

Determination of simple correlated wave functions for few-electron systems using a Jastrow factor

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Compact Jastrow-Slater-type correlated wave functions for three- and four-electron atoms and ions (Li, Be⁺, B²⁺, C³⁺, Be, B⁺, and C²⁺) are proposed. The Jastrow factor we employed consists of one-body and two-body functions including only two variational parameters in total. We found that a one-body Jastrow function with one variational parameter, which is responsible for the screening effect around the nucleus, is effective for reproducing good total energies of the three- and four-electron atomic systems if hydrogenoid orbitals are adopted in the Slater determinant. On the other hand, a determinant composed of Hartree-Fock orbitals multiplied by the same Jastrow factor was found to give rather worse results than that composed of hydrogenoid orbitals. This result clearly indicates that analytic hydrogenoid orbitals coupled with the one-body Jastrow function are useful for describing simple wave functions and understanding the physical properties of these systems.

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I. INTRODUCTION

It is well known that the mechanisms leading to excitation or ionization of two or more electrons in atomic or molecular systems in a collision cannot be understood within the independent-electron approximation model. The correlation in the many-body system due to the interactions between all the electrons must be properly taken into account. This is an important problem, and a great deal of experimental and theoretical work has been devoted to this question.

The determination of accurate wave functions for few-body Coulombic systems can be achieved in many ways and could be considered nowadays to be a resolved problem if one uses expansions of many Slater determinants [configuration interaction (CI)]. However, the interest of constructing simpler and more compact correlated wave functions still remains because of its importance in theoretical studies of inelastic processes occurring in collisions. In these problems, the wave function of the system (target) is generally needed to determine the cross sections of the inelastic processes induced by the projectile interacting with the target.

Obviously the determination of both simple and accurate wave functions for few-body systems could be a key task. The presently available accurate wave functions usually contain a lot of parameters even for few-electron systems. They also include many Slater determinants (CI) optimized in a self-consistent-field (SCF) procedure and a large number of variational parameters included in the Hylleraas-correlated term. The drawback of these approaches is that the physical

meaning of the correlation role is difficult to extract from them. Developing simpler and still accurate wave functions should provide a better understanding of the underlying physical phenomena, which are governing the electronic dynamics. Moreover, the improved comprehension of the correlation in a few-body system should be a valuable guideline to understand dynamics of larger systems.

To the best of our knowledge, no simple and accurate correlated wave function for three- or four-electron systems is presently available using the Jastrow factor. We believe that this challenge remains up to date and it motivates the present work. Hence the goal of this paper is to determine fully correlated wave functions for three- or four-electron systems. It will be shown that ground-state energies of atoms and ions with three or four electrons like Li, Be⁺, B²⁺, C³⁺, Be, B⁺, and C²⁺ can be obtained accurately with a fairly simple two-parameter wave function.

II. THEORY

The Schrödinger equation for an N -electron atomic system is written in Hartree atomic units ($m=e^2=\hbar=1$), used throughout this paper, within the nonrelativistic approximation and using the usual notation

$$\left(\sum_{i=1}^N -\frac{1}{2}\nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} + \sum_{i<j}^N \frac{1}{r_{ij}} \right) \Psi = E\Psi, \quad (1)$$

where Z is the nuclear charge of the atom or ion. The wave function Ψ , a solution of the many-body Schrödinger equation

tion, is searched within a product of two functions—namely, a Slater determinant Φ and a correlation function called Jastrow factor J :

$$\Psi = J\Phi. \quad (2)$$

This type of wave function can satisfy the antisymmetry of the wave function required for fermion systems if J is a symmetric function. The Slater determinant Φ consists of the one-body orbitals $\phi_\mu(\uparrow\downarrow, \mathbf{r}_i)$, where the arrows represent the up- and down-spin electrons. The function $J(r_i, r_{ij})$ is the Jastrow term defined below. This factor is introduced to describe accurately the electron correlations.

In the present paper, we compare the results obtained from two different Slater determinants. One is given by using Hartree-Fock orbitals Φ^{HF} , and the other is obtained from hydrogenoid orbitals Φ_0 , which are built from the antisymmetric solutions of the independent N -particle problem:

$$\left(\sum_{i=1}^N -\frac{1}{2}\nabla_i^2 - \sum_{i=1}^N \frac{Z}{r_i} \right) \Phi_m = E_m \Phi_m. \quad (3)$$

Thus, in the latter case, only the parameters in the Jastrow factor $J(r_i, r_{ij})$ are optimized. Therefore, the expectation values for the ground-state total energy are, respectively, given by

$$E_{\text{HF-}J} = \frac{\langle \Phi^{\text{HF}} J | H | \Phi^{\text{HF}} J \rangle}{\langle \Phi^{\text{HF}} J | \Phi^{\text{HF}} J \rangle}, \quad (4)$$

$$E_{\text{Hydro-}J} = \frac{\langle \Phi_0 J | H | \Phi_0 J \rangle}{\langle \Phi_0 J | \Phi_0 J \rangle}. \quad (5)$$

Here, H is the interacting many-body Hamiltonian depicted in Eq. (1). We will show that a convenient choice of the symmetric function $J(r_i, r_{ij})$ takes into account the electron-nucleus correlation and $E_{\text{hydro-}J}$ gives significantly better results than $E_{\text{HF-}J}$.

Determination of the variational parameters in the Jastrow factor has been performed in two independent ways, in order to check the numerical accuracy. The first one (approach 1) is implemented by the variational Monte Carlo (VMC) method by minimizing the variance defined by

$$\sigma^2 = \int d^3N x |H_{\text{eff}}\Phi - E\Phi|^2, \quad (6)$$

where

$$H_{\text{eff}} \equiv \frac{1}{J} H J.$$

The variance minimization is known to be effective for the optimization of the Jastrow factor [1,2]. The second one (approach 2) is made via a nonstatistical approach, using a mathematical property of the wave function when is written as a product of two functions. The interest of the transformation is the derivation of a convenient expression for the total energy of the system. We show this briefly in the following.

Assuming the factorized wave function

$$\Psi_m = \Phi_m(\uparrow\downarrow, \mathbf{r}_i) J(r_i, r_{ij}),$$

with Φ_m given in Eq. (3), the calculation of the diagonal elements $H_{mm} = \langle \Psi_m | H | \Psi_m \rangle$ or the off-diagonal matrix elements $H_{mn} = \langle \Psi_m | H | \Psi_n \rangle$ reduces to the computation of a single multivariate quadrature given below (more details about the derivation of these formulas can be found in Refs. [3–5]):

$$H_{mm} = E_m + \frac{\left\langle \Phi_m \left| \sum_i \frac{\vec{\nabla}_i J \cdot \vec{\nabla}_i J}{2} + J^2 \left(\sum_{i<j} \frac{1}{r_{ij}} \right) \right| \Phi_m \right\rangle}{\langle J\Phi_m | J\Phi_m \rangle}, \quad (7)$$

$$H_{mn} = \frac{E_m + E_n}{2} + \frac{\left\langle \Phi_m \left| \sum_i \frac{\vec{\nabla}_i J \cdot \vec{\nabla}_i J}{2} + J^2 \left(\sum_{i<j} \frac{1}{r_{ij}} \right) \right| \Phi_n \right\rangle}{\langle J\Phi_m | J\Phi_n \rangle}. \quad (8)$$

Here, Φ_m is assumed to be a real function. The explicit mathematical form of the function $J(r_i, r_{ij})$ describing the electron-nucleus and electron-electron correlations is presently chosen for the three- and four-electron atoms as

$$J(r_i, r_{ij}) = \exp \left\{ \sum_i \ln[\cosh(\lambda r_i)] + \sum_{i<j} \frac{c r_{ij}}{1 + b r_{ij}} \right\}. \quad (9)$$

The first set of brackets in the functions above describes the electron-nucleus correlation. The parameter λ can be understood as a screening parameter. Such kind of hyperbolic functions were found very efficient in the case of two-electron systems [6,7] and are extended here to three and four electrons. It can be noted that this choice fulfills the electron-nucleus cusp condition. When the i th electron is close to the nucleus, the function $\cosh(\lambda r_i)$ tends to 1 as r_i^2 , giving the limit

$$\lim_{r_i \rightarrow 0} \frac{\partial \Psi}{\partial r_i} = -Z\Psi(0), \quad (10)$$

in agreement with the cusp condition at the nucleus. It is easy to see that λ can be interpreted as a screening coefficient when $r_i \rightarrow \infty$ due to the $\exp(\lambda r_i)$ behavior of the cosh function.

The second set of brackets of Eq. (9) is the well-known factor proposed by Boys and Handy [8]. The two-body Jastrow factor includes the right description of the electron-electron cusp conditions taking $c=0.5$ or $c=0.25$ when the total spin value of the electron pair is $S=0$ or $S=1$, respectively. One should remark that the actual product runs over all the electron pairs.

Equations (7) and (8) can be written in a more convenient way considering the exponential form of J :

$$J = e^W.$$

One has

TABLE I. Ground-state energy estimates for Li, Be⁺, B²⁺, and C³⁺ calculated from the VMC method with Hartree-Fock orbitals in the Slater determinant. The optimized Jastrow parameters λ and b are also listed. The expected statistical errors in the last digit of the total energy are in parentheses. Exact values are from Ref. [9].

System	λ	b	$E_{\text{HF-J}}$	E_{exact}
Li	0.11×10^{-5}	1.00	-7.459(1)	-7.4781
Be ⁺	0.50×10^{-5}	1.39	-14.303(1)	-14.3248
B ²⁺	0.44×10^{-5}	1.75	-23.405(2)	-23.4246
C ³⁺	0.22×10^{-5}	2.09	-34.758(2)	-34.7755

$$\vec{\nabla}_i J \cdot \vec{\nabla}_i J = J^2 \vec{\nabla}_i W \cdot \vec{\nabla}_i W.$$

The expression of the ground-state energy $E = H_{00}$ corresponding to $\Psi_0 = \Phi_0 e^W$ can be written as

$$E = E_0 + \frac{\int d^{3N}x \Psi_0^2 \left[\sum_i \frac{\vec{\nabla}_i W \cdot \vec{\nabla}_i W}{2} + \sum_{i < j} \frac{1}{r_{ij}} \right]}{\langle \Psi_0 | \Psi_0 \rangle}. \quad (11)$$

This form is convenient for energy calculations. This necessitates a multidimensional quadrature performed by non-statistical methods in approach 2. Moreover, the present choice of W gives a simple analytical expression of $\vec{\nabla}_i W \cdot \vec{\nabla}_i W$.

In passing it is worthwhile to notice that Eq. (11) can constitute a simpler alternative expression for the energy that could be useful for Monte Carlo simulations in the future. The main advantage is that it does not require the calculations of the derivatives of Slater determinants, and instead only the calculations of the logarithmic gradient of the Jastrow factor plus a potential term are enough. Moreover, the formula can be extended to nondiagonal terms $\Phi_m J$ and $\Phi_n J$ —same Jastrow factor—considering Eq. (8). This could be used in the CI method.

III. RESULTS

A. Three-electron systems

The basic possibilities of the method are illustrated by determining the wave function for some three-electron ionic or atomic systems in their ground states. In Table I, we report the total energy estimates given by Eq. (4) where numerical solutions of the Hartree-Fock equation were adopted for the Slater determinant and the two parameters λ and b included

in the Jastrow factor were optimized by the VMC method minimizing variance defined by Eq. (6). Here, the Monte Carlo sampling number for the $3N$ -dimensional integration of Eqs. (4) and (6) was set to be $10^6 \times N$. It can be noticed that Hartree-Fock orbitals, which are screened within Hartree and exchange electron interactions, cancel the role of the cosh term, leading to the value $\lambda \approx 0$.

In Table II we display the total energies for the same systems calculated from Eq. (5) where hydrogenoid orbitals were utilized for the Slater determinant and only the Jastrow parameters were optimized by the VMC method minimizing the variance of Eq. (6). The optimum values of the parameters b and λ are also reported in the table. The Monte Carlo sampling number for the $3N$ -dimensional integration of Eq. (5) was again set to be $10^6 \times N$. Surprisingly, the energies listed in Table II are better than those shown in Table I. The agreement between the present results and those that can be considered as exact [9] in Table II is within 1×10^{-2} hartree. In spite of the simplicity of the present wave function including only two variational parameters, the accuracy is considered to be satisfactory. The full correlated wave function used to calculate the energy of Li($1s^2, 2s$) is explicitly written as

$$\Psi_{\text{Li}} = C 1s(r_1) [1s(r_2) 2s(r_3) - 2s(r_2) 1s(r_3)] \exp \left\{ \sum_i \ln[\cosh(\lambda r_i)] + \sum_{i < j} \frac{c r_{ij}}{1 + b r_{ij}} \right\}. \quad (12)$$

The functions $1s(r_i)$ and $2s(r_j)$ are hydrogenoid orbitals; $1s(r_i) = e^{-Z r_i}, \dots$, where Z is the nuclear charge of the atom or ion under consideration ($Z=3$ for Li, etc.), and C is a normalization constant. It is well known that the spin-assigned wave function such as Eq. (12) gives an identical expectation

TABLE II. Ground-state energy estimates for Li, Be⁺, B²⁺, and C³⁺ calculated from the VMC method with hydrogenoid orbitals in the Slater determinant. The optimized Jastrow parameters λ and b are also listed. The expected statistical errors in the last digit of the total energy are in parentheses. Exact values are from Ref. [9].

System	λ	b	$E_{\text{hydro-J}}$	E_{exact}
Li	0.67	0.83	-7.470(1)	-7.4781
Be ⁺	0.76	1.11	-14.320(1)	-14.3248
B ²⁺	0.84	1.37	-23.418(1)	-23.4246
C ³⁺	0.91	1.64	-34.765(1)	-34.7755

TABLE III. Ground-state energy estimates for Be, B⁺, and C²⁺ calculated using Eqs. (7) and (8) with hydrogenoid orbitals in the Slater determinant. The optimized Jastrow parameters λ and b in Eq. (9) are also listed. The parameter c in the Jastrow factor is always equal to 0.5. In parentheses we show the statistical error.

System	λ	b	Eq. (11)	E_{exact}
Be	0.84	1.6	-14.6489(1)	-14.6674
B ⁺	0.86	1.5	-24.3371(2)	-24.3489
C ²⁺	0.88	1.6	-36.5241(2)	-36.5349

value of any spin-independent operator as the full space-spin antisymmetric wave function [10,11]. Thus, this simplification of the wave function has been widely used in the VMC method for the calculations of the total energy and variance. Although the wave function (12) is not an eigenfunction of S^2 because of the satisfaction of the cusp conditions in the Jastrow factor, the effect of spin contamination is known to be very small [12]. It is important to recall here that the wave function is given analytically and includes only two positive parameters λ and b . Unlike the values obtained by using Hartree-Fock orbitals listed in Table I, the parameter λ shown in Table II presents nonzero values. This indicates that the $\cosh(\lambda r_i)$ one-body Jastrow factor works very well for representing the screening effect around the nucleus in these cases.

In approach 2, this analytical formula of the wave function (12) was utilized for the calculations of the total energy estimates given by Eq. (11) with the nonstatistical method and parameter optimization was performed by energy minimization. The results obtained by using this strategy coincide with those given in approach 1 by variational Monte Carlo calculations, within the numerical accuracy.

B. Four-electron systems

The energy values for the ground state 1S of four-electron atoms or ions using hydrogenoid orbitals for the Slater determinant and the Jastrow factor given in Eq. (9) are reported in Table III for the systems Be, B⁺, and C²⁺. In these cases, the $2s$ - $2p$ orbital degeneracies are taken into account by considering the interactions with the configuration $^1S (1s^2 2p^2)$. For example, the wave function of Be is explicitly chosen as $\text{Be}(1s^2, 2s^2) + d\text{Be}(1s^2, 2p^2)$. The determination of the matrix elements for the 2×2 CI is performed using Eqs. (7) and (8). The results shown have been obtained by using the VMC method.

The ground-state energy value for Be, using the two-state configuration defined above, is found to be $E = -14.6489(1)$, to be compared to the value $E = -14.6332$ deduced with a nine-parameter wave function [13] and to the value $E = -14.647$ reported by Lin *et al.* [14] obtained using a correlated quantum Monte Carlo approach, including a 42-parameter wave function. The present correlated wave func-

tion provides similar accuracy to the other sophisticated wave functions, which are optimized with a large number of parameters as mentioned above. The accurate value for the Be ground-state energy in the nonrelativistic fixed nucleus is estimated to be $E = -14.6674$; see Ref. [15].

Results for B⁺ and C²⁺ are reported in Table III. It can be seen that, for all systems considered here, the agreement with exact values deduced through much more sophisticated wave functions is good. In spite of its simplicity, the accuracy of the present wave function including only two variational parameters is gratifying.

IV. CONCLUSIONS

Determination of accurate fully correlated wave functions necessitates generally complicated trial wave functions. We show here that a suitable choice of the Jastrow factor, including only two variational parameters, can give remarkably good results which are comparable in accuracy to those derived using a more sophisticated Jastrow factor. We found also that the optimization of the proposed Jastrow factor is more efficient with hydrogenoid orbitals rather than with Hartree-Fock ones in the Slater determinant for three-electron atoms and ions. Moreover, the hydrogenoid orbitals are found to be effective for four-electron atoms and ions as well.

We hope that the simple description of the correlated wave function suggested in the present work for few-electron systems can be useful for investigating multielectron inelastic processes occurring in complex atoms. Moreover, the simple wave function possesses another possibility to be the starting point for more elaborate calculations—i.e., the configuration interaction method coupled with correlated functions that should accelerate the convergence.

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