

Derivation of Møller-Plesset Perturbation Theory

Another approach to electron correlation is Møller-Plesset perturbation theory. Qualitatively, Møller-Plesset perturbation theory adds higher excitations to Hartree-Fock theory as a non-iterative correction, drawing upon techniques from the area of mathematical physics known as many body perturbation theory.

Perturbation theory is based upon dividing the Hamiltonian into two parts:

$$\mathbf{H} = \mathbf{H}_0 + \lambda \mathbf{V}$$

such that \mathbf{H}_0 is soluble exactly. $\lambda \mathbf{V}$ is a perturbation applied to \mathbf{H}_0 , a correction which is assumed to be small in comparison to it. (Note that the perturbation operator \mathbf{V} is not related to the potential energy.) The assumption that \mathbf{V} is a small perturbation to \mathbf{H}_0 suggests that the perturbed wavefunction and energy can be expressed as a power series in \mathbf{V} . The usual way to do so is in terms of the parameter λ :

$$\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \lambda^3 \psi^{(3)} + \dots$$

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

The perturbed wavefunction and energy are substituted back into the Schrödinger equation:

$$(\mathbf{H}_0 + \lambda \mathbf{V})(\psi^{(0)} + \lambda \psi^{(1)} + \dots) = (E^{(0)} + \lambda E^{(1)} + \dots)(\psi^{(0)} + \lambda \psi^{(1)} + \dots)$$

After expanding the products, we can equate the coefficients on each side of the equation for each power of λ , leading to a series of relations representing successively higher orders of perturbation. Here are the first three such equations (after some rearranging), corresponding to powers of 0, 1, and 2 of λ :

$$\lambda^0 : (\mathbf{H}_0 - E^{(0)})\psi^{(0)} = 0$$

$$\lambda^1 : (\mathbf{H}_0 - E^{(0)})\psi^{(1)} = (E^{(1)} - \mathbf{V})\psi^{(0)}$$

$$\lambda^2 : (\mathbf{H}_0 - E^{(0)})\psi^{(2)} = (E^{(1)} - \mathbf{V})\psi^{(1)} + E^{(2)}\psi^{(0)}$$

So far, we've presented only general perturbation theory results. We'll now turn to the particular case of Møller-Plesset perturbation theory. Here, \mathbf{H}_0 is defined as the sum of the one-electron Fock operators:

$$\mathbf{H}_0 = \sum_i F^i$$

The Hartree-Fock determinant and all of the substituted determinants are eigenfunctions of \mathbf{H}_0 ; these are the solutions to the part of the divided Hamiltonian for which we have a solution. Thus:

$$\mathbf{H}_0 \psi_s = E_s \psi_s$$

for all substituted determinant wavefunctions. We'll consider each of the equations corresponding to increasing powers of λ in turn. In the first case (λ^0), by forming the inner product of each side with $\langle \psi^{(0)} |$, we obtain the following expression for $E^{(0)}$:

$$\langle \psi^{(0)} | \mathbf{H}_0 - E^{(0)} | \psi^{(0)} \rangle = 0 \Rightarrow$$

$$\langle \psi^{(0)} | \mathbf{H}_0 | \psi^{(0)} \rangle = E^{(0)} \langle \psi^{(0)} | \psi^{(0)} \rangle = E^{(0)}$$

Since the ψ 's are orthonormal, the inner product of any with itself is one, and the inner product of any distinct two of them is 0. Since \mathbf{H}_0 is the sum of Fock operators, then $E^{(0)}$ is the sum of the orbital energies:

$$E^{(0)} = \langle \psi^{(0)} | \mathbf{H}_0 | \psi^{(0)} \rangle = \sum_i \varepsilon_i$$

The expression for $E^{(1)}$ also follows easily from simple linear algebra. Once again, we begin by forming the inner product of both sides of the equation corresponding to the first power of λ with $\langle \psi^{(0)} |$:

$$\langle \psi^{(0)} | \mathbf{H}_0 - E^{(0)} | \psi^{(1)} \rangle = \langle \psi^{(0)} | E^{(1)} - \mathbf{V} | \psi^{(0)} \rangle \Rightarrow$$

$$\langle \psi^{(0)} | \mathbf{H}_0 | \psi^{(1)} \rangle - E^{(0)} \langle \psi^{(0)} | \psi^{(1)} \rangle = E^{(1)} \langle \psi^{(0)} | \psi^{(0)} \rangle - \langle \psi^{(0)} | \mathbf{V} | \psi^{(0)} \rangle$$

Now, since $\mathbf{H}_0 \psi^{(0)} = E^{(0)} \psi^{(0)}$ and \mathbf{H}_0 is an Hermitian operator (i.e., $\mathbf{H}_0 \psi^{(0)} = \psi^{(0)} \mathbf{H}_0$), the left hand side of the second equation above goes to 0, leaving this expression for $E^{(1)}$:

$$E^{(1)} = \langle \psi^{(0)} | \mathbf{V} | \psi^{(0)} \rangle$$

Adding $E(0)$ and $E(1)$ yields the Hartree-Fock energy (since $\mathbf{H}_0 + \mathbf{V}$ is the full Hamiltonian):

$$E^{(0)} + E^{(1)} = \langle \psi^{(0)} | \mathbf{H}_0 | \psi^{(0)} \rangle + \langle \psi^{(0)} | \mathbf{V} | \psi^{(0)} \rangle = \langle \psi^{(0)} | \mathbf{H}_0 + \mathbf{V} | \psi^{(0)} \rangle = \langle \psi^{(0)} | \mathbf{H} | \psi^{(0)} \rangle = E^{HF}$$

We'll now work with the equation corresponding to the second power of λ in the same way:

$$\begin{aligned} \langle \psi^{(0)} | \mathbf{H}_0 - E^{(0)} | \psi^{(2)} \rangle &= \langle \psi^{(0)} | E^{(1)} - \mathbf{V} | \psi^{(1)} \rangle + E^{(2)} \langle \psi^{(0)} | \psi^{(0)} \rangle \Rightarrow \\ E^{(2)} &= \langle \psi^{(0)} | \mathbf{V} - E^{(0)} | \psi^{(1)} \rangle = \langle \psi^{(0)} | \mathbf{V} | \psi^{(1)} \rangle \end{aligned}$$

We need to find $\psi(1)$ before we can determine $E(2)$. We will form the former as a linear combination of substituted wavefunctions and solve for the coefficients:

$$\psi^{(1)} = \sum_s a_s \psi_s \ni \mathbf{H}_0 \psi_s = E_s \psi_s$$

We will return to the equation corresponding to the first power of λ , and this time use it to find the coefficients for $\psi(1)$:

$$(\mathbf{H}_0 - E^{(0)}) \sum_s a_s \psi_s = (E^{(1)} - \mathbf{V}) \psi^{(0)}$$

We will form the inner product of both sides of this equation with an arbitrary substituted wavefunction ψ_t , and then solve for a_t :

$$\begin{aligned} \langle \psi_t | \mathbf{H}_0 - E^{(0)} | \sum_s a_s \psi_s \rangle &= \langle \psi_t | E^{(1)} - \mathbf{V} | \psi^{(0)} \rangle \Rightarrow \\ \sum_s a_s \langle \psi_t | \mathbf{H}_0 - E^{(0)} | \psi_s \rangle &= E^{(1)} \langle \psi_t | \psi^{(0)} \rangle - \langle \psi_t | \mathbf{V} | \psi^{(0)} \rangle \Rightarrow \\ \sum_s a_s (\langle \psi_t | \mathbf{H}_0 | \psi_s \rangle - \langle \psi_t | E^{(0)} | \psi_s \rangle) &= E^{(1)} \langle \psi_t | \psi^{(0)} \rangle - \langle \psi_t | \mathbf{V} | \psi^{(0)} \rangle \end{aligned}$$

The left side of the final equation is nonzero only when $s=t$, yielding:

$$a_t (E_t - E^{(0)}) = -\langle \psi_t | \mathbf{V} | \psi^{(0)} \rangle \Rightarrow a_t = \frac{\langle \psi_t | \mathbf{V} | \psi^{(0)} \rangle}{E^{(0)} - E_t}$$

This equation indicates that substitutions close in energy to the ground state make larger contributions to the perturbation. Similarly, the more strongly mixed a state is with the ground state, the larger its contribution to the perturbation. Both of these observations are in line with (quantum mechanical) intuition.

These coefficients result in the following expression for $\psi(1)$:

$$\psi^{(1)} = \sum_t \left(\frac{\langle \psi_t | \mathbf{V} | \psi^{(0)} \rangle}{E^{(0)} - E_t} \right) \psi_t$$

We can now return to the expression for $E(2)$:

$$E^{(2)} = \langle \psi^{(0)} | \mathbf{V} | \psi^{(1)} \rangle = \langle \psi^{(0)} | \mathbf{V} | \sum_t a_t \psi_t \rangle = \sum_t a_t \langle \psi^{(0)} | \mathbf{V} | \psi_t \rangle = \sum_t \frac{\langle \psi^{(0)} | \mathbf{V} | \psi_t \rangle \langle \psi_t | \mathbf{V} | \psi^{(0)} \rangle}{E^{(0)} - E_t} = - \sum_t \frac{|\langle \psi^{(0)} | \mathbf{V} | \psi_t \rangle|^2}{E^{(0)} - E_t}$$

The two factors in the numerator of the first expression in the second line are one another's complex conjugates, and so reduce to the square of its modulus in the final expression.

Note that both the numerator and denominator in the final expression are always positive expressions; in the case of the denominator, we know this because

$E(0)$ is the lowest energy eigenvalue of the unperturbed system. (The denominator reduces to a difference in orbital energies.)

In addition, the numerator will be nonzero only for double substitutions. Single substitutions are known to make this expression zero by Brillouin's theorem. Triple and higher substitutions also result in zero value since the Hamiltonian contains only one and two-electron terms (physically, this means that all interactions between electrons occur pairwise).

Thus, the value of $E(2)$, the first perturbation to the Hartree-Fock energy, will always be negative. Lowering the energy is what the exact correction should do, although the Møller-Plesset perturbation theory correction is capable of overcorrecting it, since it is not variational (and higher order corrections may be positive).

By a similar, although more elaborate process, the third and fourth order energy corrections can be derived.