

Spin Contamination in Unrestricted Hartree-Fock Wavefunctions

An unrestricted Hartree-Fock (UHF) wavefunction with N_α α spins and N_β β spins has the form

$$\psi(1,2,\dots,N) = \hat{\mathcal{A}}\phi_1\alpha(1)\phi_2\alpha(2)\cdots\phi_{N_\alpha}\alpha(N_\alpha)\phi_1\beta(N_\alpha+1)\phi_2\beta(N_\alpha+2)\cdots\phi_{N_\beta}\beta(N_\alpha+N_\beta)$$

where the α spin spatial orbitals $\{\phi_i\}_{i=1}^{N_\alpha}$ and the β spin spatial orbitals $\{\phi_i\}_{i=1}^{N_\beta}$ are eigenfunctions of different Fock operators. To show that this is an eigenfunction of \hat{S}_z we form

$$\hat{S}_z\psi = \left(\sum_{i=1}^N \hat{S}_z(i) \right) \hat{\mathcal{A}}\phi_1\alpha(1)\phi_2\alpha(2)\cdots\phi_1\beta(N_\alpha+1)\phi_2\beta(N_\alpha+2)\cdots$$

and since \hat{S}_z is symmetric with respect to electron permutations it commutes with $\hat{\mathcal{A}}$

$$\hat{S}_z\psi = \hat{\mathcal{A}} \left(\sum_{i=1}^N \hat{S}_z(i) \right) \phi_1\alpha(1)\phi_2\alpha(2)\cdots\phi_1\beta(N_\alpha+1)\phi_2\beta(N_\alpha+2)\cdots$$

and since α & β are Eigenfunctions of $\hat{S}_z(i)$ with eigenvalues $\pm\frac{1}{2}$ we have

$$\hat{S}_z\psi = \frac{1}{2}(N_\alpha - N_\beta)\psi$$

To show that ψ is not an eigenfunction of \hat{S}^2 we evaluate the expectation value

$$\langle \hat{S}^2 \rangle = \langle \psi | \hat{S}^2 | \psi \rangle = \langle \psi | \sum_{i=1}^N \hat{S}(i) \cdot \sum_{j=1}^N \hat{S}(j) | \psi \rangle = \langle \psi | \sum_{i=1}^N \hat{S}^2(i) | \psi \rangle + 2 \langle \psi | \sum_{i>j}^N \hat{S}(i) \cdot \hat{S}(j) | \psi \rangle$$

Since $\hat{S}^2(i)$ is a one electron operator its expectation value is

$$\langle \psi | \sum_{i=1}^N \hat{S}^2(i) | \psi \rangle = \sum_{i=1}^{N_\alpha} \langle \phi_i\alpha | \hat{S}^2 | \phi_i\alpha \rangle + \sum_{i=1}^{N_\beta} \langle \phi_i\beta | \hat{S}^2 | \phi_i\beta \rangle = \frac{3}{4}(N_\alpha + N_\beta) = \frac{3}{4}N$$

To evaluate the two electron terms we will use the 2 particle density matrix discussed earlier.

$$\langle \psi | \sum_{i>j}^N \hat{S}(i) \cdot \hat{S}(j) | \psi \rangle = \int_{1'2' \rightarrow 12} \hat{S}(1) \cdot \hat{S}(2) \Gamma(1,2/1',2') d\tau(1,2)$$

where after the spin operators operate on coordinates 1&2 one changes the primed coordinates to 1&2. It's convenient to use the operator equivalent

$$\hat{S}(1) \cdot \hat{S}(2) = \frac{1}{4}(2\hat{P}_{12} - 1)$$

,first noted by Dirac, where \hat{P}_{12} interchanges the SPIN variables. So we have

$$\int_{1'2' \rightarrow 12} \hat{S}(1) \cdot \hat{S}(2) \Gamma(1,2/1',2') d\tau(1,2) = \frac{1}{2} \int_{1'2' \rightarrow 12} \hat{P}_{12} \Gamma(1,2/1',2') d\tau(1,2) - \frac{1}{4} \int \Gamma(1,2/1,2) d\tau(1,2)$$

and from the definition of the two-particle density matrix

$$\int \Gamma(1,2/1,2) d\tau(1,2) = \frac{N(N-1)}{2}$$

To evaluate the remaining term we recognize that the two-particle density matrix for a single determinant wave function can be written as products of the one particle density matrix

$$\Gamma(1,2/1',2') = \frac{1}{2} \left(\gamma(1/1')\gamma(2/2') - \gamma(2/1')\gamma(1/2') \right)$$

where for the UHF wavefunction

$$\gamma(1/1') = P_{\alpha}(1,1')\alpha(1)\alpha(1') + P_{\beta}(1,1')\beta(1)\beta(1')$$

with

$$P_{\alpha}(1,1') \sum_{i=1}^{N_{\alpha}} \varphi_i(1)\varphi_i(1') \& P_{\beta}(1,1') \sum_{i=1}^{N_{\beta}} \phi_i(1)\phi_i(1')$$

and with these definitions

$$\gamma(1/1')\gamma(2/2') = \left(P_{\alpha}(1,1')\alpha(1)\alpha(1') + P_{\beta}(1,1')\beta(1)\beta(1') \right) \left(P_{\alpha}(2,2')\alpha(2)\alpha(2') + P_{\beta}(2,2')\beta(2)\beta(2') \right)$$

Then operating with \hat{P}_{12} on the spin coordinates

$$\hat{P}_{12}\gamma(1/1')\gamma(2/2') = \left(P_{\alpha}(1,1')\alpha(2)\alpha(1') + P_{\beta}(1,1')\beta(2)\beta(1') \right) \left(P_{\alpha}(2,2')\alpha(1)\alpha(2') + P_{\beta}(2,2')\beta(1)\beta(2') \right)$$

Changing the primes

$$\int_{1',2' \rightarrow 1,2} \hat{P}_{12}\gamma(1/1')\gamma(2/2') d\tau(1,2) = \int \left(P_{\alpha}(1,1)\alpha(2)\alpha(1) + P_{\beta}(1,1)\beta(2)\beta(1) \right) \left(P_{\alpha}(2,2)\alpha(1)\alpha(2) + P_{\beta}(2,2)\beta(1)\beta(2) \right) d\tau(1,2)$$

Doing the spin integrations

$$\int_{1',2' \rightarrow 1,2} \hat{P}_{12} \gamma(1/1') \gamma(2/2') d\tau(1,2) = \int (P_\alpha(1,1)P_\alpha(2,2) + P_\beta(1,1)P_\beta(2,2)) dV(1,2)$$

and then the spatial integrations

$$\int_{1',2' \rightarrow 1,2} \hat{P}_{12} \gamma(1/1') \gamma(2/2') d\tau(1,2) = N_\alpha^2 + N_\beta^2$$

In a similar way

$$\gamma(2/1') \gamma(1/2') = (P_\alpha(2,1')\alpha(2)\alpha(1') + P_\beta(2,1')\beta(2)\beta(1')) (P_\alpha(1,2')\alpha(1)\alpha(2') + P_\beta(1,2')\beta(1)\beta(2'))$$

operating with \hat{P}_{12} on the spin coordinates

$$\hat{P}_{12} \gamma(2/1') \gamma(1/2') = (P_\alpha(2,1')\alpha(1)\alpha(1') + P_\beta(2,1')\beta(1)\beta(1')) (P_\alpha(1,2')\alpha(2)\alpha(2') + P_\beta(1,2')\beta(2)\beta(2'))$$

Changing the primes

$$\int_{1',2' \rightarrow 1,2} \hat{P}_{12} \gamma(2,1') \gamma(1,2') d\tau(1,2) = \int (P_\alpha(2,1)\alpha(1)\alpha(1) + P_\beta(2,1)\beta(1)\beta(1)) (P_\alpha(1,2)\alpha(2)\alpha(2) + P_\beta(1,2)\beta(2)\beta(2)) dV(1,2)$$

doing the spin integration

$$\int_{1',2' \rightarrow 1,2} \hat{P}_{12} \gamma(2,1') \gamma(1,2') d\tau(1,2) = \int (P_\alpha(2,1)P_\alpha(1,2) + P_\alpha(2,1)P_\beta(1,2) + P_\beta(2,1)P_\alpha(1,2) + P_\beta(2,1)P_\beta(1,2)) dV(1,2)$$

and the spatial integrations

$$\int (P_\alpha(2,1)P_\alpha(1,2)) dV(1,2) = \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\alpha} \langle \varphi_i | \varphi_j \rangle = \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\alpha} \delta_{ij} = N_\alpha$$

and likewise

$$\int (P_\beta(2,1)P_\beta(1,2)) dV(1,2) = \sum_{i=1}^{N_\beta} \sum_{j=1}^{N_\beta} \langle \phi_i | \phi_j \rangle = \sum_{i=1}^{N_\beta} \sum_{j=1}^{N_\beta} \delta_{ij} = N_\beta$$

whereas we have

$$\int (P_\alpha(2,1)P_\beta(1,2)) dV(1,2) = \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \langle \varphi_i | \phi_j \rangle^2 = \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} (\Delta_{ij}^{\alpha\beta})^2$$

and

$$\int (P_\beta(2,1)P_\alpha(1,2))dV(1,2) = \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} |\langle \phi_i | \phi_j \rangle|^2 = \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} (\Delta_{ij}^{\alpha\beta})^2$$

and so

$$\int_{1',2' \rightarrow 1,2} \hat{P}_{12} \gamma(2,1') \gamma(1,2') d\tau(1,2) = N_\alpha + N_\beta + 2 \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} (\Delta_{ij}^{\alpha\beta})^2$$

The two-electron contribution is then

$$2 \langle \psi | \sum_{i>j} \hat{S}(i) \cdot \hat{S}(j) | \psi \rangle = \frac{1}{2} \left\{ N_\alpha^2 + N_\beta^2 - N - 2 \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} (\Delta_{ij}^{\alpha\beta})^2 \right\} - \frac{1}{4} N(N-1)$$

After completing the square and adding the one electron term we have

$$\langle \hat{S}^2 \rangle = \frac{N}{2} \left(\frac{N}{2} + 1 \right) - N_\alpha N_\beta - \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} (\Delta_{ij}^{\alpha\beta})^2$$

Check

Although we derived this formula assuming an UHF wavefunction it is general and we can test it using more restrictive functions. For example if we have a closed shell wavefunction with

$$N_\alpha = N_\beta = N/2 \text{ and } \{ \phi_i \}_{i=1}^{N_\alpha} = \{ \phi_i \}_{i=1}^{N_\beta} \text{ then } \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} (\Delta_{ij}^{\alpha\beta})^2 = N_\alpha = N/2$$

then

$$\langle \hat{S}^2 \rangle = \frac{N}{2} \left(\frac{N}{2} + 1 \right) - \frac{N^2}{4} - \frac{N}{2} = 0$$

as required. As another example suppose we have linear triplet methylene, $CH_2(^3\Sigma_g^-)$ with the electronic configuration

$$1\sigma_g^2 2\sigma_g^2 2\sigma_u^2 1\pi_x^1 1\pi_y^1, \text{ we have } N_\alpha = 5 \text{ \& } N_\beta = 3 \text{ and } \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} (\Delta_{ij}^{\alpha\beta})^2 = N_\beta \text{ and}$$

$$\langle \hat{S}^2 \rangle = \frac{8}{2} \left(\frac{8}{2} + 1 \right) - 5 \times 3 - 3 = 2, \text{ corresponding to } S(S+1) \text{ with } S = 1.$$

UHF for the Li atom

The UHF function for the ground state of Li is

$$\psi(1,2,3) = \hat{\mathcal{A}}1s\alpha(1)1s'\beta(2)2s\alpha(3)$$

If we expand these orbitals in term of spherical gaussians

$$1s = \sum_{i=1}^{11} C_{1s,i} \chi_i = \sum_{i=1}^{11} C_{1s,i} \left(\frac{2\gamma_i}{\pi} \right)^{3/4} e^{-\gamma_i r^2}$$

and use the VTZ basis the resulting UHF orbitals are collected in the table below.

i	γ_i	$C_{1s,i}$	$C_{1s',i}$	$C_{2s,i}$
1	5988.0	0.000133	0.000132	-0.000020
2	898.9	0.001028	0.001023	-0.000160
3	205.9	0.005284	0.005260	-0.000813
4	59.24	0.020981	0.020882	-0.003299
5	19.87	0.066525	0.066167	-0.010431
6	7.406	0.166379	0.165209	-0.027897
7	2.93	0.316303	0.313840	-0.55520
8	1.189	0.393604	0.393573	-0.098769
9	0.4798	0.188738	0.193136	-0.111737
10	0.07509	0.004872	0.005228	0.568295
11	0.028320	-0.001593	-0.001724	0.529947

Note that the $1s$ & $1s'$ are very similar but not identical as they would be in a restricted open shell wavefunction. The energy of this function is xxx and $\langle \hat{S}^2 \rangle = 0.750015629$. Using the general

$$\text{formula } \langle \hat{S}^2 \rangle = \frac{N}{2} \left(\frac{N}{2} + 1 \right) - N_\alpha N_\beta - \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \left(\Delta_{ij}^{\alpha\beta} \right)^2$$

With $N = 3, N_\alpha = 2$ & $N_\beta = 1$ and

$$\sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \left(\Delta_{ij}^{\alpha\beta} \right)^2 = \left| \langle 1s | 1s' \rangle \right|^2 + \left| \langle 2s | 1s' \rangle \right|^2 = (0.99999080)^2 + (0.00166473)^2 = 0.999984371$$

And so $\langle \hat{S}^2 \rangle = 0.750015629$ as required.

Eliminate the spin contamination

From the branching diagram discussion we know that 3 electrons in different spin orbitals give rise to two doublets and one quartet and in the Li UHF it must be the quartet that's causing the spin contamination. We can write the UHF function as

$\psi(1,2,3) = C_D\psi_D + C_Q\psi_Q$ where ψ_D & ψ_Q are eigenfunctions of \hat{S}^2

$$\hat{S}^2\psi_D = \frac{1}{2}\left(\frac{1}{2}+1\right)\psi_D = \frac{3}{4}\psi_D \quad \& \quad \hat{S}^2\psi_Q = \frac{3}{2}\left(\frac{3}{2}+1\right)\psi_Q = \frac{15}{4}\psi_Q$$

We project out the quartet component

$$\left(\hat{S}^2 - \frac{15}{4}\right)\psi(1,2,3) = \left(\hat{S}^2 - \frac{15}{4}\right)(C_D\psi_D + C_Q\psi_Q) = -3C_D\psi_D$$

We can ignore $-3C_D$ and simply renormalize the result of $\left(\hat{S}^2 - \frac{15}{4}\right)\psi(1,2,3)$.

We write $\hat{S}^2 = \hat{S}_- \hat{S}_+ + \hat{S}_z^2 + \hat{S}_z$ and note

$$\left(\hat{S}_z^2 + \hat{S}_z\right)\psi = \left(\frac{1}{4} + \frac{1}{2}\right)\psi = \frac{3}{4}\psi$$

then

$$\hat{S}_- \hat{S}_+ \psi = \hat{S}_- \hat{A} \hat{S}_+ 1s\alpha(1)1s'\beta(2)2s\alpha(3) = \hat{S}_- \hat{A} 1s\alpha(1)1s'\beta(2)2s\alpha(3)$$

and

$$\hat{S}_- \hat{A} 1s\alpha(1)1s'\alpha(2)2s\alpha(3) = \hat{A} 1s\beta(1)1s'\alpha(2)2s\alpha(3) + \hat{A} 1s\alpha(1)1s'\beta(2)2s\alpha(3) + \hat{A} 1s\alpha(1)1s'\alpha(2)2s\beta(3)$$

and so

$$\left(\hat{S}^2 - \frac{15}{4}\right)\psi = -2\psi + \hat{A} 1s\beta(1)1s'\alpha(2)2s\alpha(3) + \hat{A} 1s\alpha(1)1s'\alpha(2)2s\beta(3)$$

Since the $1s$ & $1s'$ orbitals are virtually identical the last term on the right is ~ 0 and

$$\psi_D = \left(\frac{-2\psi + \hat{A} 1s\beta(1)1s'\alpha(2)2s\alpha(3)}{\sqrt{5}}\right) = a\psi + b\psi' \quad \text{where}$$

$$\psi' = \hat{A} 1s\beta(1)1s'\alpha(2)2s\alpha(3)$$

and $a = -\frac{2}{\sqrt{5}}$ & $b = \frac{1}{\sqrt{5}}$. The energy of this function is

$$E_D = \langle \psi_D | \hat{H} | \psi_D \rangle = \langle a\psi + b\psi' | \hat{H} | a\psi + b\psi' \rangle = E_{UHF} + 2ab \langle \psi | \hat{H} | \psi' \rangle$$

where we note

$$\langle \psi | \hat{H} | \psi \rangle = \langle \psi' | \hat{H} | \psi' \rangle$$

The off diagonal term is

$$\langle \psi | \hat{H} | \psi' \rangle = \langle \hat{\mathcal{A}} 1s\alpha(1)1s'\beta(2)2s\alpha(3) | \hat{H} | \hat{\mathcal{A}} 1s\beta(1)1s'\alpha(2)2s\alpha(3) \rangle = \langle 1s\alpha(1)1s'\beta(2) | \frac{1}{r_{12}} (1 - P_{12}) | 1s\beta(1)1s'\alpha(2) \rangle$$

so

$$E_D = E_{UHF} + \frac{4}{5} J_{1s,1s'} > E_{UHF}$$

So the uncontaminated function has a higher energy than the UHF as it should since ψ_D is restricted relative to ψ_{UHF}