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Note

NOTE ON THE DENSITY MATRIX FOR AN ARBITRARY NUMBER OF CLOSED SHELLS IN A BARE COULOMB FIELD

Pawel M. KOZLOWSKI
Department of Chemistry, University of Arizona, Tucson, Arizona 85721, USA

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Abstract

An explicit relation between the density matrix and its s-state part is analyzed for electron closed shells moving in a bare Coulomb potential. The density matrix has a simple separable form in terms of $r_1 + r_2$ and $|r_1 - r_2|$. It is demonstrated that for an arbitrary number of closed shells, the off-diagonal dependence is simply polynomial in the $|r_1 - r_2|$ coordinate.

The problem of expressing the density matrix $\gamma(\boldsymbol{r}_1, \boldsymbol{r}_2)$ in terms of the electron density $\rho(\boldsymbol{r})$ remains of considerable theoretical interest. The investigation of simple model systems, for example, noninteracting electrons moving in a bare Coulomb potential $V(r) = -Ze^2/r$, can be valuable in pointing the way to relations which may have approximate validity in more complex systems. It should be pointed out that for this model, a spatial generalization of Kato's theorem reads [1]

$$\frac{\partial \rho}{\partial r} = -\frac{2Z}{a_0}\rho_s(r), \quad a_0 = \frac{\hbar^2}{me^2}, \tag{1}$$

while the density matrix has the form [2]

$$\gamma(\boldsymbol{r}_1, \boldsymbol{r}_2) = -(x-y)^{-1}\left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y}\right)\left[xy\,\gamma_s\left(\frac{x}{2}, \frac{y}{2}\right)\right], \tag{2}$$

where

$$x = r_1 + r_2 + |\boldsymbol{r}_1 - \boldsymbol{r}_2|, \quad y = r_1 + r_2 - |\boldsymbol{r}_1 - \boldsymbol{r}_2|. \tag{3}$$

The density matrix depends on just two independent coordinates x and y rather than r_1, r_2 and r_{12}. This results from the existence of additional constants of motion

which is known as the Runge–Lenz vector [3]. The electron density itself and the full density matrix are determined solely by the density matrix for s states. One can make the above relation explicit and consider the form of the density matrix for particular shells. March and Santamaria [4] investigated the relation between the density matrix and density functional theory for K plus L shells. For K shells, the result is almost trivial:

$$\gamma(r_1, r_2) = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \exp\left(-\frac{Z}{a_0}(r_1 + r_2)\right), \tag{4}$$

while for K plus L shells, the matrix has the form

$$\gamma(r_1, r_2) = \rho\left(\frac{r_1 + r_2}{2}\right) + |r_1 - r_2|^2 F\left(\frac{r_1 + r_2}{2}\right), \tag{5}$$

where

$$F(r) = -\frac{1}{64\pi}\left(\frac{Z}{a_0}\right)^5 \exp\left(-\frac{Z}{a_0} r\right), \tag{6}$$

and $\rho(r)$ is the density. The above equation has some interesting features. Only the first term makes a contribution to the diagonal density, the second still contributes to the kinetic energy. The purpose of this note is to demonstrate that the density matrix for an arbitrary number of closed shells has the following structure:

$$\gamma(r_1, r_2) = \rho\left(\frac{r_1 + r_2}{2}\right) + |r_1 - r_2|^2 F_1\left(\frac{r_1 + r_2}{2}\right) + |r_1 - r_2|^4 F_2\left(\frac{r_1 + r_2}{2}\right) + \ldots + |r_1 - r_2|^{2n} F_n\left(\frac{r_1 + r_2}{2}\right). \tag{7}$$

Again, only the first term contributes to the diagonal density, eqs. (4) and (5) are particular cases of eq. (7).

In order to demonstrate that the density matrix has the structure given by eq. (7) for an arbitrary number of closed shells, let us consider the product of two s-type radial hydrogenic wave functions:

$$R_{n0}(r) R_{n0}(r') = C_{n0}^2 \exp\left(-\tfrac{1}{2}(q + q')\right) \frac{\mathrm{d}}{\mathrm{d}q} \frac{\mathrm{d}}{\mathrm{d}q'} \left[\exp(q + q') \frac{\mathrm{d}^n}{\mathrm{d}q^n} \frac{\mathrm{d}^n}{\mathrm{d}q'^n} \left[q^n q'^n \exp\left(-(q + q')\right)\right]\right], \tag{8}$$

where C_{n0} is a normalization factor and $q = (2Z/na_0)r$ (see [5] or any standard textbook). Performing the transformation to the new coordinates:

$$u = q + q', \tag{9}$$

$$v = q - q', \tag{10}$$

the product of the radial wave functions eq. (8) becomes

$$R_{n0}(r)R_{n0}(r') = C_{n0}^2 \frac{1}{4^n} \exp\left(-\tfrac{1}{2}u\right)\left(\frac{\partial^2}{\partial u^2} - \frac{\partial^2}{\partial v^2}\right)[\exp(u)W(u,v)], \tag{11}$$

where

$$W(u,v) = \left(\frac{\partial^2}{\partial u^2} - \frac{\partial^2}{\partial v^2}\right)^n \left[(u^2 - v^2)^n \exp(-u)\right]. \tag{12}$$

Using the binomial expansion, the last expression can be rewritten as

$$W(u,v) = \sum_j \sum_i (-1)^{i+j} \binom{n}{i} \binom{n}{j} \frac{\partial^{2(n-j)}}{\partial u^{2(n-j)}} \frac{\partial^{2j}}{\partial v^{2j}} \left(u^{2(n-i)} v^{2i} \exp(-u)\right). \tag{13}$$

In the last expression, the differentiation with respect to the v coordinate can be easily carried out and leads to the result

$$W(u,v) = \sum_j \sum_i b_{ij}^n v^{2(i-j)} \frac{\partial^{2(n-j)}}{\partial u^{2(n-j)}} \left(u^{2(n-i)} \exp(-u)\right), \tag{14}$$

where

$$b_{ij}^n = (-1)^{i+j}[2(i-j)]! \binom{n}{i} \binom{n}{j}. \tag{15}$$

By changing the summation indexes, i.e. $k = i + j$ and $l = i - j$, the v coordinate can be explicitly separated:

$$W(u,v) = \sum_l v^{2l} G_l(u), \tag{16}$$

with

$$G_l(u) = \sum_k \tilde{b}_{kl}^n \frac{\partial^{2(n-\frac{1}{2}(k-l))}}{\partial v^{2(n-\frac{1}{2}(k-l))}} \left(u^{2(n-\frac{1}{2}(k+l))} \exp(-u)\right). \tag{17}$$

Substituting the above result into eq. (11), the product of two s-type functions becomes

$$R_{n0}(r)R_{n0}(r') = C_{n0}^2 \frac{1}{4^n} \exp\left(-\tfrac{1}{2}u\right)\left(\frac{\partial^2}{\partial u^2} - \frac{\partial^2}{\partial v^2}\right)\left[\exp(u) \sum_l v^{2l} G_l(u)\right]. \tag{18}$$

Finally, performing differentiation in the last equation, one obtains:

$$R_{n0}(r)R_{n0}(r') = P(u;n) + \sum_{m=1} v^{2m} Q_m(u;n), \tag{19}$$

where

$$P(u;n) = C_{n0}^2 \frac{1}{4^n} \exp\left(\tfrac{1}{2}u\right) \frac{\partial^2}{\partial u^2} G_0(u) \tag{20}$$

and

$$Q_m(u;n) = C_{n0}^2 \frac{1}{4^n} \exp\left(\tfrac{1}{2}u\right)\left[\frac{\partial^2}{\partial u^2} G_m(u) + G_m(u) + 2(m+1)(2m+1)G_{m+1}(u)\right]. \tag{21}$$

Let us return to the expression for the density matrix given by eq. (2) and the coordinates given by eq. (3). Identify u as

$$u = r_1 + r_2, \tag{22}$$

and v as

$$v = |r_1 - r_2| \tag{23}$$

(i.e. $x = u + v$ and $y = u - v$), the expression for $\gamma(r_1, r_2)$ in terms of u and v becomes:

$$\gamma(r_1, r_2) = -(2v)^{-1} \frac{\partial}{\partial v}\left[(u^2 - v^2)\gamma_s\left(\frac{u+v}{2}, \frac{u-v}{2}\right)\right]. \tag{24}$$

Evidently, from eq. (19) the density matrix for s states takes the form

$$\gamma_s\left(\frac{u+v}{2}, \frac{u-v}{2}\right) = \sum_n P(u;n) + \sum_n \sum_{m=1} v^{2m} Q_m(u;n), \tag{25}$$

and finally the density matrix becomes:

$$\gamma(r_1, r_2) = \sum_n P(u;n) + \sum_{m=1} v^{2m} \sum_n (1 + m - u^2) Q_m(u;n). \tag{26}$$

We now identify $\sum_n P(u;n)$ as the density, i.e.

$$\sum_n P(u;n) = \rho\left(\frac{r_1 + r_2}{2}\right), \tag{27}$$

and

$$\sum_n (1 + m - u^2) Q_m(u;n) = F_m\left(\frac{r_1 + r_2}{2}\right), \tag{28}$$

then eq. (26) becomes identical to the equation for the density matrix given by formula (7).