

Simple analysis of correlation in few-body Coulomb systems: Application in the diffusion Monte Carlo method

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An approach is presented in order to study the interelectronic correlation in few-electron atomic or molecular systems. The main point is that the correlation is described as a mutual collision between all the electrons. This approach allows the determination of simple wave functions for complex systems including only three parameters, with a clear physical meaning. The method is applied to study three- and four-electron systems in different states, including the so-called hollow states for lithium and beryllium. The overall results are found to be in good agreement with those deduced using much more sophisticated wave functions. Subsequently, the present wave functions are chosen as trial wave functions in the diffusion Monte Carlo method. This approach leads to a very accurate determination of the ground-state energies of lithium, lithium negative ion, and beryllium atoms, indicating that it becomes possible to deduce with very good accuracy some properties of relatively complex systems with a quite simple wave function.

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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 cannot be understood within the independent electron approximation model. Indeed the correlation in many-body systems due to the interaction 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 done on this problem.

In order to investigate the role of electronic correlations in complex atoms, a lot of experimental work has been devoted to the study of multiple excitations of atoms and molecules induced by photoabsorption or collisions with electrons. Recent papers report on the multiexcitation or ionization of the helium and lithium atoms in different initial states, including the so-called hollow atomic states [1–4]. Multielectron excited states are of special interest to probe the method of taking into account the electronic correlation, as it is expected to play an important role there. These experimental results have motivated theoretical works to improve the understanding of the various multielectron mechanisms.

Obviously the determination of both simple and accurate wave functions for few-body systems could be a key task. On the one hand, the wave function has to describe the properties of the free atomic system. On the other hand, it should also take into account its behavior in a collision or when it is placed in an electric or magnetic field, or interacting with a surface. The determination of accurate wave functions for few-body Coulomb systems can be achieved in different ways (see, for example, [5–7]) and may be considered today as a solved problem. However, the presently available accurate wave functions are always involved, including many Slater determinants, or explicitly correlated trial wave functions.

The determination of compact wave functions should be considered as an important task. They could be useful for further calculations on the system. For instance, when an atomic or molecular system is involved in a collision, one generally needs the initial- and final-state wave functions in order to calculate the corresponding cross sections. This is illustrated in many calculations relative to inelastic processes in helium-atom-like double excitation, double (photo)ionization, etc., where relatively simple correlated wave functions are often chosen to describe the different helium states. It seems of interest to be able to propose simple correlated and still accurate wave functions for three- and four-electron systems.

The purpose of the present work is to show that simple correlated wave functions can be deduced in a systematic way for few-electron atoms or molecules in different states, even when two, three, or four electrons are excited. Next we will use these functions as trial functions in a diffusion Monte Carlo method approach, and we show that we can get quasixact values for the ground-state energies of the lithium atom, lithium negative ion, and beryllium atom. The key point of the present approach is the representation of the electronic correlation in a few-body Coulomb system as a mutual collision between all the electrons of the system.

II. THEORY

In the past, Pluvinaige [8] suggested a new way to look at electron correlation in the helium atom. In his approach, based on a semiseperation property of the Schrödinger equation, the electron-electron interaction is introduced as a mutual collision due to the Coulomb repulsion. Some years later, Vainstein *et al.* [9] studied the polarization of a hydrogen atom in collision problems with electrons in a similar approach. More recently, Briggs *et al.* [10] described the

double ionization of helium by a wave function including a Coulomb wave function in order to describe the correlation in the continuum between the two escaping electrons.

The Schrödinger equation for an N -electron atomic system with nuclear charge Z is written in atomic units (used throughout this paper) within the nonrelativistic approximation and using the usual notation

$$\left(-\frac{1}{2}\Delta_{3N}-\sum_{i=1}^N\frac{1}{r_i}+\sum_{i<j=1}^N\frac{1}{r_{ij}}\right)\Psi(\mathbf{r}_i)=E\Psi(\mathbf{r}_i), \quad (1)$$

where Δ_{3N} stands for the $3N$ dimensions Laplacian. The wave function $\Psi(\mathbf{r}_i)$ will be written as a product of two functions: $\Psi(\mathbf{r}_i)=\Phi(\uparrow\downarrow\mathbf{r}_i)\Omega(r_i,r_{ij})$, where the arrows represent the up-down spin electrons. The basic idea is to include the antisymmetric part of the total wave function, related to the orbital motion of the free electrons in the nuclear field, in the determinant function $\Phi(\uparrow\downarrow\mathbf{r}_i)$, and to put the interelectronic interaction depending explicitly upon the interelectronic r_{ij} and electron-nucleus distances r_i in the symmetric function $\Omega(r_i,r_{ij})$.

Replacing the Ψ function by its product in the Schrödinger equation (1), the Δ_{3N} operator will introduce the $3N$ dot product $\nabla_{3N}\Phi(\uparrow\downarrow\mathbf{r}_i)\cdot\nabla_{3N}\Omega(r_i,r_{ij})$. We notice that it is very similar to the so-called backflow correlation; see Ref. [11] for a discussion of this term.

As explained in [12], it can be shown that for any function Ψ_m written as a product, $\Psi_m=\Phi_m\Omega$, the calculation of the diagonal elements $H_{m,m}$ or the off-diagonal matrix elements $H_{m,n}$ reduces to the computation of a single multivariate quadrature,

$$H_{m,m}=E_m+\left\langle\Phi_m\left|\frac{\nabla_{3N}\Omega\cdot\nabla_{3N}\Omega}{2}+\Omega^2\left(\sum_{i<j}1/r_{ij}\right)\right|\Phi_m\right\rangle, \quad (2)$$

$$H_{m,n}=\frac{E_m+E_n}{2}+\left\langle\Phi_m\left|\frac{\nabla_{3N}\Omega\cdot\nabla_{3N}\Omega}{2}+\Omega^2\left(\sum_{i<j}1/r_{ij}\right)\right|\Phi_n\right\rangle. \quad (3)$$

To derive these expressions, it was assumed that the functions Φ_m are the solutions of the independent N -particle problem:

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

The form of the function $\Omega(r_i,r_{ij})$ has to be chosen. In principle, any parametrization that makes Eqs. (2) and (3) convergent can be chosen for the correlation factor, as, for example that of Boys and Handy [13]. In this work, we propose a general parametrization that includes only a few variational parameters with a clear physical meaning that leads to very good results.

The $\Omega(r_i,r_{ij})$ function, which describes the electron-nucleus and electron-electron correlation, is presently defined for the lithium atoms as

$$\Omega(r_i,r_{ij})=\left(\sum_{i<j}\cosh(\lambda r_i)\cosh(\lambda r_j)\right)\times\left(\prod_{i<j}[1+0.5br_{ij}e^{-ar_{ij}}]\right) \quad (4)$$

and for beryllium as

$$\Omega(r_i,r_{ij})=\left(\sum_{i<j<k}\cosh(\lambda r_i)\cosh(\lambda r_j)\cosh(\lambda r_k)\right)\times\left(\prod_{i<j}[1+0.5br_{ij}e^{-ar_{ij}}]\right). \quad (5)$$

In Eqs. (4) and (5) the indexes i , j , and k run to the number of electrons. The cosh functions describe the electron-nucleus correlations. This choice fulfills the electron-nucleus cusp condition; see, e.g., Refs. [14,15] for details and considerations about cusp conditions. When the electron is close to the nucleus, the function $\cosh(\lambda r_i)$ tends to 1 as r_i^2 , giving the limit

$$\lim_{r_i\rightarrow 0}\frac{\partial\Psi}{\partial r_i}=-Z\Psi(0). \quad (6)$$

Moreover, such a choice insures the correct behavior at large electron-nucleus distances, i.e., the electron-electron interaction is decoupled and becomes the screen felt by an electron when it is at large distance from the nucleus. It is easy to see that λ is closely related to a familiar screening coefficient due to the exponential behavior of $\cosh(\lambda r_i)$ when $r_i\rightarrow\infty$.

The second factor on the right-hand side of Eq. (4) describes the electron–electron correlation. It can be understood—see below—that a term like $g(r_{ij})=1+0.5br_{ij}e^{-ar_{ij}}$ is simulating the Coulomb diffusion of two electrons, hence the full product represents the electron-electron correlation in the system as a mutual diffusion of all electron pairs. This parametrization fits the expansion of the Coulomb wave function ($l=0$ wave) for the small interparticle distances r_{ij} . The function $g(r_{ij})$ tends to 1 for large interelectronic distances. This means that for bound states, when an electron goes at large distances from the other, the interelectronic correlation is shifted to the screening idea; see above. This choice of the g function was found to be quite efficient [16], leading to better results than the true Coulomb wave function. The function includes the right description of the electron-electron up-down spin cusps if $b=1$ (Kato's theorem). The function $g(r_{ij})$ was first suggested by Hirschfelder [17] for the case of a two-electron problem.

III. RESULTS

The basic possibilities of the method will now be illustrated. Results concerning two–electron atoms and molecules have been previously reported [18,19], and the overall accuracy of the wave function has been tested [20]. We will present here results for different states of atomic or ionic systems with three and four electrons. We will focus our

attention on the atoms or ions: Li, He⁻, Li⁻, and Be. For the lithium atom, many states have been already determined with excellent accuracy, allowing comparison between different methods. To obtain the stability of negative ions such as He⁻ and Li⁻, one must include good correlation in their wave functions, hence these systems are a good measure of the possibilities of the present method. We study the beryllium atom to illustrate the present approach in the case of a four-electron problem. For the latter atom, we also calculate multiply excited electronic states, which, to the best of our knowledge, have never been calculated previously.

Taking into account the integration over the spin symmetries of the determinantal function, the free-particle wave function $\Phi(\uparrow\downarrow\mathbf{r}_i)$ can be simplified if only the energies of different atomic states are determined. As a proof of the outstanding simplicity of the fully correlated wave function, the expression used to calculate the ground-state energy of the lithium Li(1s²,2s) is shown here,

$$\begin{aligned} \Psi_{\text{Li}} = & C 1s(r_1)[1s(r_2)2s(r_3) - 1s(r_3)2s(r_2)] \\ & \times \left(\sum_{i < j} \cosh(\lambda r_i) \cosh(\lambda r_j) \right) \\ & \times \left(\prod_{i < j} [1 + 0.5br_{ij}e^{-ar_{ij}}] \right). \end{aligned}$$

The functions 1s(r_i) and 2s(r_i) are the usual hydrogenic orbitals, 1s(r_i) = e^{-Zr_i} , . . . , Z is the true nuclear charge of the atom or ion under consideration ($Z=3$), and C is the normalization constant. It is important to notice that these functions include only three positive parameters— λ , a , and b —that will be optimized subsequently by energy minimization. It is worth mentioning that we never did observe any variational collapse with this method.

In the case of S atomic states of three-electron ions or atoms, the multivariate integral equations (2) and (3) reduce to six dimensions, eight dimensions for non- S states. It becomes a nine dimensions quadrature in the case of S states of four-electron systems like beryllium. The multivariate integral is computed without any numerical approximation, using a new method presented in [16]. This approach was found to be efficient in many calculations. The numerical accuracy is presently at least 10^{-3} . For a four-electron problem, typically 20×10^6 points of integration are needed, leading to a quite reasonable computing time. Calculations can be easily performed on any desk computer, taking only a few minutes with a PII 300 processor.

The values of the energies of some ground or hyperexcited (resonant) states of the systems He⁻(1s,2s²), Li(1s²,2s), Li(2s²,2p)²P, Li⁻(1s²,2s²), Be(1s²,2s²), Be(1s²,3s²), and Be(2s²,2p²)¹S are presented in Table I. When 2s-2p degeneracies occur, for example in He⁻(1s,2s²) and in He⁻(1s,2p²)¹S, Li⁻(1s²,2s²), Li⁻(1s²,2p²)¹S, Be(1s²,2s²), and Be(1s²,2p²)¹S states, a diagonalization has been made between these two quasidegenerated states. In addition, the optimized values by energy minimization of the variational parameters, λ , a , and b , are given in Table I.

TABLE I. Energies of some states of He⁻, Li, Li⁻, and Be, calculated using the present correlated wave function and the corresponding variationally optimized values of the parameters λ , a , and b . In the last column, we have reported different results calculated within different approaches for comparison.

λ	a	b	State	Energy:	
				This method	Other results
0.45	0.03	0.5	He ⁻ (1s,2s ²)	-2.190	-2.1920 ^a
0.79	0.21	0.8	Li(1s ² ,2s)	-7.473	-7.4731 ^b -7.477 ^c
0.0	0.12	1.0	Li(2s ² ,2p) ² P ^o	-2.249	-2.2509 ^d
0.84	0.115	0.57	Li ⁻ (1s ² ,2s ²)	-7.480	-7.5005 ^e
0.78	0.115	0.61	Be(1s ² ,2s ²)	-14.648	-14.6332 ^b -14.647 ^c
0.49	0.08	0.8	Be(1s ² ,3s ²)	-14.156	
0.6	0.1	0.7	Be(2s ² ,2p ²) ¹ S	-4.811	
0.2	0.06	1.4	Be(3s ² ,3p ²) ¹ S	-2.261	

^aReference [21].

^bReference [11].

^cReference [22].

^dReference [6].

^eReference [26].

In all cases the agreement between the presented results and the accurate values is better than a few 10^{-3} a.u. The energy of the He⁻(1s,2s²) resonant state was recently calculated by Ho [21]. The value reported there is $E = -2.1920$ a.u. calculated with a Hylleras-type correlated function involving up to 3543 terms. This result is to be compared to the present calculated value $E = -2.190$ a.u. obtained with a much simpler wave function. The ground-state energy for the lithium atom deduced with the present method is $E = -7.473$ a.u., to be compared with $E = -7.4731$ a.u. obtained with a nine parameter correlated wave function [11] and $E = -7.477$ a.u. deduced with a 42-parameter correlated wave function [22]. The best value is known to be $E = -7.47806$ a.u. [23]. Let us quote the recent calculations using also a simple wave function for the ground state of lithium proposed by Patil [24], giving the value of the energy $E = -7.4732$ a.u.

The ground-state values for Li⁻ and Be using a single configuration are found to be, respectively, $E = -7.463$ a.u. and $E = -14.625$ a.u. With a two-state configuration-interaction wave function, the ground-state energy of Li⁻ becomes $E = -7.480$ a.u. and the energy of beryllium is found to be $E = -14.648$ a.u. The latter should be compared to the value $E = -14.6332$ a.u., deduced with a nine-parameter wave function [11], and to the recently calculated value reported by Lin *et al.* [22], $E = -14.647$ a.u., obtained using the correlated quantum Monte Carlo approach using a 42-parameter wave function. In the latter case, the present correlated wave function provides similar accuracy to other more sophisticated parametrizations. The *exact* value for the Be ground state in the nonrelativistic fixed nucleus framework is estimated to be $E = -14.6673$ a.u., see Ref. [7]. In spite of its simplicity, the accuracy of the present wave function including only three variational parameters is gratifying.

The energy values for the two-electron excited states of beryllium, $\text{Be}(1s^2,3s^2)$, are also reported in Table I, along with those of the hollow states $\text{Be}(2s^2,2p^2)$ and $\text{Be}(3s^2,3p^2)$. In these cases, the $2s$ - $2p$ and $3s$ - $3p$ degeneracies are taken into account by considering the interactions with the configuration $\text{Be}(2p^4)$, and $\text{Be}(3p^4)$ ^1S states, respectively.

IV. APPLICATION TO THE DIFFUSION MONTE CARLO METHOD

To further study the performance of the wave functions proposed in this work, we have used them as trial functions in a quantum Monte Carlo (QMC) calculation. More specifically, we shall use in this work the so-called diffusion Monte Carlo (DMC) method. We recall briefly here the main ideas underlying the DMC approach. Further details relative to this powerful approach to solve the Schrödinger equation by simulating the Green's function of the system by statistical methods can be found in, e.g., Ref. [25].

Generally speaking, the wave function is represented as a set of points in the configuration space of the system, usually called walkers, that constitutes the initial ensemble. Then the Green's function is simulated iteratively by means of random walks. Differences in QMC methods come from how this is achieved. DMC starts from the time-dependent Schrödinger equation in imaginary time, which becomes a classical diffusion equation. To determine the random walk that simulates the Green's function, a short-time approximation is invoked. Then a step of the random walk consists in an isotropic Gaussian diffusion and a branching process of the walkers. After a large number of iterations, the excited-state contributions are projected out from the initial ensemble, converging to the ground-state wave function, and then the ground-state energy can be deduced.

The systematic error introduced by the short-time approximation can be eliminated by using small time steps and extrapolating the results to zero time step. For boson systems, this method provides the exact ground-state energy (except for statistical errors). However, Fermi systems such as those studied in this work are affected by sign problems resulting from the required antisymmetry of the wave function. Here we will employ the fixed-node approximation that uses a prefix nodal surface in the configuration space of the system. The results so calculated are not exact any more; instead, an upper bound for the energy is obtained. The accuracy of such a bound is governed by the quality of the nodal surface employed in the simulation. This is the most commonly used approach in the literature.

The algorithm, as described above, is in general very inefficient due to the large fluctuations in the ensemble along the random walk introduced by the interaction potential. Practical implementations usually make use of the Monte Carlo technique known as importance sampling that greatly reduces these fluctuations. This method requires an analytical trial function that is used to bias the random walk. This is included in the algorithm by considering in the Gaussian diffusion an additional drift term proportional to the logarithmic derivative of the trial wave function and using the local

TABLE II. DMC results for Li, Li^- , and Be ground states using the present three-parameter wave function. SC, $(1s^2,2s^2)$; CI, $(1s^2,2s^2) + d(1s^2,2p^2)$; meaning, respectively, single configuration and configuration interaction wave function. The statistical error in the last figure is given in parentheses.

Atom or ion	Wave function	Energy:	
		This method	Accurate results
Li		-7.4782(2)	-7.4780 ^a
Li^-	SC	-7.4979(4)	
Li^-	CI	-7.5007(7)	-7.5005 ^b
Be	SC	-14.6566(3)	
Be	CI	-14.6667(5)	-14.6673 ^c

^aReference [23].

^bReference [26].

^cReference [7].

energy in the branching part instead of the interaction potential. The better the trial function, the smaller the fluctuations will be, and therefore the smaller the statistical error of the calculation will be. However, very involved parametrizations, which generally are time consuming, will slow down the calculation due to the fact that in each step the gradient and the Laplacian must be calculated for each walker. Hence compact and concise and still accurate wave functions are ideal. Another highly desirable requirement for a trial wave function is that it fulfill the cusp conditions, because the largest branching fluctuations tend to occur where two particles come together and the potential diverges. This effect can be minimized by the cusps in the trial function. Quantum Monte Carlo methods are computationally demanding and the statistical errors go as the inverse of the square root of the number of sampling points.

The choice of an adequate trial function that affects the statistical error in the calculation is very important. For fermion systems, the trial wave function not only affects the statistical error, but also the value obtained for the energy. This comes from the fact that the trial function also determines the location of the nodal surface. In general, very little is known about the exact location of the nodes in fermion systems. The quality of the nodal structure induced by the trial wave function will determine how close one can come to the exact result. This is usually established *a posteriori* for those systems for which exact or quasiexact solutions are available by other methods.

In Table II, we show the results obtained by using the wave function proposed in this work as a trial function in a fixed-node DMC calculation. These results show the quality of the present parametrization. In spite of the simplicity of the three-parameter wave function used, it reproduces quite accurately the many-dimension exact nodal surface. For $\text{Be}(1s^2,2s^2)$, the inclusion of the $(1s^2,2p^2)$ configuration in the trial wave function leads to a significant improvement in the variational and also in the DMC energy. The accuracy of those results makes us confident that this simple parametrization is able to incorporate reliably the most important physical effects involved in the dynamic of these systems. For $\text{Li}^- (1s^2,2s^2)$, a noticeable improvement is also obtained

in the variational energy when the near degeneracy is explicitly included in the trial wave function. However, the DMC results for the alkali-metal anion obtained with the single- and the two-configuration wave functions are very similar and both are very accurate. This tells us about the quality of the present parametrization and that the effect of the near degeneracy is more important in the variational energy than in the nodal surface, which seems to be well described by the single-configuration wave function. This is due to the fact that the nuclear charge is reduced with respect to the $\text{Be}(1s^2, 2s^2)$ case, and mean field effects, such as this near degeneracy, become relatively less important.

Our feelings are that the present description of the correlation is relatively general, and should be useful to analyze

the correlation in more complex systems. Clearly, the method is applicable also to molecules. For larger systems, the statistical methods of multivariate integration could be considered in order to perform the necessary numerical quadratures.

Finally, let us point out that these approximate very simple wave functions are of interest as trial wave functions in a DMC approach, leading to quasixact energy values of relatively complex systems such as Li^- and Be.

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- [1] P. Moretto-Capelle, D. Bordenave-Montesquieu, A. Bordenave-Montesquieu, A. Godunov, and V. Schipakov, *Phys. Rev. Lett.* **79**, 5230 (1997).
- [2] R. Wehlitz, M. T. Huang, B. D. DePaola, J. C. Levin, I. A. Sellin, T. Nagata, J. W. Cooper, and Y. Azuma, *Phys. Rev. Lett.* **81**, 1813 (1998).
- [3] M. Schulz, R. Moshhammer, W. Schmitt, H. Kollmus, B. Feuerstein, R. Mann, S. Hagmann, and J. Ullrich, *Phys. Rev. Lett.* **84**, 863 (2000).
- [4] S. Diehl, D. Cubaynes, H. L. Zhou, L. Voky, F. J. Willeumier, E. T. Kennedy, J. M. Bizau, S. T. Manson, T. J. Morgan, C. Blancard, N. Berrah, and J. Bozek, *Phys. Rev. Lett.* **84**, 1677 (2000).
- [5] F. W. King, *Phys. Rev. A* **40**, 1735 (1989).
- [6] K. T. Chung and B. Gou, *Phys. Rev. A* **52**, 3669 (1995).
- [7] J. Komasa, W. Cencek, and J. Rychlewski, *Phys. Rev. A* **52**, 4500 (1995).
- [8] P. Pluvinaige, *J. Phys. Radium* **12**, 789 (1951).
- [9] L. Vainshtein, L. Presyankov, and I. Sobel'man, *Zh. Eksp. Teor. Fiz.* **45**, 2015 (1963) [*Sov. Phys. JETP* **18**, 1383 (1964)].
- [10] H. Brauner, J. S. Briggs, and H. Klar, *J. Phys. B* **22**, 2265 (1989).
- [11] K. E. Schmidt and J. W. Moskowitz, *J. Chem. Phys.* **93**, 4172 (1990).
- [12] L. D. A. Siebbeles and C. Le Sech, *J. Phys. B* **27**, 4443 (1993).
- [13] S. F. Boys and N. C. Handy, *Proc. R. Soc. London, Ser. A* **310**, 63 (1969).
- [14] C. R. Myers, C. J. Umrigar, J. P. Sethna, and J. D. Morgan III, *Phys. Rev. A* **44**, 5537 (1991).
- [15] J. D. Talman, *Phys. Rev. Lett.* **84**, 855 (2000).
- [16] C. Le Sech and B. Silvi, *Chem. Phys.* **236**, 77 (1998).
- [17] J. O. Hirschfelder, *J. Chem. Phys.* **39**, 3154 (1963).
- [18] C. Le Sech, *Phys. Rev. A* **51**, R2668 (1995).
- [19] C. Le Sech, *J. Phys. B* **30**, L47 (1997).
- [20] A. K. Kazansky, *J. Phys. B* **31**, L579 (1998).
- [21] Y. K. Ho and Z. Yan, *Phys. Rev. A* **59**, R2559 (1999).
- [22] X. Lin, H. Zhang, and A. M. Rappe, *J. Chem. Phys.* **112**, 2650 (2000).
- [23] Z. C. Yan and G. W. F. Drake, *Phys. Rev. A* **52**, 3711 (1995).
- [24] S. H. Patil, *Eur. Phys. J. D* **6**, 171 (1999).
- [25] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in ab initio Quantum Chemistry* (World Scientific, Singapore, 1994).
- [26] C. Froese-Fischer, *J. Phys. B* **26**, 855 (1993).