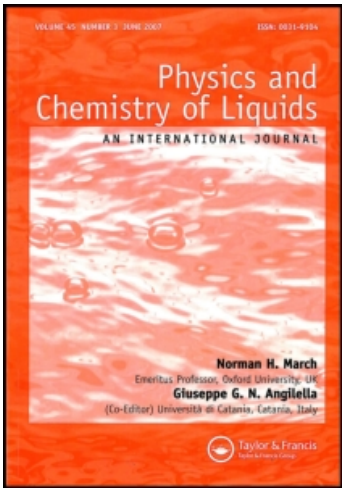

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Near-Diagonal Behaviour of First-order Density Matrix for *N* Closed Shells in a Bare Coulomb Field

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Letter

NEAR-DIAGONAL BEHAVIOUR OF FIRST-ORDER DENSITY MATRIX FOR N CLOSED SHELLS IN A BARE COULOMB FIELD

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When the first order density matrix is expanded to lowest order, it is shown that the lowest order term is characterized by a function $f(r)$ whose derivative can be expressed in terms of the diagonal electron density and the nuclear charge, for the case of N closed shells in a bare Coulomb field.

Keywords: Inhomogeneous electron liquid; Coulomb potential; electron density matrix

In a recent paper [1] we have shown that for an arbitrary number of closed shells in a bare Coulomb field, the derivative $t'(r)$ of the kinetic energy density $t(r)$ is given in terms of the ground-state electron density $n(r)$ by

$$t'(r) = \frac{1}{8}n''' - \frac{3}{4r^2}n' - \frac{3Z}{2r^2}n \qquad (1)$$

where the Coulomb potential energy is $-Z/r$ in which non-interacting electrons move.

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Subsequently [2] an expression for the kinetic energy tensor T_{ij} was derived, in the form

$$T_{ij} = \frac{r_i r_j}{r^2} t(r) + \left[\frac{3 r_i r_j}{r^2} - \delta_{ij} \right] F(r), \tag{2}$$

where the derivative of the function F is given by

$$F' = \frac{1}{8r} n'' + \frac{1}{4r^2} n' + \frac{Z}{2r^2} n. \tag{3}$$

The focus of the present letter is the near diagonal behaviour of the first-order density matrix (1DM) which can be expanded as [3]

$$\rho(\vec{r}, \vec{r}') = n\left(\frac{r + r'}{2} \right) + f\left(\frac{r + r'}{2} \right) |\vec{r} - \vec{r}'|^2 + O(|\vec{r} - \vec{r}'|^4). \tag{4}$$

One can then show that in terms of the function $f(r)$ in Eq. (4) the kinetic energy tensor

$$T_{ij} = \frac{1}{2} \left[\frac{\partial^2}{\partial r_i \partial r'_j} \rho(\vec{r}, \vec{r}') \right]_{\vec{r}' = \vec{r}} \tag{5}$$

can be expressed in the form

$$T_{ij} = \frac{r_i r_j}{8r^2} n'' - \delta_{ij} f. \tag{6}$$

Comparing Eqs. (6) and (2) and using Eq. (3) one is led to the result for the derivative of the function $f(r)$ in the density matrix expansion (4) as

$$f' = \frac{1}{4r^2} n' + \frac{Z}{2r^2} n \tag{7}$$

An alternative form of f' results from the use in Eq. (7) of the generalized Kato theorem of one of us [4]

$$n'(r) = -2Z n_s(r) \tag{8}$$

where $n_s(r)$ is the s-state density component of the total density $n(r)$. Inserting Eq. (8) into Eq. (7) yields immediately

$$f'(r) = \frac{Z}{2r^2}\left[n(r) - n_s(r)\right]. \tag{9}$$

In discussions of interacting electron assemblies, the 1DM is assuming major importance [5]. One needs to find, in fact, the 'near-diagonal' behaviour in terms of the electron density to turn a density matrix theory of the exchange-correlation potential $V_{xc}(\vec{r})$ into density functional form.

For the admittedly very simple model of a bare Coulomb potential, Eq. (4), supplemented by Eq. (7), achieves that aim. While the present result is valid for an arbitrary number of closed shells, for He-like ions of large atomic number Z, Gál, March and Nagy [6] have constructed the 1DM in terms of its diagonal density, with inclusion of weak electron–electron interaction. However, their result is restricted to the two-electron case.

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