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Bound-state plus continuum electron densities, and Slater sum, in a bare Coulomb field

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After reporting numerical studies based solely on s-states of total (s + p + d etc.) bound-state densities, which allow the range of validity of the simplest density functional theory of Thomas and Fermi to be critically assessed, two areas in which analytical progress proves possible are focused on. The first of these is the local density of states in the continuum, for which an exact formula is derived. The second concerns the Slater sum, for which an explicit differential equation is established. Prior to this, only the Bloch equation satisfied by the off-diagonal generalization of the Slater sum, namely the canonical density matrix, was available.

1. Introduction

In the important $1/Z$ expansion of the ground-state energy of an atomic ion of nuclear charge Ze and with N electrons, this energy $E(Z,N)$ is expressed as

$$E(Z,N) = Z^2\left(\epsilon_0(N) + \frac{1}{Z}\epsilon_1(N) + \frac{1}{Z^2}\epsilon_2(N) + \dots\right) \tag{1.1}$$

following Hylleraas [1], Layzer [2] and others [3]. In this expansion, $\epsilon_0(N)$ is completely determined by solution of the bare Coulomb field problem, while the higher terms in the series account for effects of screening, plus exchange and correlation. While, for fixed N, the convergence of this series is guaranteed for sufficiently large Z, for other than the lightest atoms it is essential to sum the series (1.1). As was pointed out by March and White [4] in early work, one such partial sum is afforded by the Thomas–Fermi limit of density functional theory, which leads to the result

$$E_{\mathrm{TF}}(Z,N) = Z^{7/3}f(N/Z)\,, \tag{1.2}$$

where the function $f(x)$ is known from numerical solution of the Thomas–Fermi self-consistent field problem [4]. For neutral atoms, ie $N = Z$, the term $Z^{7/3}$ from eq. (1.2) has to be corrected by a term of $O(Z^2)$ from an inner-electron correction neglected in the Thomas–Fermi (TF) approach [5–7], a Dirac–Slater exchange term [5] of $O(Z^{5/3})$ and a correlation energy of $O(Z)$ (see ref. [8] and other authors cited there). Such a development gives an excellent overall account of numerical Hartree–Fock energies calculated for individual atoms.

Such progress in calculating the ground-state energy has prompted recent parallel studies of the ground-state electron density. Two aspects are important in the present context. First of all, since the leading term in the energy expansion (1.1) is for electrons, taken as non-interacting, moving in a bare Coulomb potential $-Ze^2/r$, the ground-state electron density $\rho(r)$ in this potential is of obvious interest. For closed shells, considerable progress has proved possible. One step, for densities of s + p + d etc. states associated with closed shells, has been the derivation of an exact spatial generalization of Kato's theorem to read [9]

$$\frac{\partial \rho(r)}{\partial r} = -\frac{2Z}{a_0}\rho_s(r), \quad a_0 = \hbar^2/me^2 . \tag{1.3}$$

This has already proved valuable [10]; here we shall use it to construct the total (s + p + d etc.) density for 5 closed shells by computing solely the s-state density ρ_s and then determining $\rho(r)$ by numerical quadrature using eq. (1.3). The result for $\rho(r)$ is then utilized to make a critical assessment of the range of validity of the simplest density functional theory of Thomas and Fermi (TF).

Following this numerical study of bound states, attention will then be focused on two specific areas where analytical progress proves possible. The first of these is the local density of states in the continuum. Here, analytical forms are established, both from the (approximate) TF density functional theory and then exactly via a Green function calculation, using the work of Blinder [11] and of earlier authors. This analytical progress is summarized in section 3.

The second area in which analytical progress proves possible is in treating bound plus continuum states via the so-called Slater sum $S(r, \beta)$, defined explicitly in eq. (4.2) below. The essential result of this part of the present investigation is to establish the differential equation (4.13) for $S(r, \beta)$. Prior to the present work, one had to use the Bloch equation, which is obeyed by the off-diagonal generalization of the Slater sum, namely the canonical density matrix. Clearly it is a major simplification to be able to work directly with the diagonal matrix, or Slater sum. Section 5 constitutes a brief summary.

2. Ground-state density for closed shells in a bare Coulomb field

To obtain the ground-state density $\rho(r)$, the simplest route is to calculate the s-state density $\rho_s(r)$ in eq. (1.3) by summing the squares of the s-state hydrogenic wave functions, and then integrating eq. (1.3) to read

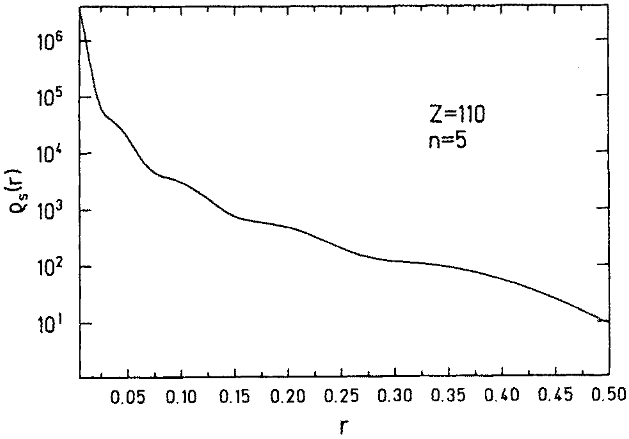

Fig. 1. The s-state density $\rho_s(r)$ calculated for doubly filled levels in a bare Coulomb field. The result is for nuclear charge 110*e* and for 5 closed shells. Atomic units are employed in all figures.

$$\rho(r) = \frac{2Z}{a_0} \int_r^\infty \rho_s(r)\, \mathrm{d}r\,. \tag{2.1}$$

As an example, fig. 1 depicts the s-state density for 5 closed shells obtained by summing the squares of the wave functions $\Phi_{n00}(r)$ from $n = 1$ to 5. The plot in fig. 1 has been produced for the specific case $Z = 110$, which corresponds to a "neutral" system in that 5 closed shells in the bare Coulomb field, with $2n^2$ electrons per closed shell, contain 110 electrons. The "ripples" in the s-state density shown become pronounced when $\rho_s(r)$ is multiplied by r^2, as illustrated in fig. 2. All plots in the paper are made in atomic units.

Using the results for $\rho_s(r)$ shown in fig. 1, eq. (2.1) has been utilized to obtain

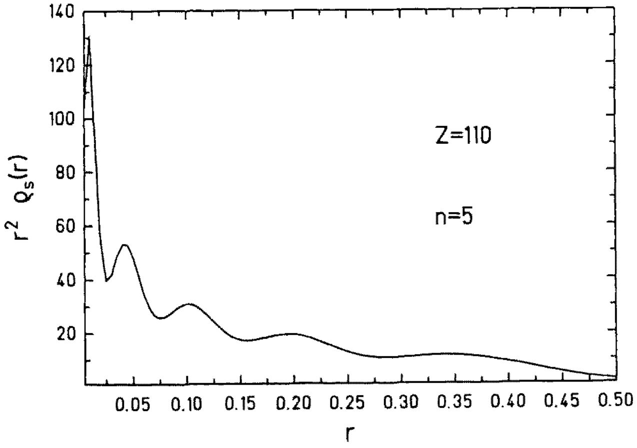

Fig. 2. r^2 times s-state density of fig. 1, to reveal "shells" more clearly.

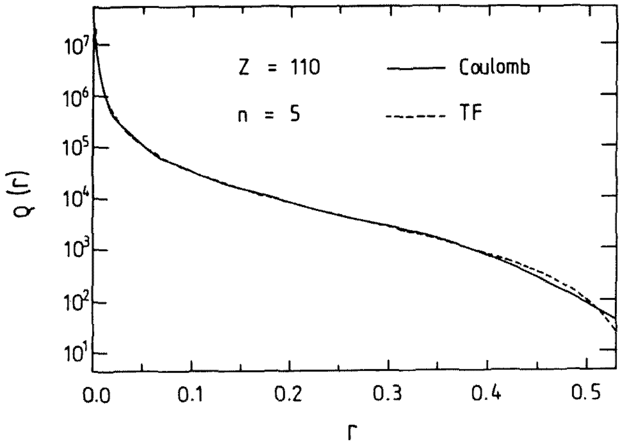

Fig. 3. Solid curve: the exact wave mechanical ground state density $\rho(r)$ calculated directly from the s-state density of fig. 1 by using eq. (2.1). The dashed curve is the result of Thomas–Fermi statistical theory as given in eqs. (2.2) and (2.3). Again $Z = 110$ and $N = Z$.

the total ground-state density $\rho(r)$ for 5 closed shells by numerical quadrature. The result is shown by the solid curve of fig. 3. It is to be stressed that in obtaining this curve, one has avoided recourse to any wave functions having angular dependence, that is p, d, etc., wave functions. For closed shell systems, as exemplified by eqs. (1.3) and (2.1), the s-state density suffices to determine $\rho(r)$. As in fig. 2 for this s-state density, fig. 4 shows $D(r) = 4\pi r^2\rho(r)$, the radial electron density. In contrast to fig. 2, where the "shells" are pronounced, in the total density $D(r)$ the shells are beginning to be smoothed out, for this example with 110 electrons. Eventually, of course, if one filled a sufficiently large number of closed shells, one must

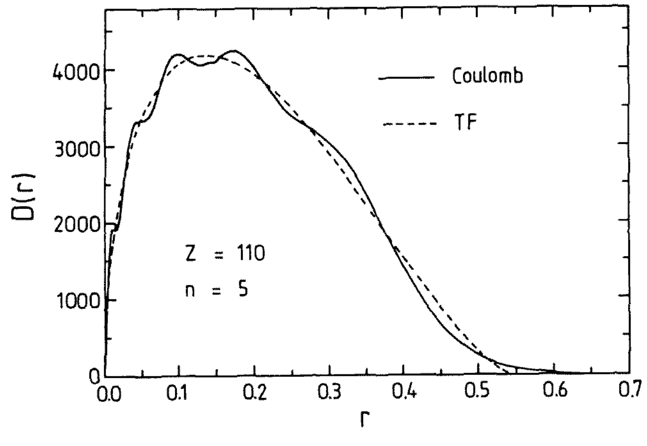

Fig. 4. Radial density $D(r) = 4\pi r^2\rho(r)$, obtained from $\rho(r)$ in fig. 3.

asymptotically approach the TF semiclassical density. This is given explicitly in the bare Coulomb field problem under discussion by

$$\rho_{\mathrm{TF}}(r) = c_3\left[\mu + \frac{Ze^2}{r}\right]^{3/2}, \quad c_3 = \frac{8\pi}{3h^3}(2m)^{3/2}. \tag{2.2}$$

The chemical potential μ is, of course, to be determined by normalization of the total electron density. In the present case it is given in atomic units by [3]

$$\mu = -\frac{1}{18^{1/3}}Z^2N^{-2/3} \tag{2.3}$$

with $N = \int \rho(r)\mathrm{d}\boldsymbol{r}$ being the total number of electrons as above. For $N = Z = 110$, the result (2.2) is shown by the dotted curve in fig. 3. The corresponding approximation to the radial density $D(r)$ is similarly shown in fig. 4. Clearly, it can be seen that especially from fig. 4 the TF statistical theory is not fully quantitative for the ground-state electron density $\rho(r)$ even for 110 electrons. Furthermore, of course, as follows from eq. (2.2) plus eq. (2.3), it has a classical cutoff radius, r_c say, given by $Ze^2/r_c = |\mu|$, while there is a singularity in the density like $r^{-3/2}$ as one approaches the point nucleus.

Using the present method based on eq. (2.1), it will be a straightforward matter in the future to repeat the calculations shown in figs. 1–4 for a larger number of closed shells. The economy of the present approach is best illustrated by noting that, as already mentioned, there are $2n^2$ electrons in a closed shell of principal quantum number n for the bare Coulomb field, of which only 2 are s electrons.

We turn next to the treatment of continuum states. In the spirit of the TF theory in eq. (2.2), this is moving from the regime of negative chemical potential μ to the case where μ is greater than zero. Here we shall focus all attention on the local density of states, to be defined precisely below.

3. Local density of states in continuum

Let us start out from the TF relation (2.2) and define $\rho(r, E)$ from it by replacing μ by the (now positive) energy E. Since we are in the continuum, let us then differentiate $\rho(r, E)$ with respect to energy E. This defines the local density of states $N(r, E)$, which is evidently given in the TF approximation by

$$N_{\mathrm{TF}}(r, E) = \frac{\partial}{\partial E}\rho_{\mathrm{TF}}(r, E) = \frac{3c_3}{2}\left[E + \frac{Ze^2}{r}\right]^{1/2}. \tag{3.1}$$

If we "switch off" the atomic potential $-Ze^2/r$ in eq. (3.1) by letting Z tend to zero, then we obtain the density of states $N(E)$ of free electrons, the resulting system being described by plane waves and having therefore translational invariance.

The object of the present section is purely analytical; to replace the approximate TF formula (3.1) for the bare Coulomb field by an exact result.

3.1. USE OF COULOMB GREEN FUNCTION

The tool we shall employ here is the Coulomb Green function, the analytical form of which has been studied by many workers [11]. To be precise, we define this Green function by

$$G(\boldsymbol{r}_1,\boldsymbol{r}_2,E)=\sum_{nlm}\frac{\psi^*_{nlm}(\boldsymbol{r}_1)\psi_{nlm}(\boldsymbol{r}_2)}{E-\epsilon_n}\,, \tag{3.2}$$

where ϵ_n are the exact levels for the Coulomb field, with Im $E>0$ for G^+.

Following Blinder [11], we employ the new independent variables

$$x=r_1+r_2+r_{12},\quad y=r_1+r_2-r_{12},\quad x\geqslant y\geqslant 0\,, \tag{3.3}$$

where $\boldsymbol{r}_1-\boldsymbol{r}_2=\boldsymbol{r}_{12}$ and $r_{12}=|\boldsymbol{r}_{12}|$. Writing $E=k^2/2$, Blinder then finds

$$G^+(x,y,k)=\frac{ik}{2\pi}\int_0^\infty \mathrm{d}s\sinh s\Big(\coth\frac{s}{2}\Big)^{2i\nu}\exp(ik\xi\cosh s)J_0(k\eta\sinh s) \tag{3.4}$$

with $\xi=(1/2)(x+y),\eta=(xy)^{1/2}$ and $\nu=Z/k$. We note from eq. (3.4) that G^+ is a function of only two space variables x and y. This, in turn, results from the fact that for the bare Coulomb field the Runge–Lenz vector is a constant of motion [12].

As Z tends to zero, ie ν tends to zero, eq. (3.4) reduces to the free-particle Green function, G_0^+ say, namely

$$G_0^+=\frac{\exp(ik|\boldsymbol{r}_1-\boldsymbol{r}_2|)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,. \qquad (3.5$$

If we take the imaginary part of G_0^+, we evidently find

$$\mathrm{Im}\ G_0^+(\boldsymbol{r}_1,\boldsymbol{r}_2,E)=\frac{\sin k|\boldsymbol{r}_1-\boldsymbol{r}_2|}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,. \tag{3.6}$$

If one now goes on to the diagonal $\boldsymbol{r}_1=\boldsymbol{r}_2=\boldsymbol{r}$ say, then eq. (3.6) yields

$$\mathrm{Im}\ G_0^+(\boldsymbol{r}_1,\boldsymbol{r}_2,E)=k=(2E)^{1/2}\,, \tag{3.7}$$

which is essentially the free-electron density of states discussed above. In fact, the above correspondence follows from the quite general result for the local density of states $N(\boldsymbol{r},E)$, namely [13]

$$N(\boldsymbol{r},E)=\frac{\partial\rho(\boldsymbol{r},E)}{\partial E}=\frac{1}{\pi^2}\mathrm{Im}\ G^+(\boldsymbol{r},\boldsymbol{r},E)\,. \tag{3.8}$$

The result (3.8), when combined with eq. (3.4) above, provides us with a route to calculate the local density of states in the bare Coulomb field.

3.2. LOCAL DENSITY OF STATES $N(r,E)$

Obviously one wants to take, from eq. (3.8), first the imaginary part of $G^+(x,y,k)$ in eq. (3.4) and secondly to go on to the diagonal $\boldsymbol{r}_1=\boldsymbol{r}_2=\boldsymbol{r}$. From the definitions of x and y in eq. (3.3), this second step is equivalent to putting $x=y=2r$.

To facilitate these two steps, we note with Blinder [11] that the substitution $\sinh s = \operatorname{csch} q$ transforms the integral in eq. (3.4) to give

$$G^{+}(x,y,k) = \frac{ik}{2\pi}\int_0^{\infty} dq\, \operatorname{csch}^2 q \exp(i[2\nu q + k\xi \coth q]) J_0(k\eta \operatorname{csch} q)\,. \tag{3.9}$$

Taking the imaginary part of eq. (3.9), one can then put $x=y=2r$ to find the result

$$N(r,E) = \frac{(2E)^{1/2}}{2\pi^3}\int_0^{\infty} dq\, \operatorname{csch}^2 q\, \cos\left[\frac{2Zq}{k} + 2kr\coth q\right] J_0(2kr \operatorname{csch} q)\,, \tag{3.10}$$

where $k^2 = 2E$. The integral can now be evaluated, with the result

$$N(r,E) = \frac{k}{4\pi^3}\sqrt{\frac{\pi\nu}{\sinh \pi\nu}}\cos\left\{\nu\gamma - \sum_{n=1}^{\infty}\left[\frac{\nu}{n} - \tan^{-1}\left(\frac{\nu}{n}\right)\right]\right\} \times \left[M'_{i\nu,1/2}(ikr)\, W'_{i\nu,1/2}(ikr) - \left(\frac{1}{4}+\frac{\nu}{kr}\right) M_{i\nu,1/2}(ikr)\, W_{i\nu,1/2}(ikr)\right]. \tag{3.11}$$

The functions M and W appearing in eq. (3.11) are Whittaker functions. The quantity γ denotes Euler's constant. It can be shown that the right-hand side of eq. (3.11) is real. The result (3.11) achieves the objective of transcending the semiclassical approximation (3.1) for this case of the bare Coulomb field.

Having discussed the quantum mechanics of bound and continuum electron densities in the Coulomb field case, we shall finally consider the calculation of the Slater sum for this same field. This, of course, involves both bound and continuum states together (see eq. (4.2) below).

4. Differential equation for Slater sum for bare Coulomb field

For a one-electron Hamiltonian $H_{\boldsymbol{r}}$ of the form

$$H_{\boldsymbol{r}} = -\frac{1}{2}\nabla_{\boldsymbol{r}}^2 + V(\boldsymbol{r})\,, \tag{4.1}$$

the Slater sum $S(\boldsymbol{r},\beta)$ is defined by

$$S(\boldsymbol{r},\beta) = \sum_{\text{all } i} \psi_i^{*}(\boldsymbol{r})\psi_i(\boldsymbol{r})\, \exp(-\beta\epsilon_i), \quad \beta = (k_{\mathrm{B}}T)^{-1}\,. \tag{4.2}$$

In eq. (4.2), $\psi_i(\boldsymbol{r})$ and ϵ_i represent, respectively, the normalized eigenfunctions and eigenvalues of the hamiltonian (4.1). The Bloch equation

$$H_r C(\boldsymbol{r}, \boldsymbol{r}', \beta) = -\frac{\partial C(\boldsymbol{r}, \boldsymbol{r}', \beta)}{\partial \beta} \tag{4.3}$$

affords a well-established route to the canonical density matrix $C(\boldsymbol{r}, \boldsymbol{r}', \beta)$. $S(\boldsymbol{r}, \beta)$ is then the diagonal element $C(\boldsymbol{r}, \boldsymbol{r}, \beta)$. However March and Murray [14] showed, for central field problems in which $V(\boldsymbol{r}) = V(|\boldsymbol{r}|)$, that a partial wave analysis could lead to $S(r, \beta)$ in the form

$$S(r, \beta) = \sum_{l=0} (2l+1) S_l(r, \beta) \tag{4.4}$$

and that $S_l(r, \beta)$ itself satisfied the differential equation

$$\frac{1}{8} \frac{\partial^3}{\partial r^3} (r^2 S_l) - \frac{l(l+1)}{2r} \frac{\partial}{\partial r} (r S_l) - \frac{1}{2} \frac{\partial V}{\partial r} (r^2 S_l) \\ - V \frac{\partial}{\partial r} (r^2 S_l) - \frac{\partial^2}{\partial r \, \partial \beta} (r^2 S_l) = 0 \,. \tag{4.5}$$

If one multiplies eq. (4.5) by $(2l+1)$ and sums over all l to form $S(r, \beta)$ in eq. (4.4), the term involving $l(l+1)$ in eq. (4.5) presents a stumbling block, and for a general central field potential $V(r)$ this summation has so far not been achieved. The resulting differential equation therefore relates S and its derivatives to this summation of S_l and its derivative $\partial S_l / \partial r$.

However, for the bare Coulomb field (cf. eq. (1.3) above), Storer [15] and later Pollock [16] have demonstrated that the canonical density matrix $C(\boldsymbol{r}, \boldsymbol{r}', \beta)$ entering eq. (4.3) can be directly related to its s-wave component $C_{l=0}(\boldsymbol{r}, \boldsymbol{r}', \beta)$. This strongly suggests for this specific model that $S(r, \beta)$ should be determined solely by $S_{l=0}(r, \beta) = S_s(r, \beta)$, the s-wave contribution in eq. (4.4). Storer introduces $P_{ns}(\mathrm{r}) = r \psi_{ns}(\mathrm{r})$ and then shows that

$$S(r, \beta) = -\frac{1}{2} \lim_{s \to 0} \frac{\partial^2}{\partial s^2} \left[\sum_{\text{all}\, n} P^*_{ns}(r+s) P_{ns}(r-s) \ \exp(-\beta \epsilon_n) \right] . \tag{4.6}$$

Expanding the RHS of eq. (4.6) around $s = 0$, one readily finds

$$\lim_{s \to 0} \frac{\partial^2}{\partial s^2} \sum_n \exp(-\beta \epsilon_n) \Big[|P_{ns}|^2 + s \big(P^{*\prime}_{ns} P_{ns} - P^*_{ns} P'_{ns} \big)_{s=0} \\ + \frac{s^2}{2} \big(P^{*\prime\prime}_{ns} P_{ns} + P^*_{ns} P''_{ns} - 2 P^{*\prime}_{ns} P'_{ns} \big)_{s=0} + O(s^3) \Big] \\ = \sum_n \exp(-\beta \epsilon_n) \big[P^{*\prime\prime}_{ns} P_{ns} + P^*_{ns} P''_{ns} - 2 P^{*\prime}_{ns} P'_{ns} \big]_{s=0} \,. \tag{4.7}$$

From the definition of S_s we find that

$$\frac{\partial^2}{\partial r^2} [r^2 S_s(r, \beta)] = \sum_n \exp(-\beta \epsilon_n) \big[P^{*\prime\prime}_{ns} P_{ns} + P^*_{ns} P''_{ns} + 2 P^{*\prime}_{ns} P'_{ns} \big] \tag{4.8}$$

and

$$-\frac{\partial}{\partial\beta}\left(r^2 S_s(r,\beta)\right) = \sum_n \epsilon_n |P_{ns}|^2 \exp(-\beta\epsilon_n)\,. \tag{4.9}$$

Furthermore, the P_{ns} are solutions of the radial Schrödinger equation

$$P''_{ns} + 2\left(\frac{Z}{r} + \epsilon_n\right)P_{ns} = 0\,. \tag{4.10}$$

Inserting eqs. (4.8)–(4.10) in eq. (4.7), the relation (4.6) finally takes the form

$$S(r,\beta) = \frac{1}{2}\frac{\partial^2}{\partial r^2}\left(r^2 S_s\right) - 4\frac{\partial}{\partial\beta}\left(r^2 S_s\right) + \frac{4Z}{r}\left(r^2 S_s\right)\,. \tag{4.11}$$

Taking the r-derivative of eq. (4.11) and returning to eq. (4.5) for s-states, ie $l = 0$, one obtains

$$\frac{\partial S}{\partial r} = -2ZS_s\,. \tag{4.12}$$

We stress that eq. (4.12) is the analogue in statistical mechanics of the quantum-mechanical spatial generalization (1.3) of Kato's theorem [9] for the bare Coulomb field. One can now substitute for S_s in eq. (4.11) when the desired differential equation for the Slater sum $S(r,\beta)$ results, namely

$$-2ZS = \frac{r^2 S'''}{2} + 2rS'' + \left[1 + 4r^2\left(\frac{Z}{r} - \frac{\partial}{\partial\beta}\right)\right]S'\,, \tag{4.13}$$

with the primes denoting the derivatives with respect to r.

Equation (4.13) has been shown to hold for the bound part of S:

$$S_b = \sum_{\substack{\text{bound}\\ \text{states}}} \exp(-\beta\epsilon_n)|\psi_{nlm}(\boldsymbol{r})|^2 \tag{4.14}$$

in earlier work [17]. However the existence of a more general relation seemed to us likely from the infinite series form of S given by Blinder [18]. By means of eq. (4.12), S_s may be calculated from Blinder's result.

5. Summary

The spatial generalization (1.3) of Kato's theorem can be used to provide a direct route to the calculation of the total density from the s-state density (see figs. 1–4 above). The analogue of eq. (1.3) for the Slater sum has been obtained here, the result being exhibited in eq. (4.12).

Specific to continuum states, again for the model of the bare Coulomb field, the local density of states $N(r,E)$ can be obtained. This is given in the form of a onedimensional quadrature in eq. (3.10). This can be evaluated as an infinite series, as in eq. (3.11).

Finally, by utilizing the result (4.12) relating the Slater sum S to its s-wave component S_s, a third order partial differential equation has been obtained for the Slater sum in a bare Coulomb field. An exact solution of this, again though in the form of an infinite series, is then known from the earlier work of Blinder [18].

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