Many-body perturbation theory

The Schroedinger equation is

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle,$$

and multiplying the latter from the left with $|\Psi_0\rangle$ gives

$$\langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E \langle \Psi_0 | \Psi_0 \rangle = E,$$

and subtracting from this equation

$$\langle \Psi_0 | \hat{\Delta} | \Psi_0 \rangle = W_0 - W_0,$$

and using the fact that the both operators $\hat{\Delta}$ and $\hat{\Delta}$ are hermitian results in

$$\Delta E = E - W_0 = \langle \Psi_0 | \hat{\Delta} | \Psi_0 \rangle,$$

which is an exact result. We call this quantity the correlation energy.

We can rewrite Schroedinger’s equation as

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle = |\Psi_0\rangle$$

$$\hat{\Delta}|\Psi_0\rangle = W_0|\Psi_0\rangle$$

and multiplying the latter from the left with $|\Psi_0\rangle$ gives

$$\langle \Psi_0 | \hat{\Delta} | \Psi_0 \rangle = W_0 - W_0,$$

and using the fact that the both operators $\hat{\Delta}$ and $\hat{\Delta}$ are hermitian results in

$$\Delta E = E - W_0 = \langle \Psi_0 | \hat{\Delta} | \Psi_0 \rangle,$$

which is an exact result. We call this quantity the correlation energy.

We assume here that we are only interested in the ground state of the system and expand the exact wave function in term of a series of Slater determinants

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{m=1}^\infty C_m |\phi_m\rangle,$$

where we have assumed that the true ground state is dominated by the solution of the unperturbed problem, that is

$$\hat{H}_0 |\Phi_0\rangle = W_0 |\Phi_0\rangle.$$

The state $|\Psi_0\rangle$ is not normalized, rather we have used an intermediate normalization $\langle \Phi_0 | \Phi_0 \rangle = 1$ since we have

$$\langle \Phi_0 | \Psi_0 \rangle = 1.$$
Many-body perturbation theory

These operators commute meaning that
\[
\hat{Q} \left( \frac{1}{\omega - \hat{H}_0} \right) \hat{Q} \left( \frac{1}{\omega - \hat{H}_0} \right) = \hat{Q} \left( \frac{1}{\omega - \hat{H}_0} \right) \hat{Q} \left( \frac{1}{\omega - \hat{H}_0} \right).
\]

With these definitions we can in turn define the wave function as
\[
|\psi_i \rangle = |\varphi_i \rangle + \frac{\hat{Q}}{\omega - \hat{H}_0} \left( \omega - \hat{E} + \hat{\Delta} \right) |\varphi_i \rangle.
\]

This equation is again nothing but a formal rewrite of Schrödinger’s equation and does not represent a practical calculational scheme. It is a non-linear equation in two unknown quantities, the energy \( \hat{E} \) and the exact wave function \( |\psi_0 \rangle \). We can however start with a guess for \( |\psi_0 \rangle \) on the right hand side of the last equation.

Many-body perturbation theory

In Brillouin-Wigner perturbation theory it is customary to set \( \omega = E \). This results in the following perturbative expansion for the energy \( \Delta E \)
\[
\Delta E = \sum_{i=0}^{\infty} \langle \varphi_0 | \hat{H}_i \left( \omega - \hat{H}_0 \right) | \varphi_0 \rangle = \langle \varphi_0 | \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \cdots | \varphi_0 \rangle.
\]

\[
\Delta E = \sum_{i=0}^{\infty} \langle \varphi_0 | \hat{H}_i \left( \omega - \hat{H}_0 \right) | \varphi_0 \rangle = \langle \varphi_0 | \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \cdots | \varphi_0 \rangle.
\]

This expression depends however on the exact energy \( E \) and is again not very convenient from a practical point of view. It can obviously be solved iteratively, by starting with a guess for \( E \) and then solve

Many-body perturbation theory

In our equations for \( |\psi_2 \rangle \) and \( \Delta E \) in terms of the unperturbed solutions \( |\varphi_i \rangle \) we have still an undetermined parameter \( \omega \) and a dependency on the exact energy \( E \). Not much has been gained thus from a practical computational point of view.

Many-body perturbation theory

Many-body perturbation theory

The most common choice is to start with the function which is expected to exhibit the largest overlap with the wave function we are searching after, namely \( |\varphi_0 \rangle \). This can again be inserted in the solution for \( |\psi_0 \rangle \) in an iterative fashion and if we continue along these lines we end up with
\[
|\psi_0 \rangle = \sum_{i=0}^{\infty} \left( \frac{\hat{Q}}{\omega - \hat{H}_0} \left( \omega - \hat{E} + \hat{\Delta} \right) \right)^i |\varphi_0 \rangle,
\]

for the wave function and
\[
\Delta E = \sum_{i=0}^{\infty} \langle \varphi_0 | \hat{H}_i \left( \omega - \hat{H}_0 \right) | \varphi_0 \rangle = \langle \varphi_0 | \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \cdots | \varphi_0 \rangle.
\]

This is now a perturbative expansion of the exact energy in terms of the interaction \( \hat{H}_i \) and the unperturbed wave function \( |\psi_0 \rangle \).

Many-body perturbation theory

Many-body perturbation theory

Defining \( E = \hat{E} \) and recalling that \( \hat{H}_0 \) commutes with \( \hat{Q} \) by construction and that \( \hat{Q} \) is an idempotent operator \( \hat{Q}^2 = \hat{Q} \). Using this equation in the above expansion for \( \Delta E \) we can write the denominator
\[
\hat{Q} \left( \frac{1}{\omega - \hat{Q} \hat{H}_0 \hat{Q}} \right) - \hat{Q} \left[ \frac{1}{\omega - \hat{Q} \hat{H}_0 \hat{Q}} \hat{Q} \right] \hat{Q} \left( \frac{1}{\omega - \hat{Q} \hat{H}_0 \hat{Q}} \right) = \hat{Q} \left( \frac{1}{\omega - \hat{H}_0} \right).
\]

In Brillouin-Wigner perturbation theory we set \( \omega = E_0 \) and obtain the following expression for the energy difference
\[
\Delta E = \sum_{i=0}^{\infty} \langle \varphi_0 | \hat{H}_i \left( \omega - E_0 \right) | \varphi_0 \rangle = \langle \varphi_0 | \hat{H}_0 \left( \omega - E_0 \right) + \hat{H}_1 \left( \omega - E_0 \right) + \hat{H}_2 \left( \omega - E_0 \right) + \cdots | \varphi_0 \rangle.
\]

Inserted in the expression for \( \Delta E \) leads to
\[
\Delta E = \langle \varphi_0 | \hat{H}_0 \left( \omega - E_0 \right) + \hat{H}_1 \left( \omega - E_0 \right) + \hat{H}_2 \left( \omega - E_0 \right) + \cdots | \varphi_0 \rangle = \langle \varphi_0 | \hat{H}_0 \left( \omega - E_0 \right) + \hat{H}_1 \left( \omega - E_0 \right) + \hat{H}_2 \left( \omega - E_0 \right) + \cdots | \varphi_0 \rangle.
\]

In RS perturbation theory we set \( \omega = W_0 \) and obtain the following expression for the energy difference
\[
\Delta E = \sum_{i=0}^{\infty} \langle \varphi_0 | \hat{H}_i \left( W_0 - E_0 \right) | \varphi_0 \rangle = \langle \varphi_0 | \hat{H}_0 \left( W_0 - E_0 \right) + \hat{H}_1 \left( W_0 - E_0 \right) + \hat{H}_2 \left( W_0 - E_0 \right) + \cdots | \varphi_0 \rangle.
\]
Many-body perturbation theory

Recalling that $\hat{Q}$ commutes with $\hat{H}_0$ and since $\Delta E$ is a constant we obtain that

$$\Delta E(\Phi_0) = \Delta E(\hat{Q} \Phi_0) = 0.$$  

Inserting this results in the expression for the energy results in

$$\Delta E = \langle \Phi_0 | \hat{H} + \hat{Q} (\hat{H}_0 - \hat{H}) + \hat{Q} (\hat{H}_0 - \hat{H}) | \Phi_0 \rangle = \Delta E(\hat{Q} | \Phi_0 \rangle),$$

being the third-order contribution.

Interpreting the correlation energy and the wave operator

We use letters $ijkl \ldots$ for states below the Fermi level and $abcd \ldots$ for states above the Fermi level. A general single-particle state is given by letters $pqrs \ldots$.

We can then expand our exact state function for the ground state as

$$|\Psi_0\rangle = \prod_{i} \hat{a}_{i}^\dagger |\Phi_0\rangle,$$

where the index $i$ defines different single-particle states up to the Fermi level. We have assumed that we have $N$ fermions. A given one-particle-one-hole $(1p1h)$ state can be written as

$$|\Psi_{1p1h}\rangle = \hat{a}_{i}^\dagger \hat{a}_{j} |\Phi_0\rangle,$$

while a 2p2h state can be written as

$$|\Psi_{2p2h}\rangle = \hat{a}_{i}^\dagger \hat{a}_{j} \hat{a}_{k}^\dagger \hat{a}_{l} |\Phi_0\rangle,$$

and a general $ApAh$ state as

$$|\Psi_{ApAh}\rangle = \hat{a}_{i}^\dagger \hat{a}_{j} \hat{a}_{k}^\dagger \hat{a}_{l} \ldots \hat{a}_{m}^\dagger \hat{a}_{n} |\Phi_0\rangle.$$
Interpreting the correlation energy and the wave operator

If we limit the attention to a Hartree-Fock basis, then we have that \( \langle \Phi_0 | \hat{H} | 2p - 2h \rangle \) is the only contribution and the contribution to the energy reduces to
\[
\Delta E^{(2)} = \frac{1}{4} \sum_{ijkl} \langle ij | \hat{v} | ab \rangle \langle ab | \hat{v} | ij \rangle (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b).
\]

Interpreting the correlation energy and the wave operator

If we compare this to the correlation energy obtained from full configuration interaction theory with a Hartree-Fock basis, we found that
\[
E - E_0 = \Delta E = \sum_{ijkl} \langle ij | \hat{v} | ab \rangle C_{ij}^{ab},
\]
where the energy \( E_0 \) is the reference energy and \( \Delta E \) defines the so-called correlation energy.

We see that if we set
\[
C_{ij}^{ab} = \frac{1}{4} \frac{\langle ab | \hat{v} | ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b},
\]
we have a perfect agreement between FCI and MBPT. However, FCI includes such \( 2p - 2h \) correlations to infinite order. In order to make a meaningful comparison we would at least need to sum such correlations to infinite order in perturbation theory.

Interpreting the correlation energy and the wave operator

Summing up, we can see that

- MBPT introduces order-by-order specific correlations and we make comparisons with exact calculations like FCI.
- At every order, we can calculate all contributions since they are well-known and either tabulated or calculated on the fly.
- MBPT is a non-variational theory and there is no guarantee that higher orders will improve the convergence.
- However, since FCI calculations are limited by the size of the Hamiltonian matrices to diagonalize (today’s most efficient codes can attach dimensionality of ten billion basis states), MBPT can function as an approximative method which gives a straightforward (but tedious) calculation recipe.
- MBPT has been widely used to compute effective interactions for the nuclear shell-model.
- But there are better methods which sum to infinite order important correlations. Coupled cluster theory is one of these methods.

Codes for computing effective Hamiltonians for the shell model or...