Lower bound on the coefficient of an exchangelike energy for a single bound electron in a screened Coulomb potential

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(Received 16 February 2011; published 27 April 2011)

The spurious self-interaction energy, which is one-half the integrated electrostatic interaction energy of a normalized electronic charge distribution with the potential field generated by itself, is calculated analytically for a $1s$-like electron charge distribution governed by an attractive screened Hulthen-type model potential. The exact result obtained is used, via an energetic cancellation constraint and a convenient Hölder's integral inequality, to deduce an analytical *lower bound* for the screening-dependent positive coefficient of a negative exchange-like energy term applied routinely in the local-density approximation to density functional theory with Coulomb potentials. The bare Coulomb case is investigated by Sobolev's integral inequality as well.

DOI: 10.1103/PhysRevA.83.044503 PACS number(s): 31.15.E−, 71.15.Mb

Introduction. While the exact density functional for the ground-state energy of a bound electron in its quantum mechanical $1s$ state in the Coulomb field of a point nucleus is self-interaction free, the approximation based on local-density approximation (LDA) of the density functional theory (DFT) is not. Therefore, the elimination of the self-interaction is an important issue [1–4]. The spurious self-interaction term is one-half the integrated electrostatic interaction energy of a normalized electronic charge distribution with the potential field generated by itself. Considering the importance of nucleus screening in the degenerate electron gases of different solid-state systems, and in plasma physics, the theoretically challenging question on the screening-dependence of bounded parameters to be used in LDA turns out to be a realistic one. By employing a well-known energetic constraint, here we derive a *lower bound* to the coefficient of an exchange-like local energy term.

Calculation. The model Hamiltonian of the present study is given by

$$H = -\frac{1}{2}\nabla^2 - Z\frac{\Lambda}{e^{\Lambda r}-1}, \tag{1}$$

where Λ is the screening parameter for the nucleus-electron interaction. Hartree atomic units, $\hbar = m_e = e^2 = 1$, are used throughout this work. One may [5] take $\Lambda = 1.75\lambda_{\rm TF}$, where $\lambda_{\rm TF} = \sqrt{4k_F/\pi}$ in the Thomas-Fermi treatment of charge polarization driven by a heavy point charge (Z) in an electron gas with Fermi momentum k_F. This is defined from the density n_0 via $k_F = (3\pi^2 n_0)^{1/3}$. The complete [6] normalized $1s$ wave function is

$$\phi_{1s}(r) = \left[\frac{Z(4Z^2-\Lambda^2)}{4\pi}\right]^{1/2} \frac{1}{\Lambda r}[e^{-(Z-\Lambda/2)r} - e^{-(Z+\Lambda/2)r}], \tag{2}$$

The critical (cr) screening parameter is $\Lambda_{\rm cr} = 2Z$, and the binding energy becomes

$$E_0(\Lambda) = \left[\frac{1}{8}(4Z^2-\Lambda^2) - \frac{Z}{2}(2Z-\Lambda)\right] = -\frac{Z^2}{2}\left(1-\frac{\Lambda}{2Z}\right)^2. \tag{3}$$

The maximum (m) in the electron density $r^2|\phi_{1s}(r)|^2$ occurs at the radius

$$r_m = \frac{1}{Z}\frac{1}{2x}\ln\frac{1+x}{1-x}, \tag{4}$$

where $x = \Lambda/2Z$. There is a weak enhancement close to the critical ($x \to 1$) screening.

The self-interaction ($E_{\rm si}$) energy, which is one-half of the integrated electrostatic interaction energy of a properly normalized spherical electronic charge distribution with the potential field generated by itself, is defined by the usual expression of electrostatics,

$$E_{\rm si} = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{n(r)n(r')}{|\mathbf{r}-\mathbf{r}'|}, \tag{5}$$

where the density is $n(r) = [\phi_{1s}(r)]^2$ in terms of the $1s$-like wave function. In order to derive a closed expression for the self-interaction in our model, we employ the convolution (Faltung) theorem and get an alternative, convenient representation,

$$E_{\rm si} = \frac{1}{2}\frac{4\pi}{(2\pi)^3}\int_0^\infty dq\,q^2\left[n(q)\,\frac{4\pi}{q^2}\,n(q)\right], \tag{6}$$

where $n(q)$ is the three-dimensional Fourier-Henkel transform of $n(r)$. This transformation of the density $n(r)$ is easy to carry out due to the result

$$\int_0^\infty dr\,\frac{\sin(qr)}{r}\,e^{-ar} = \arctan(q/a). \tag{7}$$

Performing the resulting straightforward integrations in Eq. (6), we arrive at

$$E_{\rm si}(Z,x) = \frac{1}{2}Z\left(\frac{1-x^2}{x^4}\right)\sum_{i=1}^{4} f_i(x), \tag{8}$$

where the parameter-dependence of $E_{\rm si}$ is now explicit. Here $f_1(x) = (1-2x^2)\ln(1-x^2)$, $f_2(x) = x\ln[(1-x)/(1+x)]$, $f_3(x) = 2(x^2-2)\ln(1-x^2/4)$, and $f_4(x) = 2x\ln[(2+x)/(2-x)]$. In the unscreened ($x \to 0$) limit we get $E_{si}(Z,x\to 0) = (5Z/16)$, while at the critical screening ($x \to 1$, from below) the result tends to zero as $E_{si}(Z,x \to 1) = (2Z\ln 2)(1-x)$.

The exchange-like (ex) energy in our one-electron model is defined, in a complete analogy $[n_0 \Rightarrow n(r)]$ with well-known result established for a degenerate homogeneous electron gas with density n_0, as a simple volume integral of a local energy density

$$E_{\rm ex}^{\rm LDA}(Z,x) \;=\; -4\pi \int_0^\infty dr\, r^2\, n(r)[\beta\, n^{1/3}(r)], \qquad (9)$$

where $n(r) = [\phi_{1s}(r)]^2$ as we noted above. In the exchange-only approximation one has $\beta = (3/4)(6/\pi)^{1/3}$ in a *spin-polarized* electron gas. In order to get an analytical result after substitution from Eq. (2), we use Hölder's (h) integral inequality [7] and write

$$\left|E_{\rm ex}^{\rm LDA}(Z,x)\right| \leqslant \beta_h \left(\int_0^\infty 4\pi r^2 \left[\phi_{1s}^{4/3}(r)\right]^p dr\right)^{1/p} \times \left(\int_0^\infty 4\pi r^2 \left[\phi_{1s}^{4/3}(r)\right]^q dr\right)^{1/q}, \qquad (10)$$

where $p = (3/2) > 1$ and $q = 3$, thus $p^{-1} + q^{-1} = 1$ as required. In such a way we can determine a *lower bound* for β via the cancellation constraint $[E_{\rm ex}^{\rm LDA}(Z,x) + E_{\rm si}(Z,x)] = 0$.

The first integral, the one with $p = 3/2$, is fortunately just the normalization condition. The second integral, the one that depends on the square of $n(r)$, is performed by applying first a partial integration and then a repeated use of the integral

$$\int_0^\infty \frac{e^{-ar} - e^{-br}}{r} \;=\; \ln(b/a) \qquad (11)$$

to finish the resulting integration. For the right-hand side (H) of Eq. (10), we obtain

$$H(Z,x) \;=\; \beta_h\, Z \left[\frac{1}{\pi}\left(\frac{1-x^2}{x^2}\right)^2\right]^{1/3} [F_1(x) - F_2(x)]^{1/3}, \qquad (12)$$

$$F_1(x) \;=\; (1+x)\left(3\ln\frac{2}{2+x} + \ln\frac{2+2x}{2-x}\right), \qquad (13)$$

$$F_2(x) \;=\; (1-x)\left(3\ln\frac{2-x}{2} + \ln\frac{2+x}{2-2x}\right). \qquad (14)$$

The application of Eq. (8) and Eq. (12) to our cancellation constraint results in a $\beta_h(x)$, i.e., in a screening-dependent ($x = \Lambda/2Z$) coefficient. It will be illustrated below in Fig. 1.

In the unscreened ($x \to 0$) limit we get $[H(Z,x \to 0)/\beta_h Z] = (1/2)\pi^{-1/3}$ from the closed expression, thus $\beta_h(x \to 0) = (5/8)\pi^{1/3} \simeq 0.92$ in the Coulomb ($-Z/r$) potential case. This *lower bound* is close to the $\beta = (3/4)(6/\pi)^{1/3} \simeq 0.93$ value deduced for a spin-polarized electron gas. We add, for completeness, that in the $\Lambda = 0$ case, the direct evaluation of Eq. (9) with hydrogenic density results in a value of $\beta_o = (20/27)\pi^{1/3} \simeq 1.085$, which is an optimal (o) value [8] by construction. The optimal value is very close to the so-called best (b) coefficient, $\beta_b \simeq 1.092$, derived from a sophisticated variational treatment [9] with a finite-range charge density of unit norm. Notice that the best coefficient depends on the particle number (N) monotonically. For instance, $\beta_b \simeq 1.23$ for two ($N = 2$) electrons.

It may be of some general interest to note here that in the unscreened ($\Lambda = 0$) case we can easily apply another integral

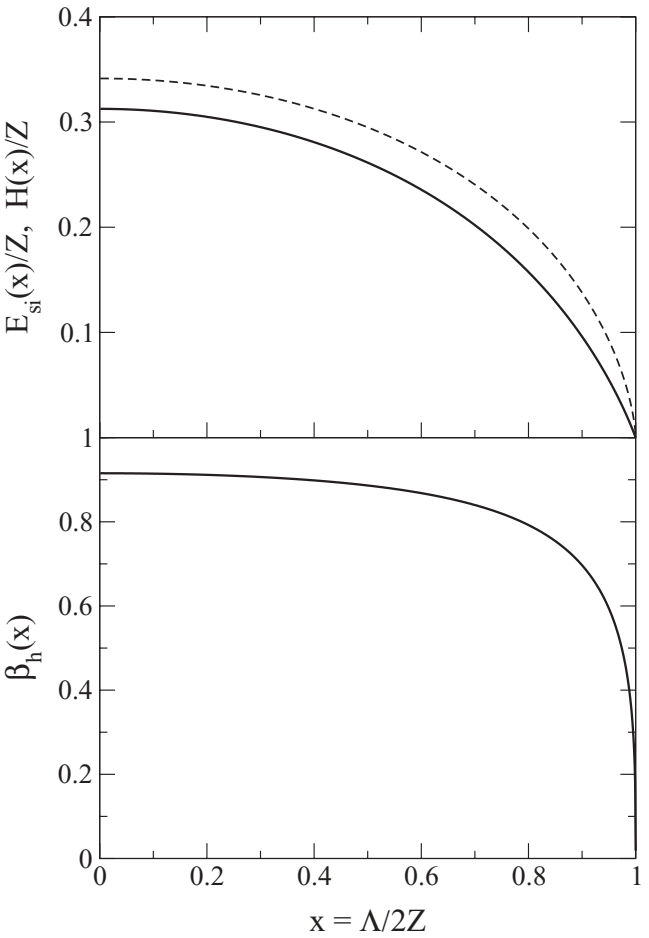

FIG. 1. The solid and dashed curves in the upper panel refer to $E_{\rm si}(x)/Z$ and $H(x)/Z$, respectively. These energies from Eqs. (8) and (12) are given in atomic units. The lower panel is devoted to the $\beta_h(x) = E_{\rm si}(x)/H(x)$ ratio, which represents the screening dependence of the coefficient of an exchange-like energy term.

inequality, Soboliev's [10,11]. Thus, instead of Eq. (10), we have

$$4\pi \int_0^\infty r^2 \phi_{1s}^q(r) dr \leqslant \left\{C(p,m)\left[4\pi \int_0^\infty [\nabla\phi_{1s}(r)]^p dr\right]^{1/p}\right\}^q, \qquad (15)$$

where $q = 8/3$ and $m = 3$, the space dimension. Via the $1 < p < m$ and $q = mp/(m-p)$ constraints, one gets $p = 24/17$. The best constant, denoted in Ref. [10] as $C(p,m)$, is given by

$$C(p,m) \;=\; \frac{1}{\sqrt{\pi}}\,\frac{1}{m^{1/p}}\left(\frac{p-1}{m-p}\right)^{(p-1)/p} \times \left[\frac{\Gamma(1+m/2)\Gamma(m)}{\Gamma(m/p)\Gamma(1+m-m/p)}\right]^{1/m}. \qquad (16)$$

Using $\phi_{1s}(r)$ from Eq. (2) with $\Lambda = 0$, after a straightforward calculation we derive, as another *lower bound*, $\beta_s \simeq 1.02$. This value is somewhat better than the value deduced via Hölder's integral inequality. It is close (from below) to the optimal value of $\beta_o \simeq 1.085$. Our finding gives further credit to the

well-known [12,13] power of Sobolev's inequality in mathematical physics.

From here on, we return to the result based on Hölder's inequality. At critical screening ($x \to 1$, from below) the asymptotic result obtained from Eq. (12) behaves as $[H(Z,x \to 1)/\beta_h Z] = [8(\ln 4 - 3\ln(3/2))/\pi]^{1/3}(1-x)^{2/3}$. Thus, based on our energetic constraint, the corresponding coefficient becomes $\beta_h(x \to 1) \simeq 1.83(1-x)^{1/3}$. This shows that the tendency to zero from above is surprisingly slow. There is, therefore, a certain stability of $\beta_h(x)$ against screening. Notice that the expectation value for the ground-state energy vanishes as $\sim(1-x)^2$. Clearly, the tendency of $\beta_h(x)$ to zero at vanishing binding is an expected general result. Direct numerical evaluation of Eq. (9) in this limit ($x \to 1$) should result in a vanishing character for the coefficient as well.

Our $\beta_h(x) \equiv E_{\rm si}(Z,x)/H(Z,x)$ coefficient, a *lower bound* in an exchange-like, local-density approximation, is exhibited in Fig. 1 (lower panel) as a function of the convenient variable $x = (\Lambda/2Z)$; $x \in [0,1]$. The curve shows that at moderate screening, say $x = 0.5$, the deviation from the limiting β_h $(x = 0) = 0.92$ value is small. However, the general character of $\beta_h(x)$ heralds that care is needed when one applies local forms of approximate density functional theory with an unmodified coefficient under screening conditions for a weakly bound state. In this frequent and important case, one can [14] use a physically motivated partitioning of the total density into a well-localized inner and more diffuse outer parts.

Concluding remarks. Wigner's pioneering [15] estimation for the maximal correlation energy per electron in a dilute electron fluid (F) is $e_F(r_s) = -(0.75/r_s) \simeq -1.21 n_0^{1/3}$, where $r_s = (9\pi/4)^{1/3} k_F^{-1}$ in three dimensions. Wigner's coefficient ($\beta_W^F \simeq 1.21$) is a rigorous upper bound [4] in this essentially *single*-electron limit. With the lower bound ($\beta_s \simeq 1.02$) derived here for an atomic case, we mark the borders for a coefficient in LDA of DFT for a single bound electron. The optimal ($\beta_o \simeq 1.085$) and variationally [9] established ($\beta_b \simeq 1.092$) values are almost exactly in the middle of the range limited by these borders.

If we measure the limiting values in terms of the exchange coefficient $\beta_p = (3/4)(3/\pi)^{1/3}$ of a homogeneous paramagnetic (p) electron gas, we obtain for illustration $(\beta_s/\beta_p) \simeq 1.38$ and $(\beta_W^F/\beta_p) \simeq 1.64$. The energy per particle in the famous Wigner lattice (L) can [4] be approximated by $e_L(r_s) = 2e_F(r_s) + 0.6/r_s$, where the first term is the interaction energy of a point-like electron with a charge-compensating sphere and the second term is the self-energy of the sphere. This commonly applied [16,17] lattice-energy yields $\beta_W^L \simeq 1.45$, which is slightly smaller then an N-independent [9,18] upper (u) bound $\beta_u \simeq 1.68$.

The lower bound derived here on the *screening-dependent* coefficient of an exchange-like energy for a single ($N = 1$) bound electron in a screened Coulomb potential could be important, for instance, in application of LDA to DFT in plasma physics. Around critical screening, i.e., at the appearance of a bound state, care is needed to avoid localized states supported by a spurious attractive exchange-like potential term based on LDA.

The author is grateful to Professors M. L. Glasser and P. Lévay for useful discussions. He thanks Professor P. M. Echenique for the warm hospitality at the DIPC.

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