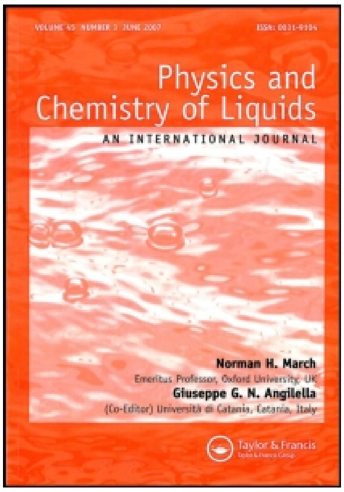

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TEN-ELECTRON CENTRAL FIELD PROBLEM: AN INHOMOGENEOUS ELECTRON LIQUID

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Recent work has been carried out on the exchange energy density $\varepsilon_x(r)$ of a ten-electron atomic ion in the (bare Coulomb) limit of large atomic number Z [Howard, I. A. *et al.* (2000). *Phys. Rev. A*, **62**, 062512]. This analytical study of $\varepsilon_x(r)$ was made possible by the existence of a closed form of the first-order (idempotent) density matrix (1DM).

Here, some generalizations are effected to a central potential energy $V(r)$ which (a) localizes the ten electrons and (b) yields closed K and L shells for these ten electrons occupying the lowest eigenstates with spin compensation. In particular, it is shown that p-shell properties alone determine the 1DM in this example of a confined inhomogeneous electron liquid.

Keywords: Inhomogeneous electron liquid; Density matrix

I. BACKGROUND AND INTRODUCTION

In very recent work, the exchange energy density $\varepsilon_x(r)$ of a ten-electron atomic ion in the (bare Coulomb) limit of large Z has been calculated analytically [1]. This has proved possible because of the existence of a relatively simple analytical form of the first-order idempotent density

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matrix [1DM] $\gamma(\mathbf{r}, \mathbf{r}')$, namely [2]

$$\gamma_{\text{coul}}(\mathbf{r},\mathbf{r}') = \rho\left(\frac{r+r'}{2}\right) + F\left(\frac{r+r'}{2}\right)|\mathbf{r}-\mathbf{r}'|^2. \tag{1.1}$$

The simplicity of the variables in Eq. (1.1) has to do with the existence of an additional constant of motion, the so-called Runge-Lenz vector [3] for the bare Coulomb field limit underlying Eq. (1.1). In that equation, $\rho(r)$ is the bare Coulomb density, while $F(r)$ is related to this quantity plus the single-particle kinetic energy density, $t[\rho]$, by

$$F(r) = \frac{1}{24}\rho''(r) - \frac{1}{3}\frac{m}{\hbar^2}t(r). \tag{1.2}$$

In Eq. (1.2), $t(r)$ is defined by the (always positive) form analogous to $(\nabla\psi)^2$ in terms of wave functions. In fact, in the bare Coulomb limit of Ref. [2],

$$F_{\text{coul}}(r) = -\frac{2}{64\pi}\left[\frac{Z}{a_o}\right]^5 \exp(-Zr/a_o) \tag{1.3}$$

for doubly occupied states, where Z is the (large) atomic number in this (non-relativistic) theory.

Defining the total kinetic energy T as

$$T = \int t(r)d\mathbf{r} \tag{1.4}$$

it was already shown in Ref. [2] that

$$T = \frac{\pi\hbar^2}{m}\int_0^\infty \rho(r)dr - \frac{12\pi\hbar^2}{m}\int_0^\infty F(r)r^2dr. \tag{1.5}$$

In this (bare Coulomb field) example, Eq. (1.5) is known to represent the total kinetic energy as a sum of T_o ($l=0$) and T_1 ($l=1$) contributions, the result T_o being simply the first term on the right-hand side of Eq. (1.5), as was established in Ref. [4].

The aim of the present work is to effect the generalization of Eqs. (1.1) and (1.5) to allow for a central field defined by a one-body potential energy $V(r)$.

II. FIRST-ORDER DENSITY MATRIX FOR TEN ELECTRONS (CLOSED K PLUS L SHELLS) FOR A GENERAL CENTRAL FIELD

For, say, Ne-like ions with atomic number Z, described in density functional theory (DFT) by a one-body potential $V(r)$ having the form

$$V(r) = V_{\mathrm{Hartree}}(r) + \frac{\delta E_{xc}[\rho]}{\delta\rho(r)} \tag{2.1}$$

where $E_{xc}[\rho]$ is the (as yet unknown) exchange-correlation energy functional, Schrödinger's one-electron equation with $V(r)$ inserted (equivalent to the so-called Slater-Kohn-Sham equations [5, 6] if that $V(r)$ giving the exact ground-state density is known) yields wavefunctions $\psi_{10}(r)$, $\psi_{20}(r)$, and p-state radial wavefunction $R_{21}(r)$ times spherical harmonics $Y_{1m}(\theta, \phi)$, with $m = -1, 0$, and 1. Taking $R_{21}(r)$ to be normalized to $(1/4\pi)$, to account for the spherical harmonic prefactor and for the three p-states, one can write the 1DM as

$$\begin{aligned}\gamma(\mathbf{r},\mathbf{r}') &= 2[\psi_{10}(r)\psi_{10}(r') + \psi_{20}(r)\psi_{20}(r')]\\ &\quad + 6R_{21}(r)R_{21}(r')\left[\frac{xx' + yy' + zz'}{rr'}\right].\end{aligned} \tag{2.2}$$

But, (recalling Eq. (1.1) in the bare Coulomb limit system of ten electrons) we know that

$$\begin{aligned}|\mathbf{r}-\mathbf{r}'|^2 &= (x-x')^2 + (y-y')^2 + (z-z')^2\\ &= (x^2+y^2+z^2) + (x'^2+y'^2+z'^2) - 2[xx'+yy'+zz']\end{aligned} \tag{2.3}$$

and hence Eq. (2.2) is readily rewritten as

$$\begin{aligned}\gamma(\mathbf{r},\mathbf{r}') &= \Gamma(r,r') - 3\frac{R_{21}(r)}{r}\frac{R_{21}(r')}{r'}|\mathbf{r}-\mathbf{r}'|^2\\ &\equiv \Gamma(r,r') - 3f(r)f(r')|\mathbf{r}-\mathbf{r}'|^2.\end{aligned} \tag{2.4}$$

The shape of Eq. (2.4) is valid for general $V(r)$ and the important fact which it reveals is that the function multiplying the term $|\mathbf{r}-\mathbf{r}'|^2$ is factorizable.

Returning to Eq. (1.1) and using the explicit (bare Coulomb) form (1.3) one sees that

$$f(r)_{\text{Coulomb}} = \frac{1}{4\sqrt{6\pi}}\left[\frac{Z}{a_o}\right]^{(5/2)} \exp(-Zr/2a_o), \tag{2.5}$$

and this is just the (appropriately normalized) radial wavefunction $R_{21}(r)$ of the p electrons divided by r. In marked contrast, $\Gamma(r, r')$ in the general 10-electron form (2.4) of the 1DM for a general central potential energy $V(r)$ is not factorizable and is of a more complicated form than $f(r)$. It is therefore important to enquire what properties associated with the 1DM (2.4) can be characterized by $f(r)$, which in turn determines the p shell ground state properties.

Evidently from Eqs. (2.2)–(2.4), one can write

$$\Gamma(r,r') = \Gamma_o(r,r') + 3f(r)f(r')(r^2 + r'^2) \tag{2.6}$$

where $\Gamma_o(r, r')$ is just the s-state ($l = 0$) density matrix. Clearly it follows that

$$\Gamma(r,r')|_{r'=r} \equiv \rho(r) = \rho_o(r) + 6r^2f^2(r) \tag{2.7}$$

the p-wave density $\rho_{l=1}(r) \equiv \rho_1(r)$ being given from Eq. (2.7) by

$$\rho_1(r) = 6r^2f^2(r). \tag{2.8}$$

Thus Eq. (2.6) can be rewritten in terms of the p ($l = 1$) density as

$$\begin{aligned}\Gamma(r,r') &= \Gamma_o(r,r') + 3\frac{\sqrt{\rho_1(r)}}{\sqrt{6}r}\frac{\sqrt{\rho_1(r')}}{\sqrt{6}r'}(r^2 + r'^2)\\ &= \Gamma_o(r,r') + \frac{1}{2}\frac{\sqrt{\rho_1(r)}}{r}\frac{\sqrt{\rho_1(r')}}{r'}[(r + r')^2 - 2rr']\\ &= \Gamma_o(r,r') + \frac{1}{2}\frac{\sqrt{\rho_1(r)}}{r}\frac{\sqrt{\rho_1(r')}}{r'}(r + r')^2 - \sqrt{\rho_1(r)}\sqrt{\rho_1(r')}.\end{aligned} \tag{2.9}$$

Putting $r' = r$ in Eq. (2.9) yields back simply $\rho(r) = \rho_o(r) + \rho_1(r)$, as it must. Finally, we show in the latter part of Appendix C that ψ_{10} and ψ_{20}, which determine the s-state matrix $\Gamma_o(r, r')$ through Eqs. (2.2) and (2.6), are both determined by $\rho_1(r)$. Hence, in principle, $\Gamma(r, r')$ in

Eq. (2.9) is a functional of $\rho_1(r)$ and thus, through (2.4) and (2.8), so is $\gamma(\mathbf{r}, \mathbf{r}')$.

III. SUMMARY AND FUTURE DIRECTIONS

The shape of the first-order density matrix (1DM) $\gamma(\mathbf{r}, \mathbf{r}')$ for filled K and L shells is settled by Eq. (2.4), with the function $f(r)$ determined by the p-state electron density through Eq. (2.8). All the angular dependence is subsumed into the factor $|\mathbf{r}-\mathbf{r}'|^2$, for any general central potential energy $V(\mathbf{r})$. Furthermore, a proof has been given that the function $F(r, r')$ in Eq. (2.4) is also completely determined, but now in principle, by the p-state density $\rho_1(r)$. However, part of this dependence can be displayed explicitly, as in Eq. (2.9).

It is obviously tempting, for the future, to contemplate variational calculations based on the 1DM discussed in the present study, both for Ne-like atomic ions and for the 'almost spherical' molecule CH_4 (see March, 1952 [8], for the simplest density functional theory [DFT] of such a molecule, namely the Thomas-Fermi method). In such a variational aproach, one would want to exploit the fact, proved here, that $\gamma(\mathbf{r}, \mathbf{r}')$ is determined in principle solely by the p-state density $\rho_1(r)$. However, we must stress that, for a valid variational method based on the 1DM generated by a given $V(r)$ (ideally given by Eq. (2.1) in terms of the exchange-correlation energy functional $E_{xc}[\rho]$, if it should become known), the 1DM characterized by the p-state density $\rho_1(r)$ must be constructed to be an idempotent 1DM, *i.e.*, it must satisfy $\gamma^2=\gamma$. Even then, by direct use of such a 1DM, one could not transcend the Hartree-Fock ground-state energy without knowing the energy functional, the essential (unknown) part of which is, of course, $E_{xc}[\rho]$ in Eq. (2.1).

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IV. APPENDIX A: *S*-STATE AND TOTAL KINETIC ENERGY DENSITIES

The purpose of this Appendix is to obtain expressions for both the s-state kinetic energy density $t_s(r)$ and for the total kinetic energy density $t(r)$. The former will be obtained using Ref. [7] and is valid for any number of s-states and for a general central potential energy $V(r)$. We use throughout the positive definite forms (corresponding to the wave function expression (1/2) $(\nabla\psi)^2$) of $t_s(r)$ and $t(r)$.

A.1. *s*-state Kinetic Energy Density $t_s(r)$

From what is essentially the differential virial equation for s-states we find

$$\frac{\partial}{\partial r}(r^2 t_s(r)) - \frac{1}{8}\frac{\partial}{\partial r}(r^2\rho_s'') + \frac{1}{4}\rho_s' = -\frac{r^2}{2}\rho_s V'(r). \tag{A1.1}$$

This equation, valid for any number of occupied s-levels and any central potential $V(r)$, can be integrated to yield

$$t_s(r) = \frac{1}{8}\rho_s''(r) - \frac{1}{4r^2}\rho_s(r) + \frac{1}{2r^2}\int_r^\infty q^2\rho_s(q)V'(q)dq. \tag{A1.2}$$

This result becomes simple for the bare Coulomb field case, for which $V'(q) = Z/q^2$, and we also have the spatial generalization of Kato's theorem:

$$\frac{\partial\rho(r)}{\partial r} = -2Z\rho_s(r). \tag{A1.3}$$

Then the final term in Eq. (A1.2) can be readily evaluated and hence in this limiting case Eq. (A1.2) simplifies to read

$$t_s^{\text{Coul}}(r) = \frac{1}{4}\left[\frac{\rho(r) - \rho_s(r)}{r^2}\right] + \frac{\rho_s''}{8}. \tag{A1.4}$$

But also, for a given central potential energy $V(r)$, $t_s(r)$ can be calculated from Eq. (A1.2) without recourse to off-diagonal information. Eq. (A1.2), however, it should be stressed, is not of DFT form since $V(r)$ enters in an essential manner.

A.2. Total Kinetic Energy Density $t(r)$ for Spin-compensated $K + L$ Shell Occupancy Only

Using Eq. (8) of Ref. [7], which is, however, essentially a one-dimensional formalism, and the equation for t_s in Section A.1, one finds, after remembering that the truly three-dimensional $t(r)$ in the present paper differs from the definition in Ref. [7] by $(1/4)\nabla^2\rho$, and after some considerable manipulation, the result

$$\frac{\partial}{\partial r}[r^2 t] = \frac{r^2}{8}\rho''' + \frac{r}{4}\rho'' + \frac{3}{4}\rho' - \rho_s' + \frac{\rho - \rho_s}{r} - \frac{1}{2}r^2\rho V'. \tag{A2.1}$$

However, we must note here first that in Appendix B, differential equations for ρ and ρ_s are also constructed for this 10-electron problem. Secondly, for the Coulomb field limiting system, $\rho'(r) = -2Z\rho_s$ and hence it is then possible to eliminate $\rho_s(r)$ from Eq. (A2.1).

V. APPENDIX B: DIFFERENTIAL EQUATIONS FOR S AND P-STATE DENSITIES

For the p-states, since we have $\rho_1(r) = 6r^2 f^2(r)$ or $f(r) = \rho_1^{1/2}/\sqrt{6}r = R_{21}(r)/r$, we can write the radial Schrödinger equation (for $l = 1$) as

$$\frac{\partial^2}{\partial r^2}\left[\frac{r\rho_1^{1/2}}{\sqrt{6}}\right] + \frac{2m}{\hbar^2}\left[\varepsilon_{21} - V(r) - \frac{\hbar^2}{mr^2}\right]\frac{r\rho_1^{(1/2)}}{\sqrt{6}} = 0, \tag{B.1}$$

with ε_{21} the eigenvalue in the potential V. Rearranged and multiplied by $\rho_1^{1/2}$, this becomes

$$\frac{\partial^2\rho_1}{\partial r^2}-\frac{1}{2\rho_1}\left(\frac{\partial\rho_1}{\partial r}\right)^2+\frac{2}{r}\frac{\partial\rho_1}{\partial r}=-\frac{4m}{\hbar^2}\rho_1\left[\varepsilon_{21}-V(r)-\frac{\hbar^2}{mr^2}\right]. \tag{B.2}$$

For the s-states, we can write $\rho_o(r)=2(\psi_{10}^2(r)+\psi_{20}^2(r))$, so that, using the radial Schrödinger equation and the definition of the s-state kinetic energy $t_o(r)=\hbar^2(\psi_{10}'^2+\psi_{20}'^2)/m$, we have

$$\frac{\partial^2\rho_o}{\partial r^2}+\frac{2}{r}\frac{\partial\rho_o}{\partial r}=\frac{4m}{\hbar^2}t_o(r)-\frac{8m}{\hbar^2}\left(\varepsilon_{10}\psi_{10}^2+\varepsilon_{20}\psi_{20}^2-\frac{1}{2}\rho_oV(r)\right). \tag{B.3}$$

Taking a further derivative then yields

$$\frac{\partial\nabla^2\rho_o}{\partial r}=\frac{8m}{\hbar^2}\left[\frac{2t_o(r)}{r}+\frac{\partial t_o}{\partial r}+\frac{\rho_o}{2}\frac{\partial V}{\partial r}\right]. \tag{B.4}$$

VI. APPENDIX C: 'EQUATION OF MOTION' FOR *Γ*(*R*, *R'*) IN EQ. (2.9)

Allowing the Laplacian ∇_r^2 to act on $\Gamma(r, r')$ in Eq. (2.9) yields, after a short calculation,

$$\begin{aligned}\nabla_r^2\Gamma &= \nabla_r^2\Gamma_o+\frac{1}{2}\frac{\rho_1^{1/2}(r')}{r'}\left[\nabla_r^2\left\{\rho_1^{1/2}(r)\frac{(r^2+r'^2)}{r}\right\}\right]\\
&= \nabla_r^2\Gamma_o+\frac{\rho_1^{1/2}(r')\rho_1^{1/2}(r)}{rr'}+\frac{\rho_1^{1/2}(r')}{r'}\rho_1^{1/2}(r)\frac{\rho_1'(r)}{\rho_1(r)}\\
&\quad+\frac{1}{4}\frac{r^2+r'^2}{rr'}[\rho_1^{1/2}(r')\rho_1^{1/2}(r)]\frac{\rho_1''(r)}{\rho_1(r)}\\
&\quad-\frac{1}{8}\frac{r^2+r'^2}{rr'}[\rho_1^{1/2}(r')\rho_1^{1/2}(r)]\frac{\rho_1'^2(r)}{\rho_1^2(r)}\end{aligned} \tag{C.1}$$

By symmetry,

$$\begin{aligned}\nabla^2_{\mathbf{r}'}\Gamma = \nabla^2_{\mathbf{r}'}\Gamma_o &+ \frac{\rho_1^{1/2}(r')\rho_1^{1/2}(r)}{rr'} + \frac{\rho_1^{1/2}(r)}{r}\rho_1^{1/2}(r')\frac{\rho_1'(r')}{\rho_1(r')}\\ &+\frac{1}{4}\frac{r^2+r'^2}{rr'}[\rho_1^{1/2}(r')\rho_1^{1/2}(r)]\frac{\rho_1''(r')}{\rho_1(r')}\\ &-\frac{1}{8}\frac{r^2+r'^2}{rr'}[\rho_1^{1/2}(r')\rho_1^{1/2}(r)]\frac{\rho_1'^2(r')}{\rho_1^2(r')}\end{aligned} \tag{C.2}$$

and therefore, by subtraction,

$$\begin{aligned}\nabla^2_{\mathbf{r}}\Gamma - \nabla^2_{\mathbf{r}'}\Gamma = \nabla^2_{\mathbf{r}}\Gamma_o &- \nabla^2_{\mathbf{r}'}\Gamma_o\\ &+\rho_1^{1/2}(r')\rho_1^{1/2}(r)\left[\frac{1}{r'}\frac{\rho_1'(r)}{\rho_1(r)} - \frac{1}{r}\frac{\rho_1'(r')}{\rho_1(r')}\right]\\ &+\frac{1}{4}\frac{r^2+r'^2}{rr'}[\rho_1^{1/2}(r')\rho_1^{1/2}(r)]\left[\frac{\rho_1''(r)}{\rho_1(r)} - \frac{\rho_1''(r')}{\rho_1(r')}\right]\\ &-\frac{1}{8}\frac{r^2+r'^2}{rr'}[\rho_1^{1/2}(r')\rho_1^{1/2}(r)]\left[\frac{\rho_1'^2(r)}{\rho_1^2(r)} - \frac{\rho_1'^2(r')}{\rho_1^2(r')}\right].\end{aligned} \tag{C.3}$$

Hence, defining $\Gamma_1 = \Gamma - \Gamma_o$, it follows that

$$\nabla^2_{\mathbf{r}}\Gamma_1 - \nabla^2_{\mathbf{r}'}\Gamma_1 = \mathcal{F}[\rho_1], \tag{C.4}$$

where the functional $\mathcal{F}$ is known from Eq. (C.3). This is the most important qualitative conclusion of this Appendix: the off-diagonal p contribution to $\Gamma(r, r')$ is determined solely by $\rho_1(r)$. Indeed, this is already evident from Eqs. (2.7) and (2.8) of the main text.

Returning briefly to the bare Coulomb field example in Section 1, if we write $rR_{nl} = P_{nl}$ then March and Santamaria [2] show that

$$\frac{P_{nl}''}{P_{nl}} - \frac{P_{n0}''}{P_{n0}} - \frac{l(l+1)}{r^2} = 0, \tag{C.5}$$

or, with $F_{nl} \equiv (P_{nl}''/P_{nl}) - (P_{n0}''/P_{n0}) = l(l+1)/r^2$, that F_{nl} satisfies

$$\frac{d^2F_{nl}}{dr^2} + \frac{3}{r}\frac{dF_{nl}}{dr} = 0. \tag{C.6}$$

This shows that P_{nl} is determined by P_{n0} for *any* central potential $V(r)$. Now for this example, $\rho_1 = 6R_{21}^2 = 6P_{21}^2/r^2$, or $P_{21} = r\rho_1^{1/2}/\sqrt{6}$, and so

$$\frac{P_{21}''}{P_{21}} = \frac{(\rho_1'/\rho_1)}{r} + \frac{1}{2}\frac{\rho_1''}{\rho_1} - \frac{1}{4}\frac{\rho_1'^2}{\rho_1^2} = \frac{P_{20}''}{P_{20}} + \frac{2}{r^2}. \tag{C.7}$$

Hence, P_{20}''/P_{20} is determined by ρ_1. Consequently,

$$\begin{aligned}\Gamma_o(r,r') &= 2[\psi_{10}(r)\psi_{10}(r') + R_{20}(r)R_{20}(r')]\\ &= 2[\psi_{10}(r)\psi_{10}(r')] + \frac{2}{rr'}P_{20}(r)P_{20}(r'),\end{aligned} \tag{C.8}$$

and so

$$\Gamma_o'' = 2\psi_{10}''(r)\psi_{10}(r') + \frac{2}{r'}P_{20}(r')\frac{d^2}{dr^2}\left\{\frac{P_{20}(r)}{r}\right\}. \tag{C.9}$$

Now since we know that

$$\begin{aligned}&\frac{1}{r}\frac{d^2}{dr^2}(rR_{n0}) + \frac{2m}{\hbar^2}[\varepsilon_{n0} - V(r)]R_{n0} = 0,\\ \text{or}\quad &\frac{P_{n0}''}{P_{n0}} = -\frac{2m}{\hbar^2}[\varepsilon_{n0} - V(r)],\end{aligned} \tag{C.10}$$

we can write

$$\frac{P_{10}''}{P_{10}} + \frac{2m}{\hbar^2}\varepsilon_{10} = \frac{2m}{\hbar^2}V(r) = \frac{P_{20}''}{P_{20}} + \frac{2m}{\hbar^2}\varepsilon_{20} \tag{C.11}$$

or

$$\frac{P_{10}''}{P_{10}} = \frac{2m}{\hbar^2}[\varepsilon_{20} - \varepsilon_{10}] - \frac{2}{r^2} + \frac{\rho_1'/\rho_1}{r^2} + \frac{1}{2}\frac{\rho''}{\rho_1} - \frac{1}{4}\frac{\rho_1'^2}{\rho_1^2}, \tag{C.12}$$

showing that ψ_{10} is determined by ρ_1 to within a constant. Hence, $\Gamma(r, r')$ in Eq. (2.5) is determined by $\rho_1(r)$ (and boundary conditions).