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Exact relation between density-matrix and density-functional theory for *K* plus *L* closed shells in a bare Coulomb field

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The explicit form of the first-order density matrix $\rho(\mathbf{r}_1,\mathbf{r}_2)$ for independent electrons moving in a bare Coulomb field is first set up for the case of K plus L closed shells. The density matrix has a simple separable form in terms of the variables r_1+r_2 and $|\mathbf{r}_1-\mathbf{r}_2|$, a property exclusive to the Coulomb potential. Also, the off-diagonal dependence is simply quadratic in $|\mathbf{r}_1-\mathbf{r}_2|$. These two properties allow $\rho(\mathbf{r}_1,\mathbf{r}_2)$ to be written solely in terms of electron and kinetic energy densities. Other implications for density-functional theory are briefly referred to.

I. INTRODUCTION

The Thomas-Fermi method, the forerunner of modern density-functional theory,[1,2] works for independent electrons moving in a common potential energy $V(\mathbf{r})$ when this quantity varies by but a small fraction of itself over a characteristic electron wavelength. That this restriction could be removed, and a formally exact relation established between electron density $\rho(\mathbf{r})$ and potential energy $V(\mathbf{r})$ for arbitrary spatial variations of V, was clearly established by March and Murray[3] by plane-wave perturbation theory to all orders in V. Their procedure was to calculate first the density matrix

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\substack{\text{occupied}\\ \text{states}}}\psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\ , \tag{1.1}$$

where $\psi_i(\mathbf{r})$ are the normalized eigenfunctions generated by $V(\mathbf{r})$, and then to go on to the diagonal $\mathbf{r}_1=\mathbf{r}_2\equiv\mathbf{r}$ to find the $\rho(\mathbf{r})-V(\mathbf{r})$ relation, to all orders in V. The subsequent work of Stoddart and March[4] demonstrated that this ρ-V relation could be inverted to give V in terms of the charge displaced by $V(\mathbf{r})$. Hence, substituting back into the perturbation series in V for the density matrix $\rho(\mathbf{r}_1,\mathbf{r}_2)$ yields this as a functional of its diagonal element $\rho(\mathbf{r})$. Unfortunately, to date, these infinite-order perturbation expansions have not been summed exactly for arbitrary V.

Nevertheless, the problem of expressing the density matrix $\rho(\mathbf{r}_1,\mathbf{r}_2)$ defined in Eq. (1.1) in terms of the electron density $\rho(\mathbf{r})$ remains of considerable theoretical interest. The present work lies in this area, and whereas the plane-wave perturbation theory referred to above is most directly relevant to perturbations in simple extended systems like nearly-free-electron metals,[3] the theory given in the present paper has been constructed with closed-shell atoms specifically in mind. To make analytic progress in relating $\rho(\mathbf{r}_1,\mathbf{r}_2)$ to its diagonal electron density $\rho(\mathbf{r})$, we consider here solely the case when the wave functions $\psi_i(\mathbf{r})$ in Eq. (1.1) are generated by the bare Coulomb potential energy $V=-Ze^2/r$ (see, for example, Ref. 5). This limit is, in fact, the leading term in the important $1/Z$ expansion of atomic theory.[6]

II. GENERATION OF $\rho(\mathbf{r}_1,\mathbf{r}_2)$ FROM ITS s-STATE COMPONENT

For this case of a bare Coulomb field, a spatial generalization of Kato's theorem has been established[7] for an arbitrary number of closed shells:

$$\frac{\partial\rho}{\partial r}=-\frac{2Z}{a_0}\rho_s(r),\quad a_0=\frac{\hbar^2}{me^2}\ , \tag{2.1}$$

where ρ_s is the s-state density component of the total density ρ. Theophilou and March[8] have shown that the diagonal relation (2.1) between total and s densities has a counterpart with density matrices, the relation being

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=-(x-y)^{-1}\left[\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right]\left[xy\rho_s\left[\frac{x}{2},\frac{y}{2}\right]\right]\ , \tag{2.2}$$

where

$$x=r_1+r_2+|\mathbf{r}_1-\mathbf{r}_2|\ ,\quad y=r_1+r_2-|\mathbf{r}_1-\mathbf{r}_2|\ . \tag{2.3}$$

Again, Eq. (2.2) is valid for an arbitrary number of closed shells generated by the bare Coulomb potential energy $-Ze^2/r$.

III. EXPLICIT DENSITY MATRIX FOR *K* PLUS *L* CLOSED SHELLS

To make Eq. (2.2) explicit, we consider the form of $\rho(\mathbf{r}_1,\mathbf{r}_2)$ below for (a) the K shell only and (b) the $K+L$ shells.

A. *K* shell

This almost trivial example follows from

$$\psi_{10}(r)=\left[\frac{Z^3}{\pi a_0^3}\right]^{1/2}\exp\left[-\frac{Zr}{a_0}\right]\ . \tag{3.1}$$

Hence, for singly occupied states considered throughout,

$$\rho_s(r_1,r_2)=\psi_{10}(r_1)\psi_{10}(r_2)\ . \tag{3.2}$$

Thus Eq. (2.2) yields

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$$\rho(r_1,r_2)=-(x-y)^{-1}\left[\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right]\left[xy\psi_{10}\left[\frac{x}{2}\right]\psi_{10}\left[\frac{y}{2}\right]\right]$$

$$=-(x-y)^{-1}\left\{y\psi_{10}\left[\frac{y}{2}\right]\left[\psi_{10}\left[\frac{x}{2}\right]+x\left[\frac{-Z}{2a_0}\right]\psi_{10}\left[\frac{x}{2}\right]\right]-x\psi_{10}\left[\frac{x}{2}\right]\left[\psi_{10}\left[\frac{y}{2}\right]+y\left[\frac{-Z}{2a_0}\right]\psi_{10}\left[\frac{y}{2}\right]\right]\right\}. \tag{3.3}$$

Clearly the xy terms cancel and we are left with the elementary result,

$$\rho(r_1,r_2)=\psi_{10}\left[\frac{x}{2}\right]\psi_{10}\left[\frac{y}{2}\right]$$

$$=\left[\frac{Z^3}{\pi a_0^3}\right]\exp\left[\frac{-Z}{a_0}\frac{(x+y)}{2}\right]. \tag{3.4}$$

But from Eqs. (2.3) it follows that $(x+y)/2=r_1+r_2$, yielding

$$\rho(r_1,r_2)=\psi_{10}(r_1)\psi_{10}(r_2)$$

as required for the K shell alone.

B. $K+L$ shells

Using the formula for the $2s$ wave function,[5]

$$\psi_{20}(r)=\frac{1}{4\sqrt{2\pi}}\left[\frac{Z}{a_0}\right]^{3/2}\left[2-\frac{Zr}{a_0}\right]\exp\left[\frac{-Zr}{2a_0}\right], \tag{3.5}$$

one has the explicit form $\rho_s(x/2,y/2)$ required in Eq. (2.2) as

$$\rho_s\left[\frac{x}{2},\frac{y}{2}\right]=\frac{1}{\pi}\left[\frac{Z}{a_0}\right]^3\left\{\exp\left[-\frac{Z}{2a_0}(x+y)\right]+\frac{1}{32}\left[2-\frac{Zx}{2a_0}\right]\left[2-\frac{Zy}{2a_0}\right]\exp\left[-\frac{Z}{2a_0}\left[\frac{x+y}{2}\right]\right]\right\}. \tag{3.6}$$

Hence it follows readily that

$$\left[\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right]\left[xy\rho_s\left[\frac{x}{2},\frac{y}{2}\right]\right]=(y-x)\left[\rho_s\left[\frac{x}{2},\frac{y}{2}\right]+\frac{xy}{128\pi}\left[\frac{Z}{a_0}\right]^5\exp\left[-\frac{Z}{4a_0}(x+y)\right]\right]. \tag{3.7}$$

The desired density matrix for closed $K+L$ shells is then from Eq. (2.2) given by

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\rho_s\left[\frac{x}{2},\frac{y}{2}\right]+xy\frac{1}{128\pi}\left[\frac{Z}{a_0}\right]^5\exp\left[-\frac{Z}{4a_0}(x+y)\right]. \tag{3.8}$$

Now we reintroduce variables $\mathbf{r}_1$ and $\mathbf{r}_2$ into the right-hand side of Eq. (3.8) and after some manipulation, in which the explicit form of ρ_s in terms of ψ_{10} and ψ_{20} is utilized, one finds

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\pi}\left[\frac{Z}{a_0}\right]^3\exp\left[-\frac{Z}{a_0}(r_1+r_2)\right]$$

$$+\frac{1}{8\pi}\left[\frac{Z}{a_0}\right]^3\exp\left[-\frac{Z}{2a_0}(r_1+r_2)\right]\left[1-\frac{Z}{2a_0}(r_1+r_2)+\frac{1}{2}\left[\frac{Z}{2a_0}(r_1+r_2)\right]^2\right]$$

$$-\frac{1}{64\pi}\left[\frac{Z}{a_0}\right]^5|\mathbf{r}_1-\mathbf{r}_2|^2\exp\left[-\frac{Z}{2a_0}(r_1+r_2)\right]. \tag{3.9}$$

In Appendix A an alternative derivation of this equation is given. The new feature apparent from Eq. (3.9) is that the final contribution of the right-hand side makes no contribution to the diagonal density $\rho(\mathbf{r}_1,\mathbf{r}_2)|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}}\equiv\rho(\mathbf{r})$. It does, of course, still contribute to the kinetic energy density, as will now be discussed further.

IV. KINETIC ENERGY DENSITY

Since the K shell is almost trivial, we turn immediately to the kinetic energy density derivable from the off-diagonal density matrix (3.9) for $K+L$ shells. As is well known, there is some ambiguity in the kinetic energy density $t(\mathbf{r})$, though none of course in its integral,

$$T=\int t(\mathbf{r})d\mathbf{r}, \tag{4.1}$$

over the whole of space. The ambiguity arises from the use of the possible operators $\nabla_{\mathbf{r}_1}\cdot\nabla_{\mathbf{r}_2}$ or $\nabla^2_{\mathbf{r}_1}$, etc. Below we consider the symmetric operator in $\mathbf{r}_1$ and $\mathbf{r}_2$, i.e., the first of the above choices.

A. $K+L$ shells

From the definition of the diagonal density $\rho(\mathbf{r}_1,\mathbf{r}_2)|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}}\equiv\rho(\mathbf{r})$ and returning to the density matrix (3.9), we emphasize its separability by writing

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\rho\left[\frac{r_1+r_2}{2}\right]+|\mathbf{r}_1-\mathbf{r}_2|^2F\left[\frac{r_1+r_2}{2}\right] . \tag{4.2}$$

Evidently

$$\nabla_{\mathbf{r}_1}\rho=\hat{\mathbf{r}}_1\rho'\left[\frac{r_1+r_2}{2}\right]+|\mathbf{r}_1-\mathbf{r}_2|^2\hat{\mathbf{r}}_1F'\left[\frac{r_1+r_2}{2}\right]+2(\mathbf{r}_1-\mathbf{r}_2)F\left[\frac{r_1+r_2}{2}\right] , \tag{4.3}$$

where $\hat{\mathbf{r}}_1$ denotes a unit vector along $\mathbf{r}_1$. Thus it follows that

$$\nabla_{\mathbf{r}_1}\cdot\nabla_{\mathbf{r}_2}\rho\,|_{\mathbf{r}_2=\mathbf{r}_1=\mathbf{r}}=\frac{1}{4}\rho''(r)-6F(r) \tag{4.4}$$

and hence the kinetic energy density $t(r)$ with this choice of kinetic energy operator has the form

$$t(r)=\frac{\hbar^2}{2m}[\tfrac{1}{4}\rho''(r)-6F(r)] . \tag{4.5}$$

The (unambiguous) total kinetic energy T defined by Eq. (4.1) is given by

$$T=\frac{\hbar^2}{8m}\int_0^\infty\rho''(r)4\pi r^2dr-\frac{3\hbar^2}{m}\int_0^\infty F(r)4\pi r^2dr . \tag{4.6}$$

Integrating the first term by parts we then find

$$T=\frac{\pi\hbar^2}{m}\int_0^\infty\rho(r)dr-\frac{12\pi\hbar^2}{m}\int_0^\infty F(r)r^2dr ; \tag{4.7}$$

this can evidently be written in this example of the $K+L$ shells as

$$T=T_s+T_p , \tag{4.8}$$

T_s having earlier been obtained[9] as the first term on the right-hand side of Eq. (4.7).

The kinetic energy contribution from the p states is evidently

$$T_p=-\frac{12\pi\hbar^2}{m}\int_0^\infty F(r)r^2dr . \tag{4.9}$$

From density-functional theory, it is clear that this term, as well as T_s given by the first term in Eq. (4.7), is a functional of the density ρ,[10,11] but presumably the functional form is somewhat complex for the p states. Explicitly, one has

$$F(r)=-\frac{1}{64\pi}\left[\frac{Z}{a_0}\right]^5\exp\left[-\frac{Z}{a_0}r\right] . \tag{4.10}$$

Substituting Eq. (4.10) into (4.9) yields

$$T_p=\frac{3}{8}\frac{\hbar^2}{m}\left[\frac{Z}{a_0}\right]^2 .$$

The total kinetic energy T for (singly occupied) $K+L$ shells is

$$T=\frac{\hbar^2}{m}\left[\frac{Z}{a_0}\right]^2 \tag{4.11}$$

and hence

$$T_s=T-T_p=\frac{5}{8}\frac{\hbar^2}{m}\left[\frac{Z}{a_0}\right]^2 , \tag{4.12}$$

which also follows from the first term in Eq. (4.7) by inserting $\rho(r)$ for (singly occupied) $K+L$ shells.

V. OFF-DIAGONAL MATRIX CHARACTERIZED SOLELY BY ELECTRON AND KINETIC ENERGY DENSITIES

This is the point to return to the objective discussed in the Introduction; namely, to express the off-diagonal density matrix $\rho(\mathbf{r}_1,\mathbf{r}_2)$ in Eq. (1.1) in terms solely of its diagonal electron density $\rho(\mathbf{r})$.

To do so for the model density-matrix (3.9) for the $K+L$ closed shells, let us focus on the structure of $\rho(\mathbf{r}_1,\mathbf{r}_2)$ which is clearly exposed in Eq. (4.2), namely,

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\rho\left[\frac{r_1+r_2}{2}\right]+|\mathbf{r}_1-\mathbf{r}_2|^2F\left[\frac{r_1+r_2}{2}\right] . \tag{5.1}$$

But now F is related to the electron density itself through Eq. (4.5), since the single-particle kinetic energy density $t(r)$ is a unique functional of the electron density $\rho(r)$. Hence, substituting for F from Eq. (4.5) into Eq. (5.1), we obtain the desired relation between $\rho(\mathbf{r}_1,\mathbf{r}_2)$ and its diagonal element, the electron density, in the form

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\rho\left[\frac{r_1+r_2}{2}\right]+|\mathbf{r}_1-\mathbf{r}_2|^2\left[\frac{1}{24}\rho''\left[\frac{r_1+r_2}{2}\right]-\frac{m}{3\hbar^2}t\left[\frac{r_1+r_2}{2}\right]\right] . \tag{5.2}$$

Without using the explicit form for F given in Eq. (4.10), we do not know t in terms of ρ. But we have, of course, the first-principles basis[3,4] that $t\equiv t[\rho]$. However, this motivates a brief further discussion of this relation, to which we now turn.

VI. IDEMPOTENCY RELATION BETWEEN SINGLE-PARTICLE KINETIC ENERGY DENSITY t AND ρ

The orthonormality of the wave functions $\psi_i(\mathbf{r})$ in Eq. (1.1) generated by the (assumed) common potential energy $V(\mathbf{r})$ leads to the idempotency condition $\rho^2=\rho$ on the density matrix, i.e.,

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\int\rho(\mathbf{r}_1,\mathbf{r})\rho(\mathbf{r},\mathbf{r}_2)d\mathbf{r} . \tag{6.1}$$

Clearly the insertion of Eq. (5.2) into Eq. (6.1) leads to a (somewhat complicated) integral equation relating the single-particle kinetic energy t to the electron density $\rho(r)$. While we are assured, because Eq. (5.2) is exact for $K+L$ closed shells in a pure Coulomb field, that the exact t and ρ must satisfy the above equation, it would be of interest if it could be established that insertion of the exact $\rho(\mathbf{r})$ would generate the single-particle kinetic energy density uniquely. This remains an open question at the time of writing. It is satisfactory though, to realize that idempotency does link t and ρ, and that *ad hoc* construction of $t[\rho]$, by modifications of the Thomas-Fermi $\rho^{5/3}$ term by summing subseries of gradient corrections, will generally lead to some violation of idempotency and hence to a loss of a variational bound on the independent-particle total energy.

Having seen the relevance of the present density-matrix model for the single-particle kinetic energy functional, we have thought it worthwhile to record in Appendix B some implications that the present considerations have for exchange energy as a functional of $\rho(\mathbf{r})$.

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APPENDIX A: DIRECT CALCULATION OF DENSITY MATRIX FOR *K* PLUS *L* SHELLS FROM BARE COULOMB FIELD WAVE FUNCTIONS

Using Eq. (1.1) for the K plus L shells, with hydrogen-like wave functions, one obtains almost immediately

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\pi}\left[\frac{Z}{a_0}\right]^3\exp\left[-\frac{Z}{a_0}(r_1+r_2)\right]+\frac{1}{8\pi}\left[\frac{Z}{a_0}\right]^3\exp\left[-\frac{Z}{2a_0}(r_1+r_2)\right]$$
$$\times\left[1-\frac{Z}{2a_0}(r_1+r_2)+\left[\frac{Z}{a_0}\right]^2\frac{r_1r_2}{4}\right.$$
$$\left.\times(1+\sin\theta_1\cos\psi_1\sin\theta_2\cos\psi_2+\sin\theta_1\sin\psi_1\sin\theta_2\sin\psi_2+\cos\theta_1\cos\theta_2)\right], \tag{A1}$$

if

$$x_i=r_i\sin\theta_i\cos\psi_i,\quad y_i=r_i\sin\theta_i\sin\psi_i,\quad z_i=r_i\cos\psi_i,\quad i=1,2$$

then Eq. (A1) becomes

$$\rho(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\pi}\left[\frac{Z}{a_0}\right]^3\exp\left[-\frac{Z}{a_0}(r_1+r_2)\right]+\frac{1}{8\pi}\left[\frac{Z}{a_0}\right]^3\exp\left[-\frac{Z}{2a_0}(r_1+r_2)\right]$$
$$\times\left[1-\frac{Z}{2a_0}(r_1+r_2)+\frac{1}{4}\left[\frac{Z}{a_0}\right]^2(r_1r_2+x_1x_2+y_1y_2+z_1z_2)\right], \tag{A2}$$

and using $|\mathbf{r}_1-\mathbf{r}_2|^2=(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2$, we obtain after a short calculation the desired Eq. (3.9).

APPENDIX B: IMPLICATIONS OF MODEL DENSITY MATRIX (5.2) FOR THE EXCHANGE ENERGY OF CLOSED-SHELL ATOMS

In independent electron theory, the exchange energy A is given in terms of the first-order density matrix $\rho(\mathbf{r}_1,\mathbf{r}_2)$ by

$$A=-\tfrac{1}{4}e^2\int\frac{[\rho(\mathbf{r}_1,\mathbf{r}_2)]^2}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2\ . \tag{B1}$$

The purpose of this appendix is to note that while the details of the exact result (3.9) for $\rho(\mathbf{r}_1,\mathbf{r}_2)$ depend on the assumption of a bare Coulomb potential, the structure exhibited in Eq. (5.2) might have more general, though now approximate validity. The main point to be made is that the insertion of the form (5.2) into Eq. (B1) leads to $A\equiv A[\rho,\rho'',t]$, and hence in this approximation the exchange energy is known as an explicit functional of ρ,ρ'' and single-particle kinetic energy density. Though the detail proliferates and will not be explored here, one obvious contribution to A that results is

$$A_1=-\tfrac{1}{4}e^2\int\left\{\left[\rho\left[\frac{r_1+r_2}{2}\right]\right]^2|\mathbf{r}_1-\mathbf{r}_2|^{-1}\right\}d\mathbf{r}_1d\mathbf{r}_2 \tag{B2}$$

with a corresponding contribution to the exchange potential $V_x(\mathbf{r})$ of density functional theory given by

$$V_{x1}(\mathbf{r})=\frac{\delta A_1}{\delta\rho(r)}\propto\int\frac{\rho\left[\dfrac{r+r_2}{2}\right]}{|\mathbf{r}-\mathbf{r}_2|}d\mathbf{r}_2\ . \tag{B3}$$

The most important conclusion, we reiterate, of this appendix is that, adopting the approximate structure (5.2) for the density matrix leads to the exchange energy as a functional solely of ρ,ρ'' and kinetic energy density t.

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