Electron Density and Natural Orbitals

A very convenient way of constructing the electron density for a system is to use the natural orbitals of the one particle density matrix $\gamma(1,1')$, These are the eigenfunctions of $\gamma(1,1')$ and since the indices on this matrix are continuous the eigenvalue problem for such a matrix is formulated in terms of the integral equation

$$\int \gamma(1,1')\varphi_i(1')d\tau(1') = \lambda\varphi_i(1)$$

where $\varphi_i(1)$ is the eigenfunction or natural orbital and λ_i is the eigenvalue of the natural orbital. These eigenvalues are often called the occupation numbers of the NO's. The natural orbitals and their eigenvalues are important because the spin density can in general be written as a sum of the squares of the natural orbitals weighted by the occupation numbers. So we can write

$$\eta(1) = \gamma(1,1) = \sum_{i=1} \lambda_i\varphi_i(1)\varphi_i^*(1)$$

We may show this as follows. If we are given $\gamma(1,1')$ we may solve for $\varphi(1)$ and λ by expanding them, as well as $\gamma(1,1')$ in a complete set of one-particle functions and discretizing the problem. Note that if $\gamma(1,1')$ is obtained from an approximate wave function, which has been constructed from a set of orthonormal orbitals $\{\phi_\mu\}_{\mu=1}^{M}$ this is a complete set in so far as the approximate $\gamma(1,1')$ is concerned. This places very few restrictions on $\gamma(1,1')$ as it may be obtained from an HF, CI, CC, etc. wave function. We first expand $\gamma(1,1')$

$$\gamma(1,1') = \sum_{\mu,\nu}^{M} \phi_\mu(1)\gamma_{\mu\nu}\phi_\nu^*(1')$$

or

$$\gamma(1,1') = \vec{\boldsymbol{\phi}}(1)\boldsymbol{\gamma}\vec{\boldsymbol{\phi}}^{+}(1')$$

where $\vec{\boldsymbol{\phi}}(1) = \left(\phi_1(1)\phi_2(1)\phi_3(1)\cdots\phi_M(1)\right)$ and

$$\vec{\phi}^{+}(1)=\begin{pmatrix}\phi_1^*(1)\\ \phi_2^*(1)\\ \vdots\\ \phi_M^*(1)\end{pmatrix}$$

and since we know $\gamma(1,1')$ we know the elements $\gamma_{\mu\nu}$ of the MxM matrix $\boldsymbol{\gamma}$. It's easy to see that $\boldsymbol{\gamma}$ is Hermitian. Expanding $\varphi(1)$ as

$$\varphi(1)=\sum_{\rho=1}^{M}\phi_\rho(1)A_\rho=\vec{\boldsymbol{\phi}}(1)\vec{\boldsymbol{A}}$$

where $$\vec{\boldsymbol{A}}=\begin{pmatrix}A_1\\ A_2\\ \vdots\\ A_M\end{pmatrix}$$

and inserting these two expansions into the eigenvalue equation results in

$$\int d\tau(1')\sum_{\mu,\nu}^{M}\phi_\mu(1)\gamma_{\mu\nu}\phi_\nu^*(1')\sum_{\rho=1}^{M}\phi_\rho(1')A_\rho=\lambda\sum_{\rho=1}^{M}\phi_\rho(1)A_\rho$$

and after integration we have

$$\sum_{\mu,\rho}^{M}\phi_\mu(1)\gamma_{\mu\rho}A_\rho=\lambda\sum_{\rho=1}^{M}\phi_\rho(1)A_\rho\equiv\lambda\sum_{\mu=1}^{M}\phi_\mu(1)A_\mu$$

or

$$\sum_{\mu=1}^{M}\phi_\mu(1)\sum_{\rho=1}^{M}\left(\gamma_{\mu\rho}A_\rho-A_\mu\lambda\delta_{\mu\rho}\right)=0$$

Since the set $\{\phi_\mu\}_{\mu=1}^{M}$ is orthogonal we have

$$\sum_{\rho=1}^{M}\left(\gamma_{\mu\rho}A_\rho-A_\mu\lambda\delta_{\mu\rho}\right)=0$$

or, more compactly

$$\boldsymbol{\gamma}\vec{\boldsymbol{A}}_i = \lambda_i \vec{\boldsymbol{A}}_i \ , i = 1,2,\cdots,M$$

Where we recognize that the Hermetian matrix has M eigenvectors. The M functions

$$\varphi_i(1) = \sum_{\rho=1}^{M} \phi_\rho(1) A_{\rho i}$$

are the natural orbitals of the system and λ_i is the occupation number of the ith natural orbital, (NO). We can express the electron density in terms of the natural orbitals as follows. First rewrite the eigenvalue equation for $\boldsymbol{\gamma}$ as

$$\boldsymbol{\gamma A} = \boldsymbol{A\lambda}$$

where $$\boldsymbol{A} = \left(\vec{\boldsymbol{A}}_1 \vec{\boldsymbol{A}}_2 \vec{\boldsymbol{A}}_3 \cdots \vec{\boldsymbol{A}}_M\right)$$

is a row vector of the column vectors $\vec{\boldsymbol{A}}_i$ and $\boldsymbol{\lambda}$ is a diagonal matrix the elements of which are the occupation numbers, $\{\lambda_i\}_{i=1}^{M}$. Since $\boldsymbol{\gamma}$ is Hermetian, $\boldsymbol{A}$ is unitary and so

$$\boldsymbol{A}^+\boldsymbol{A} = \boldsymbol{1}$$

and

$$\boldsymbol{A}^+\boldsymbol{\gamma A} = \boldsymbol{\lambda}$$

Since $\vec{\boldsymbol{\varphi}}(1) = \vec{\boldsymbol{\phi}}(1)\boldsymbol{A}$ we have

$$\gamma(1,1') = \vec{\boldsymbol{\phi}}(1)\boldsymbol{\gamma}\vec{\boldsymbol{\phi}}^+(1') = \vec{\boldsymbol{\phi}}(1)\boldsymbol{A}\boldsymbol{A}^+\boldsymbol{\gamma}\boldsymbol{A}\boldsymbol{A}^+\vec{\boldsymbol{\phi}}^+(1') = \vec{\boldsymbol{\varphi}}(1)\boldsymbol{\lambda}\vec{\boldsymbol{\varphi}}^+(1') = \sum_{i=1}^{M} \lambda_i \varphi_i(1)\varphi_i^*(1')$$

and so the electron density is given by

$$\gamma(1,1) = \sum_{i=1}^{M} \lambda_i \varphi_i(1)\varphi_i^*(1)$$