

Supersymmetric quantum-mechanical approach to atomic closed shells in a bare Coulomb field

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The model problem of atomic closed shells in a bare Coulomb field has been the subject of considerable interest following the recent demonstration by Blinder [Phys. Rev. A **29**, 1674 (1984)], with subsequent generalization by March [Phys. Lett. **111A**, 47 (1985)], that the electron density in an arbitrary closed shell in a bare Coulomb field is expressible solely in terms of its s -state contribution. The present paper will provide a simple derivation of this important relationship by application of the methods of supersymmetric quantum mechanics to the radial Coulomb problem. Using this relation, differential equations are derived which are satisfied by the electron density for an arbitrary closed shell and the Slater sum for an arbitrary number of closed shells in a bare Coulomb field.

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I. INTRODUCTION

In a recent paper on the Sturmian propagator for the Coulomb problem, Blinder [1] derived a generalization of Unsold's theorem, the diagonal form of which was subsequently used by Shakeshaft and Spruch [2] in a semiclassical evaluation of the sums of squares of bound-state Coulomb wave functions, arising in the calculation of the capture cross section of an electron into the n th level of a hydrogenlike ion by a bare ion at high velocity [3,4].

This relation may be expressed in the form

$$\rho_n(r) = [P'_{n0}(r)]^2 - P_{n0}P''_{n0}(r), \quad (1.1)$$

where $\rho_n(r)$ represents the electron density for the n th filled shell of electrons which interact with the nucleus but not with each other, and $P_{n0}(r) = rR_{n0}(r)$, where $R_{n0}(r)$ represents the s -state radial wave function of the hydrogenlike ion for the n th shell. The function $P_{n0}(r)$ satisfies the radial Schrödinger equation (in atomic units)

$$-P''_{n0}(r) + \left[-\frac{2Z}{r} + \frac{Z^2}{n^2} \right] P_{n0}(r) = 0. \quad (1.2)$$

Equation (1.1) has subsequently been used by March and co-workers to express [5] the bound-state Slater sum for the bare Coulomb field solely in terms of the s -state Slater sum to derive [6] a spatially dependent generalization of Kato's theorem [7] for atomic closed shells in a bare Coulomb field, and to express [8] both electron and kinetic-energy densities for an arbitrary closed shell in a bare Coulomb field in terms of s -state densities. These latter results for the model problem of the bare Coulomb field are of interest in density-functional theory and the bare Coulomb model itself is of significance as the leading term in the so-called $1/Z$ expansion [9,10] method in atomic theory.

The object of the present paper is to provide a simple derivation of the important result of Blinder [Eq. (1.1)] using the methods of supersymmetric quantum mechanics [11,12], or factorization [13,14], as applied to the radial Coulomb problem [15–19]. This approach leads to a

set of shift operators which connect Coulomb eigenstates corresponding to different values of angular momentum quantum number at fixed energy (i.e., at a constant value of principal quantum number). This allows the electron density of the filled shell to be expressed solely in terms of the s -state solution of the radial Schrödinger equation at a constant value of the principal quantum number. This relation can then be used to derive differential equations for the closed-shell density and kinetic-energy density corresponding to the n th closed shell, as well as for the Slater sum for an arbitrary number of closed shells for the bare Coulomb field problem. The resultant formulas differ from those derived by March [5] and March and Santamaria [8] since they start from Eq. (1.1) itself rather than from the derived extension to Kato's theorem, namely,

$$\frac{\partial \rho(r)}{\partial r} = -2Z\rho_s(r), \quad (1.3)$$

where $\rho(r)$ is the total closed-shell density and $\rho_s(r)$ is the total s -state density.

The plan of the present paper is as follows. The basic results of supersymmetric quantum mechanics, as applied to the radial Coulomb problem, are summarized in Sec. II and then used in Sec. III to provide a simple derivation of Eq. (1.1). In Secs. IV and V we use Eq. (1.1) to construct differential equations satisfied by the electron density and kinetic-energy density for an arbitrary closed shell in a bare Coulomb field. Section VI considers the Slater sum for an arbitrary number of closed shells in a bare Coulomb field, and an explicit differential equation satisfied by this Slater sum is derived. The relationship between these results and earlier results of March and co-workers [5,6,8,20] is discussed, and the paper ends with some general conclusions.

II. SUPERSYMMETRIC QUANTUM-MECHANICAL APPROACH TO THE RADIAL COULOMB PROBLEM

The method of supersymmetric quantum mechanics [11,12], which has been shown to be equivalent [21,22] to

the earlier factorization approach of Schrödinger [13,14], has been applied previously to the radial Coulomb problem [15–19] and only a summary of the main results will be presented here. The starting point is the radial Schrödinger equation for a specified value of angular momentum quantum number, namely,

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r} - 2E_{n_r,l} \right] \psi_{n_r,l}(r) = 0, \quad (2.1)$$

where n_r represents the number of radial nodes. The eigenvalues $E_{n_r,l}$ are defined by

$$2E_{n_r,l} = -\frac{Z^2}{(n_r + l + 1)^2} \equiv -\frac{Z^2}{n^2}, \quad (2.2)$$

where $n = n_r + l + 1$ is the principal quantum number. Although the energy eigenvalues are well known in this case, the method of supersymmetric quantum mechanics (or factorization) enables these eigenvalues to be determined for analytically solvable potentials directly using algebraic procedures. The essence of the method is the factorization of the Hamiltonian (or, more precisely, the Hamiltonian minus the appropriate ground state energy) in the form

$$a^\dagger(l)a(l)\psi_{n_r,l}(r) = 2\Delta E_{n_r,l}\psi_{n_r,l}(r), \quad (2.3)$$

where $\Delta E_{n_r,l} = E_{n_r,l} - E_{0,l}$.

The operators $a(l)$ and $a^\dagger(l)$ are defined by

$$a(l) = \frac{d}{dr} - \frac{l+1}{r} + \frac{Z}{l+1}, \quad (2.4)$$

$$a^\dagger(l) = -\frac{d}{dr} - \frac{l+1}{r} + \frac{Z}{l+1}. \quad (2.5)$$

If we interchange the order of the operators $a(l)$ and $a^\dagger(l)$ in the parent Hamiltonian, we generate a so-called partner Hamiltonian. This partner has the same bound-state eigenvalue spectrum as the parent, except that the ground-state energy of the parent is absent in the partner. In the present instance it can be shown [15–19] that

$$a(l)a^\dagger(l) = a^\dagger(l+1)a(l+1) + 2\Delta E_{1,l}, \quad (2.6)$$

where the partner Hamiltonian corresponds to an increase in angular momentum quantum number of one unit. The eigenvalue spectrum of the partner follows immediately from the relation

$$\begin{aligned} a(l)a^\dagger(l)(a(l)\psi_{n_r,l}(r)) \\ = (a^\dagger(l+1)a(l+1) + 2\Delta E_{1,l})(a(l)\psi_{n_r,l}(r)) \\ = 2\Delta E_{n_r,l}(a(l)\psi_{n_r,l}(r)), \end{aligned} \quad (2.7)$$

where we note that the function $a(l)\psi_{n_r,l}(r)$ is an eigenstate of the radial Coulomb Hamiltonian corresponding to angular momentum quantum number $l+1$. Hence

$$\begin{aligned} a^\dagger(l+1)a(l+1)(a(l)\psi_{n_r,l}(r)) \\ = 2\Delta E_{n_r-1,l}(a(l)\psi_{n_r,l}(r)). \end{aligned} \quad (2.8)$$

If we assume that the wave functions are normalized, then

$$a(l)\psi_{n_r,l}(r) = \sqrt{2\Delta E_{n_r,l}}\psi_{n_r-1,l+1}(r), \quad (2.9)$$

$$a^\dagger(l)\psi_{n_r-1,l+1}(r) = \sqrt{2\Delta E_{n_r,l}}\psi_{n_r,l}(r), \quad (2.10)$$

where the operators $a(l)$, $a^\dagger(l)$ act as shift operators [16,17,19,23] for the radial Coulomb problem, acting at constant energy (i.e., constant value of the principal quantum number), to decrease [increase] by one unit the number of radial nodes with corresponding increase [decrease] in the value of the angular momentum quantum number.

Note that

$$a(l)\psi_{0,l}(r) \equiv 0 \quad (2.11)$$

such that $a(l)$ acts as a destruction operator for the ground state corresponding to a specified value of angular momentum quantum number l . The operators $a(l)$ serve to connect the set of degenerate states at constant value of the principal quantum number n and in combination act as destruction operators for any such state. For example, for the state $\psi_{0,1}(r)$, corresponding to $n=2$, we have

$$a(1)a(0)\psi_{1,0}(r) \propto a(1)\psi_{0,1}(r) \equiv 0. \quad (2.12)$$

These relations demonstrate that each eigenstate at a specified value of the principal quantum number can be related to every other eigenstate via the use of the various shift operators. This will be used in the following section to devise a simple proof of Eq. (1.1).

III. DERIVATION OF RELATION BETWEEN $\rho_n(r)$ AND $P_{n,0}(r)$

As discussed in the Introduction, Blinder [1] has derived a generalization of Unsold's theorem which, in its diagonal form, reveals a significant relationship between the closed-shell electron density in a bare Coulomb field and the corresponding s -state density. This relation is

$$\begin{aligned} \rho_n(r) &\equiv \sum_{l=0}^{n-1} (2l+1)R_{n,l}^2(r) \\ &= [P'_{n,0}(r)]^2 - P_{n,0}(r)P''_{n,0}(r), \end{aligned} \quad (3.1)$$

where $\rho_n(r)$ represents the electron density for the n th closed shell, $R_{n,l}(r) = rP_{n,l}(r)$, and $P_{n,0}(r)$ satisfies the radial Schrödinger equation

$$-P''_{n,0}(r) + \left[-\frac{2Z}{r} + \frac{Z^2}{n^2} \right] P_{n,0}(r) = 0. \quad (3.2)$$

For convenience, we have omitted a factor of 2, which arises from double occupancy of each of the orbitals.

In terms of the above standard notation, the shift operators defined in Sec. II become

$$a(l)P_{n,l}(r) = \alpha_l P_{n,l+1}(r), \quad (3.3)$$

$$a^\dagger(l)P_{n,l+1}(r) = \alpha_l P_{n,l}(r), \quad (3.4)$$

where the constant of proportionality α_l is defined by the relation

$$\alpha_l^2 = Z^2 \left[\frac{1}{(l+1)^2} - \frac{1}{n^2} \right]. \quad (3.5)$$

Note that $\alpha_l = 0$ when $l = n - 1$, as required.

It is instructive to demonstrate the validity of Eq. (3.1) in the simplest case of $n = 1$, before presenting a general derivation. When $n = 1$, we have

$$a(0)P_{1,0}(r) \equiv \left[\frac{d}{dr} - \frac{1}{r} + Z \right] P_{1,0}(r) = 0, \quad (3.6)$$

so that

$$P'_{1,0}(r) = \left[\frac{1}{r} - Z \right] P_{1,0}(r). \quad (3.7)$$

Then

$$\begin{aligned} [P'_{1,0}(r)]^2 &= \left[\left[\frac{1}{r} - Z \right] P_{1,0}(r) \right]^2 \\ &= \frac{1}{r^2} P_{1,0}^2(r) + \left[-\frac{2Z}{r} + Z^2 \right] P_{1,0}^2(r). \end{aligned} \quad (3.8)$$

Applying Eq. (3.2), with $n = 1$, gives

$$[P'_{1,0}(r)]^2 = R_{1,0}^2(r) + P_{1,0}(r)P''_{1,0}(r). \quad (3.9)$$

Hence we have the result

$$\rho_1(r) \equiv R_{1,0}^2(r) = [P'_{1,0}(r)]^2 - P_{1,0}(r)P''_{1,0}(r), \quad (3.10)$$

as required.

In order to treat the general case, we proceed as follows. From Eq. (3.3), and the definition of $a(0)$, we have

$$a(0)P_{n,0}(r) \equiv P'_{n,0}(r) + (-1/r + Z)P_{n,0}(r) = \alpha_0 P_{n,1}(r). \quad (3.11)$$

Hence

$$\begin{aligned} [P'_{n,0}(r)]^2 &= [(1/r - Z)P_{n,0}(r) + \alpha_0 P_{n,1}(r)]^2 \\ &= R_{n,0}^2(r) + P_{n,0}(r)P''_{n,0}(r) + F_0(r), \end{aligned} \quad (3.12)$$

where we have used Eq. (3.3) and the relation $\alpha_0^2 = Z^2(1 - 1/n^2)$. The function $F_0(r)$ represents the remainder and is defined by

$$\begin{aligned} F_0(r) &= \alpha_0 P_{n,0}(r) [\alpha_0(r)P_{n,0}(r) + 2(1/r - Z)P_{n,1}(r)] \\ &\quad + \alpha_0^2 P_{n,1}^2(r). \end{aligned} \quad (3.13)$$

We require a recursion relation for the functions $P_{n,l}(r)$, and this is provided in the Appendix, in which use is made of the properties of the shift operators. Applying Eq. (A5) in the case $l = 0$, we have

$$\alpha_0 P_{n,0}(r) = 3 \left[-\frac{1}{r} + \frac{Z}{2} \right] P_{n,1}(r) - \alpha_1 P_{n,2}(r), \quad (3.14)$$

and substitution into Eq. (3.13) gives the result

$$\begin{aligned} F_0(r) &= 3R_{n,1}^2(r) \\ &\quad + [\alpha_1 P_{n,1}(r)] [\alpha_1 P_{n,1}(r) + 2(2/r - Z/2)P_{n,2}(r)] \\ &\quad + \alpha_1^2 P_{n,2}^2(r), \end{aligned} \quad (3.15)$$

where we have used the fact that

$$(\alpha_0^2 - \frac{3}{4}Z^2) = \left[\frac{1}{4} - \frac{1}{n^2} \right] Z^2 \equiv \alpha_1^2. \quad (3.16)$$

We note that Eq. (3.15) is expressible in the form

$$F_0(r) = 3R_{n,1}^2(r) + F_1(r), \quad (3.17)$$

where $F_l(r)$ is defined by the relation

$$\begin{aligned} F_l(r) &= [\alpha_l P_{n,l}(r)] \{ \alpha_l P_{n,l}(r) \\ &\quad + 2[(l+1)/r - Z/(l+1)] \\ &\quad \times P_{n,l+1}(r) \} + \alpha_l^2 P_{n,l+1}^2(r) \end{aligned} \quad (3.18)$$

and represents the generalization of Eq. (3.15) to arbitrary l value. It is then a straightforward matter, using Eq. (A5), to derive the recursion formula

$$\begin{aligned} F_l(r) &= \frac{2l+3}{r^2} P_{n,l+1}^2(r) + F_{l+1}(r) \\ &\equiv (2l+3)R_{n,l+1}^2(r) + F_{l+1}(r), \end{aligned} \quad (3.19)$$

which leads to the expansion

$$\begin{aligned} F_0(r) &= 3R_{n,1}^2(r) + 5R_{n,2}^2(r) + \cdots + (2n-1)R_{n,n-1}(r) \\ &= \sum_{l=1}^{n-1} (2l+1)R_{n,l}^2(r). \end{aligned} \quad (3.20)$$

Combining Eqs. (3.12) and (3.20) gives the result

$$\begin{aligned} [P'_{n,0}(r)]^2 &= P_{n,0}(r)P''_{n,0}(r) + R_{n,0}^2(r) \\ &\quad + \sum_{l=1}^{n-1} (2l+1)R_{n,l}^2(r) \end{aligned}$$

or, equivalently,

$$[P'_{n,0}(r)]^2 - P_{n,0}(r)P''_{n,0}(r) = \sum_{l=0}^{n-1} (2l+1)R_{n,l}^2(r). \quad (3.21)$$

This equation demonstrates that the electron density $\rho_n(r)$ for the n th closed shell is related to the $l=0$ solution of the radial Schrödinger equation, in the form

$$\begin{aligned} \rho_n(r) &= \sum_{l=0}^{n-1} (2l+1)R_{n,l}^2(r) \\ &= [P'_{n,0}(r)]^2 - P_{n,0}(r)P''_{n,0}(r). \end{aligned} \quad (3.22)$$

Note that the derivation has made use of the properties of the Coulomb shift operators in order to transform between the set of degenerate eigenstates at fixed value of the principal quantum number. In the following sections, we will use Eq. (3.22) to derive differential equations satisfied by the electron density and kinetic-energy density for a specified closed shell and the Slater sum associated with an arbitrary number of closed shells in a bare Coulomb field.

IV. DIFFERENTIAL EQUATION SATISFIED BY $\rho_n(r)$

The starting point here is Eq. (3.22), namely,

$$\rho_n(r) = [P'_{n,0}(r)]^2 - P_{n,0}(r)P''_{n,0}(r). \quad (4.1)$$

Since $P_{n,0}(r)$ satisfies the radial Schrödinger equation

$$-P''_{n,0}(r) + \left[-\frac{2Z}{r} + \frac{Z^2}{n^2} \right] P_{n,0}(r) = 0, \quad (4.2)$$

Eq. (4.1) becomes

$$\rho_n(r) = [P'_{n,0}(r)]^2 + \left[\frac{2Z}{r} - \frac{Z^2}{n^2} \right] P_{n,0}^2(r). \quad (4.3)$$

Differentiation with respect to r gives

$$\rho'_n(r) = -\frac{2Z}{r^2} P_{n,0}^2(r) = -2ZR_{n,0}^2(r) \equiv -2Z\rho_{n,0}(r). \quad (4.4)$$

This is the result first derived by March [6] as the spatial generalization of Kato's theorem [7] for atomic closed shells in a Coulomb field. Summation over the quantum number n gives

$$\rho'(r) = -2Z\rho_s(r), \quad (4.5)$$

where $\rho_s(r)$ represents the s -state contribution to the electron density. This result is valid for a set of closed shells in a bare Coulomb field.

In order to derive a differential equation satisfied by $\rho_n(r)$, we proceed by introducing an intermediate variable $\sigma_{n,0}(r) = P_{n,0}^2(r)$. Then, since $\sigma'_{n,0}(r) = 2P_{n,0}(r)P'_{n,0}(r)$, we have

$$[P'_{n,0}(r)]^2 = \frac{[\sigma'_{n,0}(r)]^2}{4\sigma_{n,0}(r)}. \quad (4.6)$$

Hence, from Eq. (4.3),

$$\rho_n(r) = \frac{[\sigma'_{n,0}(r)]^2}{4\sigma_{n,0}(r)} + \left[\frac{2Z}{r} - \frac{Z^2}{n^2} \right] \sigma_{n,0}(r). \quad (4.7)$$

Since $\rho'_n(r)$ is related to $\sigma_{n,0}(r)$ through Eq. (4.5), expressed in the form

$$\rho'_n(r) = -2Z\rho_{n,0}(r) = -(2Z/r^2)\sigma_{n,0}(r), \quad (4.8)$$

we can relate $\sigma_{n,0}(r)$ and its derivatives to those of $\rho_n(r)$. Thus

$$\sigma_{n,0}(r) = -\frac{r^2}{2Z}\rho'_n(r), \quad (4.9)$$

$$\sigma'_{n,0}(r) = -\frac{r}{Z} \left[\frac{r}{2}\rho''_n(r) + \rho'_n(r) \right]. \quad (4.10)$$

This allows us to rewrite Eq. (4.7) in the form

$$\rho_n(r) = -\frac{1}{2Z} \left[\frac{r^2}{4} \frac{[\rho''_n(r)]^2}{\rho'_n(r)} + r\rho''_n(r) + \rho'_n(r) \right] - \frac{r^2}{2} \left[\frac{2}{r} - \frac{Z}{n^2} \right] \rho'_n(r) \quad (4.11)$$

or, equivalently,

$$-\rho''_n(r) - \frac{r}{4} \left[\frac{\rho''_n(r)}{\rho'_n(r)} \right]^2 \rho'_n(r) + \left[\frac{Z^2 r}{n^2} - \frac{1}{r} - 2Z \right] \rho'_n(r) - \frac{2Z}{r} \rho_n(r) = 0. \quad (4.12)$$

This represents a second-order nonlinear differential equation for the electron density of the n th closed shell in the bare Coulomb problem.

It can be shown from Eq. (4.3) and its derivative that

$$\frac{\rho''_n(r)}{\rho'_n(r)} = \frac{\rho'_{n,0}(r)}{\rho_{n,0}(r)}, \quad (4.13)$$

so that Eq. (4.12) can be written in the alternative form

$$-\rho''_n(r) - \frac{r}{4} \left[\frac{\rho'_{n,0}(r)}{\rho_{n,0}(r)} \right]^2 \rho'_n(r) + \left[\frac{Z^2 r}{n^2} - \frac{1}{r} - 2Z \right] \rho'_n(r) - \frac{2Z}{r} \rho_n(r) = 0. \quad (4.14)$$

We can derive a third-order nonlinear differential equation satisfied by $\rho_n(r)$, as first derived by March [6], as follows. Using Eq. (4.2), it is straightforward to show that $\sigma_{n,0}(r) = P_{n,0}^2(r)$ satisfies the differential equation

$$-\sigma''_{n,0}(r) + \frac{1}{2} \left[\frac{\sigma'_{n,0}(r)}{\sigma_{n,0}(r)} \right]^2 \sigma_{n,0}(r) + 2 \left[-\frac{2Z}{r} + \frac{Z^2}{n^2} \right] \sigma_{n,0}(r) = 0. \quad (4.15)$$

Converting Eq. (4.15) into an equation for $\rho_{n,0}(r) = \sigma_{n,0}(r)/r^2$ produces a second-order nonlinear differential equation satisfied by the s -state density $\rho_{n,0}(r)$, namely,

$$-\rho''_{n,0}(r) + \frac{1}{2} \left[\frac{\rho'_{n,0}(r)}{\rho_{n,0}(r)} \right]^2 \rho_{n,0}(r) - \frac{2}{r} \left[\frac{\rho'_{n,0}(r)}{\rho_{n,0}(r)} \right] \rho_{n,0}(r) + 2 \left[-\frac{2Z}{r} + \frac{Z^2}{n^2} \right] \rho_{n,0}(r) = 0. \quad (4.16)$$

If we now apply Eq. (4.3) in the form $\rho_{n,0}(r) = -\rho'_n(r)/2Z$, we regain the third-order nonlinear differential equation for $\rho_n(r)$ first derived by March [6], namely,

$$r\rho_n'''(r) - \frac{r}{2} \left[\frac{\rho_n''(r)}{\rho_n'(r)} \right]^2 \rho_n'(r) + 2\rho_n''(r) + \left[4Z - \frac{2Z^2 r}{n^2} \right] \rho_n'(r) = 0. \quad (4.17)$$

Such differential equations satisfied by the electron density of the n th closed shell in the bare Coulomb problem

are of interest in density-functional theory, as has been emphasized by March [6].

V. KINETIC-ENERGY DENSITY IN A BARE COULOMB FIELD

March and Santamaria [8] have recently derived a simple equation relating the kinetic-energy density and electron density for a specified closed shell in a bare Coulomb field to the corresponding s -state densities. Here we shall provide an alternative derivation of this relation and consider some of its consequences.

The kinetic-energy density for the n th closed shell in a bare Coulomb field is defined by

$$t_n(r) = -\frac{1}{2} \sum_{l=0}^{n-1} \sum_{m=-l}^l \psi_{nlm}^*(\mathbf{r}) \nabla^2 \psi_{nlm}(\mathbf{r}) \quad (5.1)$$

with corresponding s -state density

$$t_{n0}(r) = -\frac{1}{2} \psi_{n00}^*(\mathbf{r}) \nabla^2 \psi_{n00}(\mathbf{r}) . \quad (5.2)$$

Utilizing the Schrödinger equation satisfied by the hydrogenic wave function $\psi_{nlm}(\mathbf{r})$, we have

$$-\frac{1}{2} \psi_{nlm}^*(\mathbf{r}) \nabla^2 \psi_{nlm}(\mathbf{r}) = \left[\frac{Z}{r} - \frac{Z^2}{2n^2} \right] |\psi_{nlm}(\mathbf{r})|^2 . \quad (5.3)$$

Hence

$$t_n(r) = \left[\frac{Z}{r} - \frac{Z^2}{2n^2} \right] \sum_{l=0}^{n-1} \sum_{m=-l}^l |\psi_{nlm}(\mathbf{r})|^2 . \quad (5.4)$$

Since $\psi_{nlm}(\mathbf{r}) = R_{n,l}(r) Y_{l,m}(\theta, \phi)$, we have

$$\begin{aligned} t_n(r) &= \left[\frac{Z}{r} - \frac{Z^2}{2n^2} \right] \sum_{l=0}^{n-1} R_{n,l}^2(r) \sum_{m=-l}^l |Y_{l,m}(\theta, \phi)|^2 \\ &\equiv \frac{1}{4\pi} \left[\frac{Z}{r} - \frac{Z^2}{2n^2} \right] \sum_{l=0}^{n-1} (2l+1) R_{n,l}^2(r) . \end{aligned} \quad (5.5)$$

We have made use of the addition theorem for spherical harmonics,

$$\frac{2l+1}{4\pi} P_l(\cos\alpha) = \sum_{m=-l}^l Y_{l,m}^*(\theta_1, \phi_1) Y_{l,m}(\theta_2, \phi_2) , \quad (5.6)$$

where $P_l(\cos\alpha)$ is the l th Legendre polynomial and α is the angle between the two directions (θ_1, ϕ_1) and (θ_2, ϕ_2) . In the present case, $\theta_1 = \theta_2$ and $\phi_1 = \phi_2$, so that $\alpha = 0$, and hence $P_l(1) = 1$, so that

$$\sum_{m=-l}^l |Y_{l,m}(\theta, \phi)|^2 = \frac{2l+1}{4\pi} . \quad (5.7)$$

The s -state contribution to the kinetic-energy density is given, from Eq. (5.5), by

$$t_{n0}(r) = \frac{1}{4\pi} \left[\frac{Z}{r} - \frac{Z^2}{2n^2} \right] R_{n,0}^2(r) . \quad (5.8)$$

Combining Eqs. (5.5) and (5.8) leads to the relation

$$\frac{t_n(r)}{t_{n0}(r)} = \frac{\sum_{l=0}^{n-1} (2l+1) R_{n,l}^2(r)}{R_{n,0}^2(r)} \equiv \frac{\rho_n(r)}{\rho_{n,0}(r)} . \quad (5.9)$$

This significant result is a consequence of the fact that states with constant principal quantum number and different values of angular momentum quantum number are degenerate in a central Coulomb field.

It is a straightforward matter to relate $t_{n0}(r)$ to the function $P_{n,0}(r)$, such that

$$\begin{aligned} t_{n0}(r) &= -\frac{1}{8\pi} R_{n,0}(r) \frac{1}{r} \frac{\partial^2}{\partial r^2} [r R_{n,0}(r)] \\ &= -\frac{1}{8\pi r^2} P_{n,0} P_{n,0}''(r) \end{aligned} \quad (5.10)$$

since $P_{n,0}(r) \equiv r R_{n,0}(r)$. Using the relation

$$[P_{n,0}^2(r)]'' = 2[P_{n,0}(r)'(r)]^2 + 2P_{n,0}(r)P_{n,0}''(r) , \quad (5.11)$$

Eq. (3.22) becomes

$$\rho_n(r) = \frac{1}{2} [r^2 \rho_{n,0}(r)]'' - 2P_{n,0}(r)P_{n,0}''(r) . \quad (5.12)$$

Substitution into Eq. (5.10) yields the expression for $t_n(r)$ first derived by March and Santamaria [8], namely,

$$t_n(r) = \frac{1}{4\pi} \left[\frac{\rho_n(r)}{4r^2} - \frac{1}{8r^2} [r^2 \rho_{n,0}(r)]'' \right] . \quad (5.13)$$

Other consequential relations can also be derived [8], but these will not be considered further here.

VI. BOUND-STATE SLATER SUM FOR BARE COULOMB PROBLEM

In this section we shall consider the bound-state Slater sum for the bare Coulomb problem, defined by

$$S(r, \beta) = \sum_n \sum_{l=0}^{n-1} \sum_{m=-l}^l |\psi_{nlm}(\mathbf{r})|^2 e^{-\beta \epsilon_n} , \quad (6.1)$$

where $\beta = 1/k_B T$, $\psi_{nlm}(\mathbf{r})$ represents the hydrogenic wave function corresponding to quantum numbers (n, l, m) , and $\epsilon_n = -Z^2/2n^2$. As first demonstrated by March [5], using the result of Blinder [1], this bound-state Slater sum can be expressed in terms of the corresponding s -state sum. For completeness, we shall rederive this result here and proceed to identify a differential equation satisfied by the bound-state Slater sum $S(r, \beta)$.

Since

$$\sum_{m=-l}^l |\psi_{nlm}(\mathbf{r})|^2 = R_{n,l}^2(r) \sum_m |Y_{l,m}(\theta, \phi)|^2 , \quad (6.2)$$

and by use of Eq. (5.7), we have the result

$$\begin{aligned} S(r, \beta) &= \frac{1}{4\pi} \sum_n \sum_{l=0}^{n-1} (2l+1) R_{n,l}^2(r) e^{-\beta \epsilon_n} \\ &= \frac{1}{4\pi} \sum_n \rho_n(r) e^{-\beta \epsilon_n} . \end{aligned} \quad (6.3)$$

Using Eq. (3.22) this becomes

$$S(r, \beta) = \frac{1}{4\pi} \sum_n \{ [P'_{n0}(r)]^2 - P_{n0}(r)P''_{n0}(r) \} e^{-\beta\epsilon_n}. \quad (6.4)$$

The corresponding s -state sum is

$$S_0(r, \beta) = \frac{1}{4\pi} \sum_n \rho_{n0}(r) e^{-\beta\epsilon_n} = \frac{1}{4\pi r^2} \sum_n P_{n0}^2(r) e^{-\beta\epsilon_n}. \quad (6.5)$$

From Eqs. (6.4) and (6.5), it is straightforward to derive the relation

$$S(r, \beta) = \frac{1}{2} \frac{\partial^2}{\partial r^2} [r^2 S_0(r, \beta)] - 4 \frac{\partial}{\partial \beta} [r^2 S_0(r, \beta)] + 4Zr S_0(r, \beta). \quad (6.6)$$

From Eqs. (4.4) and (6.3), we have

$$\begin{aligned} \frac{\partial}{\partial r} S(r, \beta) &= \frac{1}{4\pi} \sum_n \rho'_n(r) e^{-\beta\epsilon_n} = -\frac{2Z}{4\pi} \sum_n \rho_{n0}(r) e^{-\beta\epsilon_n} \\ &= -2Z S_0(r, \beta). \end{aligned} \quad (6.7)$$

If we now differentiate Eq. (6.6) with respect to r , we find

$$\begin{aligned} \frac{\partial}{\partial r} S(r, \beta) &= \frac{1}{2} \frac{\partial^3}{\partial r^3} [r^2 S_0(r, \beta)] - 4 \frac{\partial^2}{\partial r \partial \beta} [r^2 S_0(r, \beta)] \\ &\quad + 4Z \frac{\partial}{\partial r} [r S_0(r, \beta)] - 4Z S_0(r, \beta), \end{aligned} \quad (6.8)$$

and this is equal to $-2Z S_0(r, \beta)$, from Eq. (6.7). The resultant third-order differential equation is equivalent, for the specific case of the bare Coulomb potential, to a result first derived by March and Murray [20]. The application of Eq. (6.7) to Eq. (6.8) results in a fourth-order differential equation [5] satisfied by the Slater sum for the bare Coulomb problem. However, if we use Eq. (6.7) to define an explicit relationship between $S_0(r, \beta)$ and $\partial S(r, \beta)/\partial r$, incorporation into Eq. (6.6) produces a third-order differential equation satisfied by the Slater sum for the bare Coulomb problem, namely,

$$\begin{aligned} S(r, \beta) &= -\frac{r^2}{4Z} \frac{\partial^3}{\partial r^3} S(r, \beta) - \frac{r}{Z} \frac{\partial^2}{\partial r^2} S(r, \beta) \\ &\quad - \frac{1}{2Z} \frac{\partial}{\partial r} S(r, \beta) - 2r \frac{\partial}{\partial r} S(r, \beta) \\ &\quad + \frac{2r^2}{Z} \frac{\partial^2}{\partial r \partial \beta} S(r, \beta). \end{aligned} \quad (6.9)$$

There does not appear to be a corresponding relation for the total closed-shell electron density $\rho(r)$ in the bare Coulomb field, although a formal expression can be obtained by considering the limit $\beta=0$ in Eq. (6.9). This difficulty arises from the explicit appearance of the energy eigenvalues ϵ_n within the summation over n , for which no further simplification appears possible.

VII. CONCLUSIONS

We have presented a simple proof of the relationship, first derived by Blinder, between the electron density and the corresponding s -state density, for a closed shell in a bare Coulomb field, based on the use of the shift operators which arise naturally in the supersymmetric treatment of the radial Coulomb problem. These shift operators act at constant value of the principal quantum number and hence at constant energy. This result between the density of a specified closed shell and the corresponding s -state density may be generalized to an arbitrary number of closed shells. In addition, it is possible to derive differential equations satisfied by the electron density within a specified closed shell and the Slater sum for an arbitrary number of closed shells. These equations are somewhat simpler than those derived previously. In addition, a proof is presented for the simple relation between the kinetic-energy and electron densities in a single closed shell, and the corresponding s -state densities. The results derived here may have relevance in density-functional theory, where the problem of noninteracting electrons in a bare Coulomb field is of importance since it represents an exactly solvable model.

APPENDIX

Here we shall derive a simple recursion formula for the states $P_{n,l}(r)$ using the shift operators which act at specified value of the principal quantum number. We have, from Eqs. (3.3) and (3.4),

$$a^\dagger(l) P_{n,l+1}(r) = \alpha_l P_{n,l}(r), \quad (A1)$$

$$a(l+1) P_{n,l+1}(r) = \alpha_{l+1} P_{n,l+2}(r). \quad (A2)$$

Equation (A1) is expressible in the form

$$\alpha_l P_{n,l}(r) = -P'_{n,l+1}(r) + \left[-\frac{l+1}{r} + \frac{Z}{l+1} \right] P_{n,l+1}(r) \quad (A3)$$

while Eq. (A2) becomes

$$\begin{aligned} \alpha_{l+1} P_{n,l+2}(r) &= P'_{n,l+1}(r) + \left[-\frac{l+2}{r} + \frac{Z}{l+2} \right] P_{n,l+1}(r). \end{aligned} \quad (A4)$$

Elimination of $P'_{n,l+1}(r)$ from Eqs. (A3) and (A4) yields the desired recursion relation

$$\begin{aligned} \alpha_l P_{n,l}(r) &= (2l+3) \left[-\frac{1}{r} + \frac{Z}{(l+1)(l+2)} \right] P_{n,l+1}(r) \\ &\quad - \alpha_{l+1} P_{n,l+2}(r). \end{aligned} \quad (A5)$$

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