

Electron and kinetic energy densities for an arbitrarily closed shell in a bare Coulomb field from s -state densities

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It is known from previous work that the total electron density matrix for closed-shell atoms in a bare Coulomb field is determined solely by the corresponding s -state contribution. In keeping with this philosophy, an expression is derived for the closed-shell electron density $\rho_n(r)$ and kinetic energy density $t_n(r)$ in terms only of s -state components $\rho_{no}(r)$ and $t_{no}(r)$ for arbitrary quantum number n . A proposal for the generalization of the present model for any central field of force is given in the Appendix.

I. INTRODUCTION

One of us has shown, for the model of the bare Coulomb field which has significance in atomic physics in the important $1/Z$ expansion,¹ that Kato's theorem has the spatial generalization²

$$\frac{\partial \rho(r)}{\partial r} = -\frac{2Z}{a_0} \rho_s(r), \quad a_0 = \frac{\hbar^2}{me^2} \quad (1.1)$$

for an arbitrary number of closed shells with nuclear charge Ze . In Eq. (1.1) $\rho(r)$ is the total electron density with s -state contribution $\rho_s(r)$.

Subsequently, Theophilou and March³ have given the total density matrix solely in terms of the s -state density matrix. Here, we derive a relation between the closed-shell density $\rho_n(r)$ and its corresponding s -state density $\rho_{no}(r)$ for arbitrary quantum number n . This latter result has a counterpart when the n th-shell kinetic energy density $t_n(r)$ is expressed only in terms of $\rho_{no}(r)$ and its s -state contribution $t_{no}(r)$.

To begin this program we show first that the radial wave function $R_{nl}(r)$ is determined solely by $R_{no}(r)$ for arbitrary principal and orbital quantum numbers n and l , respectively; this statement can in fact be generalized to any central field (cf. Appendix). Then using an earlier result of one of us for the s -state kinetic energy density in terms of the total density $\rho(r)$ in the bare Coulomb model,⁴ a direct way of generating the total density $\rho_n(r)$ for the n th closed shell from its s -state contribution $\rho_{no}(r)$ is exhibited. Our previous result for the $K+L$ shells⁵ is recovered from this expression as a simple check of its validity. The final section of the paper deals with the generalization of these results to kinetic energy densities.

II. DIFFERENTIAL EQUATION RELATING RADIAL WAVE FUNCTION R_{nl} TO R_{no}

It is well known that for any central field the total wave function $\psi_{nlm}(r)$ is the product of a radial wave function $R_{nl}(r)$ and a spherical harmonic $Y_l^m(\theta, \phi)$. The radial function for an arbitrary central potential energy $V(r)$ satisfies the wave equation

$$\frac{d^2}{dr^2}(rR_{nl}) + \frac{2m}{\hbar^2} \left[\epsilon_{nl} - V(r) - \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] rR_{nl} = 0. \quad (2.1)$$

It will be convenient below to denote the product rR_{nl} by P_{nl} , which evidently from Eq. (2.1) satisfies the equation

$$\frac{P_{nl}''}{P_{nl}} + \frac{2m}{\hbar^2} \left[\epsilon_{nl} - V(r) - \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] = 0. \quad (2.2)$$

It is clear that if we write Eq. (2.2) for the special case of s states, i.e., $l=0$, and note that for the bare Coulomb field the eigenvalues are independent of l , then subtracting the s -state expression corresponding to Eq. (2.2) from Eq. (2.2) itself yields immediately

$$\frac{P_{nl}''}{P_{nl}} - \frac{P_{no}''}{P_{no}} - \frac{l(l+1)}{r^2} = 0. \quad (2.3)$$

This equation makes abundantly clear the philosophy underlying the present work. Given the s -state radial wave function $R_{no} = r^{-1}P_{no}$, Eq. (2.3) shows that, at least in principle, the general angular momentum state P_{nl} can be determined without recourse to the (bare Coulomb) potential energy. This is sufficiently interesting for us to record in the Appendix the corresponding equation for a general central potential $V(r)$ for which the eigenvalues depend on both n and l .

Having established this point in terms of wave functions, we now turn to one of the main aims of the paper; to relate the total electron density $\rho_n(r)$ for the n th closed shell to its s -state contribution.

III. RELATION BETWEEN $\rho_n(r)$ AND S -STATE CONTRIBUTION $\rho_{no}(r)$

As in our earlier example on $K+L$ shells,⁵ we shall consider, to be definite, singly occupied levels. Then the s -state density $\rho_{no}(r)$ is immediately given by

$$\rho_{no}(r) = R_{no}^2(r) = P_{no}^2(r)/(4\pi r^2). \quad (3.1)$$

If we now define the kinetic energy t_{no} for the s states by

$$t_{no}(r) = -\frac{\hbar^2}{2m} \psi_{noo} \nabla^2 \psi_{noo}, \quad (3.2)$$

then in terms of P_{no} and its derivatives this becomes

$$t_{no}(r) = -\frac{\hbar^2}{2m} \frac{P_{no}}{(4\pi r^2)} P_{no}'' \quad (3.3)$$

or in terms of the s -state density contribution $\rho_{no}(r)$ to the closed-shell density $\rho_n(r)$,

$$t_{no}(r) = -\frac{\hbar^2}{2m} \rho_{no}(r) \frac{P_{no}''}{P_{no}}. \quad (3.4)$$

However, we next note that one of us has obtained an alternative expression⁴ for $t_{no}(r)$ in terms of $\rho_n(r)$ and $\rho_{no}(r)$, namely, when we allow for difference in definitions of the kinetic energy density,⁶

$$t_{no}(r) = \frac{\hbar^2}{4m} \frac{\rho_n(r)}{r^2} - \frac{\hbar^2}{8m} \frac{1}{r^2} \frac{\partial^2}{\partial r^2} (r^2 \rho_{no}). \quad (3.5)$$

Hence, equating (3.4) and (3.5) yields for $\rho_n(r)$ the result

$$\rho_n(r) = -2r^2 \rho_{no}(r) \frac{P_{no}''}{P_{no}} + \frac{1}{2} \frac{\partial^2}{\partial r^2} (r^2 \rho_{no}). \quad (3.6)$$

But from Eq. (3.1) it readily follows that

$$2P_{no}' = 4\pi P_{no}^{-1} (r^2 \rho_{no}' + 2r \rho_{no}), \quad (3.7)$$

and a further differentiation yields

$$2 \frac{P_{no}''}{P_{no}} = -\frac{4\pi}{P_{no}^2} \left[\frac{P_{no}'}{P_{no}} (r^2 \rho_{no}' + 2r \rho_{no}) - (r^2 \rho_{no}'' + 4r \rho_{no}' + 2\rho_{no}) \right]. \quad (3.8)$$

Using Eq. (3.7) for P_{no}' this becomes

$$2 \frac{P_{no}''}{P_{no}} = \frac{(-4\pi)}{P_{no}^2} \left[\frac{4\pi}{2P_{no}^2} (r^2 \rho_{no}' + 2r \rho_{no})^2 - (r^2 \rho_{no}'' + 4r \rho_{no}' + 2\rho_{no}) \right]. \quad (3.9)$$

Inserting this in the first term on the right-hand side of Eq. (3.6) and using Eq. (3.1) to eliminate P_{no}^2 yields after some algebra

$$\rho_n(r) = \rho_{no}(r) + \frac{1}{2} r^2 \left[\frac{(\rho_{no}')^2}{\rho_{no}} - \rho_{no}'' \right]. \quad (3.10)$$

Thus, for arbitrary principal quantum number n , a remarkably simple expression emerges in terms of the s -state density ρ_{no} for the sum of p , d , etc., contributions to the density of the n th closed shell. Since knowledge of s -state properties in a bare Coulomb field determines the n th closed shell and therefore the total electron density, this motivates the subsequent discussion of the counterpart of expression (3.10) for kinetic energy densities.

IV. RELATION BETWEEN $t_n(r)$ AND S -STATE CONTRIBUTION $t_{no}(r)$

Here, we turn to the derivation of an expression for the kinetic energy density $t_n(r)$ for the n th closed shell in terms only of the s -state contributions $t_{no}(r)$ and $\rho_{no}(r)$. As before, we find that the ratio P_{nl}''/P_{nl} can be written in terms of the radial wave function R_{nl} and derivatives as

$$\frac{P_{nl}''}{P_{nl}} = \frac{1}{r(R_{nl})^2} \left[r R_{nl} R_{nl}'' + \frac{d}{dr} R_{nl}^2 \right], \quad (4.1)$$

considering that the density matrix for the subshell nl is defined in the form

$$\begin{aligned} \rho_{nl}(r, r_1) &= \sum_{m=-l}^l \rho_{nlm}(\mathbf{r}, \mathbf{r}_1) \Big|_{\phi_1=\theta} \\ &= R_{nl}(r) R_{nl}(r_1) \\ &\quad \times \sum_{m=-l}^l Y_l^m(\theta, \phi) Y_l^{*m}(\theta_1, \phi_1) \Big|_{\phi_1=\phi}. \end{aligned} \quad (4.2)$$

Then Eq. (4.1) becomes

$$\frac{P_{nl}''}{P_{nl}} = \frac{1}{r \rho_{nl}(r)} \left[r \frac{d^2}{dr_1^2} \rho_{nl}(r, r_1) \Big|_{r_1=r} + \frac{d}{dr} \rho_{nl}(r) \right], \quad (4.3)$$

where $\rho_{nl}(r)$ is the diagonal density matrix obtained from (4.2). Inserting Eqs. (3.4) and (4.3) in (2.3) one obtains

$$\begin{aligned} \frac{d^2}{dr_1^2} \rho_{nl}(r, r_1) \Big|_{r_1=r} + \frac{1}{r} \frac{d}{dr} \rho_{nl}(r) + \frac{2m}{\hbar^2} \frac{\rho_{nl}(r)}{\rho_{no}(r)} t_{no}(r) \\ - \frac{l(l+1)}{r^2} \rho_{nl}(r) = 0. \end{aligned} \quad (4.4)$$

In order to find an expression for $t_n(r)$ in terms of $t_{no}(r)$ we shall define the kinetic energy density $t_{nl}(r)$ for the subshell nl in the form

$$\begin{aligned} t_{nl}(r) &= -\frac{\hbar^2}{2m} \nabla_1^2 \rho_{nl}(\mathbf{r}, \mathbf{r}_1) \Big|_{\mathbf{r}_1=\mathbf{r}} \\ &= -\frac{\hbar^2}{2m} \nabla_1^2 \left[R_{nl}(r) R_{nl}(r_1) \right. \\ &\quad \left. \times \sum_{m=-l}^l Y_l^m(\theta, \phi) Y_l^{*m}(\theta_1, \phi_1) \right] \Big|_{\mathbf{r}_1=\mathbf{r}}. \end{aligned} \quad (4.5)$$

After operating ∇_1^2 over the radial and angular functions that depend on the coordinates with subindex 1 and using the result in (4.4) one finds that

$$\begin{aligned} t_{nl}(r) &= \frac{\rho_{nl}(r)}{\rho_{no}(r)} t_{no}(r) \\ &\quad + \frac{\hbar^2}{2m} \frac{1}{r} \frac{d}{dr_1} [\rho_{nl}(r_1) - 2\rho_{nl}(r, r_1)] \Big|_{r_1=r}. \end{aligned} \quad (4.6)$$

This expression is reduced further if we take into account

the fact that $\rho_{nl}(r, r_1)$ can be written from (4.2) in terms of the diagonal density $\rho_{nl}(r)$ as

$$\rho_{nl}(r, r_1) = \sqrt{\rho_{nl}(r)\rho_{nl}(r_1)}, \quad (4.7)$$

hence the second term in the right-hand side member of Eq. (4.6) vanishes and it becomes

$$t_{nl}(r) = \frac{\rho_{nl}(r)}{\rho_{no}(r)} t_{no}(r). \quad (4.8)$$

Finally, summing over l we arrive at

$$t_n(r) = \frac{\rho_n(r)}{\rho_{no}(r)} t_{no}(r). \quad (4.9)$$

This last equation is one of the important expressions given in the paper since it is possible to obtain the kinetic energy density for the n th closed shell from the density $\rho_n(r)$ and s -state contributions $t_{no}(r)$ and $\rho_{no}(r)$. We can avoid the use of the factor $t_{no}(r)$ in (4.9) by means of Eq. (3.5); in this case Eq. (4.9) is

$$t_n(r) = \frac{\rho_n(r)}{\rho_{no}(r)} \frac{\hbar^2}{4m} \frac{1}{r^2} \left[\rho_n(r) - \frac{1}{2} \frac{\partial^2}{\partial r^2} (r^2 \rho_{no}) \right]. \quad (4.10)$$

Therefore the total kinetic energy for the n th shell is given in the form

$$\begin{aligned} T_n &= \int t_n(r) d^3\mathbf{r} \\ &= \frac{\pi\hbar^2}{m} \left[\int_0^\infty \frac{\rho_n^2(r)}{\rho_{no}(r)} dr \right. \\ &\quad \left. - \frac{1}{2} \int_0^\infty \frac{\rho_n(r)}{\rho_{no}(r)} \frac{\partial^2}{\partial r^2} (r^2 \rho_{no}) dr \right], \quad (4.11) \end{aligned}$$

which is a general expression for T_n in the bare Coulomb field. It is clear that if we use the relation for $\rho_n(r)$ in terms of $\rho_{no}(r)$ as given in Eq. (3.10) then T_n can be expressed as a function solely of $\rho_{no}(r)$, which was one of the main aims of the paper. Finally, we shall derive a new expression for T_n by using the results (3.10) and (4.9). Inserting (3.10) into (4.9) and taking back (3.5) we arrive at

$$T_n = \frac{\pi\hbar^2}{m} \int_0^\infty \rho_n(r) dr + \int t_{no} \frac{r^2}{2} \left[\frac{(\rho'_{no})^2}{\rho_{no}^2} - \frac{\rho''_{no}}{\rho_{no}} \right] d^3\mathbf{r}. \quad (4.12)$$

From here we can see that when we carry out the sum

over n , the first term represents the s -state contribution to the kinetic energy (see Ref. 5), and the second the kinetic energy coming from the remaining subshells.

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APPENDIX

In order to obtain the general angular momentum state $P_{nl}(r)$ for any central field in terms of the s -state function $P_{no}(r)$, we shall proceed to find a similar equation to that given in (2.3). Allowing for the fact that in general the eigenvalues of the Schrödinger equation depend on the quantum numbers n and l , a similar procedure to that used to obtain Eq. (2.3) yields

$$\frac{P''_{nl}}{P_{nl}} - \frac{P''_{no}}{P_{no}} - \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2} (\epsilon_{nl} - \epsilon_{no}) = 0. \quad (A1)$$

For simplicity, we write

$$F_{nl} = \frac{P''_{nl}}{P_{nl}} - \frac{P''_{no}}{P_{no}}. \quad (A2)$$

Hence Eq. (A1) can be expressed in the form

$$r^2 F_{nl} + \frac{2m}{\hbar^2} r^2 (\epsilon_{nl} - \epsilon_{no}) - l(l+1) = 0. \quad (A3)$$

Differentiating the Eq. (A3) once to eliminate l , then dividing by r and differentiating again to eliminate the eigenvalues, we arrive at the following equation:

$$\frac{d^2}{dr^2} F_{nl} + \frac{3}{r} \frac{d}{dr} F_{nl} = 0. \quad (A4)$$

This last result shows that in principle the general angular momentum function P_{nl} is completely determined by the s -state function P_{no} for any central potential $V(r)$. As an example of this result in the bare Coulomb field, we deduce immediately from the second term in Eq. (3.10) the relation

$$\frac{3}{4\pi} R_{21}^2 = \frac{r^2}{2} \left[\frac{(\rho'_{20})^2}{\rho_{20}} - \rho''_{20} \right] \quad (A5)$$

where the functions R_{21} and ρ_{20} are related to P_{21} and P_{20} , respectively, in the form $R_{21} = P_{21}/r$ and $\rho_{20} = P''_{20}/(4\pi r^2)$, hence relating P_{21} to P_{20} .

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⁶It is clear that the linearity of this equation allows the sum over an arbitrary number of closed shells to be carried out to yield the total s -state kinetic energy density in terms of the total electron density and its s -state contribution.