Pauli potential from Heilmann-Lieb electron density obtained by summing hydrogenic closed-shell densities over the entire bound-state spectrum

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Independently, in the mid-1980s, several groups proposed to bosonize the density-functional theory (DFT) for fermions by writing a Schrödinger equation for the density amplitude $\rho(\mathbf{r})^{1/2}$, with $\rho(\mathbf{r})$ as the ground-state electron density, the central tool of DFT. The resulting differential equation has the DFT one-body potential $V(\mathbf{r})$ modified by an additive term $V_P(\mathbf{r})$ where P denotes Pauli. To gain insight into the form of the Pauli potential $V_P(\mathbf{r})$, here, we invoke the known Coulombic density, $\rho_\infty(r)$ say, calculated analytically by Heilmann and Lieb (HL), by summation over the entire hydrogenic bound-state spectrum. We show that $V_{P\infty}(r)$ has simple limits for both r tends to infinity and r approaching zero. In particular, at large r, $V_{P\infty}(r)$ precisely cancels the attractive Coulomb potential $-Ze^2/r$, leaving $V(r) + V_{P\infty}(r)$ of $O(r^{-2})$ as r tends to infinity. The HL density $\rho_\infty(r)$ is finally used numerically to display $V_{P\infty}(r)$ for all r values.

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I. INTRODUCTION

In the mid-1980s, several groups from around the world independently proposed to bosonize density-functional theory for fermions, which uses the ground-state electron density $\rho(\mathbf{r})$ as its main tool [1]. The bosonized result, which emerged, is very simply stated; it is a Schrödinger equation for the so-called density amplitude $\rho(\mathbf{r})^{1/2}$, namely,

$$\nabla^2 \rho(\mathbf{r})^{1/2} + \frac{2m}{\hbar^2}[\epsilon - V(\mathbf{r}) - V_P(\mathbf{r})]\rho(\mathbf{r})^{1/2} = 0. \quad (1)$$

An important early review focusing on the basis for Eq. (1) is that of Levy and Görling [2], and a very recent overview is by one of us [3].

The aim of the present Brief Report is to gain insight into the form of the Pauli potential [4–6] $V_P(\mathbf{r})$ entering Eq. (1) by invoking the analytical study, in the fermion framework already referred to, for the bare Coulombic density, denoted in the following as $\rho_\infty(r)$, by Heilmann and Lieb (HL) [7]. The subscript ∞, on the electron density $\rho(r)$, indicates that HL summed the closed-shell hydrogenic electron densities characterized by the principal quantum number over all its allowed values from 1 to ∞. The essential achievement of HL was then to exactly connect the Thomas-Fermi large r known asymptotic behavior cited explicitly in Eq. (8) with the readily accessible electron density $\rho_\infty(r = 0)$ at the nucleus. In their exact analysis, $\rho_\infty(r)$ was given in somewhat complex double integral forms [compare Eqs. (12)–(14) for some simplification], but, nevertheless, it is entirely practicable from their study to compute $\rho_\infty(r)$ for a specified numerical accuracy at any chosen value of r. Therefore, in order to expose the potential sum $V(\mathbf{r}) + V_P(\mathbf{r})$ entering Eq. (1), we evaluate $\nabla^2\rho^{1/2}/\rho^{1/2}$ for the special case of an arbitrary number of closed shells generated by the bare Coulomb potential given by

$$V(r) = -Ze^2/r. \quad (2)$$

To do so, it will prove helpful to appeal to the so-called spatial generalization of Kato's theorem [8] for the potential (2), as derived by one of us [9]. This reads

$$\frac{\partial \rho(r)}{\partial r} = -\frac{2Z}{a_0}\rho_s(r), \qquad a_0 = \frac{\hbar^2}{me^2}, \quad (3)$$

where $\rho_s(r)$ denotes the $l = 0$ component extracted from the total closed-shell Coulomb density $\rho(r)$ under discussion.

First of all then, to find $\nabla^2\rho^{1/2}/\rho^{1/2}$ referred to earlier, we can write that

$$\frac{d}{dr}\rho^{1/2} = \frac{1}{2}\rho^{-1/2}\rho' = -\frac{Z}{a_0}\rho^{-1/2}\rho_s, \quad (4)$$

where, in the second step of Eq. (4), the result (3) has been invoked. From Eq. (4) and a further differentiation with respect to r, we can write the central equation of this Brief Report, namely,

$$V + V_P - \epsilon = -\frac{\hbar^2 Z}{2ma_0}\left(\frac{Z}{a_0}\frac{\rho_s^2}{\rho^2} + \frac{\rho_s'}{\rho} + \frac{2}{r}\frac{\rho_s}{\rho}\right). \quad (5)$$

II. USE OF THE HL DENSITY

To gain insight into Eq. (5), let us next appeal to the HL Coulomb density $\rho^{\mathrm{HL}}(r)$, defined in terms of the normalized hydrogenic wave functions $\Psi_{nlm}(\mathbf{r})$ as

$$\rho_N(r) = \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \Psi_{nlm}(\mathbf{r})\Psi^*_{nlm}(\mathbf{r}), \quad (6)$$

$$\rho^{\mathrm{HL}} \equiv \rho_\infty = \lim_{N\to\infty} \rho_N. \quad (7)$$

From the Thomas-Fermi statistical method (see, e.g., Ref. [10]), it follows almost immediately that, as $r \to \infty$,

$$\rho_\infty(r)|_{r\to\infty} = K/r^{3/2}. \quad (8)$$

Hence, it follows from Eq. (3) that $\rho_{s\infty}(r)$ is proportional to $r^{-5/2}$. Then, using Eq. (5) in this HL limit, the ratio ρ_s/ρ, which enters there, is proportional to r^{-1} as $r \to \infty$. But it also follows at large r that ρ_s'/ρ is proportional to r^{-2}, while it is already clear from the HL study that $\epsilon = 0$ in their limiting case of $\rho_\infty(r)$. Thus, we readily reach a further important result from Eq. (5): namely, that

$$V(r) + V_{P\infty}(r)|_{r\to\infty} = \frac{\mathrm{const}}{r^2} + \cdots. \quad (9)$$

Using the explicit Coulomb form of $V(r)$ in Eq. (2), we are led to the desired large r limit of the Pauli potential $V_{P\infty}(r)$:

$$V_{P\infty}(r) \to \frac{Ze^2}{r} + O(r^{-2}), \qquad r \to \infty. \quad (10)$$

Turning to the other limit, namely, $r \to 0$, $\rho'/\rho \to -2Z/a_0$ from Eq. (3) as $\rho \to \rho_s$ in this case. Hence, the final term in Eq. (5) precisely cancels the Coulomb term $V(r)$. Using Kato's theorem for the s density, it follows that $\rho_s'/\rho_s \to -2Z/a_0$ as $r \to 0$ to yield

$$V_{P\infty}(r)|_{r\to 0} = \frac{1}{2}\frac{\hbar^2}{m}\left(\frac{Z}{a_0}\right)^2. \quad (11)$$

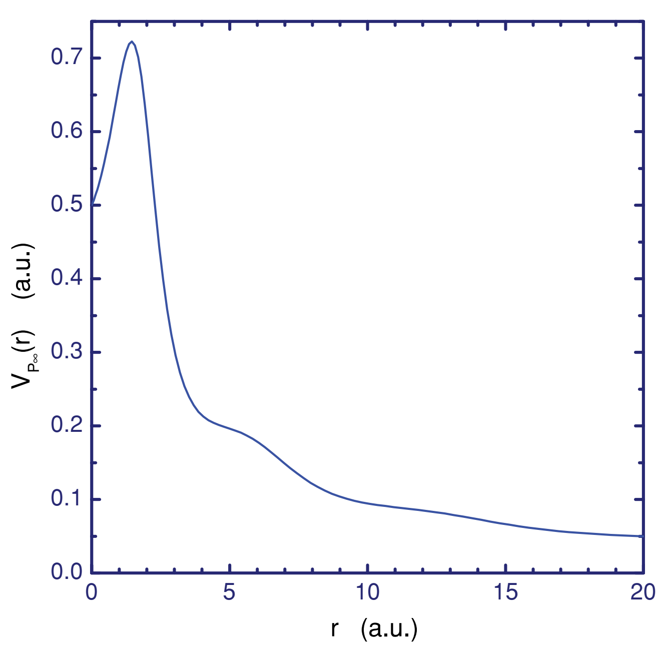

FIG. 1. (Color online) Form of the Pauli potential $V_{P\infty}(r)$ as calculated from Eq. (5). Input for Eq. (5) is the HL density $\rho_\infty(r)$, $\rho_{s\infty}(r)$, thus, obtained from Eq. (3), with ϵ finally set equal to zero.

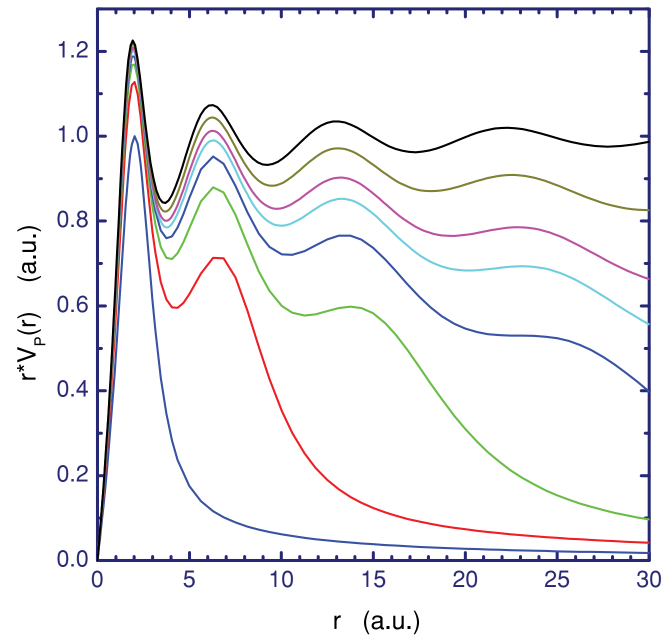

FIG. 2. (Color online) Form of $rV_{PN}(r)$ for some closed-shell cases derived for ρ_N of Eq. (6). The curves are shown for $N = 2,3,4,5,6,7,10,\infty$ from bottom to top, respectively.

Prompted by these attractively simple limits of the Pauli potential $V_{P\infty}(r)$ as $r \to \infty$ and $r \to 0$, respectively, we have utilized the series expansions for $\rho_\infty(r)$ recorded by HL to calculate numerically intermediate values of $V_{P\infty}(r)$ from Eq. (5). In what follows, $Z = 1$ and atomic units are used. The (typographical error corrected to be $w \Rightarrow w^{-3/2}$) first integral representation as given in HL Eq. (2.4) is our starting expression to give a similar representation for the s-only density. In particular, Eq. (3) can be applied as $\rho_{s\infty}(r) = -\rho'_\infty(r)/2$. After some algebra, using the $[u^{-k}J_k(u)]' = -u^{-k}J_{k+1}(u)$ identity for the Bessel functions (see, e.g., Sec. 9.1.30 in Ref. [11]), we obtain the integral as

$$\rho_{s\infty}(r) = (2\pi r)^{-2}\int_0^\infty x e^{-x}\phi^2 \int_0^\pi w^{-1} \times J_4(2\phi\sqrt{2rw})\, d\theta\, dx, \quad (12)$$

where the functions,

$$\phi(x) = \sqrt{\frac{x}{1-e^{-x}}}, \quad (13)$$

$$w(x,\theta) = 1 + e^{-x} - 2e^{-x/2}\cos(\theta) \quad (14)$$

are those of HL's Eqs. (2.5) and (2.6).

The result for $V_{P\infty}(r)$ is displayed in Fig. 1. The limiting behavior of the Pauli potential can be checked, at $r \to 0$, it is indeed $V_{P\infty}(0) = 1/2$, and for large r, it converges to $1/r$, in particular, $V_{P\infty}(20) = 1/20 \pm 10^{-4}$. Marks of the shell structure can be observed for $r < 15$ a.u.; further shells are outside the plot range and are quenched by the hyperbolic asymptotic envelop. In order to demonstrate how the shells appear in the Pauli potential, in Fig. 2, we plot $V_{PN}(r)$ multiplied by r first, for some finite closed-shell cases together with the limiting potential.

To summarize, we have gained some insight into the Pauli potential $V_P(r)$ occurring in bosonized Eq. (1) for the density amplitude $\rho(\mathbf{r})^{1/2}$. This has been achieved predominantly by making use of the analytic density $\rho_\infty(r)$ of HL for the bare Coulomb potential [7].

The central analytical results of this Brief Report are then displayed in Eqs. (5), (9), (10), and (12). While Eq. (5) holds quite generally for any arbitrary number of closed shells generated by the bare Coulomb potential (2), the limiting forms in Eqs. (10) and (11) hold for sufficiently large and sufficiently small r, respectively. Finally, $V_{P\infty}(r)$ has been evaluated numerically for the case of $Z = 1$ in Eq. (2) and is displayed in Fig. 1. For comparison, numerical values of $rV_P(r)$ for some finite numbers of closed-shell cases are plotted in Fig. 2.

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