**One and two particle density matrices for single determinant HF wavefunctions**

**One particle density matrix**

Given the Hartree-Fock wavefunction

\[ \psi(1,2,3,\cdots,N) = \hat{A}\phi_1(1)\phi_2(2)\phi_3(3)\cdots\phi_N(N) \]

The electronic energy is

\[ \langle \psi | \hat{H} | \psi \rangle = \sum_{i=1}^{N} \langle \phi_i(1) | \hat{j}(1) | \phi_i(1) \rangle + \sum_{i<j} \langle \phi_i(1) \phi_j(2) | g(1,2)(1-\hat{P}_{12}) | \phi_i(1) \phi_j(2) \rangle \]

The one electron contribution may be written as

\[ \sum_{i=1}^{N} \langle \phi_i(1) | \hat{f}(1) | \phi_i(1) \rangle = \int d\tau(1) \hat{f}(1) \sum_{i=1}^{N} \phi_i(1) \phi_i^*(1') \bigg|_{\tau \rightarrow 1} \]

from which we deduce

\[ \gamma(1,1') = \sum_{i=1}^{N} \phi_i(1) \phi_i^*(1') \]

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

\[ \phi_1(1) = \phi_1(\vec{r}_1)\alpha(1), \quad \phi_2(1) = \phi_1(\vec{r}_1)\beta(1), \quad \phi_3(1) = \phi_2(\vec{r}_2)\alpha(1), \cdots, \quad \phi_N(1) = \phi_{N/2}(\vec{r}_{N/2})\beta(1) \]

and the one particle density matrices becomes

\[ \gamma_{\text{RHF}}(1,1') = \sum_{i=1}^{N/2} \phi_i(\vec{r}_1)\phi_i^*(\vec{r}_{1'}) \left( \alpha(1)\alpha^*(1') + \beta(1)\beta^*(1') \right) \]

and so the electron density may be written as

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

where \( \rho_{\text{RHF}}^\alpha(\vec{r}) \) and \( \rho_{\text{RHF}}^\beta(\vec{r}) \) are the densities of \( \alpha \) & \( \beta \) 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 \textit{unrestricted} HF wavefunction
\[
\psi_{UHF}(1,2,3,\cdots,N) = \hat{A} \left( \chi_1(\alpha(1)\chi_2(\alpha(2))\cdots\chi_{N_a}(\alpha(\alpha(N_a + 1))\phi_1(\beta(N_a + 2))\phi_2(\beta(N_a + 2))\cdots\phi_{N_\beta}(\beta(N_a + N_\beta)) \right)
\]

Where \( \{\chi_i\}_{i=1}^{N_a} \) and \( \{\phi_i\}_{i=1}^{N_\beta} \) are the \( \alpha \) & \( \beta \) spatial orbitals, then the spin densities \( \rho_{UHF}^\alpha(\vec{r}) \) and \( \rho_{UHF}^\beta(\vec{r}) \) are not the same
\[
\rho_{UHF}^\alpha(\vec{r}) = \sum_{i=1}^{N_a} \chi_i(\vec{r})\chi_i^*(\vec{r}) \quad \text{&} \quad \rho_{UHF}^\beta(\vec{r}) = \sum_{j=1}^{N_\beta} \phi_j(\vec{r})\phi_j^*(\vec{r})
\]

and at a given point \( \vec{r} \) there is an imbalance in the number of \( \alpha \) & \( \beta \) 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
\[
\int Q(\vec{r}) dV = \int (\rho_{UHF}^\alpha(\vec{r}) - \rho_{UHF}^\beta(\vec{r})) dV = N_\alpha - N_\beta
\]

\textit{Two particle density matrices}

We may rewrite the two-electron contribution to the energy of a single determinant wavefunction as
\[
\sum_{i<j}^N \langle \phi_i(1)\phi_j(2)\rangle_g(1,2)(1-\hat{P}_{12})\mid \phi_i(1)\phi_j(2) \rangle = \int d\tau(1,2)g(1,2)\sum_{i<j}^N \phi_i^*(1)\phi_j^*(2)(1-\hat{P}_{12})\phi_i(1)\phi_j(2)
\]
that allows us to write the two-particle density matrix as
\[ \Gamma(1,2|\text{l},2) = \sum_{i<j}^{N} \phi_i^*(1) \phi_j^*(2)(1 - \hat{P}_{12}) \phi_i(1) \phi_j(2) \]

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

\[ \Gamma(1,2|\text{l},2) = \sum_{i<j}^{N} \phi_i^*(1) \phi_j^*(2)(1 - \hat{P}_{12}) \phi_i(1) \phi_j(2) = \frac{1}{2} \sum_{i,j}^{N} \phi_i^*(1) \phi_j^*(2)(1 - \hat{P}_{12}) \phi_i(1) \phi_j(2) \]

then

\[ \Gamma(1,2|\text{l},2) = \frac{1}{2} \sum_{i,j}^{N} \phi_i^*(1) \phi_j^*(2)(1 - \hat{P}_{12}) \phi_i(1) \phi_j(2) = \frac{1}{2} (\gamma(1,1) \gamma(2,2) - \gamma(2,1) \gamma(1,2)) \]

Being able to express \( \Gamma \) in terms of \( \gamma \) 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

\[ \Gamma_{\text{uncorr}}(1,2|\text{l},2) = \frac{1}{2} \frac{\gamma(1,1) \gamma(2,2)}{N(N-1)} \]

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

\[ \Gamma(1,2|\text{l},2) = \tau(1,2) \Gamma(1,2|\text{l},2)_{\text{uncorr}} = \frac{1}{2} \frac{\gamma(1,1) \gamma(2,2)}{N(N-1)} \tau(1,2) \]

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
\[
\Gamma(1,2|1,2) = \frac{1}{2}(\gamma(1,1)\gamma(2,2) - \gamma(2,1)\gamma(1,2))
\]

and the definition of \( \gamma \) we may write for the UHF function

\[
\Gamma_{UHF}(1,2|1,2) = P^{\alpha\alpha,\alpha\alpha}(\vec{r}_1,\vec{r}_2)\alpha(1)\alpha^*(1)\alpha(2)\alpha^*(2) + P^{\alpha\beta,\beta\alpha}(\vec{r}_1,\vec{r}_2)\alpha(1)\beta(2)\beta^*(2) + P^{\beta\alpha,\alpha\beta}(\vec{r}_1,\vec{r}_2)\beta(1)\alpha^*(1)\alpha(2)\beta^*(2) + P^{\beta\beta,\alpha\beta}(\vec{r}_1,\vec{r}_2)\beta(1)\beta^*(1)\beta(2)\beta^*(2)
\]

where

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

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

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

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

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

and

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

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

\[
\int P^{\alpha\alpha}(\vec{r}_1, \vec{r}_2) dV_1 dV_2 = \frac{1}{2} N_\alpha (N_\alpha - 1)
\]

\[
\int P^{\beta\beta}(\vec{r}_1, \vec{r}_2) dV_1 dV_2 = \frac{1}{2} N_\beta (N_\beta - 1)
\]

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

\[
\int P^{\alpha\beta\alpha}(\vec{r}_1, \vec{r}_2) dV_1 dV_2 = \int \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \phi_i^*(\vec{r}_1) \phi_j^*(\vec{r}_1) \phi_j(\vec{r}_2) \phi_i(\vec{r}_2) dV_1 dV_2
\]

Since the \( \alpha \) & \( \beta \) orbitals are not eigenfunctions of the same Fock operator they need not be orthogonal and so

\[
\Delta_{ij} = \int \phi_i^*(\vec{r}) \phi_j(\vec{r}) dV
\]

and therefore

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

In a similar fashion

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