

### *Natural Orbitals for the $H_2$ molecule in the Heitler-London approximation*

Lets calculate the natural orbitals as a function of internuclear separation for  $H_2$  using the Heitler-London wavefunction

$$\psi(1,2) = \frac{a(1)b(2) + b(1)a(2)}{\sqrt{2 + 2S_{ab}^2}} \left( \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \right)$$

where  $a$  &  $b$  are atomic orbitals on center  $a$  and  $b$  and  $S_{ab} = \langle a|b \rangle$  is the overlap between these orbitals. In the original Heitler-London study the orbitals were kept as  $H$  1s functions for all inter-nuclear separations and while this wave-function is accurate at large separations it becomes increasingly less so as the as the bond gets shorter. In more recent applications the orbitals are optimized at each separation and the resulting wave-function (called a GVB wave-function) is rather good. The subsequent formalism is the same for either scenario. To find the density matrix for this wave-function we return to its definition and write

$$\gamma(1,1') = 2 \int \psi(1,2) \psi^*(1',2) dV(2) d\xi(1)$$

The spin integration contributes 1 and the subsequent spatial integration over electron 2 results in

$$\gamma(1,1') = \frac{a(1)a(1') + a(1)b(1')S_{ab} + b(1)a(1')S_{ab} + b(1)b(1')}{1 + S_{ab}^2}$$

or

$$\gamma(1,1') = \chi(1) A \chi^+(1')$$

where we have defined the row vector  $\chi(1) = (a(1) \ b(1))$  and its adjoint and the two by two matrix

$$A = \frac{1}{D} \begin{pmatrix} 1 & S_{ab} \\ S_{ab} & 1 \end{pmatrix}$$

with  $D = 1 + S_{ab}^2$ . The natural orbitals of the system must be linear combinations of  $a$  &  $b$  so lets write this relationship as  $\bar{\varphi} = \bar{\chi} C$  where the natural orbitals are the elements of the vector  $\varphi = (\varphi_1 \ \varphi_2)$  and  $C$  is to be determined. We then have the eigenvalue equation

$$\int \bar{\chi}(1) A \bar{\chi}^+(1') \bar{\chi}(1') \bar{C}_i dV(1') = \lambda_i \bar{\chi}(1) \bar{C}_i$$

and after integration

$$\bar{\chi}(1)(A\Delta\bar{C}_i - \lambda_i\bar{C}_i) = 0$$

where  $\Delta = \langle \bar{\chi} | \bar{\chi} \rangle = \begin{pmatrix} 1 & S_{ab} \\ S_{ab} & 1 \end{pmatrix}$

The coefficients,  $C$ , that define the natural orbitals and the occupation numbers  $\lambda_i$  are determined by the eigenvalue equation

$$A\Delta\bar{C}_i = \lambda_i\bar{C}_i$$

In this problem  $A = \frac{\Delta}{D}$ , so we need to solve  $\Delta^2\bar{C}_i = \lambda_i D\bar{C}_i$ . The results are

$$C = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \& \lambda = \begin{pmatrix} \frac{(1+S_{ab})^2}{(1+S_{ab}^2)} & 0 \\ 0 & \frac{(1-S_{ab})^2}{(1+S_{ab}^2)} \end{pmatrix}$$

The natural orbitals are not normalized and if we normalize them to unity and label them according to their inversion symmetry we have

$$\varphi_g = \frac{a+b}{\sqrt{2+2S_{ab}}} \text{ with the occupation number } \lambda_g = \frac{(1+S_{ab})^2}{1+S_{ab}^2} \text{ and}$$

$$\varphi_u = \frac{a-b}{\sqrt{2-2S_{ab}}} \text{ with the occupation number } \lambda_u = \frac{(1-S_{ab})^2}{1+S_{ab}^2}$$

The electron density associated with this wavefunction is

$$\eta(\vec{r}) = \lambda_g \varphi_g^2(\vec{r}) + \lambda_u \varphi_u^2(\vec{r})$$