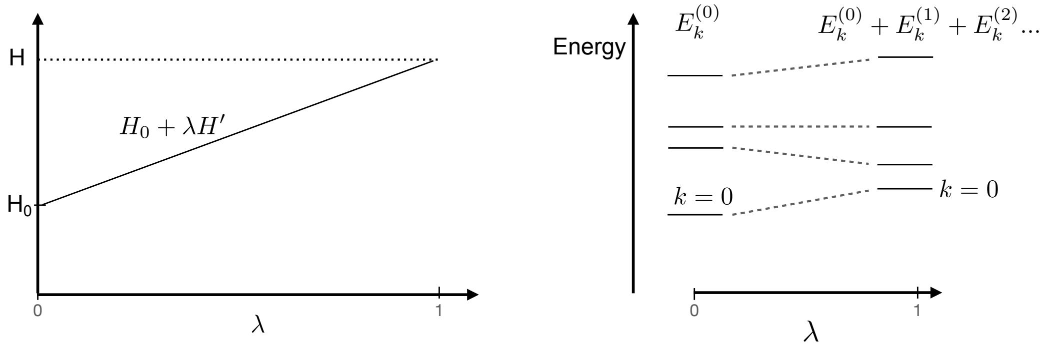

Figure 6. Left: Illustration of the change from zeroth order Hamiltonian approximation to the full Hamiltonian as the parameter λ is increased from 0 to 1.
Right: Corresponding change in the energy levels where the estimate is a sum of perturbation corrections.

Example: The vibration of a diatomic molecule is a good example of the use of perturbation theory. The zeroth order problem is the harmonic approximation and anharmonicity is then introduced as a perturbation. Let the minimum energy distance between the atoms be r_0 and Taylor expand the potential about this point

$$v(r) = v(r_0) + (r - r_0)v'(r_0) + \frac{(r-r_0)^2}{2}v''(r_0) + \frac{(r-r_0)^3}{3!}v'''(r_0) + ...$$

$$= a\tilde{r}^2 + b\tilde{r}^3 + ...$$

Here, we have chosen the zero of energy such that $v(r_0) = 0$, used the fact that $v'(r_0) = 0$ (v is at a minimum at r_0) and defined $\tilde{r} \equiv r - r_0$. Only the quadratic term from the expansion is included in H_0

$$H_0 = -\frac{\hbar^2}{2\mu}\frac{d^2}{d\tilde{r}^2} + a\tilde{r}^2$$

which gives the harmonic oscillator Hamiltonian, and then the rest of the terms are treated as a perturbation

$$H' = b\tilde{r}^3 + ...$$

One clear effect of the perturbation is that $\Delta n = \pm 2$ transitions become possible when the perturbation H' is turned on while they are not allowed for the pure harmonic oscillator.

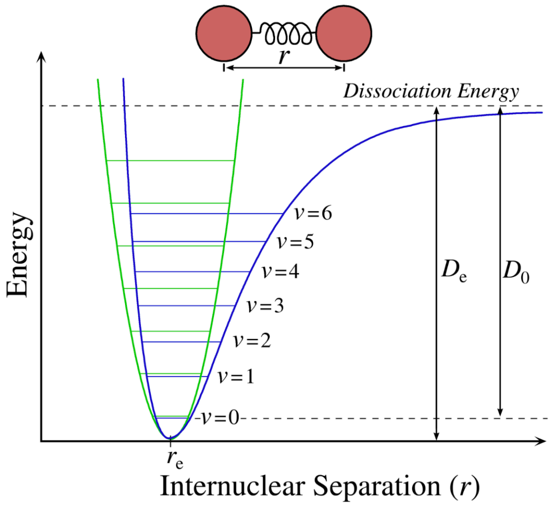

Figure 7. Illustration of the harmonic approximation to the energy curve for a diatomic and the effect anharmonicity has on the energy levels.

We want to find the eigenstates $|\psi>$ and eigenvalues W such that

$$H|\psi>= W|\psi> .$$

Assume H' is small and expand both $|\psi>$ and W in a power series expansion:

$$|\psi>= |\psi_0> + \lambda|\psi_1> + \lambda^2|\psi_2> + \lambda^3|\psi_3> + ...$$

$$W = W_0 + \lambda W_1 + \lambda^2 W_2 + \lambda^3 W_3 + ...$$

These expansions do not always converge, but there are many cases where they converge fast enough that only the first few terms need to be included. This occurs when H' is sufficiently small. Substitute these expressions into the Schrödinger equation

$$\overbrace{(H_0 + \lambda H')}^{H}\ \overbrace{(\psi_0 + \lambda\psi_1 + \lambda^2\psi_2 + ...)}^{\psi} = \overbrace{(W_0 + \lambda W_1 + \lambda^2 W_2 + ...)}^{W}\ \overbrace{(\psi_0 + \lambda\psi_1 + \lambda^2\psi_2 + ...)}^{\psi}.$$

This equation holds for any value of λ, so we can equate coefficients of equal powers of λ.
To 0-th order:

$$H_0|\psi_0>= W_0|\psi_0> \quad \text{or} \quad (H_0-W_0)|\psi_0>=0.$$

To 1-st order:

$$\lambda(H_0|\psi_1>+H'|\psi_0>)=\lambda(W_1|\psi_0>+W_0|\psi_1>)$$

or, after rearrangement of terms

$$(H_0-W_0)|\psi_1>=(W_1-H')|\psi_0>.$$

To 2-nd order:

$$\lambda^2(H_0|\psi_2>+H'|\psi_1>)=\lambda^2(W_0|\psi_2>+W_1|\psi_1>+W_2|\psi_0>)$$

or

$$(H_0-W_0)|\psi_2>=(W_1-H')|\psi_1>+W_2|\psi_0>.$$

etc.
Zeroth order solution: The zeroth order equation is just the Schrödinger equation for the unperturbed problem. To proceed, one of the unperturbed eigenstates is chosen as the zeroth order approximation

$$|\psi_0>=|u_m>$$

$$W_0=E_m^{(0)}.$$

Each state needs to be treated separately and the procedure is different depending on whether the energy level E_m is degenerate or not.

Case A: E_m is non-degenerate

Consider the case where E_m is non-degenerate. Note that any multiple of $|\psi_0>$ can be added to any of the other terms, $|\psi_s>$, and the equations remain unchanged because

$$(H_0-W_0)|\psi_0>=0.$$

For example, if $|\psi_1>$ is a solution to the first order equation then so is $|\psi_1>+a\,|\psi_0>$

$$\begin{aligned}(H_0-W_0)(|\psi_1>+a|\psi_0>) &= (H_0-W_0)|\psi_1>+a(H_0-W_0)|\psi_0>\\ &= (H_0-W_0)|\psi_1>\\ &= (W_1-H')|\psi_0>.\end{aligned}$$

Therefore, we can choose the s-th order correction to the state, where $s>0$, to be orthogonal to the zeroth order estimate, i.e. $<\psi_0|\psi_s>=0$.

The first order correction to the energy can be obtained from the first order equation by left multiplying with $<\psi_0|$ and using the fact that (H_0-W_0) is Hermitian and can be taken to operate to the left, to give $<\psi_0|H_0-W_0|\psi_1>=0$. The first order equation then becomes

$$0=<\psi_0|W_1-H'|\psi_0>=W_1<\psi_0|\psi_0>-<\psi_0|H'|\psi_0>$$

So

$$W_1=\frac{<\psi_0|H'|\psi_0>}{<\psi_0|\psi_0>}.$$

The calculation of the first order correction to the energy level is therefore quite simple and only requires knowledge of the zeroth order solution.

Similarly, for the second order equation

$$\begin{aligned}0 &= <\psi_0|W_1-H'|\psi_1>+W_2<\psi_0|\psi_0>\\ &= 0-<\psi_0|H'|\psi_1>+W_2<\psi_0|\psi_0>\end{aligned}$$

and the second order correction to the energy is

$$W_2 = \frac{<\psi_0|H'|\psi_1>}{<\psi_0|\psi_0>}.$$

In order to evaluate the second order correction to the energy level, only the zeroth and first order correction to the state vector are needed. This is a reflection of the fact that the expectation value of the Hamiltonian is stationary for the eigenstates.
Generally, for any $s > 0$:

$$W_s = \frac{<\psi_0|H'|\psi_{s-1}>}{<\psi_0|\psi_0>}.$$

It is sufficient to know $|\psi>$ to order $s-1$ in order to finding W to order s.

The perturbation corrections to the wave function, i.e. the state vector, can be found in a similar way. The first order correction, $|\psi_1>$, is expanded in the set of the orthonormal eigenstates of H_0

$$|\psi_1>=\sum_n a_n|u_n> .$$

This can be done because the eigenstates of H_0 form a complete set for functions satisfying the same boundary conditions and therefore also the first order correction. The expression above assumes that all the eigenstates of H_0 are bound states, i.e. only discrete spectrum. More generally, there could also be a continuous part of the spectrum and the expansion would then be of the form

$$|\psi_1>=\sum_n a_n|u_n> + \int_0^\infty dk\ a_k|u_k> .$$

The $\sum_n$ includes the discrete spectrum of the eigenstates and the integral $\int_0^\infty$ includes the continuum spectrum.

The expansion of $|\psi_1>$ can now be substituted into the first order equation

$$(H_0 - W_0)|\psi_1>=(W_1 - H')|\psi_0> .$$

Since we are studying how much the $E_m^{(0)}$ level changes when the perturbation H' is applied, we take $W_0 = E_m^{(0)}$, $|\psi_0>=|u_m>$

$$\sum_{n\neq m} a_n(E_n^{(0)} - E_m^{(0)})|u_n>=(W_1 - H')|u_m>$$

The $n = m$ term is left out in the summation because we must have $a_m = 0$ since $<\psi_1|\psi_0>= 0$, i.e., $<\psi_1|u_m>= 0$. Left multiplying with $<u_\ell|$ gives

$$\sum_{n\neq m} a_n(E_n^{(0)} - E_m^{(0)})\underbrace{<u_\ell|u_n>}_{\delta_{\ell n}} = W_1<u_\ell|u_m> - <u_\ell|H'|u_m>$$

$$a_\ell(E_\ell^{(0)} - E_m^{(0)}) = - <u_\ell|H'|u_m>$$

$$a_\ell = \frac{<u_\ell|H'|u_m>}{E_m^{(0)} - E_\ell^{(0)}} \qquad \ell \neq m$$

Having obtained an explicit expression for the first order correction to the state vector, it is now possible to write the second order correction to the eigenvalue only in terms of the solution to the known, zeroth order quantities. The second order equation, obtained from the λ^2 terms, is

$$(H_0 - W_0)|\psi_2>=(W_1 - H')|\psi_1> + W_2|\psi_0>$$

The second order correction to the energy is

$$W_2 = E_m^{(2)} = \frac{<\psi_0|H'|\psi_1>}{<\psi_0|\psi_0>}.$$

It can now be written more explicitly in terms of the zeroth-order states. Using the solution for $|\psi_1>$ and choosing $|\psi_0>=|m>$,

$$|\psi_1>=\sum_{n\neq m} a_n|n> \quad \text{with} \quad a_n=\frac{<n|H'|m>}{E_m^{(0)}-E_n^{(0)}}\,,$$

gives

$$E_m^{(2)}=<m|H'|\sum_{n\neq m}\frac{<n|H'|m>}{E_m^{(0)}-E_n^{(0)}}|n>$$

$$=\sum_{n\neq m}\frac{<m|H'|n><n|H'|m>}{E_m^{(0)}-E_n^{(0)}}.$$

Using the fact that H' is Hermitian gives

$$E_m^{(2)}=\sum_{n\neq m}\frac{|<n|H'|m>|^2}{E_m^{(0)}-E_n^{(0)}}.$$

The second order correction to the state vector is again obtained by expanding in the eigenstates of H_0

$$|\psi_2>=\sum_{n\neq m} a_n^{(2)}|n>$$

and substituting into the λ^2 equation

$$\sum_{n\neq m}(E_n^{(0)}-E_m^{(0)})a_n^{(2)}|n>=\sum_{\ell\neq m} a_\ell^{(1)}(W_1-H')|\ell>+W_2|m>\,.$$

Left multiplying by $<k|$ gives

$$a_k^{(2)}=\sum_{n\neq m}\frac{<k|H'|n><n|H'|m>}{(E_m^{(0)}-E_k^{(0)})(E_m^{(0)}-E_n^{(0)})}-\frac{<k|H'|m><m|H'|n>}{(E_m^{(0)}-E_k^{(0)})^2}.$$

Case B: $E_m^{(0)}$ is two-fold degenerate (optional)

Assume now that the energy level we are studying is two-fold degenerate

$$W_0=E_m^{(0)}=E_\ell^{(0)}.$$

The unperturbed state can be any linear combination of the two:

$$|\psi_0>=a_m|m>+a_\ell|\ell>\,.$$

Substitute this into the first order equation:

$$(H_0-W_0)|\psi_1>=(W_1-H')|\psi_0>$$

$$=(W_1-H')(a_m|m>+a_\ell|\ell>).$$

(1) Left multiply by $<m|$

$$(E_m^{(0)}-W_0)<m|\psi_1>=W_1(a_m<m|m>+a_\ell<m|\ell>)-(a_m<m|H'|m>+a_\ell<m|H'|\ell>)$$

Similar to the non-degenerate case, we choose $|\psi_1>$ to be orthogonal to $|m>$ and $|\ell>$. So

$$0=W_1a_m-a_m<m|H'|m>-a_\ell<m|H'|\ell>$$

or

$$(< m|H'|m > -W_1)a_m + < m|H'|\ell > a_\ell = 0.$$

(2) Similarly, left multiply by $< \ell|$ and get

$$< \ell|H'|m > a_m + (< \ell|H'|\ell > -W_1)a_\ell = 0.$$

This set of coupled equations for a_m and a_ℓ only has nontrivial solutions when the determinant of the matrix:

$$\begin{matrix} < m|H'|m > -W_1 & < m|H'|\ell > \\ < \ell|H'|m > & < \ell|H'|\ell > -W_1 \end{matrix}$$

vanishes. This determines the first order correction to the energy. By expanding the determinant we get

$$W_1^2 - (< m|H'|m > + < \ell|H'|\ell >)W_1 + < m|H'|m >< \ell|H'|\ell > - \Big| < m|H'|\ell > \Big|^2 = 0.$$

There are two solutions to this quadratic equation

$$W_{1\pm} = \frac{1}{2}\Big[< m|H'|m > + < \ell|H'|\ell >) \pm \sqrt{(< m|H'|m > - < \ell|H'|\ell >)^2 + 4| < m|H'|\ell > |^2}.$$

If the square root is non-zero, the states are no longer degenerate, i.e. the degeneracy is lifted.

If $< m|H'|m > + < \ell|H'|\ell >= 0$, the splitting is symmetric $|W_{1+}| = |W_{1-}|$. Under H_0 the system can be in a state that is any linear combination of $|m >$ and $|\ell >$. As H' is turned on, only two linear combinations are allowed. After determining W_{1+} and W_{1-}, the expansion coefficients a_m^+, a_ℓ^+ and a_m^-, a_ℓ^- can be found from equations (1) and (2) above.

The first order correction to the state can again be found by expanding in the complete set of zeroth order solutions

$$|\psi_1 >= \sum_{\substack{n\neq m \\ \neq \ell}} a_n|n > \quad .$$

The ℓ and m terms are excluded in the sum since $|\psi_1 >$ has been chosen to be orthogonal to those states. The first order equation is

$$(H_0 - W_0)|\psi_1 >= (W_1 - H')|\psi_0 > \quad .$$

Left multiplying by $< k|$ gives

$$\sum_n (E_k^{(0)} - E_m^{(0)})a \overbrace{< k|n >}^{\delta_{kn}} = W_1 < k|\psi_0 > - < k|H'|\psi_0 >$$

$$(E_k^{(0)} - E_m^{(0)})a_k = - < k|H'|m > a_m - < k|H'|\ell > a_\ell$$

$$a_k = \frac{< k|H'|m > a_m + < k|H'|\ell > a_\ell}{E_m^{(0)} - E_k^{(0)}}.$$

If

$$< m|H'|m >=< \ell|H'|\ell >$$

and

$$< m|H'|\ell >= 0$$

then the degeneracy is not lifted, $W_{1-} = W_{1+}$, and we need to go to second order.

C. Many-body Perturbation Method

Now apply perturbation theory to the electronic structure problem, i.e. the task of estimating the energy of a system of N electrons. The Hamiltonian is partitioned as

$$H \;=\; H_0 + H'$$

where H_0 is the Hartree-Fock Hamiltonian

$$H_0 \;=\; \sum_i f(i) \;=\; \sum_i [h(i) + v^{HF}(i)]$$

and

$$H' \;=\; \sum_{i<j} r_{ij}^{-1} \;-\; \sum_i v^{HF}(i)$$

is the perturbation. Here, $v^{HF}(i)$ denotes the Coulomb and exchange interaction of electron i with the rest of the electrons in the Hartree-Fock approximation. From the expression for the Hartree-Fock energy, one can see that

$$v^{HF}\chi_a(x_1) \;=\; \sum_b \int dx_2 \frac{|\chi_b(x_2)|^2}{r_{12}} \chi_a(x_1) \;-\; \sum_b \int dx_2 \frac{\chi_b^*(x_2)\chi_a(x_2)}{r_{12}} \chi_b(x_1)$$

and the expectation value of v^{HF} for orbital a is

$$[a|v^{HF}|a] \;=\; \sum_b [aa|bb] - [ab|ba] \;.$$

The indices i and j are used for electrons, while a and b are used for orbitals.

The Hartree-Fock Slater determinant, $|\Psi_0>$, is an eigenfunction of H_0

$$H_0\; |\Psi_0> = \; E_0^{(0)}\; |\Psi_0>$$

with eigenvalue

$$E_0^{(0)} \;=\; \sum_a \epsilon_a$$

where ϵ_a is the orbital energy for orbital a. This is the zeroth order perturbation energy. Note that this is not the same as the Hartree-Fock estimate of the energy of the system, $E_0^{HF} =< \Psi_0|H|\Psi_0>$, which involves the exact Hamiltonian.

To first order, the correction to the energy is

$$\begin{aligned} E_0^{(1)} &= < \Psi_0|H'|\Psi_0> \\ &= < \Psi_0|\sum_{i<j} r_{ij}^{-1}|\Psi_0> \;-\; < \Psi_0|\sum_i v^{HF}(i)|\Psi_0> \\ &= \; \frac{1}{2}\sum_a\sum_b([aa|bb] - [ab|ba]) - \sum_a [a|v^{HF}|a] \end{aligned}$$

The second sum is just twice the first sum so the final result is

$$E_0^{(1)} \;=\; -\frac{1}{2}\sum_a\sum_b [aa|bb] - [ab|ba] \;.$$

When this correction is added to $E_0^{(0)}$, the result is the Hartree-Fock energy

$$E_0^{HF} \;=\; E_0^{(0)} \;+\; E_0^{(1)} \;=\; \sum_a \epsilon_a - \frac{1}{2}\sum_{ab}[aa|bb] - [ab|ba] \;.$$

The first order perturbation result therefore does not add any correlation energy.

In order to get a non-zero estimate of the correlation energy, one needs to go to second order or higher in the perturbation. The second order correction to the energy of the ground state (setting m=0 in the equation derived above for $E_m^{(2)}$) gives

$$E_0^{(2)} \ = \ \sum_n \ \frac{|<0|H'|n>|^2}{E_0^{(0)} - E_n^{(0)}}$$

where the sum runs over all states except n=0. Here, $|0>$ denotes $|\Psi_0>$ and $|n>$ denotes a Slater determinant corresponding to electron configurations of higher energy where one or more electron has been promoted to a virtual orbital. It turns out that single excitation Slater determinants do not give a non-zero contribution to $E_0^{(2)}$, i.e.

$$<\Psi_0|H'|\Psi_a^r> = \ 0 \ .$$

This is referred to as Brillouin theorem and can be illustrated as follows. Writing out the expression

$$<\Psi_0|H'|\Psi_a^r> = [a|h|r] + \sum_b([ar|bb] - [ab|br])$$

$$= <a|f|r>$$

shows that this is an off-diagonal element of the Fock matrix. By choice of the orbitals in the Hartree-Fock procedure, the Fock matrix is diagonal, i.e. $<a|f|r> = \epsilon_a \delta_{ar}$, and here a and r are not the same, so $<a|f|r> = 0$. This again shows mathematical advantage of the particular choice of orbitals made when the Hartree-Fock equations are derived. If the calculations are carried out with a different choice of orbitals (for example so-called natural orbitals), single excitation Slater determinants do contribute to the correlation energy.

The triple and higher order excitation determinants also do not give a non-zero contribution because the perturbation includes only pairwise interactions between the electrons. As a result of this and Brillouin theorem, only the double excitation determinants, $|\Psi_{ab}^{rs}>$, give a non-zero contribution. The matrix elements are (note, the one-electron operator, h, does not give a contribution because the determinants differ by two orbitals)

$$<\Psi_0|\sum_{i<j} r_{ij}^{-1}|\Psi_{ab}^{rs}> = \ [ar|bs] - [as|br]$$

and the energy eigenvalues of the double excitation determinants are $E_0^{(0)} - \epsilon_a - \epsilon_b + \epsilon_r + \epsilon_s$, that is

$$H_0|\Psi_{ab}^{rs}> = \ (E_0^{(0)} \ - \epsilon_a - \epsilon_b + \epsilon_r + \epsilon_s) \ |\Psi_{ab}^{rs}> \ .$$

The expression for the second order energy then becomes

$$E_0^{(2)} \ = \ \sum_{a<b}\sum_{r<s} \ \frac{|<\Psi_0|\sum_{i<j}\frac{1}{r_{ij}}|\Psi_{ab}^{rs}>|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

$$= \ \sum_{a<b}\sum_{r<s} \ \frac{|[ar|bs] - [as|br]|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \ .$$

Note that the second-order energy can be expressed as a sum over contributions from each pair of electrons in occupied orbitals

$$E_0^{(2)} \ = \ \sum_{a<b} e_{ab}$$

and the contribution from each pair involves a sum over pairs of virtual orbitals

$$e_{ab} \ = \ \sum_{r<s} \ \frac{|[ar|bs] - [as|br]|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \ .$$

The estimate of the energy to second order is referred to as the MP2 approximation to the energy of the system

$$E_0^{MP2} \;=\; E_0^{(0)} \;+\; E_0^{(2)}$$

since $E_0^{(1)}$=0.

The MP2 calculations only add single and double excited determinants to the Hartree-Fock estimate. So, it can be compared with a CI expansion that gets truncated at doubly excited determinants, so-called CISD. The advantage of MP2 over CISD is that MP2 is size consistent. It is, therefore, more applicable to calculations of binding energy. However, it is not variational and the energy can therefore become lower than the true ground state energy. MP2 is currently the most popular post-Hartree-Fock method. The computational effort scales as the number of basis functions to the fifth power, K^5.