Electron correlation, post-HF methods

Hartree-Fock (HF) is a variational method, with the exact Hamiltonian (albeit non-relativistic) and approximate wave-function in the form of a Slater determinant (SD).

The Slater determinant accounts for exchange perfectly (the wave-function is anti-symmetric for particle interchange, following Pauli).

HF is exact for one-electron systems (the hydrogen atom, . . .).

HF is approximate for two- and more-electron systems. The probability of the electron to be somewhere is specifically correlated with the "location" of the other electrons: The pair-correlation function $g(\mathbf{r}', \mathbf{r})$ drops below the HF value. The real $g(\mathbf{r}', \mathbf{r}) < g(\mathbf{r}', \mathbf{r})_{\mathrm{HF}} < 1$ (exchange already forbids electrons with the same spin sitting at the same spot) and the real $E < E_{\mathrm{HF}}$ for two and more electrons.
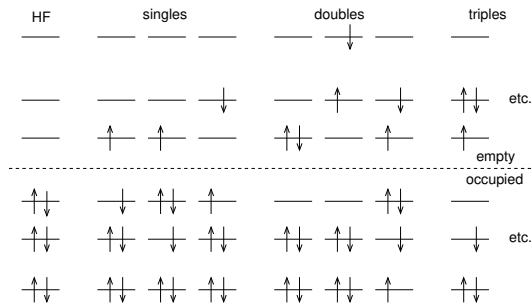
The correlation energy is the HF energy minus and the exact ground state energy (if we take the correlation energy to be positive). HF (almost) always yields too high energy. It cannot yield too low energy.

Post-HF methods: (a) configuration interaction, (b) coupled cluster methods, (c) Møllet-Plesset perturbation theory, (d) multi-reference methods. And . . .

Configuration interaction

Start from HF, with a basis (M) larger than the number of occupied MOs ($N/2$): $M > N/2$. You get empty MOs.

Fix the orbitals $\phi_k(\mathbf{r})$, and build Ansatz with Slater determinants with zero, one, two, three, etc., electrons "kicked into" the empty orbitals.

$$\Phi_{\text{CI}} = C_0 \Phi_{\text{HF}} + \underbrace{\sum C_i^S \Phi_i^S}_{\text{singles}} + \underbrace{\sum C_i^D \Phi_i^D}_{\text{doubles}} + \underbrace{\sum C_i^T \Phi_i^T}_{\text{triples}} + \cdots + \underbrace{\sum C_i^N \Phi_i^N}_{N \text{ excit.}}$$

Configuration interaction

$$\Phi_{CI} = C_0 \Phi_{HF} + \sum_{\text{singles}} C_i^S \Phi_i^S + \sum_{\text{doubles}} C_i^D \Phi_i^D + \sum_{\text{triples}} C_i^T \Phi_i^T + \cdots + \sum_{N \text{ excit.}} C_i^N \Phi_i^N$$

This is a variational method: one has to determine the expansion coefficients such that energy is minimal with the constraint that the WF is normalized:

$$E = \min \langle \Phi_{CI} | \hat{H} | \Phi_{CI} \rangle \text{ with } \langle \Phi_{CI} | \Phi_{CI} \rangle = 1$$

This can be expressed as an eigenvalue problem in the basis of determinants (so **H** is a matrix, **c** is a vector):

$$\mathbf{Hc} = E\mathbf{c}$$

The lowest eigenvalue is the ground state energy.

There is much structure in **H**, e.g., matrix elements between determinants with more than three different orbitals are zero, as $\hat{H}$ has only one- and two-electron operators.

In **full CI** we have all possible determinants in the sum. Then (if the basis is complete) we get the exact ground state energy!

Configuration interaction

$$\Phi_{CI} = C_0 \Phi_{HF} + \underbrace{\sum C_i^S \Phi_i^S}_{\text{singles}} + \underbrace{\sum C_i^D \Phi_i^D}_{\text{doubles}} + \underbrace{\sum C_i^T \Phi_i^T}_{\text{triples}} + \cdots + \underbrace{\sum C_i^N \Phi_i^N}_{N \text{ excit.}}$$

In practice we cannot keep the full expansion. Too expensive! Truncate:

▶ **CIS** (S = singles)

$$\Phi_{CIS} = C_0 \Phi_{HF} + \underbrace{\sum C_i^S \Phi_i^S}_{\text{singles}}$$

This yields no improvement over HF.

▶ **CID** (D = doubles)

$$\Phi_{CID} = C_0 \Phi_{HF} + \underbrace{\sum C_i^D \Phi_i^D}_{\text{doubles}}$$

This gives the big gain!

▶ **CISD** singles & doubles

$$\Phi_{CISD} = C_0 \Phi_{HF} + \underbrace{\sum C_i^S \Phi_i^S}_{\text{singles}} + \underbrace{\sum C_i^D \Phi_i^D}_{\text{doubles}}$$

In conjunction with doubles the singles help (and are relatively few). Nevertheless the computational cost scales as M^6.

Configuration interaction

In practice often one can also leave out excitations from core states, which speeds things up considerably also.

Apart from the unfavorable scaling, CI also has the drawback of not being size-consistent.

Consider a single molecule calculated with CISD. It has double excitations. Consider a second single molecule calculated with CISD. It also has double excitations. So the both together feature quadrupole excitations... But treating the complex (at "infinite" intermolecular distance) at the CISD level only gives up to (and including) double excitations.

So, a single CISD calculation on both molecules together yields a higher energy than two CISD calculations on the single molecules. This is not very desirable.

Of course, in full CI this problem does not exist.

Maybe it is better to use the criterion of size-extensivity...

Coupled-cluster methods

We start again with the HF SD: Φ_0.

The CC wave function:

$$\Phi_{CC} = e^{\hat{T}} \Phi_0 \quad \text{where} \quad \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N$$

Here $\hat{T}$ is the cluster operator. $\hat{T}_1$ are the single excitations, $\hat{T}_2$ the double, etc.

$$\hat{T}_1 \Phi_0 = \sum_{ij} t_i^j \hat{\tau}_i^j \Phi_0$$

Singles: Removing a single electron from orbital i ($i \leq N/2$) and adding it to an empty orbital j ($N/2 + 1 \leq j \leq M$) . The t_i^j are the expansion coefficients to be determined.

Doubles:

$$\hat{T}_2 \Phi_0 = \sum_{kl} \sum_{ij} t_{ki}^{lj} \hat{\tau}_k^l \hat{\tau}_i^j \Phi_0$$

The exponent is defined by its series expansion:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \ldots$$

Coupled-cluster methods

Now, e.g., cut at triples, $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$ (i.e. CCSDT), do a Taylor expansion, and re-order the summation (in order of increasing number of excitations):

$$e^{\hat{T}} = 1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \frac{1}{2!}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)^2 + \frac{1}{3!}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3)^3 + \dots$$

$$= 1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right) + \left(\hat{T}_3 + \hat{T}_2\hat{T}_1 + \frac{1}{6}\hat{T}_1^3\right) + \dots$$

We can now insert the expansion (truncated in $\hat{T}$ beyond $\hat{T}_3$) into the Schrödinger equation:

$$\hat{H}\Phi_{\text{CCSDT}} = E_{\text{CCSDT}}\Phi_{\text{CCSDT}}$$

Solving this will yield the coefficients t_i^j, t_{ki}^{lj}, t_{mki}^{nlj} and E_{CCSDT}.

Note: We still have terms of all orders excitation in the Taylor expansion (until we have exhausted our basis set). Hence there is no problem with size-extensivity.

Again, we have a hierarchy of methods: CCSD, CCSDT, CCSDTQ.

One can also do the highest order of the excitations in perturbation theory: CCSD(T), CCSDT(Q). CCSD(T) is the most popular and very accurate.

Møller-Plesset perturbation theory

We want to solve ($i = 1, 2, 3, \ldots$ labels the state, WF and (increasing) energy):

$$\hat{H}\Phi_i = E_i\Phi_i \tag{1}$$

We know everything about the unperturbed Hamiltonian, its eigenstates and energies:

$$\hat{H}_0\Phi_i^{(0)} = E_i^{(0)}\Phi_i^{(0)}$$

We now write:

$$\hat{H} = \hat{H}_0 + \lambda\Delta\hat{H} \tag{2}$$

And expand:

$$\Phi_i = \Phi_i^{(0)} + \lambda\Phi_i^{(1)} + \lambda^2\Phi_i^{(2)} + \lambda^3\Phi_i^{(3)} + \ldots \tag{3}$$

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \lambda^3 E_i^{(3)} + \ldots \tag{4}$$

Inserting 2, 3 and 4 into the eigenvalue equation 1 and isolating the same powers of λ. This yields (recursive) relations for terms in 3 and 4.

E.g., (choosing λ^1):

$$E_i^{(1)} = \langle\Phi_i^{(0)}|\Delta\hat{H}|\Phi_i^{(0)}\rangle \quad , \quad E_i^{(2)} = \sum_{j\neq i} \frac{|\langle\Phi_j^{(0)}|\Delta\hat{H}|\Phi_i^{(0)}\rangle|^2}{E_i^{(0)} - E_j^{(0)}} \quad , \quad \text{etc.}$$

In practice we have to truncate at some power of λ.

Perturbation theory basics

Help slide:

$$\left(\hat{H}_0 + \lambda \Delta \hat{H} \right) \left(|\Phi_i^0\rangle + \lambda|\Phi_i^1\rangle + \lambda^2|\Phi_i^2\rangle + \dots \right)$$

$$= \left(E_i^0 + \lambda E_i^1 + \lambda^2 E_i^2 + \dots \right) \left(|\Phi_i^0\rangle + \lambda|\Phi_i^1\rangle + \lambda^2|\Phi_i^2\rangle + \dots \right)$$

λ^0:
$$\hat{H}_0|\Phi_i^0\rangle = E_i^0|\Phi_i^0\rangle$$

λ^1:
$$\langle\Phi_i^0|\hat{H}_0|\Phi_i^1\rangle + \langle\Phi_i^0|\Delta\hat{H}|\Phi_i^0\rangle = \langle\Phi_i^0|E_i^0|\Phi_i^1\rangle + \langle\Phi_i^0|E_i^1|\Phi_i^0\rangle$$

$$\text{so that} \quad \langle\Phi_i^0|\Delta\hat{H}|\Phi_i^0\rangle = \langle\Phi_i^0|E_i^1|\Phi_i^0\rangle = E_i^1$$

Insert back (right) and insert complete set (left)

$$\hat{H}_0|\Phi_i^1\rangle + \sum_j |\Phi_j^0\rangle\langle\Phi_j^0|\Delta\hat{H}|\Phi_i^0\rangle = E_i^0|\Phi_i^1\rangle + |\Phi_i^0\rangle\langle\Phi_i^0|\Delta\hat{H}|\Phi_i^0\rangle$$

$$\Rightarrow \langle\Phi_k^0|(E_i^0 - \hat{H}_0)|\Phi_i^1\rangle = \langle\Phi_k^0|\sum_{j\neq i} |\Phi_j^0\rangle\langle\Phi_j^0|\Delta\hat{H}|\Phi_i^0\rangle$$

$$\Rightarrow (E_i^0 - E_k^0)\langle\Phi_k^0|\Phi_i^1\rangle = \langle\Phi_k^0|\Delta\hat{H}|\Phi_i^0\rangle \quad \text{next use:} \quad |\Phi_i^1\rangle = \sum_k |\Phi_k^0\rangle\langle\Phi_k^0||\Phi_i^1\rangle \quad \text{etc.}$$

Note: this is too simple, consider $k = i$ and degenerate case.

Møller-Plesset perturbation theory

We again start from Hartree-Fock, but now from the HF equation:

$$\hat{f}(1)\psi_k(1) = \epsilon_k \psi_k(1)$$

(here, for convenience, with spin orbitals)

We sum the $\hat{f}$ operator for all occupied states and obtain the Fock operator:

$$\hat{F} = \sum_i^N \hat{f}(i)$$

The HF SD is an eigenfunction of $\hat{F}$ by construction.

We now split of the Fock operator from the Hamiltonian:

$$\hat{H} = \hat{F} + (\hat{H} - \hat{F}) \equiv \hat{H}_0 + \Delta\hat{H}$$

This is the "Møller-Plesset" choice (well, they formulated differently).

One achieves that the zeroth order WF is just the HF WF, which is a pretty good first approximation already.

Møller-Plesset perturbation theory

The zeroth order energy is (we suppress the label $i = 0$):

$$\hat{F}\Phi^{(0)} = 2\sum_{i}^{N/2} \epsilon_i \Phi^{(0)} = E^{(0)}\Phi^0$$

The first order energy (**MP1**) is:

$$E^{(0)} + E^{(1)} = \langle \Phi^{(0)}|\hat{H}_0 + \Delta H|\Phi^{(0)}\rangle = \langle \Phi^{(0)}|\hat{H}|\Phi^{(0)}\rangle = E_{\text{HF}}$$

(so $E^{(1)}$ are our "double counting corrections" for HF).

So one cannot yet cut at the first order. The main gain comes for **MP2**:

$$E \approx E^{(0)} + E^{(1)} + E^{(2)}$$

Of course, the expressions are somewhat more complicated ... however, in the expression for $E^{(2)}$ we have matrix elements

$$\langle \Phi_j^{(0)}|\Delta\hat{H}|\Phi_i^{(0)}\rangle$$

For the ground state: $\Phi_i^{(0)} \rightarrow \Phi_{\text{gs}}^{(0)}$ is our ground state HF Slater determinant. As $\Delta\hat{H}$ is a sum of two-particle operators, the only $\Phi_j^{(0)}$ that matter are SDs with double excitations.

Møller-Plesset perturbation theory

A few "final" remarks on MPn:

MP4 is often done.

Convergence with n of **MPn** can be tricky, i.e. not smooth. In particular one has to be careful with systems with a small "gap".

MPn is not variational. **MPn** is size-extensive.

Multi-reference methods

Help slide:

$s_{A/B}$ is "1s" on hydrogen atom A/B

HF wave function (N is normalisation):

$$\Psi_1 = \frac{1}{N} \left(s_A(\mathbf{r}_1) + s_B(\mathbf{r}_1)\right)\left(s_A(\mathbf{r}_2) + s_B(\mathbf{r}_2)\right) \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

$$\sim s_A(\mathbf{r}_1) s_A(\mathbf{r}_2) + s_A(\mathbf{r}_1) s_B(\mathbf{r}_2) + s_B(\mathbf{r}_1) s_A(\mathbf{r}_2) + s_B(\mathbf{r}_1) s_B(\mathbf{r}_2)$$
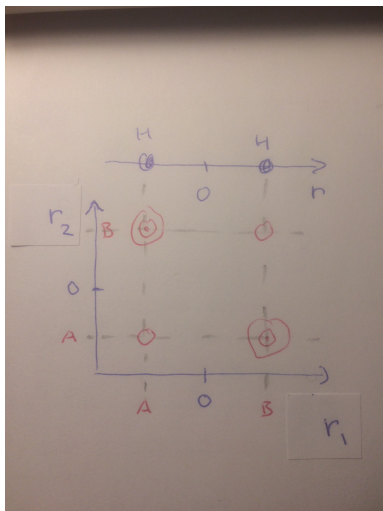
Both electrons excited into the the first empty state (anti-bonding σ^*)

$$\Psi_2 = \frac{1}{\tilde{N}} \left(s_A(\mathbf{r}_1) - s_B(\mathbf{r}_1)\right)\left(s_A(\mathbf{r}_2) - s_B(\mathbf{r}_2)\right) \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$
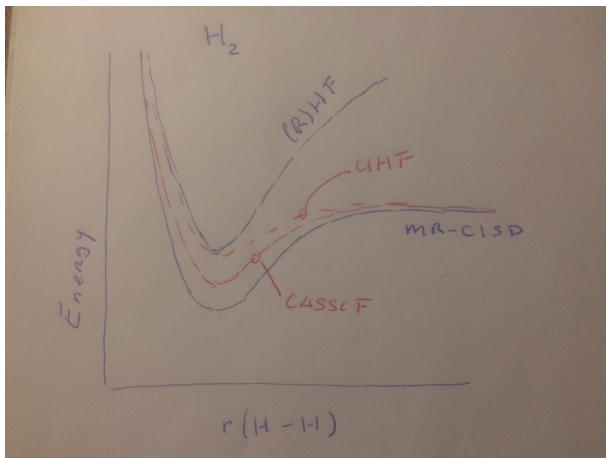
CID:

$$\Psi_{CID} = c_1 \Psi_1 + c_2 \Psi_2$$

Multi-reference methods

If H_2 is dissociated, the probability density for electron 1 at A and electron 2 at B (and vice versa) should become progressively larger than the density for both electrons at A or both electrons at B.

Multi-reference methods

Sketch of H_2 dissociation curve. For H_2, UHF, CASSCF and MR-CISD all yield the correct dissociation limit, contrary to standard HF. For a general diatomic molecule one expects in the dissociation limit: $E(\text{UHF}) > E(\text{CASSCF}) > E(\text{MR-CISD})$.

Multi-reference methods

MCSCF = Multi-configuration self-consistent field (methods)

To be used when a single Slater determinant is *not* a good starting point for, e.g., a perturbation expansion. So, if, in a CI expansion, the coefficient of any determinant other than the HF ground state is considerable. One then also needs *to optimize the orbitals from which the determinants are build*.

A classic example, H_2:

- ▶ In HF the likelihood to find (a) both electrons near one proton is the same as (b) finding one near one proton and the other near the other proton.
- ▶ In CI this is cured by considering (one additional) determinant build from an anti-bonding orbital. This makes (b) more likely.
- ▶ Now you dissociate the H_2. The CI clearly helps: the electrons are not localized simultaneously at the same proton. However, this "configuration" is very different from the "reference" HF for which the orbitals are optimized. So the shape of the orbitals in not good... and needs to be optimized again for the additional determinant (in full CI you get the right numbers, but the price is to have very many determinants).
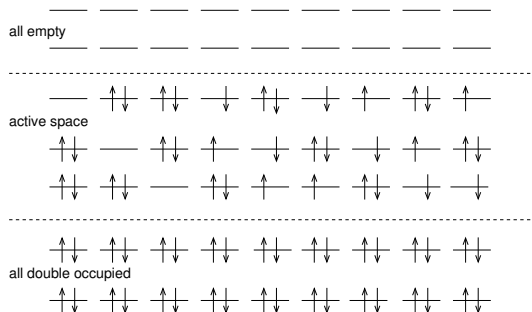
Note that in practice we "break symmetry" and do HF for the H atom.

Multi-reference methods

This method has an "active" space in which all electron distributions (i.e. "complete") are considered. Below the active space has 3 orbitals containing 4 electrons.

Not only the coefficients of these nine determinants are optimized, but also the expansion coefficients of the orbitals in the MOs.

Multi-reference methods

The MCSCF calculation can be a first step ... so on top of, e.g., a CASSCF you do a CISD, allowing excitation from and into orbitals outside the active space, but now keeping the orbitals fixed: an MR-CISD (multi-reference CISD).

The MR-step serves to account for "static correlation", the kind where a single Slater determinant is just not sufficient (N_2 dissociation is another text-book example). The CISD step accounts then (much more efficient) for the "dynamic correlation" (e.g. van der Waals interaction).

A "final" remark: the better you account for correlation, the better needs to be the quality of your basis set. You cannot get away with 6-31G or so. There is a huge variety of basis sets... something like cc-pv$X$Z, with $X = D, T, Q, 5, \ldots$