One and two particle density matrices for single determinant HF wavefunctions

One particle density matrix

Given the Hartree-Fock wavefunction

$$\psi(1,2,3,\cdots,N) = \hat{\mathcal{A}}\varphi_1(1)\varphi_2(2)\varphi_3(3)\cdots\varphi_N(N)$$

The electronic energy is

$$\left\langle\psi\left|\hat{H}\right|\psi\right\rangle = \sum_{i=1}^{N}\left\langle\varphi_i(1)\left|\hat{f}(1)\right|\varphi_i(1)\right\rangle + \sum_{i<j}^{N}\left\langle\varphi_i(1)\varphi_j(2)\left|g(1,2)(1-\hat{P}_{12})\right|\varphi_i(1)\varphi_j(2)\right\rangle$$

The one electron contribution may be written as

$$\sum_{i=1}^{N}\left\langle\varphi_i(1)\left|f(1)\right|\varphi_i(1)\right\rangle = \int d\tau(1)\hat{f}(1)\sum_{i=1}^{N}\varphi_i(1)\varphi_i^*(1')\Big|_{1'\to1}$$

from which we deduce

$$\gamma(1,1') = \sum_{i=1}^{N}\varphi_i(1)\varphi_i^*(1')$$

and we see that the natural orbitals of a single determinant wavefunction are simply the occupied spin orbitals of the system. If we are dealing with a RHF wavefunction these spin orbitals may be partitioned into pairs of doubly occupied spatial orbitals and so

$$\varphi_1(1) = \phi_1(\vec{r}_1)\alpha(1),\ \varphi_2(1) = \phi_1(\vec{r}_1)\beta(1),\ \varphi_3(1) = \phi_2(\vec{r}_1)\alpha(1),\cdots,\varphi_N(1) = \phi_{N/2}(\vec{r}_1)\beta(1)$$

and the one particle density matrices becomes

$$\gamma_{RHF}(1,1') = \sum_{i=1}^{N/2}\phi_i(\vec{r}_1)\phi_i^*(\vec{r}_{1'})\Big(\alpha(1)\alpha^*(1') + \beta(1)\beta^*(1')\Big)$$

and so the electron density may be written as

$$\rho_{RHF}(1) = \gamma_{RHF}(1,1) = \alpha(1)\alpha^*(1)\rho_{RHF}^{\alpha}(\vec{r}_1) + \beta(1)\beta^*(1)\rho_{RHF}^{\beta}(\vec{r}_1)$$

where $\rho_{RHF}^{\alpha}(\vec{r})$ and $\rho_{RHF}^{\beta}(\vec{r})$ are the densities of α & β electrons and for the RHF wave-function these are identical

$$\rho_{RHF}^{\alpha}(\vec{r}) = \rho_{RHF}^{\beta}(\vec{r}) = \sum_{i=1}^{N/2} \phi_i(\vec{r})\phi_i^*(\vec{r})$$

and since

$$\int \rho_{RHF}^{\xi}(\vec{r})dV = N/2, \text{ where } \xi = \alpha \text{ or } \beta$$

we have

$$\int \rho_{RHF}(1)d\tau(1) = N$$

If however we have an *unrestricted HF wavefunction*

$$\psi_{UHF}(1,2,3,\cdots,N) = \hat{A}\left(\chi_1\alpha(1)\chi_2\alpha(2)\cdots\chi_{N_\alpha}\alpha(N_\alpha)\phi_1\beta(N_\alpha+1)\phi_2\beta(N_\alpha+2)\cdots\phi_{N_\beta}\beta(N_\alpha+N_\beta)\right)$$

Where $\{\chi_i\}_{i=1}^{N_\alpha}$ and $\{\phi_i\}_{i=1}^{N_\beta}$ are the α & β spatial orbitals, then the spin densities $\rho_{UHF}^{\alpha}(\vec{r})$ and $\rho_{UHF}^{\beta}(\vec{r})$ are not the same

$$\rho_{UHF}^{\alpha}(\vec{r}) = \sum_{i=1}^{N_\alpha} \chi_i(\vec{r})\chi_i^*(\vec{r}) \ \& \ \rho_{UHF}^{\beta}(\vec{r}) = \sum_{i=1}^{N_\beta} \phi_i(\vec{r})\phi_i^*(\vec{r})$$

and at a given point $\vec{r}$ there is an imbalance in the number of α & β electrons. One often defines a spin density (rather than a spin density difference) as

$$Q(\vec{r}) = \rho_{UHF}^{\alpha}(\vec{r}) - \rho_{UHF}^{\beta}(\vec{r})$$

which quantifies this imbalance as a function of $\vec{r}$. Note that

$$\int Q(\vec{r})dV = \int\left(\rho_{UHF}^{\alpha}(\vec{r}) - \rho_{UHF}^{\beta}(\vec{r})\right)dV = N_\alpha - N_\beta$$

Two particle density matrices

We may rewrite the two-electron contribution to the energy of a single determinant wavefunction as

$$\sum_{i<j}^{N}\left\langle \varphi_i(1)\varphi_j(2)\left|g(1,2)(1-\hat{P}_{12})\right|\varphi_i(1)\varphi_j(2)\right\rangle = \int d\tau(1,2)g(1,2)\sum_{i<j}^{N}\varphi_i^*(1)\varphi_j^*(2)(1-\hat{P}_{12})\varphi_i(1)\varphi_j(2)$$

that allows us to write the two-particle density matrix as

$$\Gamma(1,2|1,2) = \sum_{i<j}^{N} \varphi_i^*(1)\varphi_j^*(2)(1-\hat{P}_{12})\varphi_i(1)\varphi_j(2)$$

In this special case of a single determinant wavefunction can re-write Γ in terms of γ as follows. First the summation is changed so that it's unrestricted

$$\Gamma(1,2|1,2) = \sum_{i<j}^{N} \varphi_i^*(1)\varphi_j^*(2)(1-\hat{P}_{12})\varphi_i(1)\varphi_j(2) = \frac{1}{2}\sum_{i,j}^{N} \varphi_i^*(1)\varphi_j^*(2)(1-\hat{P}_{12})\varphi_i(1)\varphi_j(2)$$

then

$$\Gamma(1,2|1,2) = \frac{1}{2}\sum_{i,j}^{N} \varphi_i^*(1)\varphi_j^*(2)(1-\hat{P}_{12})\varphi_i(1)\varphi_j(2) = \frac{1}{2}\left(\gamma(1,1)\gamma(2,2) - \gamma(2,1)\gamma(1,2)\right)$$

Being able to express Γ in terms of γ is a property of the Hartree-Fock wavefunction and reflects the limited electron correlation in such a wavefunction. For example for totally uncorrelated motion of the electrons we expect

$$\int \psi(1,2,\cdots,N)\psi^*(1,2,\cdots,N)\,d\tau(3,\cdots,N) =$$
$$\left(\int \psi(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)\,d\tau(2,3,\cdots,N)\right)\left(\int \psi(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)\,d\tau(1,3,\cdots,N)\right)$$

or, in terms of the density matrices

$$\Gamma_{uncorr}(1,2|1,2) = \frac{1}{2}\frac{\gamma(1,1)\gamma(2,2)}{N(N-1)}$$

Rewriting the relationship between Γ and γ we express the effect of electron correlation due to antisymmetry as $\tau(1,2)$

$$\Gamma(1,2|1,2) = \tau(1,2)\Gamma(1,2|1,2)_{uncorr} = \frac{1}{2}\frac{\gamma(1,1)\gamma(2,2)}{N(N-1)}\tau(1,2)$$

where

$$\tau(1,2) = \frac{N}{N-1}\left(1 - \frac{\gamma(1,2)\gamma(2,1)}{\gamma(1,1)\gamma(2,2)}\right)$$

The analysis of the two-electron density matrix is a bit more complicated. Using the general form for a single determinant wave-function

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

and the definition of γ we may write for the UHF function

$$\begin{aligned}
\Gamma_{UHF}(1,2|1,2) = {} & P^{\alpha\alpha;\alpha\alpha}(\vec{r}_1,\vec{r}_2)\alpha(1)\alpha^*(1)\alpha(2)\alpha^*(2) + \\
& P^{\alpha\alpha;\beta\beta}(\vec{r}_1,\vec{r}_2)\alpha(1)\alpha^*(1)\beta(2)\beta^*(2) + P^{\beta\beta;\alpha\alpha}(\vec{r}_1,\vec{r}_2)\beta(1)\beta^*(1)\alpha(2)\alpha^*(2) + \\
& P^{\alpha\beta;\beta\alpha}(\vec{r}_1,\vec{r}_2)\alpha(1)\beta^*(1)\beta(2)\alpha^*(2) + P^{\beta\alpha;\alpha\beta}(\vec{r}_1,\vec{r}_2)\beta(1)\alpha^*(1)\alpha(2)\beta^*(2) + \\
& P^{\beta\beta;\beta\beta}(\vec{r}_1,\vec{r}_2)\beta(1)\beta^*(1)\beta(2)\beta^*(2)
\end{aligned}$$

where

$$P^{\alpha\alpha;\alpha\alpha}(\vec{r}_1,\vec{r}_2) = \frac{1}{2}\left(\rho^\alpha(\vec{r}_1)\rho^\alpha(\vec{r}_2) - \sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\alpha}\varphi_i(\vec{r}_1)\varphi_j^*(\vec{r}_1)\varphi_j(\vec{r}_2)\varphi_i^*(\vec{r}_2)\right)$$

$$P^{\alpha\alpha;\beta\beta}(\vec{r}_1,\vec{r}_2) = \frac{1}{2}\rho^\alpha(\vec{r}_1)\rho^\beta(\vec{r}_2)$$

$$P^{\beta\beta;\alpha\alpha}(\vec{r}_1,\vec{r}_2) = \frac{1}{2}\rho^\beta(\vec{r}_1)\rho^\alpha(\vec{r}_2)$$

$$P^{\alpha\beta;\beta\alpha}(\vec{r}_1,\vec{r}_2) = -\frac{1}{2}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\varphi_i(\vec{r}_1)\phi_j^*(\vec{r}_1)\phi_j(\vec{r}_2)\varphi_i^*(\vec{r}_2)$$

$$P^{\beta\alpha;\alpha\beta}(\vec{r}_1,\vec{r}_2) = -\frac{1}{2}\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\alpha}\phi_i(\vec{r}_1)\varphi_j^*(\vec{r}_1)\varphi_j(\vec{r}_2)\phi_i^*(\vec{r}_2)$$

and

$$P^{\beta\beta;\beta\beta}(\vec{r}_1,\vec{r}_2) = \frac{1}{2}\left(\rho^\beta(\vec{r}_1)\rho^\beta(\vec{r}_2) - \sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\beta}\phi_i(\vec{r}_1)\phi_j^*(\vec{r}_1)\phi_j(\vec{r}_2)\phi_i^*(\vec{r}_2)\right)$$

Note that $P^{\alpha\beta;\beta\alpha}(\vec{r}_1,\vec{r}_2) = \left(P^{\beta\alpha;\alpha\beta}(\vec{r}_1,\vec{r}_2)\right)^*$

These components of $\Gamma(1,2|1,2)$ have the following interpretation:

$P^{\alpha\alpha;\alpha\alpha}(\vec{r}_1,\vec{r}_2)dV_1dV_2$ represents the probability that an electron with α spin will be at the terminus of $\vec{r}_1$ in the volume element dV_1 while simultaneously another electron, also with α spin will be at the terminus of $\vec{r}_2$ in the volume element dV_2. $P^{\alpha\alpha;\beta\beta}(\vec{r}_1,\vec{r}_2)dV_1dV_2$ represents the probability that an electron with α spin will be at the terminus of $\vec{r}_1$ in the volume element dV_1 while simultaneously another electron, with β spin will be at the terminus of $\vec{r}_2$ in the volume element dV_2. $P^{\beta\beta;\alpha\alpha}(\vec{r}_1,\vec{r}_2)dV_1dV_2$ and $P^{\beta\beta;\beta\beta}(\vec{r}_1,\vec{r}_2)dV_1dV_2$ have similar interpretations. However its not clear how one should interpret the terms $P^{\alpha\beta;\beta\alpha}(\vec{r}_1,\vec{r}_2)dV_1dV_2$ and $P^{\beta\alpha;\alpha\beta}(\vec{r}_1,\vec{r}_2)dV_1dV_2$. Note the normalization of these probabilities

$$\int P^{\alpha\alpha;\alpha\alpha}(\vec{r}_1,\vec{r}_2)dV_1\,dV_2 = \frac{1}{2}N_\alpha\left(N_\alpha-1\right)$$

$$\int P^{\beta\beta;\beta\beta}(\vec{r}_1,\vec{r}_2)dV_1\,dV_2 = \frac{1}{2}N_\beta\left(N_\beta-1\right)$$

$$\int P^{\alpha\alpha;\beta\beta}(\vec{r}_1,\vec{r}_2)dV_1\,dV_2 = \int P^{\beta\beta;\alpha\alpha}(\vec{r}_1,\vec{r}_2)dV_1\,dV_2 = \frac{1}{2}N_\alpha N_\beta$$

$$\int P^{\alpha\beta;\alpha\beta}(\vec{r}_1,\vec{r}_2)dV_1\,dV_2 = -\frac{1}{2}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int \varphi_i(\vec{r}_1)\phi_j^*(\vec{r}_1)\phi_j(\vec{r}_2)\varphi_i^*(\vec{r}_2)\,dV_1\,dV_2$$

Since the α & β orbitals are not eigenfunctions of the same Fock operator they need not be orthogonal and so

$$\Delta_{ij} = \int \varphi_i^*(\vec{r})\phi_j(\vec{r})\,dV$$

and therefore

$$\int P^{\alpha\beta;\beta\alpha}(\vec{r}_1,\vec{r}_2)dV_1\,dV_2 = -\frac{1}{2}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\Delta_{ij}\Delta_{ij}^* = -\frac{1}{2}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\left|\Delta_{ij}\right|^2$$

In a similar fashion

$$\int P^{\beta\alpha;\alpha\beta}(\vec{r}_1,\vec{r}_2)dV_1\,dV_2 = -\frac{1}{2}\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\alpha}\Delta_{ji}\Delta_{ji}^* = -\frac{1}{2}\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\alpha}\left|\Delta_{ji}\right|^2$$