Introduction to HF instability

Tóth Zsuzsanna

Let us start from the HF-wavefunction:

$$|\mathrm{HF}\rangle = \prod_{i=1}^{n} \phi_i^+ |\mathrm{vac}\rangle$$

Now let us mix the occupied orbitals with virtual orbitals.

(Note: there is no point mixing the occupied orbitals between each other, since the energy depends only on the subspace of occupied orbitals, independent from the actual choice of orbitals.)

$$\phi_i^+ \quad \longrightarrow \quad \phi_i^+ + \sum_{a=1}^{m} c_{ai}\phi_a^+ = \left(1 + \sum_{a=1}^{m} c_{ai}\phi_a^+\phi_i^-\right)\phi_i^+$$

The new determinant wavefunction:

$$\begin{aligned} |\mathrm{HF}\rangle \quad \longrightarrow \quad |\Psi\rangle &= \prod_{i=1}^{n}\left(1 + \sum_{a=1}^{m} c_{ai}\phi_a^+\phi_i^-\right)|\mathrm{HF}\rangle = \\ &= \prod_{i=1}^{n}\prod_{a=1}^{m}(1 + c_{ai}\phi_a^+\phi_i^-)|\mathrm{HF}\rangle = \\ &= \exp\Big(\sum_{i=1}^{n}\sum_{a=1}^{m} c_{ai}\phi_a^+\phi_i^-\Big)|\mathrm{HF}\rangle \end{aligned}$$

(i, j are indices for occupied, a, b for virtual orbitals) The Ψ is not normalised:

$$\langle\Psi|\Psi\rangle = 1 + \sum_{i=1}^{n}\sum_{a=1}^{m}|c_{ai}|^2 + \mathcal{O}(c^4)$$

$$\langle\Psi|\Psi\rangle^{-1} = 1 - \sum_{i=1}^{n}\sum_{a=1}^{m}|c_{ai}|^2 + \mathcal{O}(c^4)$$

$$\begin{aligned} \langle\Psi|H|\Psi\rangle &= \langle\mathrm{HF}|\prod_{i=1}^{n}\prod_{a=1}^{m}(1 + c_{ai}^*\phi_i^+\phi_a^-)H\prod_{j=1}^{n}\prod_{b=1}^{m}(1 + c_{bj}\phi_b^+\phi_j^-)|\mathrm{HF}\rangle = \\ &= E_{HF} + \sum_{i,j=1}^{n}\sum_{a,b=1}^{m}\left[c_{ai}^*c_{bj}\langle\phi_i^+\phi_a^-H\phi_b^+\phi_j^-\rangle + \frac{1}{2}\left(c_{ai}^*c_{bj}^*\langle\phi_i^+\phi_a^-\phi_j^+\phi_b^-H\rangle + c_{ai}c_{bj}\langle H\phi_a^+\phi_i^-\phi_b^+\phi_j^-\rangle\right)\right] + \mathcal{O}(c^4) \\ &= E_{HF} + \sum_{k,l=1}^{n\cdot m}\left[c_k^*c_lA_{kl} + \frac{1}{2}\left(c_k^*c_l^*B_{kl} + c_kc_lB_{kl}^\dagger\right)\right] + \mathcal{O}(c^4), \end{aligned}$$

where $k = (a, i)$ and $l = (b, j)$ multiindices. Set $A' = A - E_{HF} I$.

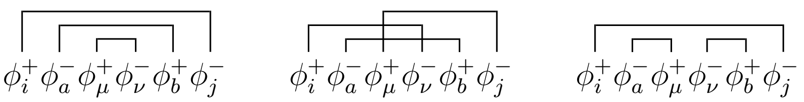
$$\begin{aligned}
\Delta E &= \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} - E_{HF} \\
&= \sum_{k,l=1}^{n \cdot m} \left[c_k^* c_l A'_{kl} + \frac{1}{2} \left(c_k^* c_l^* B_{kl} + c_k c_l B_{kl}^\dagger \right) \right] + \mathcal{O}(c^4) \\
&= \frac{1}{2} \begin{pmatrix} c^* & c \end{pmatrix} \left(\begin{array}{c|c} A' & B \\ \hline B^\dagger & A' \end{array} \right) \begin{pmatrix} c* \\ c \end{pmatrix}
\end{aligned}$$

The Hartree-Fock wavefunction is stable if for every c the energy difference $\Delta E > 0$, which means that the stability matrix is positive definite and all the eigenvalues are positive. If there is a negative eigenvalue, the HF wavefunction is instable.

Now let us calculate the elements of the A and B matrices.

$$\begin{aligned}
A'_{kl} &= \langle \mathrm{HF} | \phi_i^+ \phi_a^- (H - E_{HF}) \phi_b^+ \phi_j^- | \mathrm{HF} \rangle = -E_{HF} \delta_{kl} + A_{kl}^{1el} + A_{kl}^{2el} = \\
&= \sum_{\mu\nu} h_{\mu\nu} \langle \mathrm{HF} | \phi_i^+ \phi_a^- \phi_\mu^+ \phi_\nu^- \phi_b^+ \phi_j^- | \mathrm{HF} \rangle + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} [\mu\nu|\lambda\sigma] \langle \mathrm{HF} | \phi_i^+ \phi_a^- \phi_\mu^+ \phi_\nu^+ \phi_\sigma^- \phi_\lambda^- \phi_b^+ \phi_j^- | \mathrm{HF} \rangle
\end{aligned}$$

Contractions for the first term:

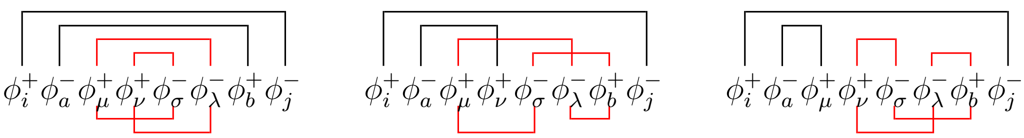


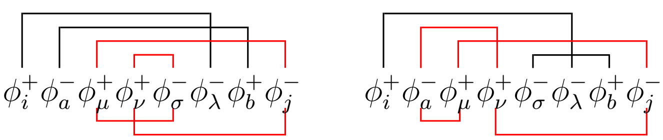
$$\langle \mathrm{HF} | \phi_i^+ \phi_a^- \phi_\mu^+ \phi_\nu^- \phi_b^+ \phi_j^- | \mathrm{HF} \rangle = \delta_{ij} \delta_{ab} \delta_{\mu\nu} n_\mu - \delta_{i\nu} \delta_{ab} \delta_{j\mu} + \delta_{ij} \delta_{a\mu} \delta_{b\nu}$$

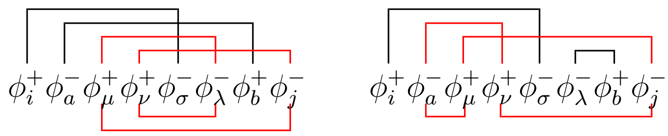
The one-electron term is:

$$A_{kl}^{1el} = \delta_{kl} \sum_{\mu}^{occ} h_{\mu\mu} - \delta_{ab} h_{ij} + \delta_{ij} h_{ab}$$

The contractions for the second term:







The two electron term:

$$A_{kl}^{2el} = \frac{1}{2}\left(\delta_{kl}\sum_{\mu\nu}^{occ}[\mu\nu||\mu\nu] + \delta_{ij}\left(\sum_{\mu}^{occ}[\mu a||\mu b] + \sum_{\nu}^{occ}[a\nu||b\nu]\right) + \delta_{ab}\left(\sum_{\sigma}^{occ}[\sigma j||i\sigma] + \sum_{\lambda}^{occ}[j\lambda||\lambda i]\right) - 2[bi||aj]\right) =$$

$$= \frac{1}{2}\delta_{kl}\sum_{\mu\nu}^{occ}[\mu\nu||\mu\nu] + \delta_{ij}\sum_{\mu}^{occ}[\mu a||\mu b] - \delta_{ab}\sum_{\sigma}^{occ}[\sigma j||\sigma i] - [bi||aj]$$

Finally the matrix element of A':

$$A'_{kl} = \delta_{kl}\left(-E_{HF} + \sum_{\mu}^{occ} h_{\mu\mu} + \frac{1}{2}\sum_{\mu\nu}^{occ}[\mu\nu||\mu\nu]\right) + \delta_{ij}\left(h_{ab} + \sum_{\mu}^{occ}[\mu a||\mu b]\right) - \delta_{ab}\left(h_{ij} + \sum_{\mu}^{occ}[i\mu||j\mu]\right) - [bi||aj]$$

$$= \delta_{ij} f_{ab} - \delta_{ab} f_{ij} - [bi||aj]$$

Now let us calculate the matrix elements of B:

$$B_{kl} = \langle \mathrm{HF}|\phi_i^+\phi_a^-\phi_j^+\phi_b^- H|\mathrm{HF}\rangle = \frac{1}{2}\sum_{\mu\nu\lambda\sigma}[\mu\nu|\lambda\sigma]\langle \mathrm{HF}|\phi_i^+\phi_a^-\phi_j^+\phi_b^-\phi_\mu^+\phi_\nu^+\phi_\sigma^-\phi_\lambda^-|\mathrm{HF}\rangle$$

The i, j indices must coincide with λ, σ and a, b must coincide with μ, ν. Thus:

$$\langle \mathrm{HF}|\phi_i^+\phi_a^-\phi_j^+\phi_b^-\phi_\mu^+\phi_\nu^+\phi_\sigma^-\phi_\lambda^-|\mathrm{HF}\rangle = (\delta_{i\lambda}\delta_{j\sigma} - \delta_{j\lambda}\delta_{i\sigma})(\delta_{a\mu}\delta_{b\nu} - \delta_{b\mu}\delta_{a\nu})$$

$$B_{kl} = \frac{1}{2}\left([ab||ij] + [ba||ji]\right) = [ab||ij]$$

Special case: RHF

A'	$\phi_j^\alpha \to \phi_b^\alpha$	$\phi_j^\beta \to \phi_b^\beta$	$\phi_j^\alpha \to \phi_b^\beta$	$\phi_j^\beta \to \phi_b^\alpha$
$\phi_i^\alpha \to \phi_a^\alpha$	A_{11}	A_{12}		
$\phi_i^\beta \to \phi_a^\beta$	A_{12}	A_{11}		
$\phi_i^\alpha \to \phi_a^\beta$			A_{33}	
$\phi_i^\beta \to \phi_a^\alpha$				A_{33}

$$A_{11} = \delta_{ij} f_{ab} - \delta_{ab} f_{ij} - [bi||aj],$$

where f is with spatial orbitals.

$$A_{12} = [ja|bi]$$

$A_{33} = \delta_{ij} f_{ab} - \delta_{ab} f_{ij} - [bi|aj]$

B	$\phi_j^\alpha \rightarrow \phi_b^\alpha$	$\phi_j^\beta \rightarrow \phi_b^\beta$	$\phi_j^\alpha \rightarrow \phi_b^\beta$	$\phi_j^\beta \rightarrow \phi_b^\alpha$
$\phi_i^\alpha \rightarrow \phi_a^\alpha$	$[ab\|\|ij]$	$[ab\|ij]$		
$\phi_i^\beta \rightarrow \phi_a^\beta$	$[ab\|ij]$	$[ab\|\|ij]$		
$\phi_i^\alpha \rightarrow \phi_a^\beta$				$-[ij\|ba]$
$\phi_i^\beta \rightarrow \phi_a^\alpha$			$-[ij\|ba]$	