Analytic inhomogeneous electron liquid and its density for model spin-compensated two-electron atomic ions with Coulomb confinement: an exact nonrelativistic Hamiltonian

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Analytic inhomogeneous electron liquid and its density for model spin-compensated two-electron atomic ions with Coulomb confinement: an exact nonrelativistic Hamiltonian

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In earlier work, Howard and March (HM) proposed an analytic ground-state electron density $\rho(r)$ starting from the s-wave model of the He atom. Subsequently Ancarani has constructed by numerical methods a variational approach for this s-wave model with a lower energy than the HM result. This clearly means that the HM $\rho(r)$ is not the ground-state electron density of the He s-wave model. Therefore, we derive here an exact nonrelativistic Hamiltonian, with strong radial correlation plus Coulomb confinement, for which the HM $\rho(r)$ is indeed the ground-state electron density.

Keywords: Inhomogeneous electron liquids; Two-electron model atoms; Radial correlation; Exact Hamiltonian

The s-wave model of Helium-like atomic ions is the simplest system in which two electrons, confined by a spherical Coulomb potential, interact via long-range Coulomb forces. This model has been used by Temkin [1] in describing the s-wave scattering in the electron-hydrogen system.

Howard and March (HM) [2] have earlier proposed a closed analytic form of electron density $\rho(r)$ for a two-electron spin-compensated atomic ion, taking the s-wave model of atomic He as their starting point. However, Ancarani [3] has recently obtained variationally a lower energy than that of HM for this s-wave Hamiltonian, and therefore the HM density $\rho(r)$ cannot be an exact ground-state property for this case. We here derive the exact nonrelativistic Hamiltonian, with purely radial correlation as in the

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s-wave model, having the HM density $\rho(r)$ as its ground-state density. The merit of this derivation is that few exact analytic solutions with Coulomb confinement exist in the presence of strong interparticle repulsion, in contrast to harmonically confined models.

The Howard and March wavefunction (HM) is simply expressed as

$$\Psi(r_>, r_<) = C \exp[-(Z-1)r_> - Zr_<] \tag{1}$$

where $r_> = (r_1 + r_2 + |r_1 - r_2|)/2$ and $r_< = (r_1 + r_2 - |r_1 - r_2|)/2$.

The validity of the Howard and March assumption has been rightly criticized by Ancarani [3] and Serra [4] because it violates the variational principle. The origin of this failure is in the discontinuity of the derivative of HM wavefunction at $r_1 = r_2$. The main objective of the Howard and March work [2] and of the subsequent detailed analysis of their wavefunction in direct and momentum space, given by Amovilli and March [5], was in the analytical results of potential interest in density functional theory of realistic atomic models. Similar derivations have been revealed fruitful for Moshinsky, Hooke and mixed models (see, for example, [6,7]). The question addressed in this Letter is whether the HM wave function is the exact ground-state wave function of a modified Hamiltonian. This question has an affirmative answer: an 'artificial' atom Hamiltonian can be constructed explicitly. Considering the discontinuity of the derivative, one can show that the HM wavefunction is the exact ground-state wave function of the Hamiltonian

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

which differs from the He-like *s*-wave model by the presence of the δ function. The operator in equation (2) can be viewed as a model Hamiltonian for a special type of 'artificial' atom which differs from that of the *s*-wave model of Helium by an interaction term which introduces an artificial radial correlation. We believe that this model Hamiltonian, by changing the strength of the $1/r_>$ interaction and, accordingly, of the δ term, could be of potential interest in the search of a Schrödinger like equation for the pair density amplitude in the approach suggested recently by Nagy and Amovilli [8].

With respect to the above Hamiltonian, the HM wave function has eigenvalue $-Z^2/2 - (Z-1)^2/2$ and is not separable in the variables r_1 and r_2, namely

$$\Psi(r_1, r_2) = C \exp\left[-\left(Z - \frac{1}{2}\right)(r_1 + r_2) + \frac{1}{2}|r_1 - r_2|\right]. \tag{3}$$

As a two electron wave function dependent only on r_1 and r_2, the HM wavefunction satisfies automatically the angular momentum condition $l_1 = l_2 = L = 0$. At this point it is interesting to make a comparison with the exact ground state of the *s*-wave model of Helium. This comparison has not correctly been exposed in the works of Serra [4] and Ancarani [3].

For functions of r_1 and r_2 and, of course, for a spherical symmetry confinement, *s*-wave model Hamiltonians can be introduced by the average of the full Hamiltonian over such a distribution, namely

$$\left\langle \Phi(r_1, r_2)|\hat{h}(1) + \hat{h}(2) + g(12)|\Phi(r_1, r_2) \right\rangle = \left\langle \Phi(r_1, r_2)|\hat{H}_s|\Phi(r_1, r_2) \right\rangle \tag{4}$$

where

$$\hat{h} = -\frac{1}{2}\nabla^2 + v(r) \tag{5}$$

and $g(12)$ is the interparticle interaction potential energy. In terms of the zeroth order Laplace's expansion [9], the *s*-wave Hamiltonian is

$$\hat{H}_s = \hat{h}(1) + \hat{h}(2) + g_0(r_>, r_<) \tag{6}$$

where

$$g_0(r_>, r_<) = \sum_{j=0}^{\infty} \frac{r_<^{2j}}{2j!!(2j+1)!!} \left[\frac{1}{r_>} \left(\frac{\partial}{\partial r_>} \right)^{2j} r_> g(r_>) \right]. \tag{7}$$

If the above Hamiltonian is Hermitian, the function $\Phi(r_1, r_2)$ which minimizes the mean value over the full Hamiltonian is also the ground-state wave function of the *s*-wave Hamiltonian (6). Serra [4] follows this route to approximate the ground-state of the He-like *s*-wave model. If we call Ψ_S such a function, we have

$$E_S = \left\langle \Psi_S(r_1, r_2)|\hat{h}(1) + \hat{h}(2) + 1/r_{12}|\Psi_S(r_1, r_2) \right\rangle$$
$$\leq \left\langle \Phi(r_1, r_2)|\hat{h}(1) + \hat{h}(2) + 1/r_{12}|\Phi(r_1, r_2) \right\rangle \tag{8}$$

from the variational principle. Equations (2) and (8) allow a comparison between HM and Serra's wave functions. If we look at the He-like *s*-wave model we have immediately

$$E_{HM} = \left\langle \Psi_{HM}|\hat{h}(1) + \hat{h}(2) + 1/r_{12}|\Psi_{HM} \right\rangle$$
$$= -\frac{Z^2}{2} - \frac{(Z-1)^2}{2} - \left\langle \Psi_{HM}|\delta(r_1 - r_2)|\Psi_{HM} \right\rangle \tag{9}$$

which leads to

$$E_{HM} = -\frac{Z^2}{2} - \frac{(Z-1)^2}{2} - \frac{6(Z-1)^2(2Z^2 - 3Z + 1)}{(2Z-1)(32Z^2 - 50Z + 20)} > E_S. \tag{10}$$

It is interesting to remark, as resulting from equation (10), that the difference between the two energies E_{HM} and E_S is of order Z at very large Z.

Instead, if we apply the variational principle to the Hamiltonian (2) we can state also that

$$E_S + \langle \Psi_S | \delta(r_1 - r_2) | \Psi_S \rangle \; > \; -\frac{Z^2}{2} - \frac{(Z-1)^2}{2} \tag{11}$$

where

$$\langle \Psi_S | \delta(r_1 - r_2) | \Psi_S \rangle = 8\pi^2 \int_0^\infty \Psi_S(r,r)^2 r^4 \mathrm{d}r. \tag{12}$$

This is the correct way to compare the energies associated with the two wave functions above and not as Serra and Ancarani did in their comments.

Subsequent to [2], we have analyzed various other two-electron artificial atoms [6,7], where the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is known with interaction $u(r_{12})$ but for harmonic confinement, in contrast to the Coulombic confinement in the Hamiltonian (2). The considerable merit of the present work is that this is an exactly solvable Hamiltonian with a nontrivial repulsive interparticle interaction for such Coulombic confinement. Already, Howard and March [2] have given the differential equation satisfied by the ground-state electron density $\rho(r)$, defined from equation (3) by

$$\rho(r_1) = 2 \int \Psi^2(r_1, r_2) \mathrm{d}\mathbf{r}_2 \tag{13}$$

namely

$$(a_0 + a_1 r + a_2 r^2)\rho'' + (b_0 + b_1 r + b_2 r^2)\rho' + (c_0 + c_1 r + c_2 r^2)\rho = 0 \tag{14}$$

with coefficients given in table 2 of reference [2]. Moreover, the entanglement of the HM wave function is demonstrated from the one-particle density matrix obtained subsequently by Amovilli and March [5]. This, of course, remains exactly valid for the solvable model corresponding to the new Hamiltonian (2), representing Coulomb confinement plus the modified artificial atom interaction displayed there. In view of the present analytic intractability of the He atom ground state wave function, it would be of considerable interest if generalizations of the new Hamiltonian (2) exhibited here for Coulomb confinement could be effected for other interparticle interactions. Already, for harmonic confinement, Holas *et al.* [10] have given a quite general integral for the density $\rho(r)$ and its off-diagonal generalization $\gamma(\mathbf{r}_1, \mathbf{r}_2)$ for an arbitrary inter-Fermion interaction $u(r_{12})$.

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