
Approximate Ansatz for the Expansion of the Spherically Averaged Wave Function in Terms of Interelectronic Separation r_{12} for the Hookean Atom, Atomic Ions, and the H_2 Molecule

C. AMOVILLI,¹ Á. NAGY,² N. H. MARCH³

¹*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy*

²*Department of Theoretical Physics, University of Debrecen, POB 5, H-4010 Debrecen, Hungary*

³*Department of Physics, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium, and University of Oxford, Oxford, England*

Received 17 January 2003; accepted 8 May 2003

DOI 10.1002/qua.10705

ABSTRACT: For the two-electron Hookean atom, it is first emphasized that, for a specific force constant $k = 1/4$, the ground-state wave function has a simple dependence on the interelectronic separation r_{12} , namely, $(1 + \frac{1}{2}r_{12})\exp(-\frac{1}{8}r_{12}^2)$. For this two-electron model, therefore, the study of Rassolov and Chipman on the electron–electron cusp conditions on the spherically averaged wave function for the N electron atomic ions can be generalized to all orders in the interelectronic separation r_{12} . This Hookean model has therefore been used to give some justification for an ansatz for the spherically averaged wave function in atomic ions with N electrons for $N \geq 2$. Several approximate two-electron wave functions satisfying the Rassolov and Chipman conditions were tested and found to give excellent results. Another ansatz has been tested numerically on the ground state of two-electron atomic ions and the H_2 molecule. Finally, for the Hookean atom a partial differential equation that is essentially for the pair correlation density is given in the Appendix.

© 2003 Wiley Periodicals, Inc. *Int J Quantum Chem* 95: 21–29, 2003

Introduction

The two-electron problem, and in particular He-like ions, has been extensively studied by accurate quantum chemical techniques, but an ex-

act analytic solution of the ground-state spatial wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ has not proved feasible to date. The present study represents a modest step along the road to achieving this objective.

Early work of Kestner and Sinanoglu [1] pointed to the fact that the electron correlation energy in the ground state of the He atom was probably not sensitive to the precise form of the electron–nuclear

Correspondence to: C. Amovilli; e-mail: amovilli@dcc.i.unipi.it

interaction but dominantly determined by the Coulombic repulsion e^2/r_{12} , where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, between the two (spin-paired) electrons. These authors therefore proposed the so-called two-electron Hookean atom, for which the Hamiltonian is, in a.u.,

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}k(r_1^2 + r_2^2) + r_{12}^{-1}, \quad (1)$$

that is, the two Coulombically repelling electrons are harmonically confined, with spring constant k . In later work, for $k = 1/4$, an exact ground-state wave function was shown to be [2–8]

$$\Psi = C \exp\left(-\frac{R^2}{2}\right) \left(1 + \frac{r_{12}}{2}\right) \exp\left(-\frac{r_{12}^2}{8}\right), \quad (2)$$

where \mathbf{R} is the center of mass coordinate $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$. In recent work, Amovilli and March [9] constructed the near-diagonal behavior of the first-order density matrix based on this model and emphasized the dependence of the correlation kinetic energy on the electron–electron cusp condition first discussed by Kato [10] and later by Bingel [11]. In an earlier article, on the other hand, the wave function at coincidence of the Hookean atom was studied by March et al. [12].

Here, our focus will be on approximations generalizing the cusp condition of Rassolov and Chipman [13] (see also Nagy and Sen [14]) in the power series expansion of the spherically averaged wave function in the interatomic separation r_{12} and on the partial differential equation satisfied by $(\rho g)^{1/2}$ in the Hookean model, with ρ the ground-state density and $g(\mathbf{r}_1, \mathbf{r}_2)$ the pair correlation density, this being set out in the Appendix.

From the investigation of Rassolov and Chipman [13] we can expand the spherically averaged wave function $\bar{\Psi}$ in the interatomic separation r_{12} of a chosen pair of electrons

$$\bar{\Psi} = \Psi^{(0)} + \Psi^{(1)}r_{12} + \Psi^{(2)}r_{12}^2 + \Psi^{(3)}r_{12}^3 + \dots + \Psi^{(n)}r_{12}^n + \dots \quad (3)$$

The low-order coefficients in Eq. (3) were shown in Ref. [13] to satisfy

$$\Psi^{(1)} = \frac{1}{2} \Psi^{(0)}, \quad (4)$$

which is the Kato [10] electron–electron cusp condition. The new result of Rassolov and Chipman [13] was to relate $\Psi^{(3)}$ to $\Psi^{(2)}$ and $\Psi^{(0)}$:

$$\Psi^{(3)} = \frac{1}{3} \Psi^{(2)} - \frac{1}{48} \Psi^{(0)}. \quad (5)$$

Approximate Wave Functions Satisfying the Rassolov–Chipman Conditions for the Hookean Atom

Let us bring these low-order results immediately into contact with the exact wave function [Eq. (2)] for the two-electron Hookean atom. The dependence on r_{12} can then be readily expanded to all orders as the sum of a series with even powers of r_{12} plus an odd power series:

$$\bar{\Psi} \propto \left(1 + \frac{r_{12}}{2}\right) \sum_{j=0}^{\infty} (-1)^j \frac{r_{12}^{2j}}{8^j j!}. \quad (6)$$

One can write from Eq. (6) the forms of $\Psi^{(0)} - \Psi^{(3)}$ in Eq. (3) explicitly, and in particular it is readily verified that Eq. (6) satisfies the specific known cusp conditions (4) and (5).

However, it is plain from Eq. (6) that in the Hookean model the coefficients of the even and odd series in powers of r_{12} are intimately related and in particular $\Psi^{(3)}/\Psi^{(0)} = -\frac{1}{16}$.

As emphasized in Ref. [13], in the general case of an atomic ion in Eq. (5) $\Psi^{(2)}$ itself is not determined and depends on the detailed model adopted. Nevertheless, it seems of interest to construct a more general ansatz for the spherically averaged wave function, which embraces not only the general results (4) and (5) but also the detailed Hookean atom form.

The original Eq. (3) can be rewritten as

$$\bar{\Psi} = \Psi^{(0)} + \Psi^{(2)}r_{12}^2 + \dots + \left[\frac{1}{2} \Psi^{(0)} + \left(\frac{1}{3} \Psi^{(2)} - \frac{1}{48} \Psi^{(0)}\right)r_{12}^2\right]r_{12} + \dots, \quad (7)$$

where we applied the relationships (4) and (5) relating the odd and even low-order terms. Now an approximate Gaussian summation motivated by Eq. (2) yields

TABLE I

Total energy minus $(3/2)\sqrt{k}$ (E) for two electrons in a harmonic external potential with spring constant k determined from Eq. (8).

k	$-\Psi^{(2)}/\Psi^{(0)}$	E	$2/\sqrt{k}$	E^{Taut}	λ	E^{pert}
0.001335	0.00299	0.19660	54.73806	0.16442*	5.23154	0.15685
0.002500	0.00447	0.24082	40.00000	0.20744	4.47214	0.20287
0.010000	0.01081	0.36932	20.00000	0.35000*	3.16228	0.34852
0.040000	0.02838	0.60067	10.00000	0.59899	2.23607	0.59835
0.250000	0.12469	1.25000	4.00000	1.25000*	1.41421	1.24991
1.000000	0.29938	2.23033	2.00000	2.22899	1.00000	2.23009
4.000000	0.63625	4.05980	1.00000	4.05634	0.70711	4.05787
25.00000	1.58438	9.22108	0.40000	9.22913	0.44721	9.21103
100.0000	3.08125	17.47154	0.20000	17.54788	0.31623	17.44867

E^{Taut} is the energy E obtained by the interpolation formula of Taut [4]. An asterisk denotes that these are the exact values instead of numbers obtained by the interpolation formula. E^{pert} denotes energies from accurate perturbation calculations [16]. λ is the expansion parameter for the perturbation theory and corresponds to $1/k^{1/4}$. All values are in a.u.

$$\bar{\Psi} = \Psi^{(0)} \exp \left[\left(\frac{\Psi^{(2)}}{\Psi^{(0)}} \right) r_{12}^2 \right] + \frac{1}{2} \Psi^{(0)} r_{12} \exp \left[\left(\frac{2}{3} \frac{\Psi^{(2)}}{\Psi^{(0)}} - \frac{1}{24} \right) r_{12}^2 \right]. \quad (8)$$

This in turn leads back to $\bar{\Psi}$ as $\bar{\Psi}_{\text{Hookean}}$ plus an extra term

$$\delta\Psi = -\frac{1}{2} \Psi^{(0)} r_{12} \exp \left[\left(\frac{\Psi^{(2)}}{\Psi^{(0)}} \right) r_{12}^2 \right] \times \left[1 - \exp \left(-\frac{1}{3} \frac{\Psi^{(2)}}{\Psi^{(0)}} - \frac{1}{24} \right) \right]. \quad (9)$$

This extra term (9) goes to zero because $\Psi^{(2)} = -\frac{1}{8}\Psi^{(0)}$ in the Hookean case. Equation (8) therefore is an approximate summation, correct to third order in r_{12} in the general case, and embracing exactly Eq. (2) for the Hookean model.

The approximate wave function (8) was applied for two electrons in a harmonic external potential with arbitrary spring constant k . The ratio $\Psi^{(2)}/\Psi^{(0)}$ was determined by minimizing the internal energy E . Table I presents the energy E for different values of the spring constant k . The energy E is compared with the value given by the interpolation formula suggested by Taut [4] (in three cases, denoted by an asterisk, the exact results are presented instead of the values obtained by the Taut interpolation formula). All energies correspond to the total energy minus $(3/2)\sqrt{k}$.

In a wide range of k the results shows that the ansatz (8) is a good one-parameter approximation to the exact ground-state wave function of a Hookean atom and of course is exact when $k = 1/4$.

As a next step we start from Taut's general solutions for two electrons in an arbitrary harmonic confining potential. One can satisfy both cusp and Rassolov–Chipman conditions by the function

$$\bar{\Psi} = \Psi^{(0)} \left(1 + \frac{1}{2} r_{12} + t r_{12}^2 \right) \exp \left[-\left(\frac{1}{8} - 2t \right) r_{12}^2 \right], \quad (10)$$

which is exact for $k = 0.25$ ($t = 0$) and for $k = 0.01$ ($t = 1/20$). In other cases t is a variational parameter to be optimized. This form looks similar to the Hylleraas function with three parameters for helium [15]:

$$\Psi = 1.331 [1 + 0.292 r_{12} + 0.131 (r_1 - r_2)^2] \times \exp[-1.816(r_1 + r_2)]. \quad (11)$$

For comparison purposes the energies from accurate perturbation calculations [16] and from Hartree–Fock (HF) calculations performed with an even-tempered Gaussian basis set of 12 functions are also added to Table II. The Taut interpolation formula is good enough for $k < 1$ while the perturbation calculation is good for $k > 1$. So, the last two columns show the percentages of correlation energy recovered by the two approximations discussed here.

TABLE II

Total energy minus $(3/2)\sqrt{k}$ ($E(t)$) for two electrons in a harmonic external potential with spring constant k determined from Eq. (10). Comparison with energies of Table I and from HF Calculations.

k	t	$E(t)$	$E(HF)$	$-E_{\text{corr}}$	E % of E_{corr}	$E(t)$ % of E_{corr}
0.001335	0.05837	0.16447	0.18672	0.02232	—	99.8
0.002500	0.05663	0.20754	0.23179	0.02435	—	99.6
0.010000	0.04999	0.35000	0.37916	0.02916	33.7	100.0
0.040000	0.03683	0.59881	0.63247	0.03348	95.0	100.0
0.250000	0.00000	1.25000	1.28851	0.03851	100.0	100.0
1.000000	-0.05539	2.23013	2.27153	0.04144	99.4	99.9
4.000000	-0.15528	4.05802	4.10153	0.04366	95.6	99.6
25.00000	-0.42208	9.22035	9.25814	0.04711	78.7	80.2
100.0000	-0.82925	17.51685	17.49985	0.05118	55.3	—

t is the variational parameter in Eq. (10). $E(t)$ is the internal energy determined from Eq. (10) with the variational parameter t . All values are in a.u.

Finally, for this model atom, because the perturbative solution is an infinite series in r_{12} times the exponential $\exp[-(1/4)\sqrt{kr_{12}^2}]$, we also tested a more flexible function

$$\bar{\Psi} = \left[1 + \frac{1}{2} r_{12} + q r_{12}^2 + \left(\frac{\sqrt{k}}{24} - \frac{1}{48} + \frac{q}{3} \right) r_{12}^3 \right] \times \exp\left[-\frac{1}{4} \sqrt{kr_{12}^2} \right], \quad (12)$$

which is a third-order polynomial times the noninteracting solution. This third approximation satisfies cusp and Rassolov–Chipman conditions and has a linear variational parameter q . As can be seen from Table III this function is better than the previous two. The last column shows how much of the correlation energy is included in $E(q)$. The wave function (12) includes one more exact solution, more precisely that corresponding to $k = 0.001335$ (see Ref. [4]).

Approximate Wave Functions Satisfying the Cusp and Rassolov–Chipman Conditions for Two-Electron Atomic Ions

Now, we turn to the case of the He atom and two-electron ions. An approximate wave function may be written in the form satisfying the Rassolov–Chipman conditions

$$\Psi = e^{-\zeta(r_1+r_2)} \left\{ 1 + \frac{1}{2} r_{12} + \frac{3}{16} (r_1 - r_2)^2 + \left[3t - \frac{\zeta}{6} \right] \frac{r_{12}^2}{(r_1 + r_2)} + t \frac{r_{12}^3}{(r_1 + r_2)} \right\}, \quad (13)$$

where ζ and t are variational parameters.

The Rassolov–Chipman condition is easily verified by putting first

$$r_1 + r_2 = 2R + \frac{(1 - \mu^2)}{4R} r_{12}^2 + O(r_{12}^4)$$

$$(r_1 - r_2)^2 = \mu^2 r_{12}^2 + O(r_{12}^4), \quad (14)$$

TABLE III

Total energy minus $(3/2)\sqrt{k}$ ($E(q)$) for two electrons in a harmonic external potential with spring constant k determined from Eq. (12) and amount of correlation energy recovered.

k	q	$E(q)$	$E(q)$ % of E_{corr}
0.001335	0.06500	0.16442	100.0
0.002500	0.06100	0.20749	99.8
0.010000	0.05000	0.35000	100.0
0.040000	0.03500	0.59880	100.0
0.250000	0.00000	1.25000	100.0
1.000000	-0.04400	2.23016	99.9
4.000000	-0.11300	4.05818	99.3
25.00000	-0.26000	9.21231	97.3
100.0000	-0.43400	17.45121	95.0

$E(q)$ is the internal energy determined from Eq. (12) with the linear variational parameter q . All values are in a.u.

TABLE IV
Electronic energy for the two-electron atomic ions considered in this work.

Ion	ζ	t	E	E^{lit}	% of E_{corr}	E^{KPTT}	% of E_{corr}
H ⁻	0.780	0.00843	-0.52402	-0.52775	91	-0.5265	97
He	1.855	0.03011	-2.90153	-2.90372	95	-2.9000	91
Li ⁺	2.885	0.07271	-7.27712	-7.27991	94	-7.2749	89
Be ²⁺	3.905	0.12209	-13.65088	-13.65557	89	-13.6499	87
B ³⁺	4.920	0.17417	-22.02419	-22.03097	85	-22.0249	87
C ⁴⁺	5.930	0.22725	-32.39753	-32.40625	81	-32.4000	86
N ⁵⁺	6.935	0.28059	-44.77104	-44.78145	77	-44.7750	86
O ⁶⁺	7.940	0.33463	-59.14472	-59.15660	74	-59.1500	85

The second and third columns show the optimal value of the variational parameters ζ and t of Eq. (13). E is the total energy obtained with these parameters. E^{lit} denotes the best values found in the literature [18]. The sixth column shows how much of the correlation energy is included in E . For comparison the last two columns present the variational energy calculated by Kleinekathöfer et al. [20] and the percentage of correlation energy obtained by them. All values are in a.u.

where

$$\mu = \frac{\vec{R} \cdot \vec{r}_{12}}{Rr_{12}}, \quad (15)$$

and then by spherical averaging according to

$$\bar{F} = \frac{1}{2} \int_{-1}^1 F(\mu) d\mu \quad (16)$$

for a general function of μ .

The best HF and exact energies in the literature are -2.86168 and -2.90372 a.u., respectively. The correlation energy is then -0.04204 a.u. Table IV presents the variational total energy for the He atom and two-electron ions considered in this work. The second and third columns show the optimal value of the variational parameters ζ and t . E is the total energy obtained with these parameters. E^{lit} denotes the best values found in the literature [17–19] reported with a truncation at 10^{-5} a.u. The next column shows how much of the correlation energy is included in E . The results are good enough although not so good as in the Hookean model. But, in this case we do not have separability and there is also one more variable. The Hylleraas three-terms function [Eq. (11)], which shows an energy of -2.90243 a.u., looks slightly better than the present ansatz [Eq. (13)], but the Hylleraas expression has three variational parameters, while we have only two in Eq. (13). Moreover, it is interesting to remark that the present ansatz [Eq. (13)] leads to better result than a full configuration interaction function obtained with a standard cc-pVTZ basis set.

For comparison, Table IV presents the variational results of Kleinekathöfer et al. [20]. Their variational

wave function satisfies the electron–nucleus and electron–electron cusps and the correct asymptotic behaviour. To ensure the latter the wave function explicitly contains the energy that is determined self-consistently. Their one-parameter wave function, however, does not exactly satisfy the Rassolov–Chipman condition. For He, Li⁺, and Be²⁺ our present approach leads to a better performance with two variational parameters. It, however, becomes worse for higher Z because we have not considered at all the problem of the electron–nucleus cusp. It is likely that a synthesis of the approach of Kleinekathöfer et al. and ours would lead to excellent results.

It is interesting to note the behavior of t for large atomic numbers; It becomes linear in Z :

$$t \approx \frac{(Z-2)}{18}. \quad (17)$$

Moreover, ζ also tends to Z . So, at some point there is a cancellation in one coefficient and for large Z the working ion wave function tends to

$$\Psi \approx e^{-Z(r_1+r_2)} \left\{ 1 + \frac{1}{2} r_{12} + \frac{3}{16} (r_1 - r_2)^2 - \frac{1}{3} \frac{r_{12}^2}{(r_1 + r_2)} + \frac{(Z-2)}{18} \frac{r_{12}^3}{(r_1 + r_2)} \right\}, \quad (18)$$

which gives a substantial fraction of correlation up to high values of Z .

A closed form of the energy as a function of Z can be obtained from Eq. (18). Grouping the terms with the same Z powers one has

$$E = \frac{-Z^2 - 0.96648Z + 0.50823 + 0.58666/Z - 0.22548/Z^2 + 0.09726/Z^3}{1 + 1.59149/Z + 0.35886/Z^2 - 0.76735/Z^3 + 0.38356/Z^4}, \quad (19)$$

in which the coefficients have been evaluated by numerical integration. In Table V we compare the energies calculated by means of Eq. (19) with the HF large Z corresponding estimates, namely, $-(Z - 5/16)^2$, for some two-electron atomic ions in the range of Z between 30 and 90. In all cases more than 65% of correlation energy is recovered.

Approximate Wave Function for the H_2 Molecule

The Rassolov–Chipman conditions are important for molecules as well. To demonstrate it the H_2 molecule is studied. We select the working function

$$\Psi = e^{-\alpha(\xi_1 + \xi_2)} \left\{ 1 + \frac{1}{2} r_{12} + c_1 r_{12}^2 + c_2 r_{12}^3 + c_3 (\eta_1 - \eta_2)^2 \right\}, \quad (20)$$

where α and c_j are variational parameters. ξ_j and η_j are essentially elliptical coordinates, here defined as

$$\xi_j = \frac{r_{jA} + r_{jB}}{D} \quad \eta_j = \frac{r_{jA} - r_{jB}}{D}, \quad (21)$$

D being the internuclear distance. The term in $(\eta_1 - \eta_2)^2$ has been introduced because this combination of variables enters in the Heitler–London valence

TABLE V
Energies calculated by Eq. (19), large Z HF estimates, namely, $-(Z - 5/16)^2$, their difference, and percent of correlation energy included for some two-electron atomic ions.

Z	E	$-(Z - 5/16)^2$	ΔE	% E_{corr}
40	-1575.13165	-1575.09766	-0.03400	72
50	-2468.88076	-2468.84766	-0.03310	70
60	-3562.63010	-3562.59766	-0.03244	69
70	-4856.37959	-4856.34766	-0.03193	69
80	-6350.12918	-6350.09766	-0.03152	67
90	-8043.87883	-8043.84766	-0.03117	66

All values are in a.u.

bond (VB) wave function (see below). Expression (20) is also similar to the low-order Kołos–Wolniewicz expansion [21]. Figure 1 presents the energy as a function of the internuclear separation. For comparison, the HF values and the results of Kołos and Wolniewicz are also shown. The percentage of correlation energy recovered by the use of function (20) reduces from 85 at D near 0.5 a.u. to 75 at D close to 3 a.u., a result that shows that the role of cusp conditions becomes less important in going toward the H_2 dissociation. Expression (20) is not forced to satisfy the Rassolov–Chipman condition but the optimal c_j reflect some relevant behavior. Expanding Eq. (20) near $r_{12} \rightarrow 0$ and after spherical averaging we have

$$\begin{aligned} \bar{\Psi} = \exp\left[-\frac{2\alpha}{D}(R_A + R_B)\right] \times & \left\{ 1 + \frac{1}{2} r_{12} \right. \\ & + \left[-\frac{\alpha}{6} \left(\frac{1}{R_A} + \frac{1}{R_B} \right) + c_1 \right. \\ & + \left. \left. \frac{2}{3D^2} (1 - \cos \phi) c_3 \right] r_{12}^2 \right. \\ & + \left. \left[-\frac{\alpha}{12} \left(\frac{1}{R_A} + \frac{1}{R_B} \right) + c_2 \right] r_{12}^3 + O(r_{12}^4) \right\}, \quad (22) \end{aligned}$$

where R_A and R_B are, respectively, the distances between the two-electron center of mass and the nuclei A and B and ϕ is the angle between the two segments R_A and R_B .

In Table VI the optimal parameters α , c_1 , c_2 , and c_3 are presented for the H_2 molecule at several internuclear distances D . As expected, α is essentially proportional to D while instead it is interesting to note that c_3 is proportional to D^2 . There is some balance in Eq. (22). Thinking to the Rassolov–Chipman conditions it looks approximately as follows:

$$\frac{1}{3} \left[-\frac{\alpha}{6} \left(\frac{1}{R_A} + \frac{1}{R_B} \right) + c_1 \right] \approx -\frac{\alpha}{12} \left(\frac{1}{R_A} + \frac{1}{R_B} \right) \quad (23)$$

$$\frac{1}{3} \times \frac{2}{3D^2} (1 - \cos \phi) c_3 - \frac{1}{48} \approx c_2, \quad (24)$$

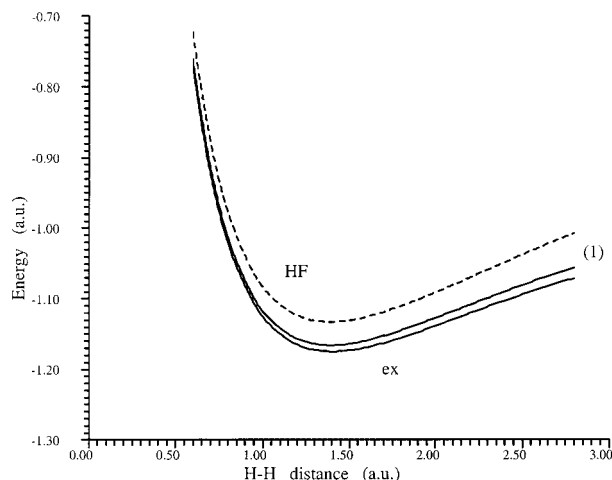


FIGURE 1. Total energy of H_2 molecule as a function of internuclear separation (1). HF values and exact results of Kotos and Wolniewicz (ex) are also shown.

although, of course, R_A , R_B , and ϕ are variables and not constant numbers.

Our work is somehow related to that of Patil and coworkers [22], who constructed a variational wave function with one parameter that satisfies nucleus–electron and electron–electron cusp conditions and has a correct asymptotic behavior. In our wave function neither the nucleus–electron nor the correct asymptotic fall were explicitly taken into account. We might expect that a simple variational wave function satisfying all the conditions mentioned above would result in even more accurate energies.

Note that the Heitler–London wave function is

$$\Psi_{\text{HL}} = e^{-\zeta r_{1A}} e^{-\zeta r_{2B}} + e^{-\zeta r_{1B}} e^{-\zeta r_{2A}}, \quad (25)$$

which becomes in the elliptical coordinates (21)

$$\begin{aligned} \Psi_{\text{HL}} &= e^{-0.5\zeta D(\xi_1 + \eta_1)} e^{-0.5\zeta D(\xi_2 - \eta_2)} + e^{-0.5\zeta D(\xi_1 - \eta_1)} e^{-0.5\zeta D(\xi_2 + \eta_2)} \\ &= e^{-0.5\zeta D(\xi_1 + \xi_2)} [e^{-0.5\zeta D(\eta_1 - \eta_2)} + e^{0.5\zeta D(\eta_1 - \eta_2)}] \\ &= e^{-0.5\zeta D(\xi_1 + \xi_2)} \left[2 + \frac{1}{4} \zeta^2 D^2 (\eta_1 - \eta_2)^2 + \dots \right], \end{aligned} \quad (26)$$

showing both the difference and resemblance to our working function (20).

Summary and Future Directions

It has been amply demonstrated here that the Rassolov–Chipman study of the electron–electron cusp conditions on the spherically averaged wave function for N electron atomic ions is a helpful tool in facilitating variational approaches to two-electron systems. It is important to emphasize that the Rassolov–Chipman condition among $\Psi^{(0)}$, $\Psi^{(2)}$, and $\Psi^{(3)}$ [Eq. (5)] is an exact statement when r_{12} tends to 0 for any given external potential. This turns out to be true not only for single-center atomic ions but for the H_2 molecule as well.

In the present study, the model Hookean atom has provided a useful yardstick in constructing such variational wave functions. Thus, several choices have been focused on because they contain exact limits for this model atom for specific chosen values of its force constant. Our approximation [Eq. (12)] for the Hooke model is the best one-parameter wave function (at least in the range of the spring constant considered).

We draw attention in this summary to the valuable approximation (18) to the correlated ground-state wave function for two-electron atomic ions in the (nonrelativistic) limit of large atomic number Z . The wave function already embodies a substantial fraction of the correlation energy up to large values

TABLE VI
Optimal parameters α , c_1 , c_2 , and c_3 of Eq. (20) for the H_2 molecule at internuclear distance D .

D	α	c_1	c_2	c_3
0.6	0.473	-0.18550	0.04847	0.04207
0.7	0.543	-0.13368	0.02767	0.05611
0.8	0.607	-0.10931	0.01859	0.07401
1.0	0.725	-0.09089	0.01198	0.12084
1.2	0.833	-0.08524	0.00992	0.18249
1.3	0.885	-0.08396	0.00940	0.21939
1.4	0.935	-0.08334	0.00904	0.26091
1.5	0.983	-0.08285	0.00876	0.30714
1.6	1.031	-0.08223	0.00856	0.35832
1.8	1.122	-0.08235	0.00827	0.47914
2.0	1.212	-0.08224	0.00814	0.62650
2.2	1.297	-0.08305	0.00812	0.80691
2.4	1.382	-0.08418	0.00827	1.02602
2.6	1.464	-0.08656	0.00850	1.29238
2.8	1.565	-0.09190	0.01001	1.61159

All values are in a.u.

of Z , and also a closed form (19) has been obtained for the corresponding ground-state energy.

That the approach adopted here is valuable beyond single-center atomic ions is then demonstrated by explicit calculations of the ground state of the H_2 molecule. This again shows clearly that the Rassolov–Chipman conditions are important for multicenter problems in quantum chemistry.

As to future directions, note that according to a recent article [23] the two-electron problem can play an important role in the solution of the many-electron problem. As a first step, it would be of obvious interest if the progress reported here in constructing two-electron variational wave functions compatible with the Rassolov–Chipman conditions could be subsumed into a variational treatment of the ground state of Be or the corresponding four-electron atomic ion sequence. Beyond the electron–electron cusp and the Rassolov–Chipman conditions, the electron–nucleus cusp and the correct asymptotic behavior are also of importance. A variational wave function satisfying all these conditions would lead to even better results.

Appendix: Partial Differential Equation for Pair Correlation Function

To propose a differential equation for $(\varrho g)^{1/2}$ we start from the definition

$$\varrho(\mathbf{r})g(\mathbf{r}, \mathbf{r}') = \varrho(\mathbf{r})\varrho(\mathbf{r}') + \varrho(\mathbf{r})\varrho_{xc}(\mathbf{r}, \mathbf{r}'), \quad (27)$$

with

$$\int \varrho_{xc}(\mathbf{r}, \mathbf{r}')d\mathbf{r}' = -1 \quad \text{for all } \mathbf{r}. \quad (28)$$

In the special case of the HF pair function we have

$$\varrho(\mathbf{r})g_x(\mathbf{r}, \mathbf{r}') = \varrho(\mathbf{r})\varrho(\mathbf{r}') - |\gamma(\mathbf{r}, \mathbf{r}')|^2. \quad (29)$$

On the other hand,

$$\varrho(\mathbf{r})g(\mathbf{r}_1, \mathbf{r}_2) = \Gamma(\mathbf{r}_1, \mathbf{r}_2) = |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2. \quad (30)$$

The last equality follows from the fact that we have a two-electron system. From Eq. (2) we obtain

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = |\Psi|^2 = C^2 e^{-R^2} \left(1 + \frac{r_{12}}{2}\right)^2 \exp\left(-\frac{r_{12}^2}{4}\right). \quad (31)$$

Comparing Eqs. (30) and (31) the relation

$$P(r_1, r_2, r_{12}) = \frac{2}{C} (\varrho g)^{1/2} = (2 + r_{12})e^{-(r_1^2 + r_2^2)/4} \quad (32)$$

can be gained. The derivation of Eq. (32) with respect to r_{12} leads to

$$p = \frac{\partial P}{\partial r_{12}} = e^{-(r_1^2 + r_2^2)/4} \quad (33)$$

Thus, p satisfies a Schrödinger equation for two noninteracting but harmonically confined particles:

$$[\nabla_{r_1}^2 + \nabla_{r_2}^2]p(r_1, r_2, r_{12}) + 2\left[\varepsilon - \frac{1}{8}(r_1^2 + r_2^2)\right] \times p(r_1, r_2, r_{12}) = 0. \quad (34)$$

This is a partial differential equation for the pair correlation function and valid for the model Hookean atom with $k = 1/4$. It should be interesting to generalize Eq. (34) to a different case by means of an effective potential $U(\mathbf{r}_1, \mathbf{r}_2)$.

From the body of the text, it seems that, more in general but now only approximately, the square root of the wave function for the two spin-paired electrons at coincidence satisfies a one-particle Schrödinger equation, but this is an area needing deeper study in the future.

ACKNOWLEDGMENTS

This work was supported by Grant OTKA T042505. This publication is based on work sponsored by the Bilateral Scientific and Technological Cooperation between Hungary and Flanders (Project B-2/01). C.A. acknowledges financial support from MIUR (Italy).

References

1. Kestner, N. R.; Sinanoglu, O. *Phys Rev* 1962, 128, 2687.
2. Samanta, A.; Ghosh, S. K. *Phys Rev* 1990, A42, 1178; Samanta, A.; Ghosh, S. K. *J Chem Phys* 1991, 94, 517; Samanta, A.; Ghosh, S. K. *Chem Phys Lett* 1991, 180, 121.

3. Kais, S.; Herschbach, D. R.; Levine, R. D. *J Chem Phys* 1989, 91, 7791.
4. Taut, M. *Phys Rev* 1993, A48, 3561.
5. King, H. F. *Theor Chim Acta* 1996, 94, 345.
6. Qian, Z.; Sahni, V. *Phys Rev* 1998, A57, 2527.
7. March, N. H.; Gál, T.; Nagy, Á. *Chem Phys Lett* 1998, 292, 384.
8. Cioslowski, J.; Pernal, K. *J Chem Phys* 2000, 113, 8434.
9. Amovilli, C.; March, N. H. *Phys Rev* 2003, A67, 022509.
10. Kato, T. *Commun Pure Appl Math* 1957, 10, 151.
11. Bingel, W. A. *Theor Chim Acta* 1966, 5, 341.
12. March, N. H.; Amovilli, C.; Klein, D. J. *Chem Phys Lett* 2000, 325, 645.
13. Rassolov, V. A.; Chipman, D. M. *J Chem Phys* 1996, 104, 9908.
14. Nagy, Á.; Sen, K. D. *J Chem Phys* 2001, 115, 6300.
15. Hylleraas, E. A. *Z Physik* 1929, 54, 347.
16. Benson, J. M.; Byers Brown, W. *J Chem Phys* 1970, 53, 3880.
17. Pekeris, C. L. *Phys Rev* 1958, 112, 1649.
18. Manby, F. R.; Knowles, P. J. *Chem Phys Lett* 1999, 310, 561.
19. Thakkar, A.; Koga, T. *Theor Chem Acc* 2003, 109, 36.
20. Kleinekathöfer, U.; Patil, S. H.; Tang, K. T.; Toennies, J. P. *Phys Rev* 1996, A54, 2840.
21. Kołos, W.; Wolniewicz, L. *J Chem Phys* 1964, 41, 3663.
22. Patil, S. H.; Tang, K. T.; Toennies, J. P. *J Chem Phys* 1999, 111, 7278.
23. Nagy, Á. *Phys Rev* 2002, A66, 022505. For further references see also two recent books: Coleman, A. J.; Yukalov, V. I. *Reduced Density Matrices: Coulson's Challenge*; Springer-Verlag: New York, 2000; Cioslowski, J. *Many-Electron Densities and Reduced Density Matrices*; Kluwer/Plenum: New York, 2000.