Models including electron correlation in relation to Fock's proposed expansion of the ground-state wave function of He-like atomic ions

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(Received 13 December 2010; revised manuscript received 9 November 2011; published 22 December 2011)

Here attention is first drawn to the importance of gaining insight into Fock's early proposal for expanding the ground-state wave function for He-like atomic ions in hyperspherical coordinates. We approach the problem via two solvable models, namely, (i) the s-term model put forth by Temkin [Phys. Rev. **126**, 130 (1962)] and (ii) the Hookean atom model proposed by Kestner and Sinanoglu [Phys. Rev. **128**, 2687 (1962)]. In both cases the local kinetic energy can be obtained explicitly in hyperspherical coordinates. Separation of variables occurs in both model wave functions, though in a different context in the two cases. Finally, a **k**-space formulation is proposed that should eventually result in distinctive identifying characteristics of Fock's nonanalyticities for He-like atomic ions when both electrons are close to the nucleus.

DOI: 10.1103/PhysRevA.84.062119 PACS number(s): 03.65.Ge, 01.55.+b, 02.30.Hq

I. INTRODUCTION

Because of the present intractability of the exact analytic solution of the Schrödinger solution for the ground-state of He-like atomic ions, we approach the problem here via two solvable models. The first model we discuss was put forth by Kestner and Sinanoglu [1], who proposed the replacement of the Coulomb confinement form of the external potential $V_{\rm ext}(\vec{r})$ by a harmonic restoring potential given by $\frac{1}{2}kr^2$ but retaining the full Coulombic interaction e^2/r_{12}. It was natural to refer to this model as the two-electron Hookean atom. The model's great merit is that the center-of mass motion can be separated from the relative motion (see, for instance, Ref. [2]). Kais *et al.* quote the exact ground-state wave function $\Psi(\vec{r}_1,\vec{r}_2)$ for the solvable case of the Hamiltonian $H_{\rm Hooke} = -\nabla_1^2 - \nabla_2^2 + e^2/r_{12} + (k/2)(r_1^2 + r_2^2)$ for $k = \frac{1}{4}$ a.u. as

$$\Psi(\vec{r}_1,\vec{r}_2) = N_0\big(1 + \tfrac{1}{2}|\vec{r}_1 - \vec{r}_2|\big)\exp\big[-\tfrac{1}{4}\big(r_1^2 + r_2^2\big)\big], \quad (1)$$

which corresponds to ground-state energy $E_0 = 2$ a.u. ($E_{\rm HF} = 2.039\,325$ a.u., where $E_{\rm HF}$ represents the Hartree-Fock energy). Following Fock's proposal [3], we immediately rewrite Eq. (1) in hyperspherical coordinates R, Θ, and α defined by

$$R = \sqrt{r_1^2 + r_2^2}, \quad r_1 = R\cos\alpha, \quad r_2 = R\sin\alpha, \quad \cos\Theta = \frac{\vec{r}_1\cdot\vec{r}_2}{r_1 r_2} \quad (2)$$

to obtain

$$\Psi(R,\alpha,\Theta) = \Psi_g(R) - \sqrt{1 - \sin 2\alpha\cos\Theta}\,\frac{\partial\Psi_g(R)}{\partial R}, \quad (3)$$

where $N_0\exp[-\frac{1}{4}R^2] = \Psi_g(R)$.

For He-like atomic ions Fock proposed expanding the ground-state wave function for small R in a form involving not only non-negative-integer powers of R, but also positive-integer powers of $\ln R$. We refer to the important subsequent work of Refs. [4–9], which have demonstrated the convergence and usefulness of Fock's expansion. It is also relevant here to note two recent papers on the Hookean model [10,11].

Here we note that while Eq. (3) is not directly separable in hyperspherical coordinates, it is the sum of a part $\Psi_g(R)$, independent of the angles α and Θ, plus a piece with an R dependence determined by $\partial\Psi_g(R)/\partial R$, times the known function $\sqrt{1 - \sin 2\alpha\cos\Theta}$ of angles α and Θ. Clearly, both R-dependent parts can be expanded to all orders in R^2 and there are no logarithmic terms at small R. Since for small R both electrons are near the origin of harmonic confinement, it is clear that e^2/r_{12} alone for small r_{12} does not lead to Fock-like nonanalytic terms for small r. Thus, Coulomb confinement with $V_{\rm ext}(r) = -Z/r$ replacing the harmonic form needs to be invoked in He if Fock's nonanalytic behavior is to be recovered.

This leads us directly to a second model, proposed by Temkin [12], which is now referred to as the Temkin-Poet [13] model for He-like atomic ions. Particularly relevant to this study is Ref. [14], where it is pointed out that the wave function considered by Howard and March [15], namely,

$$\Psi_{\rm HM}(\vec{r}_1,\vec{r}_2) = C\exp\left[-(Z - 1/2)(r_1 + r_2) + \frac{|r_1 - r_2|}{2}\right], \quad (4)$$

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is the exact ground-state wave function for the Hamiltonian

$$\hat{H}'_s = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_>} + \delta(r_1 - r_2). \quad (5)$$

This differs from the Temkin-Poet model $H_{\rm TP} = \hat{H}'_s - \delta(r_1 - r_2)$ by the presence of the δ function, with the quantity $r_>$ given by

$$r_> = \tfrac{1}{2}(r_1 + r_2 + |r_1 - r_2|) = \max(r_1, r_2). \quad (6)$$

As put forth in Ref. [12], only the s term in the expansion of $1/r_{12}$ is retained to obtain the Hamiltonian in Eq. (5). Inserting hyperspherical coordinates from Eq. (2) into the Howard-March (HM) wave function in Eq. (4) then yields

$$\Psi_{\rm HM} = C\exp\Big[-(Z-1/2)R(\sin\alpha+\cos\alpha) + \frac{R}{2}|\sin\alpha - \cos\alpha|\Big], \quad (7)$$

with no explicit dependence on Θ.

II. LOCAL-ENERGY AND KINETIC-ENERGY OPERATORS IN HYPERSPHERICAL COORDINATES

When the ground-state wave function Ψ is written in terms of the hyperspherical coordinates R, α, and Θ described above, we find it convenient to work with the local L ground-state energy E_L defined by

$$E_L = \frac{\hat{H}\Psi(R,\alpha,\Theta)}{\Psi(R,\alpha,\Theta)} = -\frac{\frac{1}{2}\big[\nabla_1^2 + \nabla_2^2\big]\Psi}{\Psi} + U(R,\alpha,\Theta). \quad (8)$$

Here $U(R,\alpha,\Theta)$ is the total potential energy entering the Hamiltonian $\hat{H}$. At this point we return to the Hookean atom with $k = 1/4$ and note immediately that $U_{\rm external} = U_{\rm ext}$ is given by

$$U_{\rm ext}(r_1, r_2) = \tfrac{1}{8}\big(r_1^2 + r_2^2\big) = \tfrac{1}{8}R^2 \quad (9)$$

in hyperspherical coordinates. This, of course, is a crucial simplification and means that the entire dependence of $U(R,\alpha,\Theta)$ on α and Θ for this Hookean atom model comes from the Coulomb repulsion potential energy $e^2/|\vec{r}_1 - \vec{r}_2|$.

Writing the kinetic-energy operator (following, e.g., Macek [16]) in hyperspherical coordinates, the He-atom ground-state Schrödinger equation reads

$$-\frac{1}{2}\left[\frac{\partial^2}{\partial R^2} + \frac{5}{R}\frac{\partial}{\partial R} - \frac{\Lambda^2}{R^2}\right]\Psi - \left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}}\right)\Psi = E\Psi,$$

where Λ^2 is Casimir's operator [cf. Eq. (12)]. We can immediately use the Hookean atom wave function Ψ in Eq. (1) to calculate the kinetic-energy term on the right-hand side of Eq. (8) as

$$E_{\rm LK} = \frac{12\sin^2\Theta + 16\cos\Theta\cos^2(2\alpha)\csc(2\alpha) - 8\phi + 2[r(12 - R^2) - 12]\phi^2 - (R^4 - 16R^2 + 12)\phi^3 + 12\phi^4}{16R\phi^3(\alpha,\Theta)\big[1 + \frac{R}{2}\phi(\alpha,\Theta)\big]}. \quad (10)$$

Here $\phi(\alpha,\Theta) = \sqrt{1 - \sin(2\alpha)\cos\Theta}$, while the potential-energy term $U(R,\alpha,\Theta)$ is

$$U(R,\alpha,\Theta) = \frac{1}{8}R^2 + \frac{e^2}{R\phi(\alpha,\Theta)}. \quad (11)$$

Given the explicit kinetic-energy operator

$$\hat{T}(R,\alpha) = -\frac{1}{2}\left[\partial_R^2 + \frac{5}{R}\partial_R + \frac{1}{R^2}\big[\partial_\alpha^2 + 4\cot(2\alpha)\partial_\alpha\big]\right], \quad (12)$$

we write the potential-energy entering $\hat{H}'_s$ in Eq. (5) as

$$U(R,\alpha) = -\frac{1}{R}[\mu(\alpha) - \delta(\sin\alpha - \cos\alpha)]. \quad (13)$$

It should be noted that here we have used the relation

$$\delta(Rx) = \frac{1}{R}\delta(x) \quad (14)$$

and have defined $\mu(\alpha)$ in Eq. (13) as

$$\mu(\alpha) = (Z - 1/2)(\sec\alpha + \csc\alpha) + \frac{1}{2}\frac{|\sin\alpha - \cos\alpha|}{\sin\alpha\cos\alpha}. \quad (15)$$

The total energy is $E_{\rm HM} = -(Z^2 - Z + 1/2)$, while the local kinetic energy is $E^K_{\rm HM} = \frac{1}{R}\mu(\alpha) - (Z^2 - Z + 1/2)$. The wave function in Eq. (4) has been written in the form

$$\Psi_{\rm HM}(R,\alpha) = Ce^{-R\lambda(\alpha)}, \quad (16)$$

where

$$\lambda(\alpha) = (Z - 1/2)(\sin\alpha + \cos\alpha) - \tfrac{1}{2}|\sin\alpha - \cos\alpha|. \quad (17)$$

For the HM model it is in $\ln\Psi_{\rm HM}$ that the variables R and α separate, in contrast to the Hookean atom Ψ in Eq. (3). The quantity $y(\alpha) = \lambda(\alpha)$ must satisfy the two differential equations

$$y'' + 4\cot(2\alpha)y' + 5y = (2Z - 1)(\sec\alpha + \csc\alpha) + \frac{|\sin\alpha - \cos\alpha|}{\sin\alpha\cos\alpha}$$

and

$$(y')^2 + y^2 = 2(Z^2 - Z + 1/2).$$

III. DETAILED TREATMENT OF BOTH MODELS IN k SPACE

We turn now to the representations of our models in **k** space. It is convenient to introduce a dummy integration vector $\vec{R}$ whose magnitude is the coordinate R.

The Hookean atom is the simplest to start with. The angle-independent term $\Psi_g(R)$ clearly has a Gaussian Fourier transform and the Fourier transform of Eq. (3) is

$$\Phi(k,\alpha,\Theta) = 4\pi N_0\left\{2\sqrt{\pi}e^{-k^2} - \left[2+\sqrt{\pi}\left(\frac{1}{k}-2k\right)e^{-k^2}\mathrm{Erf}i(k)\right] \times \sqrt{1-\sin(2\alpha)\cos\Theta}\right\}. \quad (18)$$

[Here $\mathrm{Erf}i(z)$ denotes the error function of an imaginary argument.] Similarly, the Fourier transform of the Howard-March wave function in Eq. (4) is

$$\Phi_{\mathrm{HM}}(k,\alpha) = \frac{8\pi C\lambda}{(k^2+\lambda^2)^2}, \quad (19)$$

where $\lambda = (Z-1/2)(\cos\alpha+\sin\alpha) - \frac{1}{2}|\cos\alpha-\sin\alpha|$.

For the Howard-March and Temkin-Poet models we have

$$E\Psi(R,\alpha) - U(R,\alpha)\Psi(R,\alpha) = \hat{T}(R,\alpha)\Psi(R,\alpha), \quad (20)$$

where we write

$$\hat{T}(R,\alpha) = \frac{1}{2}\left[\Delta_R + \frac{1}{R^2}\Delta_\alpha\right], \quad \Delta_R = \partial_R^2 + \frac{5}{R}\partial_R, \quad (21)$$

$$\Delta_\alpha = \partial_\alpha^2 + 4\cot(2\alpha)\partial_\alpha, \quad U(R,\alpha) = -\frac{1}{R}f(\alpha), \quad (22)$$

where $f=\mu$ for the Temkin-Poet case and $\mu - 2^{-1/2}\delta(\alpha-\pi/4)$ for the Howard-March case. The Fourier transform on the left-hand side of Eq. (20) with respect to the vector $\vec{R}$ gives

$$E\Phi(k,\alpha) + \frac{f(\alpha)}{2\pi^2}\int\frac{d\vec{k}'}{|\vec{k}-\vec{k}'|^2}\Phi(\vec{k}',\alpha), \quad (23)$$

where Φ denotes the Fourier transform of Ψ. We next evaluate the right-hand side of Eq. (20), which can be written, by expressing Ψ as an inverse Fourier transform and expanding the kernel $e^{-i\vec{k}\cdot\vec{R}}$ in spherical Bessel functions,

$$4\pi\int_0^\infty \hat{T}(R,\alpha)[j_0(k'R)\Phi(k',\alpha)]k'^2dk' = 2\pi\int_0^\infty\left\{\left[j_0(k'R)+\frac{3}{k'R}j_1(k'R)\right]\Phi(k',\alpha) - \frac{j_0(k'R)}{(k'R)^2}\Delta_\alpha\Phi(k',\alpha)\right\}k'^4dk'. \quad (24)$$

The Fourier transform of Eq. (24) is

$$\frac{4\pi^3}{k^2}\Phi(k,\alpha) + \frac{12\pi^2}{k}\int_0^\infty\left\{\left[\ln\left|\frac{k+k'}{k-k'}\right| - \frac{2kk'}{|k^2-k'^2|}\right]\Phi(k',\alpha) - \pi kk'k_<\Delta_\alpha\Phi(k',\alpha)\right\}k'dk'. \quad (25)$$

Consequently, both the Howard-March and Temkin-Poet model equations have the form

$$(E-4\pi^3k^2)\Phi(k,\alpha) + \frac{f(\alpha)-12\pi^3}{\pi k}\int_0^\infty\ln\left|\frac{k+k'}{k-k'}\right|\Phi(k',\alpha)k'dk' + 12\pi^3\int_0^\infty k'^2k_<\Delta_\alpha\Phi(k',\alpha)dk' = 0. \quad (26)$$

Remarkably, Eq. (26) with the Howard-March value of E is a solution of Eq. (20), whereas it is not, for any values of E and $\lambda(\alpha)$, for the Temkin-Poet model. The reason, of course, is that the second derivative in Δ_α operating on Eq. (16) produces the δ function necessary to cancel that in $f(\alpha)$, but the latter is absent in the Temkin-Poet case.

We have focused on the two model wave functions in Eqs. (3) and (7) in hyperspherical coordinates so far because Eq. (3) for the Hookean atom involves e^2/r_{12} exactly, while Eq. (4) has Coulomb confinement through the Hamiltonian $\hat{H}_s'$ in Eq. (5), but a modified electron-electron interaction in which the s-wave term only, namely, $e^2/r_>$, is retained, plus an additional radial correlation through the δ-function contribution to $\hat{H}_s'$. The Hookean atom results presented here then make it clear that for small R, Fock-like terms in the He atom wave function must arise from an interplay between Coulomb confinement and the full electron-electron interaction e^2/r_{12}; while Coulomb confinement is exactly incorporated in the model Hamiltonian $\hat{H}_s'$ in Eq. (5), the electron-electron interaction terms are too primitive to yield terms like $R^2\ln R$, for instance, at small R.

IV. A THIRD MODEL WITH HARMONIC CONFINEMENT BUT INVERSE SQUARE INTERPARTICLE INTERACTION

We think it will be of interest to mention here yet a third exactly solvable model in which the wave function itself has clear nonanalytic behavior at small R. This is the case for the wave function derived by Crandall *et al.* [17] for the two-electron model, $H_c = -(\nabla_1 2+\nabla_2^2)/2 + (\omega/2)(r_1^2+r_2^2) + \lambda/r_{12}^2$, which parallels the Hookean atom by having harmonic confinement, but with an inverse quadratic interaction instead of e^2/r_{12} as in the Hookean model. The Crandall ground-state wave function $\Psi(\vec{r}_1,\vec{r}_2)$ has the explicit form

$$\Psi_C(\vec{r}_1,\vec{r}_2) = \exp\left[-m\omega r_1^2/2\hbar\right]\exp\left[-m\omega r_2^2/2\hbar\right]r_{12}^\gamma, \quad (27)$$

where γ measures the strength of the repulsive coupling through

$$\gamma = [(1+4\lambda m/\hbar^2)^{1/2}-1]/2. \quad (28)$$

For γ nonintegral, as is usually the case for this model, we note below two features of the nonanalyticity, reflected in the term r_{12}^γ (which in hyperspherical coordinates is proportional to R^γ), times a known function of α and Θ. First, a physical property, the ground-state density $n(r) = \int\Psi_C^2(\vec{r},\vec{r}')d\vec{r}'$, has

been obtained from Eq. (27) by Capuzzi *et al.* [18], which for the artificial two-electron atom reads

$$n(r) = \frac{(m\omega/\hbar)^{3/2}}{2^{a-1}\pi^{3/2}} \exp[-2m\omega r^2/\hbar]\, {}_1F_1\left(\frac{3}{2}+\gamma; \frac{3}{2}; \frac{m\omega r^2}{\hbar}\right). \tag{29}$$

The corresponding x-ray scattering factor $f(k)$, which is the Fourier transform of $n(r)$, can be calculated analytically from Eq. (29), with the result

$$f(k) = 2e^{-k^2a^2/2}\, {}_1F_1\left(-\gamma; \tfrac{3}{2}; \tfrac{1}{4}k^2a^2\right), \tag{30}$$

where $a = \sqrt{\hbar/2m\omega}$. Writing Eq. (27) in hyperspherical coordinates and then taking the Fourier transform with respect to R, we find that in $\mathbf{k}$ space, the wave function of Crandall *et al.* is nonanalytic at small R and has the large-k behavior

$$\Phi_C(k,\alpha,\Theta) = f(\alpha,\Theta)\frac{1}{k^{\gamma+3}}, \tag{31}$$

where $f(\alpha,\Theta)$ is known.

V. DISCUSSION

Finally, returning to the specific Fock proposal of $\ln R$ behavior in the He atom, we note that White and Stillinger [19], using first-order perturbation theory on the angle-averaged wave function $\exp[-Z^*R]$ in Ref. [19] as the unperturbed result, found a term $R^2 \ln R$ times an angular function in He. In this regard, we consider the asymptotic behavior of the Fourier transforms below that are relevant to this work:

$$\begin{aligned} F(k) &= \int dR\, e^{i\mathbf{k}\cdot\mathbf{R}} R^\alpha e^{-aR^2} \\ &= \frac{2\pi}{a^{(\alpha+3)/2}}\Gamma(1+\alpha/2)\, {}_1F_1\left(\frac{\alpha+3}{2}; \frac{3}{2}; -\frac{k^2}{4a}\right) \\ &\quad - \frac{\pi^{3/2}2^{\alpha/2+2}\alpha}{k^{\alpha+3}}\frac{\Gamma(1+\alpha/2)}{\Gamma(1-\alpha/2)}, \end{aligned} \tag{32}$$

for large k and $\alpha \neq 0,2,4,\ldots$, and

$$\begin{aligned} G(k) &= \int d\vec{R}\, e^{\mathbf{k}\cdot\mathbf{R}} R^2 \ln R\, e^{-aR^2} \\ &= \frac{\pi\Gamma(5/2)}{a^{5/2}}\left\{\frac{\partial}{\partial s}\, {}_1F_1\left(s; \frac{3}{2}; -\frac{k^2}{4a}\right)\Big|_{s=5/2}\right. \\ &\quad \left. + \left[\psi\frac{5}{2} - \ln a\right]\left(1 - \frac{k^2}{6a}\right)e^{-k^2/4a}\right\}. \end{aligned} \tag{33}$$

For large k,

$$G(k) \sim \frac{2\pi^{3/2}[\ln a - \psi(5/2)]}{a^2}\frac{e^{-k^2/4a}}{k}. \tag{34}$$

The nonanalyticity in Eq. (31) is clearly reflected at large k in Eq. (32), while Eq. (33) is relevant to He itself in the context of the White-Stillinger first-order perturbation calculation [19].

VI. CONCLUSION

Following Fock's proposal [3], we have expressed the exact ground-state wave function for two solvable models in hyperspherical coordinates. While both wave functions are compact, we have been able to pull them together in $\vec{k}$ space, leading to a common equation [Eq. (26)]. This is one of our principal results. Returning to Fock's ideas though, the Hookean atom model as presented above reveals that in hyperspherical coordinates, Fock-like terms in the He atom wave function for small R can arise only from the interplay between Coulomb confinement and the full electron-electron interaction e^2/r_{12}. We have also stressed that, while Coulomb confinement is exactly incorporated in the Hamiltonian $\hat{H}_s'$ in Eq. (5), the electron-electron interaction terms included there are still too primitive to yield terms having, for example, the Fock term $R^2 \ln R$ at small R.

ACKNOWLEDGMENTS

M.L.G. thanks the Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid. N.M.H. acknowledges the University of Valladolid and wishes to thank Professor J. A. Alonso. This work has been supported by the Spanish Ministerio de Educación y Ciencia (Project MTM2005-09183).

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