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Bound-state position and momentum densities and Slater sum for closed shells in a bare Coulomb field

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Some generalizations are effected here of the work of Heilmann and Lieb [Phys. Rev. A **52**, 3628 (1995)], who summed the squares of all the normalized bound-state wave functions for the hydrogen atom. One of their main results is shown to be equivalent to a spatial generalization of Kato's theorem. Their asymptotic evaluation of the above sum for large r is used to obtain a property of the bound-state Slater sum in the high-temperature limit. The corresponding momentum space density is also briefly discussed. [S1050-2947(96)00412-X]

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Motivated by the recent study of Heilmann and Lieb [1] (HL), we consider here the electron density for a bare Coulomb field. This is defined in terms of the hydrogenic bound-state wave functions $\psi_{nlm}(\mathbf{r})$, normalized such that

$$\int \psi_{nlm}(\mathbf{r})\psi^*_{nlm}(\mathbf{r})d\mathbf{r}=1 \tag{1}$$

by

$$\rho_{\mathcal{N}}(r)=\sum_{n=1}^{\mathcal{N}}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\psi_{nlm}(\mathbf{r})\psi^*_{nlm}(\mathbf{r}). \tag{2}$$

Following the pioneering work of Feynman, Metropolis, and Teller [2], who introduced temperature effects into the Thomas-Fermi theory, the simplest density-functional theory to be referred to again briefly below, we shall generalize the work of HL to embrace the bound-state (only) Slater sum $S_b(r,\beta)$:

$$S_b(r,\beta)=\sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\psi_{nlm}(\mathbf{r})\psi^*_{nlm}(\mathbf{r})\exp(-\beta\epsilon_n),$$

$$\beta=(k_BT)^{-1}, \tag{3}$$

where ϵ_n are the hydrogenic levels $-Z^2/2n^2$ in units of e^2/a_0, with a_0 the Bohr radius $\hbar^2/me^2$. Following [1], we shall often scale from the case of hydrogen where $Z=1$. In the context of the Slater sum, which is seen from Eq. (3) to involve the Boltzmann factor $\exp(-\beta\epsilon_n)$, it is known from the work of March and Murray [3] that the Fermi-Dirac statistics [2] can be obtained from the Boltzmann form, albeit by a somewhat complicated transform procedure.

Returning now to the electron density defined in Eq. (2), the present author [4] has obtained the spatial generalization of Kato's theorem [5] for an arbitrary number of closed shells $\mathcal{N}$ as

$$\frac{\partial\rho_{\mathcal{N}}(r)}{\partial r}=-2\rho_{\mathcal{N}s}(r), \quad a_0=Z=1, \tag{4}$$

where $\rho_{\mathcal{N}s}(r)$ is the s-state ($l=0$) contribution to the total electron density $\rho_{\mathcal{N}}(r)$. This result (4), in the limit in which the number of closed shells $\mathcal{N}$ tends to infinity, can readily be seen to be equivalent to Eq. (2.12) of HL, when their Eqs. (1.24) and (1.25) are also used with the orbital angular momentum quantum number l set equal to zero.

One of the achievements of the study of HL is to evaluate $\rho_\infty(r)$ asymptotically for large r as

$$\rho_\infty(r)=Ar^{-3/2}, \quad A=2^{1/2}(3\pi^2)^{-1}, \quad r\to\infty, \tag{5}$$

where the constant A is precisely equal to the Thomas-Fermi constant in the form of $\rho_\infty(r)$ at, however, small r. Using Eq. (4), one finds immediately for the s-state density $\rho_{\infty s}(r)$,

$$\rho_{\infty s}(r)=\tfrac{3}{4}Ar^{-5/2}, \quad r\to\infty. \tag{6}$$

For any finite number $\mathcal{N}$ of closed shells, $\rho_{\mathcal{N}}(r)$ and $\rho_{\mathcal{N}s}(r)$ fall off exponentially, with the rate of falloff dominated by the factor $\exp(-2r/\mathcal{N})$ at sufficiently large distances from the nucleus. HL determine the maximum value of $\rho_\infty(r)$ as $\rho_\infty(r=0)\simeq0.383$, which is, of course, solely due to the s states. The generalized Kato theorem tells us that, since $\rho_{\infty s}(r)>0$, $\partial\rho_\infty(r)/\partial r$ is negative for all finite r and this is also true for an arbitrary number of closed shells $\mathcal{N}$ from Eq. (4).

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Let us turn next to the bound-state Slater sum $S_b(r,\beta)$ defined in Eq. (3) (see also [6]). March and Murray [3] (see also [7]) derived the differential equation relating the Slater sum $S_b(r,\beta)$ to its s-state ($l=0$) component $S_{bO}(r,\beta)$ as (setting $Z=1$)

$$\frac{\partial}{\partial r} S_b(r,\beta)=\frac{1}{2}\frac{\partial^3}{\partial r^3}[r^2 S_{b0}(r,\beta)]-4\frac{\partial^2}{\partial r\partial\beta}[r^2 S_{b0}(r,\beta)]+4\frac{\partial}{\partial r}[rS_{b0}(r,\beta)]-4S_{b0}(r,\beta) \tag{7}$$

and this is equal to $-2S_{b0}(r,\beta)$ from the spatial generalization (4) of Kato's theorem. Independently, Pfalzner, Lehmann, and March [8] (see also [9]) and Cooper [7] have derived a third-order differential equation satisfied by the Slater sum for the bare Coulomb problem, namely (again with $Z=1$),

$$S_b(r,\beta)=-\frac{r^2}{4}\frac{\partial^3}{\partial r^3}S_b(r,\beta)-r\frac{\partial^2}{\partial r^2}S_b(r,\beta)-\frac{1}{2}\frac{\partial}{\partial r}S_b(r,\beta)-2r\frac{\partial}{\partial r}S_b(r,\beta)+2r^2\frac{\partial^2}{\partial r\partial\beta}S_b(r,\beta). \tag{8}$$

Now let us employ the definition (3) to form the derivatives on the right-hand side (rhs) of Eq. (8), e.g.,

$$\frac{\partial}{\partial\beta}S_b(r,\beta)=\sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\psi_{nlm}(\mathbf{r})\psi^*_{nlm}(\mathbf{r})(-\epsilon_n)\times\exp(-\beta\epsilon_n). \tag{9}$$

Because of the separability of the individual terms in the summation on the rhs of Eq. (9), the r derivative and the $\beta\to 0$ limit are interchangeable. One can rewrite Eq. (8) as

$$\rho_\infty(r)\equiv S_b(r,\beta)|_{\beta\to 0}=-\frac{r^2}{4}\frac{\partial^3}{\partial r^3}\rho_\infty(r)-r\frac{\partial^2}{\partial r^2}\rho_\infty(r)-\frac{1}{2}\frac{\partial}{\partial r}\rho_\infty(r)-2r\frac{\partial}{\partial r}\rho_\infty(r)+2r^2\frac{\partial^2}{\partial r\partial\beta}S_b(r,\beta)|_{\beta\to 0}. \tag{10}$$

Using the large-r form (5) in Eq. (10) yields, to $O(r^{-3/2})$, after a short calculation,

$$\frac{\partial^2}{\partial r\partial\beta}S_b(r,\beta)|_{\beta\to 0}=-\frac{A}{r^{7/2}},\quad r\to\infty, \tag{11}$$

with only the last two terms on the rhs of Eq. (10) contributing to $O(r^{-3/2})$. Evidently, using the HL form (2.1) of $\rho_\infty(r)$, one can obtain further terms in the large-r result (11).

Since Kato's generalized theorem gives $\partial S_b/\partial r=-2S_{bO}$, we also obtain from Eq. (11), to leading order at large r,

$$\frac{\partial S_{b0}}{\partial\beta}(r,\beta)\bigg|_{\beta\to 0}=\frac{A}{2r^{7/2}}. \tag{12}$$

But

$$S_{b0}(r,\beta)=\sum_{n=1}^{\infty}\psi_{n00}(r)\psi^*_{n00}(r)\exp(-\beta\epsilon_n) \tag{13}$$

and hence

$$\frac{\partial S_{b0}(r,\beta)}{\partial\beta}\bigg|_{\beta\to 0}=\sum_{n=1}^{\infty}\psi^{(r)}_{n00}\psi^*_{n00}(r)(-\epsilon_n). \tag{14}$$

Thus one has the summation in Eq. (14) for large r as

$$\sum_{n=1}^{\infty}\psi_{n00}(r)\psi^*_{n00}(r)\frac{1}{2n^2}=\frac{A}{2r^{7/2}}\quad\text{as}\quad r\to\infty, \tag{15}$$

whereas from Eq. (6) above

$$\sum_{n=1}^{\infty}\psi_{n00}(r)\psi^*_{n00}(r)=\frac{3}{4}\frac{A}{r^{5/2}}\quad\text{as}\quad r\to\infty. \tag{16}$$

Finally, we turn to the momentum density $n(p)$ for an arbitrary number of closed shells $\mathcal{N}$. Fock [10] was the first to obtain this density for the mth closed shell in a bare Coulomb field as

$$n_m(p)=16p_m^5m^2/\pi^2(p_m^2+p^2)^4,\quad p_m=Z/m. \tag{17}$$

Summing this over $\mathcal{N}$ closed shells yields

$$n_{\mathcal{N}}(p)=\sum_{m=1}^{\mathcal{N}}n_m(p). \tag{18}$$

First consider $p=0$, i.e.,

$$n_{\mathcal{N}}(0)=\sum_{m=1}^{\mathcal{N}}n_m(0)=\frac{16\Sigma_1^{\mathcal{N}}m^5}{\pi^2Z^3}=\frac{4}{3\pi^2Z^3}[\mathcal{N}(\mathcal{N}+1)]^2(2\mathcal{N}^2+2\mathcal{N}-1). \tag{19}$$

For the number of closed shells $\mathcal{N}\gg 1$ this tends to $(8/3\pi^2Z^3)\mathcal{N}^6$, which is simply the result of replacing the discrete summation Σm^5 by an integration.

The term of $O(p^2)$ can also be calculated exactly for arbitrary $\mathcal{N}$, to yield

$$n_{\mathcal{N}}(p)=n_{\mathcal{N}}(0)-n_2p^2\cdots n_2=\frac{16\sum_1^{\mathcal{N}}m^7}{\pi^2Z^5}. \tag{20}$$

The m^7 sum is again calculable for arbitrary $\mathcal{N}$ to yield

$$n_2=\frac{2}{3\pi^2Z^5}[\mathcal{N}(\mathcal{N}+1)]^2[3\mathcal{N}^4+6\mathcal{N}^3-\mathcal{N}^2-4\mathcal{N}+2], \tag{21}$$

which readily gives back the integral limit $2\mathcal{N}^3/\pi^2 Z^5$ in the limit of very large $\mathcal{N}$.

In the opposite extreme of large momentum p, one readily finds from Eqs. (17) and (18)

$$n_{\mathcal{N}}(p) = \frac{16Z^5}{\pi^2 p^3} \sum_1^{\mathcal{N}} \frac{1}{m^3}. \tag{22}$$

In the limit $\mathcal{N}\rightarrow\infty$, the summation yields the Riemann ζ function, evaluated at argument 3 and having the value 1.202 06. Thus, some generalizations can be effected following the elegant study of HL, the electron density here being considered in some cases for an arbitrary number of closed shells both in **r** and **p** spaces.

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