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Multiconfiguration wave functions for quantum Monte Carlo calculations of first-row diatomic molecules

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We use the variance minimization method to determine accurate wave functions for first-row homonuclear diatomic molecules. The form of the wave function is a product of a sum of determinants and a generalized Jastrow factor. One of the important features of the calculation is that we are including low-lying determinants corresponding to single and double excitations from the Hartree–Fock configuration within the space of orbitals whose atomic principal quantum numbers do not exceed those occurring in the Hartree–Fock configuration. The idea is that near-degeneracy correlation is most effectively described by a linear combination of low-lying determinants whereas dynamic correlation is well described by the generalized Jastrow factor. All the parameters occurring in both the determinantal and the Jastrow parts of the wave function are optimized. The optimized wave functions recover 79%–94% of the correlation energy in variational Monte Carlo and 93%–99% of the correlation energy in diffusion Monte Carlo. © 1996 American Institute of Physics. [S0021-9606(96)01125-7]

I. INTRODUCTION

One advantage of the quantum Monte Carlo (QMC) method versus conventional quantum chemistry methods, e.g., configuration interaction (CI), is the freedom in the choice of the functional form of the wave function. It is possible to construct a compact and accurate wave function if its functional form incorporates the analytical features of the true wave function. CI, for example, uses an expansion in determinants of single-particle orbitals that is slowly convergent because it cannot reproduce the cusps in the wave function at the electron–electron coalescences.¹ On the other hand, if the functional form is sufficiently flexible to have the correct analytic structure at the electron–nucleus, electron–electron and possibly higher body coalescence points, then, a relatively compact wave function with 50–100 free parameters can be found that yields energies comparable to a CI wave function with millions of determinants.

In QMC methods, the interelectron cusp is built into the wave function by multiplying one or a sum of determinants corresponding to the Hartree–Fock (HF) configuration or a small set of multiconfiguration self-consistent-field (MCSCF) configurations with a Jastrow factor. The Jastrow factor is a function of the interelectron distances so that it directly correlates electrons with one another. Despite the freedom available in the construction of the Jastrow factor, a very simple form has been used in most cases. A generalized Jastrow factor that also includes electron–electron–nucleus correlation terms has been successfully applied to atomic systems^{2,3} and is here modified to treat multicenter systems. The other component of the wave function is the determinantal part. Although a single determinant wave function has often been employed, it is well known that the nondynamic

part of the electronic correlation, originating from the near-degeneracy of the molecular orbitals, can be efficiently described by the use of a linear combination of determinants. In the present work, this idea is pursued in the construction of the trial wave functions for molecules and leads to accurate results when combined with a generalized Jastrow factor for the description of the so called dynamic component of the electronic correlation.

Since the statistical error, the computational time and the difficulty in obtaining good trial wave functions increase with atomic number, some of the more interesting QMC calculations of finite and extended systems have been valence-only (pseudopotential) calculations.⁴ However, there is some evidence that the errors introduced in QMC by using pseudopotentials calculated within the local density approximation⁵ or HF⁶ are not negligible. Hence, in this paper we will restrict ourselves to calculations performed without the pseudopotential approximation. Some accurate all-electron QMC calculations of fairly light molecules are available in the literature (two recent reviews are Refs. 7 and 8) but the only attempt to systematically study the performance of QMC methods for first row molecules⁹ does not provide encouraging results. The authors used a simple form of the Jastrow factor and a single determinant wave function and they recover a progressively smaller fraction of the correlation energy for molecules of increasing size, N₂ being the largest molecule studied. Their variational correlation energy for the homonuclear diatomic molecules ranges between 14% and 40% and the magnitude of the Green's function Monte Carlo (GFMC) errors is so large (5%–14%) that it is difficult to judge the significance of the results. Other authors performed calculations on first row molecules^{10–14} but not in

a systematic way so that little insight is gained on the overall success and limitations of QMC methods. Here, we present both single configuration and multiconfiguration calculations of first-row homonuclear diatomic molecules from Li_2 to F_2 for which we obtained results superior to previous QMC calculations for molecules. However, we still did not achieve chemical accuracy (1 kcal/mol = 0.0016 Hartree/molecule). Since our wave functions are the result of a nonlinear optimization of the variance of the local energy on a relatively small set of configurations, better results may quite possibly be found by further optimizing the parameters in our wave functions. Nevertheless, our results provide a benchmark to which future molecular QMC calculations can be compared.

In Sec. II, the functional form of the trial wave function is described. In Sec. III, we briefly present the variance optimization method used to determine the parameters that enter in the molecular wave functions, the variational Monte Carlo (VMC) and the diffusion Monte Carlo (DMC) methods. In Sec. IV, we report the ground state energies we obtained for the first row diatomic molecules with our trial wave functions in VMC and DMC and compare them with the results of other authors. We also present the values obtained in VMC for the root mean square fluctuation of the local energy and the autocorrelation time of the local energy. In Appendix A, we briefly discuss the source of spin contamination in our wave functions and three more general forms of the wave function than the one used in the rest of the paper. In Appendix B, we list the parameters that enter in the most accurate wave function for each molecule.

II. FUNCTIONAL FORM OF THE WAVE FUNCTION

The most commonly used wave function in QMC is a sum of determinants of single-particle orbitals multiplied by a simple Jastrow factor:

$$\Psi = \left(\sum_n d_n D_n^\uparrow D_n^\downarrow \right) J(r_{ij}). \quad (1)$$

D_n^\uparrow and D_n^\downarrow are the Slater determinants of single particle orbitals for the up and down electrons, respectively. The orbitals are a linear combination of Slater basis functions multiplied by spherical harmonics centered on the atoms:

$$\phi(\mathbf{r}_i) = \sum_{\alpha k} c_{k\alpha} N_{k\alpha} r_{i\alpha}^{n_{k\alpha}-1} e^{-\zeta_{k\alpha} r_{i\alpha}} Y_{l_{k\alpha} m_{k\alpha}}(\hat{\mathbf{r}}_{i\alpha}), \quad (2)$$

where \mathbf{r}_i is the position of electron i and $\mathbf{r}_{i\alpha}$ is its position with respect to the nucleus α . The sum over α denotes a sum over the nuclei and the sum over k is over the basis functions centered on the nuclei. $N_{k\alpha}$ is the normalization of the radial part of the basis function and is equal to $[(2\zeta_{k\alpha})^{2n_{k\alpha}+1}/(2n_{k\alpha}!)]^{1/2}$. As opposed to a Gaussian basis set, a Slater basis is suitable to describe the electron–nucleus cusp. The determinants are expressed in terms of symmetry orbitals and are constructed to have the space and spin symmetry of the ground state. For a homonuclear diatomic molecule, we want the wave function to be an eigenstate of the component of the total angular momentum along the axis of the molecule, L_z , and of the spin operators S^2 and S_z where

S is the total spin operator. In most earlier work, a single determinant wave function was used with the orbitals frozen to be the HF orbitals. We believe that in order to obtain wave functions that have a good variational energy and a small root mean square fluctuation of the local energy, it is important to relax the HF orbitals when the determinantal part is multiplied by a Jastrow factor: the optimal determinant when no Jastrow is present is not the optimal determinant in the presence of the Jastrow. Therefore, we optimize the exponents $\{\zeta_{k\alpha}\}$ of the basis functions, the coefficients $\{c_{k\alpha}\}$ of the expansion of the orbitals in the Slater basis and the coefficients multiplying the determinants $\{d_{ij}\}$. Algebraic relations exist among the coefficients $\{c_{k\alpha}\}$ because the orbitals belong to the irreducible representations of the point group of the molecule. Symmetry requirements on the determinants yield constraints also among the coefficients $\{d_{ij}\}$. As a consequence, there is a considerable reduction in the number of free parameters.

A simple, commonly used Jastrow factor is

$$J(r_{ij}) = \prod_{i < j} \exp\left(\frac{b r_{ij}}{1 + b' r_{ij}}\right), \quad (3)$$

where the product is over all pairs of electrons. Imposing the electron–electron cusp condition ($\partial J / \partial r_{ij} = J/2$ for unlike spin and $J/4$ for like spin electrons when $r_{ij} = 0$) fixes the value of b to 1/2 for antiparallel spin electrons and 1/4 for parallel spin electrons. Therefore, if we want to satisfy the electron–electron cusp conditions both for antiparallel and parallel spin electrons, we are forced to use a different Jastrow factor for like and unlike spin electrons. However, the use of a nonsymmetrical Jastrow factor yields a wave function that is not an eigenstate of S^2 although the determinantal part is constructed to be an eigenstate of both S^2 and S_z . To the best of our knowledge, this has never been mentioned in the literature. Therefore, we have the choice of having a wave function that is not an eigenstate of S^2 or violating the cusp conditions for parallel spin electrons by correlating them with the same Jastrow factor as the antiparallel ones. (It is preferable to sacrifice the parallel spin electron cusp condition than the antiparallel one since it is unlikely for two parallel spin electrons to be close.) Here, in common with most earlier work, we choose to satisfy the cusp conditions by using a nonsymmetrical Jastrow factor, with the understanding that we are breaking the spin symmetry and that our wave functions will be contaminated by other spin components. This choice is motivated by the fact that the nonsymmetrical Jastrow yields wave functions that have about 15% smaller fluctuation of the local energy. Moreover, spin contamination does not affect the energy obtained in fixed-node DMC. The Jastrow factor does not alter the spatial symmetry, determined by the determinantal part, because it depends on the interelectron coordinates and is therefore completely symmetric under spatial rotations and reflections. In Appendix A, we discuss the source of spin contamination and related issues in some more detail.

The generalized Jastrow factor $J(r_i, r_j, r_{ij})$ we use is a modification of the form introduced by Umrigar *et al.*² which

yields good wave functions for atoms by explicitly introducing electron–electron–nucleus correlation. This form is a generalization of the Boys and Handy¹⁵ form. Subsequently, other authors,^{10,16} using arguments based on backflow wave functions, arrived at a similar functional form but they include only a subset of the possible terms. Our generalized Jastrow factor is written as a product of terms of increasing body-order correlation. Thus, we consider up to three-body correlation by including terms to describe the electron–nucleus correlation, A_{ai} , the electron–electron correlation, B_{ij} , and the electron–electron–nucleus correlation, C_{aij} :

$$J(r_i, r_j, r_{ij}) = \prod_{ai} \exp(A_{ai}) \prod_{ij} \exp(B_{ij}) \prod_{aij} \exp(C_{aij}). \quad (4)$$

The electron–nucleus A term could be omitted from the Jastrow factor provided that a sufficiently large single particle basis is used in constructing the determinantal part. We omit three electron correlations since, due to the exclusion principle, it is unlikely for more than two electrons to be close because at least two of them must have the same spin. Therefore, we think we have included the most significant contributions to the electronic correlation. The importance of three electron and higher order terms is discussed in Ref. 17. In order to ensure that the Jastrow factor is well behaved at large interparticle distances, we express the generalized Jastrow factor in terms of scaled coordinates:

$$R_{i\alpha} = (1 - e^{-\kappa r_{i\alpha}})/\kappa, \quad U = (1 - e^{-\kappa r_{ij}})/\kappa. \quad (5)$$

These scaled variables approach the value $1/\kappa$ as the unscaled ones go to infinity. It is not necessary to introduce scaled distances if the Jastrow factor is a ratio of two polynomials of the same degree in the interparticle coordinates. However, also in this case, the use of scaled variables would result in a faster convergence in the polynomial order and a more controlled behavior in the limit of large interparticle distances.

The three terms in the generalized Jastrow factor as functions of U , $S = R_{i\alpha} + R_{j\alpha}$ and $T = R_{i\alpha} - R_{j\alpha}$ are

$$A_{ai} = \frac{a R_{i\alpha}}{1 + a' R_{i\alpha}}, \quad (6)$$

$$B_{ij} = \frac{b U}{1 + b' U}, \quad (7)$$

$$C_{aij} = \frac{P(\{c\}, U, S, T) + F(\{f\}, U, S, T)}{1 + P'(\{c'\}, U, S, T)} + F'(\{f\}, U, S, T). \quad (8)$$

P and P' are polynomials in U , S , and T . We discuss later how we choose the degree of the two polynomials. F and F' contain nonanalytic terms in U , S , and T :

$$\begin{aligned} F + F' = & f_1 \Phi_{2,1} + f_2 \Phi_{2,0} + f_3 \Phi_{3,1} + (f_4 U + f_5 S) R \\ & + (f_6 U^3 + f_7 S^3 + f_8 U^2 S + f_9 U S^2) / R \\ & + [f_{10} U^3 + f_{11} S^3 + f_{12} U^2 S + f_{13} U S^2 \\ & + (f_{14} U + f_{15} S) T^2] \ln[R/(1+R)], \end{aligned} \quad (9)$$

where R is the hyperradius, $R = (R_{i\alpha}^2 + R_{j\alpha}^2)^{1/2}$. F contains the terms $(f_2, f_4 - f_9)$ and F' the terms $(f_1, f_3, f_{10} - f_{15})$. F appears in the numerator of the ratio because it contains second order terms whose coefficients are related to those in the polynomials P and P' through the cusp conditions. All the terms in F and F' are nonanalytic in the interparticle coordinates. They are motivated by the Fock expansion for the helium atom and are introduced to cure the discontinuity that occurs in the local energy when the two electrons collapse onto the nucleus.¹⁸ In the above expression, we present the sum of F and F' instead of the separate contributions so that the order of the first three terms and the remaining twelve terms reflects the order in which they appear in the Fock expansion. The ground state wave function of helium cannot be expanded in a power series of the interparticle coordinates^{19,20} but there exists an expansion in powers of the hyperradius and its logarithm called the Fock expansion:²⁰

$$\Psi(r_1, r_2, r_{12}) = \sum_{k=0}^{\infty} \sum_{p=0}^{[k/2]} \psi_{k,p} R^k (\ln R)^p = \sum_{k=0}^{\infty} \sum_{p=0}^{[k/2]} \Psi_{k,p}, \quad (10)$$

where the coefficients $\psi_{k,p}$ are in general complicated functions of the hyperangles. Fock derived an explicit expression for $\psi_{0,0}$ and $\psi_{1,0}$ and the functional form of $\psi_{2,1}$ but not its prefactor. Ermolaev²¹ showed that it is possible to derive recursively in closed form all $\psi_{k,p}$ with $k = 2p + 1$ and $k = 2p$, such as $\psi_{2,1}$, $\psi_{3,1}$, $\psi_{4,2}$, etc., and obtained explicit expressions for $\psi_{2,1}$ and $\psi_{3,1}$. The correct expression for $\psi_{4,2}$ can be found in Ref. 22; all earlier expressions by other authors are erroneous. Numerous efforts to solve for $\psi_{2,0}$ were unsuccessful until the mid-1980's when Gottschalk, Abbott, and Maslen²³ made extensive use of computer algebra to obtain a complicated but closed form expression for $\psi_{2,0}$ in terms of elementary functions and the Lobachevsky function. The expressions of $\psi_{0,0}$, $\psi_{1,0}$, $\psi_{2,1}$, and $\psi_{2,0}$ are reported in Eq. (14) of Ref. 18, while $\psi_{3,1}$ is given in Eq. (74) of Ref. 22.

One problem with the inclusion in a trial wave function of the lowest terms of the Fock expansion, is that the expansion does not satisfy the cusp conditions when truncated at any finite order. However, an exponential form of the Fock expansion does have the correct cusps at any order.¹⁸ If we indicate by $\Phi_{k,p}$ the term in the exponent of the exponentiated expansion, $\Phi_{1,0}$ yields a wave function that satisfies the cusp conditions given that all the other terms are cusplless, so it cures the divergence of the local energy at the electron–nucleus and electron–electron coalescence points. Note that $\Phi_{1,0}$ does not appear in Eq. (9) because it is analytic in the interparticle coordinates and is included in the A and B terms [Eq. (8)]. Introducing $\Phi_{2,1}$ and $\Phi_{2,0}$ eliminates the disconti-

nuity of the local energy at the three body coalescence and the addition of $\Phi_{3,1}$ results in a finite rather than infinite slope in the local energy at that point as discussed in Ref. 18. Since we know the lowest order terms of the Fock expansion, we can simply include them in the wave function by setting the coefficients f_1 – f_3 to one in Eq. (9). In this case one should note that the use of scaled variables [Eq. (5)] in the expression of $\Phi_{2,1}$ and the expansion of the denominator in Eq. (8) generate terms in the unscaled variables that contribute to $\Phi_{3,1}$ and have to be canceled by properly defining the coefficients f_{10} – f_{15} . Similarly, the scaled variables in $\Phi_{1,0}$ and the denominator in Eq. (8) generate second order terms that contribute to $\Phi_{2,0}$ and are canceled by properly fixing the coefficients of U^2 , US , S^2 , and T^2 in the polynomial P [Eq. (8)]. An alternative approach to the use of the exact $\Phi_{2,0}$ and $\Phi_{3,1}$, is to implement the two sets of terms f_4 – f_9 and f_{10} – f_{15} that are, respectively, $\Phi_{2,0}$ -like and $\Phi_{3,1}$ -like terms. The f_4 – f_9 terms are the first few terms in an infinite series expansion of $\Phi_{2,0}$ in U/R and S/R and the f_{10} – f_{15} terms are the six terms that make up $\Phi_{3,1}$. These terms enter in the expression of $\Phi_{2,0}$ and $\Phi_{3,1}$ with coefficients determined by the Fock expansion but can instead be treated as variationally independent in order to provide additional freedom. In particular, $\Phi_{3,1}$ is a higher order term so that we expect that, in a variational calculation, the coefficients of its constituents become quite different from the ideal value. Another motivation in the use of the $\Phi_{2,0}$ -like terms is that the computation of $\Phi_{2,0}$ is fairly expensive. Here, we fix the coefficient f_1 of the lower order term $\Phi_{2,1}$ to one and we use the $\Phi_{2,0}$ -like and $\Phi_{3,1}$ -like terms. In our Fock motivated terms as well as in $\Phi_{2,1}$ and $\Phi_{3,1}$, we use $\ln(R/(1+R))$ instead of the $\ln R$ in the exponentiated Fock expansion in Ref. 18, to enforce that the logarithm does not change sign. The inclusion of the Fock terms results in a small but significant reduction in the fluctuations of the local energy which is not attainable by simply adding more analytic terms in the Jastrow part.

Imposing the electron–electron and electron–nucleus cusp conditions yields algebraic relations among the variational parameters of the trial wave function. For simplicity, we constrain the coefficients in C to not contribute to the cusp conditions ($\partial C/\partial r_{ij}=0$ at $r_{ij}=0$ and $\partial C/\partial r_{i\alpha}=0$ at $r_{i\alpha}=0$) so that the electron–electron cusp condition is satisfied as in the simple wave function by setting b to 1/2 for antiparallel spin electrons and to 1/4 for parallel spin electrons. The electron–nucleus cusp condition ($\partial \hat{\Psi}/\partial r_{i\alpha} = -Z\Psi$ at $r_{i\alpha}=0$, where the hat denotes a spherical average) relates the coefficient a of the Jastrow factor to the parameters of the determinantal part through the equations

$$\sum_n d_n \frac{\partial \hat{D}_n^\dagger \hat{D}_n^\downarrow}{\partial r_{i\alpha}} = -(Z+a) \sum_n d_n D_n^\uparrow D_n^\downarrow \quad \text{at } r_{i\alpha}=0, \quad (11)$$

that are satisfied if the single-particle orbitals ϕ 's obey the similar equations $\partial \phi/\partial r_{i\alpha} = -(Z+a)\phi$ at $r_{i\alpha}=0$.

The electron–electron–nucleus term in the wave function [Eq. (8)] is written as a ratio of two complete polynomials P and P' in the interparticle coordinates. This form was successfully applied to atomic wave functions^{2,3} and now we investigate it within molecular systems. For all the first row homonuclear molecules, we generated a set of wave functions by using a ratio of two fourth order polynomials and another set with a simple fifth order polynomial ($P'=0$). The two Jastrow factors have approximatively the same number of terms once all the dependencies among the parameters have been taken in consideration. For all the molecules, we obtain roughly equally good variational energies with the two Jastrow factors. For the molecule we studied most carefully, Li_2 , the variance of the local energy is slightly smaller for the rational polynomial than the single polynomial. For the heaviest molecules, the situation is reversed, but we believe this is due to our failure to find the global minimum. Our empirical finding is that the optimization process requires fewer steps for the polynomial than for the rational polynomial. Another advantage of using a single polynomial is that it is simpler to impose the cusp conditions. Consequently, we adopt the wave function in [Eq. (8)] with P being a fifth order polynomial and $P'=0$.

In the most general case, the terms A_{ai} , B_{ij} , and C_{aij} depend on the spins of electrons i and j . Their functional form is obviously independent of the spin values but different sets of coefficients could be involved depending on the spins of the electrons. However, as already mentioned, the Jastrow part should be symmetric in the interelectron coordinates to yield a wave function with a definite spin while imposing the electron–electron cusp conditions results in a different b coefficient for like and unlike spin electrons. We choose to satisfy both interelectron cusp conditions but we limit the asymmetry of the Jastrow factor to the b term with the hope that, the less asymmetric the Jastrow factor is, the less the admixture of other spin components. Consequently, we choose the C term to have the same set of coefficients for any pair of electrons. In Appendix A 2, we discuss an even better choice for the coefficients b' [Eq. (8)] for antiparallel and parallel spin electrons in order to further reduce spin contamination. We summarize the constraints in our wave function:

$$a^\uparrow = a^\downarrow, \quad a'^\uparrow = a'^\downarrow, \quad b^{\uparrow\downarrow} = 1/2, \quad b^{\uparrow\uparrow} = b^{\downarrow\downarrow} = 1/4, \\ b'^{\uparrow\downarrow} = b'^{\uparrow\uparrow} = b'^{\downarrow\downarrow}, \quad c^{\uparrow\downarrow} = c^{\uparrow\uparrow} = c^{\downarrow\downarrow}, \quad f^{\uparrow\downarrow} = f^{\uparrow\uparrow} = f^{\downarrow\downarrow}.$$

Observe that we introduce the nonanalytic terms, $\{f\}$, not only for antiparallel but also for parallel spin electrons. These terms are motivated by the Fock expansion for two electrons in a 1S state so that they are physically motivated only for antiparallel spin electrons. However, we include them also for like spin electrons in an attempt to reduce the degree of asymmetry in the Jastrow factor. Moreover, omitting the nonanalytic terms for parallel spin electrons could result in the $\{c\}$ coefficients being unequal for like and unlike spin electrons since imposing the cusp conditions in the absence of the $\Phi_{2,0}$ -like terms for the parallel spin electrons yields relations among the coefficients different from the an-

tiparallel spin case. Note, that the a coefficient has always to be equal for up and down spin electrons because it enters in equations [Eq. (11)] and is therefore related to the parameters of the determinantal part that are spin independent. In Appendix A 3, we discuss the form of two spin unrestricted wave functions that can be obtained when some of the above constraints in the Jastrow and in the determinantal part are relaxed.

A fifth order polynomial in U , S , and T has 55 coefficients but, if we impose symmetry with respect to the interchange of electronic coordinates, no odd powers of T are allowed and the number of coefficients is 33. If the five electron–electron and five electron–nucleus cusp conditions are imposed, the number of free parameters reduces to 23. There are in addition six $\Phi_{2,0}$ -like and six $\Phi_{3,1}$ -like terms. Imposing the cusp conditions on the latter reduces the number of coefficients multiplying the $\Phi_{2,0}$ -like and $\Phi_{3,1}$ -like terms to ten. The wave functions presented in this paper include only three of these ten parameters because the inclusion of the additional terms was found to result in only a tiny improvement. The two b coefficients are fixed by the electron–electron cusp conditions. Including the coefficients a , a' , b' , and κ , we have a total of 30 free parameters in the Jastrow part of the wave function.

In order to obtain the starting parameters in the optimization of the determinantal part, we perform a restricted HF calculation with the quantum chemistry package GAMESS and we fit the resulting HF orbitals to a Slater basis set. Next, all the parameters in the determinantal and in the Jastrow part are optimized. The resulting wave function is then used as a starting point to add additional configuration state functions corresponding to single and double excitations from the HF configuration. The active space is the space of the orbitals whose atomic principle quantum number does not exceed those occurring in the HF configuration. To select these additional configurations, we obtain a MCSCF wave function using GAMESS and we add the configurations with a large weight in the GAMESS output to our best single configuration wave function. The optimal parameters in the new determinantal and Jastrow part are found by further optimizations of all the parameters.

III. METHOD

A. Variance minimization method

The wave function presented in the previous section has a large number of parameters, of the order of 60. To optimize such a complicated wave function, the variance minimization method has been shown to be a stable method^{2,24} as opposed to total energy minimization which is feasible only for wave functions with very few parameters. The method consists of the minimization of the variance of the local energy over a set of N_c configurations $\{R_i\}$ sampled from the square of the best wave function available before we start the optimization, Ψ_0 :

$$\sigma_{\text{opt}}^2[\Psi] = \sum_i^{N_c} \left[\frac{\mathcal{H}\Psi(R_i)}{\Psi(R_i)} - E_{\text{guess}} \right]^2 w(R_i) \bigg/ \sum_i^{N_c} w(R_i). \quad (12)$$

E_{guess} is a guess for the energy of the state we are interested in or, alternatively, the average energy over the sample of configurations. The weights $w(R_i) = |\Psi(R_i)/\Psi_0(R_i)|^2$ are introduced to allow the nodes of the wave function to freely move during the optimization and to provide the correct weighting. We do not allow the ratio of the weights to the average weight to exceed a maximum value; otherwise, it is possible for the optimizer to achieve a small value of σ_{opt} by having a few configurations gain a very large weight and a local energy that is very close to E_{guess} . 3000 configurations are usually sufficient even for a 54 dimensional space and a total of about 60 parameters as for F_2 .

We choose to minimize the variance instead of the energy because the former is more stable. The minimum of the variance is known and equal to zero while, if the energy is minimized over a finite and necessarily small set of configurations, it is possible to obtain an average energy over the configurations that is arbitrarily lower than the true value. Moreover, if the exact wave function could be written as a function of n parameters, the minimization of the variance over a set of n configurations would be equivalent to a fit and would give the exact answer while energy minimization would encounter the above problems. However, there is a drawback to minimizing the variance: the set of parameters that minimizes the variance does not precisely correspond to the parameters for the minimum energy except in the ideal case of the trial wave function being the true wave function. However, setting the guessed energy lower than the variational energy in the above scheme is approximately equivalent to a simultaneous minimization of the variance and of the energy.²⁵

B. Variational/Metropolis Monte Carlo

Monte Carlo configurations are sampled from Ψ^2 and the expectation value of the energy is obtained from

$$E_{\text{VMC}} = \frac{1}{N} \sum_i^N \frac{\mathcal{H}\Psi(R_i)}{\Psi(R_i)}. \quad (13)$$

We use a very efficient accelerated Metropolis method²⁶ that allows us to simultaneously make large Monte Carlo moves and have a high acceptance. Consequently, the autocorrelation time for the expectation values calculated is small as shown in the next section.

C. Diffusion Monte Carlo

The imaginary-time evolution operator $\exp(-\mathcal{H}\tau)$ is used to project out the ground state from the trial wave function within the fixed-node and the short-time approximations.²⁷ Since we use an efficient algorithm with a very small time-step error,³ the time-step error coming from the short-time approximation is negligible but the fixed-node error limits the accuracy of the results we obtain.

TABLE I. Total energies of Li_2 in VMC (E_{VMC}) and DMC (E_{DMC}) with increasing number of configuration state functions (CSF). We list the configurations omitting the core doubly occupied molecular orbital $1\sigma_g$. E_c^{VMC} and E_c^{DMC} are the percentages of correlation energy in VMC and DMC. σ_{VMC} is the root mean square fluctuation of the local energy in VMC. The numbers in parentheses are the statistical errors in the last digit. Energies are in Hartree atomic units.

Additional CSF	E_{VMC}	E_{DMC}	E_c^{VMC} (%)	E_c^{DMC} (%)	σ_{VMC}
$2\sigma_g^2$	-14.973 43(7)	-14.991 1(1)	82.26(5)	96.5(1)	0.112
$2\sigma_u^2$	-14.977 45(6)	-14.990 9(1)	85.51(4)	96.4(1)	0.098
$1\pi_{ux}^2 + 1\pi_{uy}^2$	-14.984 04(5)	-14.992 3(1)	90.83(4)	97.5(1)	0.086
$3\sigma_g^2$	-14.988 50(4)	-14.993 8(1)	94.43(4)	98.7(1)	0.086

IV. RESULTS AND CONCLUSIONS

We have calculated both single and multiconfiguration wave functions for the first-row homonuclear diatomic molecules, Li_2 , Be_2 , B_2 , C_2 , N_2 , O_2 , and F_2 . The configurations and parameters of the multiconfiguration wave functions are listed in Appendix B. All trial wave functions are optimized at the experimental bond length. The experimental bond lengths are those quoted in Ref. 28 with the exception that the bond length of Be_2 is taken from Ref. 29. In order to calculate the correlation energy recovered by our wave functions in VMC and DMC, we need the HF energies and the exact nonrelativistic, infinite nuclear mass energies. We used the HF energies calculated by Cade and Wahl at the experimental bond length.²⁸ For Be_2 , we were not able to find a HF calculation at the experimental bond length, so we give the result of a linear interpolation between the HF energy at $4.75 a_0$ ³⁰ and at $4.00 a_0$.²⁸ We estimated the exact energies as the sum of the accurate nonrelativistic, infinite nuclear mass atomic energies by Davidson *et al.*³¹ and the experimental dissociation energies corrected for the zero point motion as given in Ref. 32. For B_2 , we use a theoretical estimate of the dissociation energy³³ because the experimental value has only been determined with an uncertainty of 14 kcal/mol.³² For Be_2 , the dissociation energy is from Ref. 30 and for Li_2 from Ref. 34.

We use three measures of goodness to judge the quality of a wave function: the standard deviation of the local energy in VMC, σ_{VMC} , the VMC energy, E_{VMC} , and the DMC energy, E_{DMC} . In general, we find a strong, but not perfect, correlation between these three measures. For atomic systems with a strong multiconfigurational nature, it is known that the inclusion of configuration state functions beyond the one corresponding to the HF configuration yields a significant improvement in all three quantities. In the case of a Be atom, there is a single additional configuration beyond the HF configuration which makes a large contribution, resulting in a reduction in σ_{VMC} by more than a factor of 2. Consequently, the single configuration wave function gives mediocre energies, 76% and 90% of the correlation energy in VMC and DMC, respectively, but the two-configuration wave function recovers 99.2% and 99.9% of the correlation energy in VMC and DMC,³ respectively.

In Table I, we show the effect of including configuration state functions beyond the HF configuration for Li_2 . Here, there is not a single important additional configuration but

several configurations make smaller but significant contributions. Hence, the percentage of correlation energy gained using a single configuration is higher than in the case of Be. As more configurations are added, there is an improvement in all three quantities of interest, σ_{VMC} , E_{VMC} , and E_{DMC} (except that the one- and two-configuration E_{DMC} and the three- and four-configuration σ_{VMC} are the same within the statistical error) but the best result achieved for Li_2 is not as good as for the two-configuration Be wave function.

In Table II, we list the total energies obtained in VMC and DMC and σ_{VMC} obtained with our best single-determinant and multideterminant wave functions. In Fig. 1, we plot the percentage of correlation energy recovered. The use of an efficient accelerated Metropolis algorithm²⁶ and a small time step error DMC algorithm³ allowed us to obtain small statistical errors within acceptable computer time. The percentage of correlation energy recovered is 67.8%–82.3% for single-configuration and 79.1%–94.4% for multiconfiguration wave functions in VMC. The corresponding numbers are 88.1%–96.5% and 92.5%–98.7% in DMC. For the single-configuration wave functions, the smallest percentage of correlation energy recovered is not for the heaviest molecules but rather for the molecules in the middle of the row due to the strong multiconfigurational nature of their true ground state. For the multiconfiguration wave functions, the smallest percentage moves more to the right of the row where, possibly, excitations to the next shell become important. Since the wave functions are obtained by nonlinear optimization, it is possible to get stuck in a local minimum. From the shape of the curves it seems likely that we have failed to find the optimal wave function parameters for O_2 . There is considerable resemblance in the shapes of the VMC and DMC curves and the multiconfiguration energies are consistently better than their single-configuration counterparts. Therefore, it is clear that when more configurations are added to the HF one, not only do σ_{VMC} and E_{VMC} improve but also the shape of the nodal surface, which limits the accuracy of the fixed-node DMC energies, improves.

In going from Li_2 to F_2 , the root mean square fluctuation of the local energy, σ_{VMC} , increases by more than a factor of 10 for both the single and the multiconfiguration wave functions. The dependence of σ_{VMC} on Z appears to be considerably faster than linear for small Z but slower than linear for large Z . This factor should be taken into account in figuring the scaling of the computational cost of QMC methods with

TABLE II. Total energies in VMC (E_{VMC}) and DMC (E_{DMC}) for our best single and multiconfiguration state function wave functions. E_c^{VMC} and E_c^{DMC} are the percentages of correlation energy recovered in VMC and DMC. σ_{VMC} is the root mean square fluctuation of the local energy in VMC and T_{corr} is the autocorrelation time of the local energy in VMC. The numbers in parentheses are the statistical errors in the last digit. In the second column, we list the number of configuration state functions (CSF) and the number of different determinants (D) in the wave function. R_0 is the experimental bond length, E_{HF} the HF energy and E_0 the exact, nonrelativistic, infinite nuclear mass energy. Bond lengths are in Bohrs and energies are in Hartree atomic units.

Molecule	CSF,D	R_0	E_{HF}	E_0	E_{VMC}	E_{DMC}	E_c^{VMC} (%)	E_c^{DMC} (%)	σ_{VMC}	T_{corr}
Li ₂	1,1	5.051	-14.871 52	-14.995 4	-14.973 43(7)	-14.991 1(1)	82.26(5)	96.5(1)	0.112	1.39
	4,5				-14.988 50(4)	-14.993 8(1)	94.43(4)	98.7(1)	0.086	1.06
Be ₂	1,1	4.63	-29.132 42	-29.338 54(5)	-29.278 2(1)	-29.317 6(4)	70.70(7)	89.8(2)	0.242	1.45
	5,16				-29.312 9(1)	-29.330 1(2)	87.56(6)	95.9(1)	0.215	1.35
B ₂	1,1	3.005	-49.090 88	-49.415(2)	-49.311 5(3)	-49.377 8(8)	68.06(8)	88.5(2)	0.432	1.60
	6,11				-49.360 2(2)	-49.397 9(6)	83.10(7)	94.7(2)	0.408	1.15
C ₂	1,1	2.348 1	-75.406 20	-75.923(5)	-75.756 7(5)	-75.861 3(8)	67.82(9)	88.1(2)	0.707	1.71
	4,16				-75.828 2(4)	-75.890 1(7)	81.66(7)	93.6(1)	0.641	1.27
N ₂	1,1	2.068	-108.992 8	-109.542 3	-109.375 6(6)	-109.487(1)	69.7(1)	89.9(2)	0.935	1.46
	4,17				-109.437 6(5)	-109.505(1)	80.94(8)	93.1(2)	0.863	1.10
O ₂	1,1	2.282	-149.665 9	-150.326 8	-150.150 7(6)	-150.268(1)	73.4(1)	91.0(2)	1.09	1.40
	4,7				-150.188 5(5)	-150.277(1)	79.08(8)	92.5(2)	1.05	1.10
F ₂	1,1	2.68	-198.770 1	-199.529 9	-199.364 7(7)	-199.478(2)	78.26(9)	93.2(2)	1.23	1.22
	2,2				-199.410 1(6)	-199.487(1)	84.23(8)	94.3(1)	1.19	0.97

atomic number. In order to estimate this scaling, it is necessary to have a systematic study of several molecules, such as in this paper. For this purpose, it would in fact be useful to also have results on some second-row homonuclear diatomic molecules.

In Fig. 2, we show the autocorrelation time of the local energy in VMC, T_{corr} , calculated as explained in Ref. 26. The quantities shown in Fig. 1 depend on the wave function alone whereas T_{corr} has also a strong dependence on the particular form of Metropolis algorithm used. We used the single-electron accelerated Metropolis algorithm described in Ref. 26 with $\Delta_r=5$ and $\Delta_\theta=\pi/2$. The plot shows the number of Monte Carlo moves of each electron required to decorrelate the local energy. The most important point to be noticed is that T_{corr} is nearly independent of atomic number and that its value is remarkably small confirming the efficiency of the algorithm used. On the other hand, if a simple Metropolis algorithm is used, T_{corr} increases rapidly with atomic number since, in this case, the typical size of a Monte Carlo move scales as $1/Z$ where Z is the atomic number. Since atomic sizes are roughly independent of Z , the number of Monte Carlo moves required to move a distance of the size of an atom is proportional to Z^2 . Therefore, for the simple algorithm, an extra factor, possibly as large as Z^2 , should be included in estimating the scaling of the computational cost with atomic number.

For all the molecules, the value of T_{corr} is smaller for the multiconfiguration wave functions than the single-configuration ones. A likely reason for this is that adding more configurations not only reduces the magnitude of the fluctuations of the local energy, σ_{VMC} , but increases also the frequency of the oscillations. Since the electrons have to travel a shorter distance to go from a given region to a region where the error of the local energy has the opposite sign, the value of T_{corr} is reduced. It is somewhat larger in the middle of the row than at the ends indicating that the regions in configuration space that have a given sign of the error of

local energy are larger there. Occasionally, we have found exceptions to the decrease of T_{corr} as more configuration state functions are added to the HF one. For Be₂, we tested one, two, three, four, and five configuration wave functions and found that the smallest T_{corr} occurred for the two configuration wave function. The autocorrelation times in DMC (not shown in the plots) is larger than in VMC and we found in all cases studied, including Be₂, that adding more configuration state functions results in a reduction of the autocorrelation time.

In Table III, we compare with the results obtained by other authors in VMC. A difficulty in the comparison is that somewhat different values are used in the literature for E_{HF} and E_0 . For consistency, we always use the values of E_{HF} and E_0 given in Table I in order to obtain the percentages of correlation energy recovered. Subramaniam *et al.*⁹ use a simple Jastrow factor and a determinantal part with the orbitals frozen to be the HF orbitals. Similarly, no optimization of the determinantal component of the wave function is done by Schmidt *et al.*¹⁰ but a more sophisticated form of the Jastrow factor is used leading to a larger gain in correlation energy. The results of Sun *et al.*¹³ differ from the previous two because the parameters entering in the determinantal part are optimized. In addition, they include three-configuration state functions (four determinants) in their wave function, so they do better than Schmidt *et al.* in spite of using a simple Jastrow factor. For completeness, we also compare with the results obtained by conventional quantum chemistry methods. Peterson *et al.*³² give a benchmark study of the basis set dependence of different single and double excitation CI methods. In the last column of Table III, we list their estimate of the complete basis set result for a multireference single and double excitation CI from a complete active space self-consistent-field (CASSCF+1+2) calculation. To extrapolate the complete basis set values, they employ several basis sets of increasing size, the largest being a quadruple zeta consisting of *spdfg* functions augmented with additional

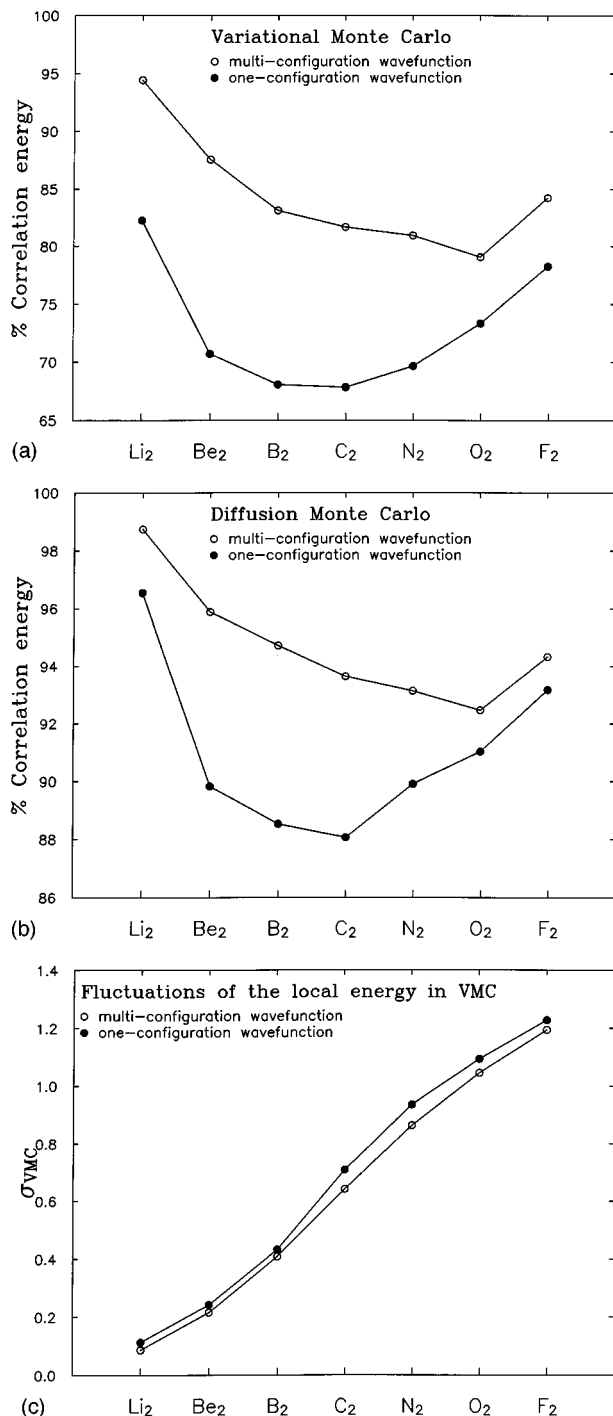


FIG. 1. Percentage of correlation energy in (a) VMC and, (b) DMC, and (c) root mean square fluctuation σ_{VMC} with one-configuration (solid circle) and multiconfiguration (open circle) wave functions.

diffuse functions for each angular momentum.

There are only a few DMC or Green function Monte Carlo (GFMC) results for homonuclear diatomics available and we will mention only the best results from each research group. Subramaniam *et al.*⁹ calculate the GFMC energies for Li₂, B₂, C₂, and N₂ but the statistical errors they report are so large (ranging from 5% for Li₂ to 14% for N₂) that it is not possible to make a meaningful comparison with our

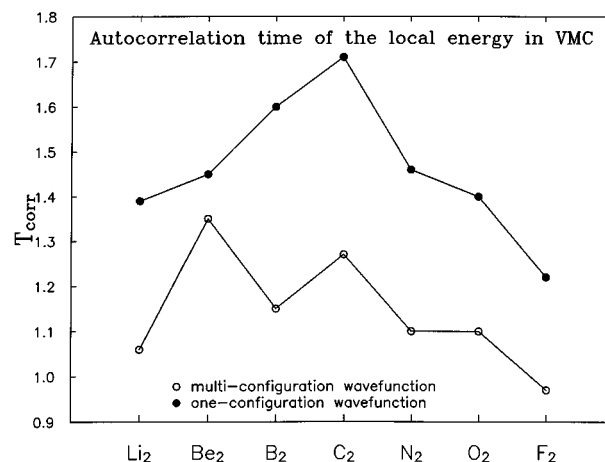


FIG. 2. Autocorrelation time of the local energy in VMC, T_{corr} , using the accelerated Metropolis algorithm of Ref. 26, for one-configuration (solid circle) and multiconfiguration (open circle) wave functions.

DMC results. For N₂, Reynolds *et al.*¹¹ obtain 89.3% of the correlation energy in DMC for a single configuration wave function. For Li₂, Sun *et al.*¹³ present DMC energies for both single configuration and three-configuration wave functions. For their optimized multiconfiguration wave function, they obtain 96.8(6)% of the DMC correlation energy. However, they find that the same functional form with unoptimized parameters taken from a MCSCF calculation yields 99.3(3)% of the DMC correlation energy and they attribute the reduced correlation energy in the optimized wave function to the introduction of spurious nodes upon optimization. Since they do not give the parameters of the unoptimized wave function, it was not possible for us to independently confirm their result. If their finding holds for other molecules as well, it would make DMC calculations much more useful: one would freeze the determinantal part obtained from a MCSCF calculation and just optimize the Jastrow factor in order to reduce the variance. However, it appears that similarly good results are not found for other molecules since such results for other molecules have not appeared in the literature.

In summary, all the VMC and DMC energies reported in this paper (with the possible exception of a DMC result for Li₂) are better than those in the literature. However, due to the nature of nonlinear optimization, it is quite possible that further optimization could result in somewhat better wave functions. There is a near redundancy in the wave functions. Consequently, we can often find several wave functions with very different parameters that are nearly equivalent by all three measures of goodness, σ_{VMC} , E_{VMC} , and E_{DMC} . Bigger improvement could be obtained by including a larger number of configuration state functions, higher body-order correlations in the Jastrow factor or inventing more innovative forms of the wave function.

The wave functions presented in Appendix B are certainly good in the regions of configuration space where they are appreciable but may be poor in the tail regions. If the ionization energy of the molecule is known, it is possible to

TABLE III. Comparison of the percentage correlation energy obtained in VMC by various authors. The numbers in parentheses are the statistical errors in the last digit. In the last column, we list the complete basis set extrapolations of CASSCF+1+2 calculations.

	Present work	Subramaniam <i>et al.</i> (Ref. 9)	Schmidt <i>et al.</i> (Ref. 10)	Sun <i>et al.</i> (Ref. 13)	Peterson <i>et al.</i> (Ref. 32)
Li ₂	94.43(4)	40(2)	70	76.6(6)	...
B ₂	83.10(7)	20(5)	66.8
C ₂	81.66(7)	15(3)	76.6
N ₂	80.94(8)	14(9)	55	...	74.8
O ₂	79.08(8)	75.3
F ₂	84.23(8)	76.2

incorporate this information into the wave function to improve its asymptotic form. We have done this in some earlier work but, in this paper, we decided to study what is obtained without providing any external experimental or theoretical input aside from the bond length.

ACKNOWLEDGMENTS

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APPENDIX A: SPIN CONTAMINATION

1. Source of spin contamination: An example

In Sec. II, we mentioned that the use of a nonsymmetrical Jastrow factor for unlike and like spin electrons yields a wave function that is not an eigenstate of S^2 but an admixture of different spin components. Here, we take the Li atom as an example to show how spin contamination enters in the wave function.

A QMC wave function for Li with two electrons in a $1s$ orbital and one spin up electron in a $2s$ orbital is given by

$$\psi_{\text{QMC}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = [1s(r_1)2s(r_2) - 1s(r_2)2s(r_1)] \times 1s(r_3)g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \quad (\text{A1})$$

where electron 1 and 2 are up spin electrons, electron 3 is a down spin electron and $g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is the Jastrow factor. In order to satisfy the cusp conditions both for antiparallel and parallel spin electrons, $g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ cannot be symmetric under the interchange of an up and a down spin electron coordinate ($2 \leftrightarrow 3$ and $1 \leftrightarrow 3$) and a possible choice is

$$g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = J_p(r_{12})J_a(r_{13})J_a(r_{23}), \quad (\text{A2})$$

where $J_p(r_{ij})$ and $J_a(r_{ij})$ are simple Jastrow factors [Eq. (3)] for parallel and antiparallel spin electrons, respectively.

The full space-spin wave function corresponding to ψ_{QMC} is

$$\psi = \mathcal{A}[\psi_{\text{QMC}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\chi_{\uparrow}(s_1)\chi_{\uparrow}(s_2)\chi_{\downarrow}(s_3)]. \quad (\text{A3})$$

where \mathcal{A} is the antisymmetrizer and χ_{\uparrow} and χ_{\downarrow} are single electron spin wave functions. ψ can be expanded and rewritten as (using an abbreviated notation for the space and spin coordinates)

$$\begin{aligned} \psi = & +1s(1)2s(2)1s(3)\chi_{\uparrow}(2)[\chi_{\uparrow}(1)\chi_{\downarrow}(3)g(1,2,3) \\ & - \chi_{\uparrow}(3)\chi_{\downarrow}(1)g(3,2,1)] + 1s(2)2s(3)1s(1)\chi_{\uparrow}(3) \\ & \times [\chi_{\uparrow}(2)\chi_{\downarrow}(1)g(2,3,1) - \chi_{\uparrow}(1)\chi_{\downarrow}(2)g(1,3,2)] \\ & + 1s(3)2s(1)1s(2)\chi_{\uparrow}(1)[\chi_{\uparrow}(3)\chi_{\downarrow}(2)g(3,1,2) \\ & - \chi_{\uparrow}(2)\chi_{\downarrow}(3)g(2,1,3)]. \end{aligned} \quad (\text{A4})$$

It is clear that, if $g(1,2,3)$ is not completely symmetric in the interchange of the particle coordinates, g cannot be factorized from all the terms in the above expression and the wave function ψ is no longer a doublet. Therefore, if the parallel and antiparallel spin electrons cusp conditions are satisfied, ψ is not an eigenstate of S^2 because the determinantal part in ψ_{QMC} is multiplied by a nonsymmetrical factor. The spin contamination for a given wave function can be calculated.³⁵ For the form of the wave functions used in the present paper, the spin contamination for Li is only of the order of 10^{-5} . Yet smaller values of the spin contamination can be obtained by a simple modification of the wave function as explained in the next section.

2. A wave function with small spin contamination

As explained in Sec. II, we use a restricted form of the Jastrow factor where only the b coefficients are different for antiparallel and parallel spin electrons. This choice was made in order to ensure a small degree of asymmetry and, consequently, a small admixture of higher spin components. More recently, we came to the realization that a better choice would have been to impose that the logarithmic derivatives of the B term in the Jastrow factor [Eq. (8)] are equal for parallel and antiparallel spin electrons at large interelectron distances. This yields different values of b' [Eq. (8)] for antiparallel and parallel spin electrons, b'_a and b'_p respectively, that are related through the scale factor κ as

$$b'_p = \kappa \left[\frac{1}{\sqrt{2}} \left(1 + \frac{b'_a}{\kappa} \right) - 1 \right]. \quad (\text{A5})$$

TABLE IV. Parameters of the single-particle orbitals in the determinantal part as described in the text. “×” means that the coefficient was not varied and “...” that the coefficient is zero by symmetry. The orbitals are not orthonormal.

	1s	1s	2s	2s	2p _x	2p _x	2p _x	2p _z	2p _z	2p _z	3s
Li₂											
ζ	3.279 959 89	2.288 312 06	2.738 805 40	0.685 778 32	0.962 586 00	0.764 443 97	×	0.937 040 20	0.810 015 56	×	×
1σ _g	0.496 680 36	1	0.686 206 29	−0.010 848 61	×	0.003 818 59	0.002 734 88	×	×
1σ _u	0.488 796 39	1	0.677 360 88	0.008 840 97	×	0.018 267 01	−0.000 000 15	×	×
2σ _g	−0.526 544 17	0	−0.607 238 26	1	×	0.244 617 58	−0.340 754 01	×	×
2σ _u	0.010 701 61	0	−0.008 494 43	1	×	−0.208 083 81	0.267 929 25	×	×
3σ _g	0.035 053 75	0	0.001 525 70	1	×	0.384 833 71	−0.646 646 14	×	×
1π _{ux}	−0.419 395 65	1	×	×	×
Be₂											
ζ	4.621 899 68	2.772 647 28	1.502 252 14	1.068 230 41	2.268 895 25	0.859 750 54	×	3.796 411 94	0.754 935 44	×	×
1σ _g	0.121 998 50	1	−0.029 008 78	0	×	−0.020 063 27	−0.002 422 83	×	×
1σ _u	0.120 485 78	1	−0.067 604 40	0.064 220 96	×	−0.016 613 06	0.009 269 10	×	×
2σ _g	0.012 377 74	0	−0.378 420 47	1	×	0.000 455 83	0.181 684 91	×	×
2σ _u	0.009 870 50	0	−0.330 329 06	1	×	−0.001 303 60	−0.240 975 03	×	×
3σ _g	0.001 157 96	0	−0.125 621 06	0	×	−0.001 944 53	1	×	×
1π _{ux}	−0.028 815 78	1	×	×	×
1π _{gx}	−0.036 034 77	1	×	×	×
B₂											
ζ	5.258 588 82	3.898 585 48	1.422 122 01	0.710 478 97	2.397 240 31	1.018 373 09	×	5.145 633 30	1.494 723 96	×	×
1σ _g	0.528 048 33	1	0	0.004 358 52	×	−0.039 767 80	0.001 530 91	×	×
1σ _u	0.530 780 79	1	0.025 006 48	−0.001 888 13	×	−0.037 573 49	−0.000 002 43	×	×
2σ _g	0.195 436 28	0	1	0.033 050 34	×	0.000 000 88	0.187 854 75	×	×
2σ _u	0.131 719 80	0	1	0.703 660 78	×	−0.009 126 32	−0.380 119 72	×	×
3σ _g	0.042 935 44	0	0	−0.046 218 85	×	0.010 131 71	1	×	×
1π _{ux}	0.214 387 15	1	×	×	×
1π _{gx}	0.090 221 42	1	×	×	×
C₂											
ζ	5.425 738 79	5.172 118 76	2.067 258 62	1.142 229 37	2.905 107 68	1.285 994 59	×	6.259 723 37	1.994 114 33	×	×
1σ _g	1	0	0.368 986 60	0.174 584 58	−0.021 092 62	0.182 973 38	×	×
1σ _u	0.761 566 41	1	0.026 492 75	0.011 141 66	−0.044 444 75	−0.000 000 05	×	×
2σ _g	0	1	−0.260 575 13	−0.131 046 73	−0.027 209 89	−0.134 693 11	×	×
2σ _u	1	0	0.473 574 51	0.827 745 40	−0.028 736 24	−0.302 921 32	×	×
3σ _g	0	0	−0.129 056 85	−0.095 839 20	0.013 522 43	1	×	×
1π _{ux}	0.293 541 04	1	×	×	×
1π _{gx}	0.105 038 47	1	×	×	×
N₂											
ζ	7.161 651 00	5.240 017 65	2.084 486 47	1.222 733 17	4.599 208 78	1.903 541 96	1.064 415 79	6.899 826 78	2.573 077 01	1.309 750 16	×
1σ _g	0.979 730 29	1	0	0.015 558 65	−0.067 687 21	0	0.002 133 59	×
1σ _u	0.981 781 83	1	0	−0.042 651 60	−0.069 275 59	0.008 798 30	−0.040 608 51	×
2σ _g	0.301 699 94	0	1	0.340 832 22	−0.012 656 13	0	−0.344 787 96	×
2σ _u	0.283 550 97	0	1	0.310 676 72	−0.017 820 05	−0.156 499 32	−0.581 801 47	×
3σ _g	0.082 564 49	0	0	−0.548 055 25	0.021 799 05	0.768 741 68	1	×
3σ _u	−0.105 019 86	0	0	1	0.017 738 74	−0.008 809 04	0.842 354 16	×
1π _{ux}	0.108 186 58	1	0.465 990 05	×
1π _{gx}	0.080 949 31	1	0.997 726 26	×
O₂											
ζ	8.378 930 35	5.835 853 77	2.032 278 45	1.117 201 07	5.474 902 40	2.013 211 22	1.227 504 43	6.340 787 60	3.888 267 89	1.866 014 12	×
1σ _g	0.840 191 74	1	0	0.006 438 07	−0.029 019 70	0.011 750 25	−0.002 745 64	×
1σ _u	0.840 045 81	1	0	0.018 927 31	−0.029 034 30	0.016 688 54	−0.010 000 14	×
2σ _g	0.152 114 08	0	1	0.026 278 79	−0.006 420 20	0.009 825 70	−0.141 721 09	×
2σ _u	0.118 959 16	0	1	0.177 084 63	−0.005 814 12	−0.017 408 28	−0.171 509 33	×
3σ _g	0.030 932 24	0	0	−0.200 878 96	0.024 339 22	0.094 692 19	1	×
3σ _u	−0.043 659 13	0	0	−0.105 485 94	0.034 553 39	−0.010 210 80	1	×
1π _{ux}	0.072 597 13	1	0.411 070 15	×
1π _{gx}	0.067 292 26	1	0.506 047 53	×
F₂											
ζ	9.405 631 59	4.609 155 07	6.866 467 67	2.289 154 12	6.342 922 63	1.824 098 85	1.038 695 93	6.405 630 26	1.858 361 13	×	1.636 311 16
1σ _g	1	−0.239 129 88	0.406 533 28	0	−0.005 110 00	0.008 248 67	×	0.000 036 17
1σ _u	1	−0.150 139 42	0.355 711 37	0	−0.006 112 89	0.002 609 79	×	0.003 653 79
2σ _g	0	−0.558 146 09	0.252 644 81	1	−0.000 000 63	−0.054 546 80	×	0.021 166 84

TABLE IV. (Continued.)

	1s	1s	2s	2s	2p _x	2p _x	2p _x	2p _z	2p _z	2p _z	3s
2σ _u	0	-0.571 202 35	0.267 183 04	1	-0.003 310 32	-0.083 072 65	×	0.134 416 97
3σ _g	0	-0.100 993 09	0.047 842 63	0	0.057 951 16	1	×	-0.046 630 35
3σ _u	0	0.233 375 98	-0.119 166 28	0	0.046 604 48	1	×	0.302 133 44
1π _{ux}	0.059 650 82	1	0.062 783 23	×	...
1π _{gx}	0.059 071 12	1	0.178 090 41	×	...

If instead we require that B is equal for parallel and antiparallel spin electrons at large interparticle distances, we obtain the above relation with the $\sqrt{2}$ replaced by a 2.

From some preliminary tests, the optimization of b'_a and b'_p yields values related by the above expression with the $\sqrt{2}$ substituted by an optimal value of about 1.5. Therefore, the optimal value seems to differ slightly from $\sqrt{2}$ in the direction of 2. The corresponding wave functions have a consistently better σ_{VMC} with respect to the minimally unrestricted wave functions presented in this paper.

3. General spin unrestricted wave functions

An alternative approach to the one adopted in this paper and the one presented in the previous subsection could be to relax the constraints on the Jastrow factor.

The first wave function we present represents the most general wave function we can construct. It corresponds to the wave function of a spin-polarized system and has the largest number of variational parameters. An up-spin electron can correlate to the nucleus differently than a down-spin electron and the terms for two up-spin and two down-spin electrons are described by two different sets of coefficients. Furthermore, the coefficients of the terms with odd powers of T in the antiparallel spin Jastrow factor need no longer vanish. As far as the determinantal wave function is concerned, we no longer have to construct it to be an eigenstate of S^2 . As a consequence, up and down orbitals, ϕ_i^\uparrow and ϕ_i^\downarrow can now be different. The second wave function corresponds to a wave function for a spin-unpolarized system. An up-spin and a down-spin electron are correlated to the nucleus in the same way. Therefore, although the coefficients are different for parallel and antiparallel spin electrons, they are equal for two up-spin electrons and two down-spin electrons. The determinantal part has still to be an eigenstate of S^2 with equal up and down orbitals. This ensures that the up and down spin densities are equal. In both wave functions, the b coefficient is different for like and unlike spin electrons as imposed by the electron-electron cusp condition. We summarize the two cases by listing the relations among the different kinds of coefficients:

1. $b^{\uparrow\downarrow} = 1/2$, $b^{\uparrow\uparrow} = b^{\downarrow\downarrow} = 1/4$,
2. $a^\uparrow = a^\downarrow$, $a'^\uparrow = a'^\downarrow$, $b^{\uparrow\downarrow} = 1/2$, $b^{\uparrow\uparrow} = b^{\downarrow\downarrow} = 1/4$,
 $b'^{\uparrow\uparrow} = b'^{\downarrow\downarrow}$, $c^{\uparrow\uparrow} = c^{\downarrow\downarrow}$, $\phi_i^\uparrow = \phi_i^\downarrow$.

For the lightest molecules, after generating an optimal restricted wave function, we tried relaxing some constraints

allowing the antiparallel spin electron coefficients to differ from the parallel ones. We still kept the nonanalytic terms for the parallel spin electrons equal to the antiparallel ones. Despite the much higher variational freedom now available, in our limited experimentation, we were unable to obtain wave functions of significantly better quality than the minimally unrestricted ones described in the rest of the paper.

APPENDIX B: MOLECULAR WAVE FUNCTIONS

We list the parameters entering in the molecular wave functions of Li_2 , Be_2 , B_2 , C_2 , N_2 , O_2 , and F_2 . The symmetry of the ground state is $^3\Sigma_g^-$ for B_2 and O_2 and $^1\Sigma_g^+$ for the other molecules.

In Table IV, we report the parameters of the single orbitals in the determinantal part. We only list the exponents and coefficients on one center. The exponents are equal on the other center and the coefficients are obtained from symmetry considerations. For a σ_g orbital, a coefficient of an s basis function is simply replicated on the other center while the coefficient of a p_z function changes sign. The opposite rule applies to a σ_u orbital. For π_u orbitals, the signs of the coefficients are the same on the two centers while they are opposite for π_g orbitals. We also list only the coefficients and exponents of the p_x basis functions in the π_x orbitals. To construct a π_y orbital, we take the coefficients and exponents of the p_y functions to be equal to those of the p_x functions of the corresponding π_x orbital. Different numbers of basis functions were used for the different molecules and the “×” symbol as an entry in the table means that the coefficient was not varied. The “...” symbol means that the coefficient is strictly zero by symmetry. The orbitals are not constructed to be orthonormal. Each orbital can be multiplied by a constant to make the largest coefficient equal to one if the coefficients of the determinants are properly redefined. This accounts for one coefficient in each orbital being equal to “1”. Orbitals belonging to the same irreducible representation of the point group of the molecule can pivot each other without modifying their symmetry character. Some coefficients have been set to “0” through pivoting. As a consequence of the pivoting, the orbitals cannot be directly compared to Hartree-Fock or MCSCF orbitals. There is only one π orbital of a given symmetry and, consequently, these do not get pivoted. Hence, it may appear surprising that the $1\pi_u$ orbitals of Li_2 have a node. However, it should be noted that the presence of this node does not imply that the wave function has additional nodes. We tested our wave functions for additional nodes as follows. We selected random Monte Carlo configu-

TABLE V. Configuration state functions in the determinantal part of the wave function. We omit the core double occupied molecular orbitals ($1\sigma_g^2, 1\sigma_u^2$). The configuration state functions are not orthonormal because the orbitals are not.

Molecule	Configuration	Coefficient	Determinants
Li ₂	$(2\sigma_g^2)$	1	
	$2\sigma_g^2 \rightarrow 2\sigma_u^2$	-0.258 198 38	
	$2\sigma_g^2 \rightarrow 1\pi_u^2$	-0.163 002 08	
	$2\sigma_g^2 \rightarrow 3\sigma_u^2$	-0.636 632 64	$\pi_{ux}^2 + \pi_{uy}^2$
Be ₂	$(2\sigma_g^2, 2\sigma_u^2)$	1	
	$2\sigma_u^2 \rightarrow 3\sigma_g^2$	-0.173 925 99	
	$2\sigma_u^2 \rightarrow 1\pi_u^2$	-0.058 205 12	
	$2\sigma_g^2 2\sigma_u \rightarrow 1\pi_u 1\pi_g$	-0.050 885 38	
		0.025 342 38	$\begin{aligned} & \pi_{ux}^2 + \pi_{uy}^2 \\ & \sigma_g^+ \sigma_u^- \pi_{ux}^- \pi_{gx}^+ - \sigma_g^+ \sigma_u^- \pi_{ux}^- \pi_{gx}^- - \sigma_g^- \sigma_u^+ \pi_{ux}^+ \pi_{gx}^+ + \sigma_g^- \sigma_u^+ \pi_{ux}^+ \pi_{gx}^- \\ & + \sigma_g^+ \sigma_u^- \pi_{uy}^- \pi_{gy}^+ - \sigma_g^+ \sigma_u^- \pi_{uy}^- \pi_{gy}^- - \sigma_g^- \sigma_u^+ \pi_{uy}^+ \pi_{gy}^+ + \sigma_g^- \sigma_u^+ \pi_{uy}^+ \pi_{gy}^- \\ & \sigma_g^+ \sigma_u^- \pi_{ux}^- \pi_{gx}^+ - \sigma_g^+ \sigma_u^- \pi_{ux}^- \pi_{gx}^- - \sigma_g^- \sigma_u^+ \pi_{ux}^+ \pi_{gx}^+ + \sigma_g^- \sigma_u^+ \pi_{ux}^+ \pi_{gx}^- \\ & + \sigma_g^+ \sigma_u^- \pi_{uy}^- \pi_{gy}^+ - \sigma_g^+ \sigma_u^- \pi_{uy}^- \pi_{gy}^- - \sigma_g^- \sigma_u^+ \pi_{uy}^+ \pi_{gy}^+ + \sigma_g^- \sigma_u^+ \pi_{uy}^+ \pi_{gy}^- \end{aligned}$
B ₂	$(2\sigma_g^2, 2\sigma_u^2, 1\pi_{ux}, 1\pi_{uy})$	1	
	$2\sigma_u^2 \rightarrow 3\sigma_g^2$	-0.460 208 91	
	$1\pi_{ux} 1\pi_{uy} \rightarrow 1\pi_{gx} 1\pi_{gy}$	-0.243 152 78	
	$2\sigma_g^2 \rightarrow 3\sigma_g^2$	0.203 022 69	
	$2\sigma_u \pi_u \rightarrow 3\sigma_g \pi_g$	0.182 349 51	
		0.068 683 04	$\begin{aligned} & 2\sigma_g^+ 3\sigma_g^- - 2\sigma_g^- 3\sigma_g^+ \\ & \sigma_u^+ \pi_{ux}^+ \sigma_g^+ \pi_{gy}^- - \sigma_u^+ \pi_{ux}^+ \sigma_g^- \pi_{gy}^- - \sigma_u^- \pi_{uy}^+ \sigma_g^+ \pi_{gx}^- + \sigma_u^- \pi_{uy}^+ \sigma_g^- \pi_{gx}^- \\ & \sigma_u^- \pi_{ux}^+ \sigma_g^+ \pi_{gy}^+ - \frac{1}{2} (\sigma_u^+ \pi_{ux}^+ \sigma_g^+ \pi_{gy}^- + \sigma_u^+ \pi_{ux}^+ \sigma_g^- \pi_{gy}^-) \\ & - (\sigma_u^- \pi_{uy}^+ \sigma_g^+ \pi_{gx}^- - \frac{1}{2} (\sigma_u^+ \pi_{uy}^+ \sigma_g^+ \pi_{gx}^- + \sigma_u^+ \pi_{uy}^+ \sigma_g^- \pi_{gx}^-)) \end{aligned}$
C ₂	$(2\sigma_g^2, 2\sigma_u^2, 1\pi_{ux}^2, 1\pi_{uy}^2)$	1	
	$2\sigma_u^2 \rightarrow 3\sigma_g^2$	-0.198 094 65	
	$2\sigma_u 1\pi_u \rightarrow 3\sigma_g 1\pi_g$	-0.107 496 97	
	$1\pi_u^2 \rightarrow 1\pi_g^2$	-0.417 315 80	$\begin{aligned} & \sigma_u^+ \pi_{ux}^- \pi_{gx}^+ \sigma_g^- - \sigma_u^+ \pi_{ux}^- \pi_{gx}^- \sigma_g^+ - \sigma_u^- \pi_{uy}^+ \pi_{gx}^+ \sigma_g^- + \sigma_u^- \pi_{uy}^+ \pi_{gx}^- \sigma_g^+ \\ & + \sigma_u^+ \pi_{uy}^- \pi_{gy}^+ \sigma_g^- - \sigma_u^+ \pi_{uy}^- \pi_{gy}^- \sigma_g^+ - \sigma_u^- \pi_{ux}^+ \pi_{gy}^+ \sigma_g^- + \sigma_u^- \pi_{ux}^+ \pi_{gy}^- \sigma_g^+ \\ & \pi_{ux}^2 \pi_{gy}^2 + \pi_{uy}^2 \pi_{gx}^2 \\ & - \frac{1}{2} (\pi_{ux}^+ \pi_{uy}^- \pi_{gx}^+ \pi_{gy}^- - \pi_{ux}^+ \pi_{uy}^- \pi_{gx}^- \pi_{gy}^- - \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^+ \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^- \pi_{gy}^-) \end{aligned}$
N ₂	$(2\sigma_g^2, 2\sigma_u^2, 3\sigma_g^2, 1\pi_{ux}^2, 1\pi_{uy}^2)$	1	
	$1\pi_u^2 \rightarrow 1\pi_g^2$	-0.156 464 50	
		-0.035 651 88	$\begin{aligned} & \pi_{ux}^2 \pi_{gy}^2 + \pi_{uy}^2 \pi_{gx}^2 \\ & - \frac{1}{2} (\pi_{ux}^+ \pi_{uy}^- \pi_{gx}^+ \pi_{gy}^- - \pi_{ux}^+ \pi_{uy}^- \pi_{gx}^- \pi_{gy}^- - \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^+ \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^- \pi_{gy}^-) \\ & \pi_{ux}^+ \pi_{uy}^- \pi_{gx}^+ \pi_{gy}^- + \pi_{ux}^+ \pi_{uy}^- \pi_{gx}^- \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^+ \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^- \pi_{gy}^- \\ & - 2(\pi_{ux}^+ \pi_{uy}^+ \pi_{gx}^- \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^+ \pi_{gy}^-) \\ & \sigma_g^+ \pi_{ux}^- \sigma_u^+ \pi_{gx}^- - \sigma_g^+ \pi_{ux}^- \sigma_u^- \pi_{gx}^- - \sigma_g^- \pi_{ux}^+ \sigma_u^+ \pi_{gx}^- + \sigma_g^- \pi_{ux}^+ \sigma_u^- \pi_{gx}^- \\ & + \sigma_g^+ \pi_{uy}^- \sigma_u^+ \pi_{gy}^- - \sigma_g^+ \pi_{uy}^- \sigma_u^- \pi_{gy}^- - \sigma_g^- \pi_{uy}^+ \sigma_u^+ \pi_{gy}^- + \sigma_g^- \pi_{uy}^+ \sigma_u^- \pi_{gy}^- \end{aligned}$
	$3\sigma_g 1\pi_u \rightarrow 3\sigma_u 1\pi_g$	0.163 433 28	
O ₂	$(2\sigma_g^2, 2\sigma_u^2, 3\sigma_g^2, 1\pi_{ux}^2, 1\pi_{uy}^2, 1\pi_{gx}, 1\pi_{gy})$	1	
	$1\pi_{ux} 1\pi_{uy} \rightarrow 1\pi_{gx} 1\pi_{gy}$	-0.186 814 63	
	$3\sigma_g^2 \rightarrow 3\sigma_u^2$	-0.192 568 92	
	$3\sigma_g 1\pi_u \rightarrow 3\sigma_u 1\pi_g$	0.141 542 93	$\sigma_g^+ \sigma_u^- \pi_{ux}^+ \pi_{gy}^+ - \sigma_g^+ \sigma_u^+ \pi_{ux}^+ \pi_{gy}^- - \sigma_g^+ \sigma_u^- \pi_{uy}^+ \pi_{gx}^+ + \sigma_g^- \sigma_u^+ \pi_{uy}^+ \pi_{gx}^+$
F ₂	$(2\sigma_g^2, 2\sigma_u^2, 3\sigma_g^2, 1\pi_{ux}^2, 1\pi_{uy}^2, 1\pi_{gx}, 1\pi_{gy})$	1	
	$3\sigma_g^2 \rightarrow 3\sigma_u^2$	-0.408 395 32	

rations, we fixed the positions of five of the six electrons and plotted contours of the nodal surface when the sixth electron was moved in a plane. (In fact, the nodal surface depends only on the position of the remaining two electrons of the same spin.) This was done for a few positions of the five electrons, a few planes and three different wave functions. One wave function was a single-configuration wave function whereas the other two were four-configuration wave functions, the suspect one of Table IV and another with nodeless $1\pi_u$ orbitals. We found no instances where the suspect wave function had additional nodes compared to the other two wave functions. Moreover, in all cases, the nodes of the two four-configuration wave function were closer to each other than to the nodes of the one-configuration wave function.

Hence, we have no reason to discard the wave function of Table IV; it yields energies that are 0.0003(1) and 0.0002(1) Hartree lower in VMC and DMC than the four-configuration wave function with nodeless $1\pi_u$ orbitals.

In Table V, we list the configuration state functions in the determinantal part of the wave functions and their coefficients. We always omit the core double occupied molecular orbitals ($1\sigma_g^2, 1\sigma_u^2$). The first configuration listed for each molecule is the HF configuration and, for each additional configuration, we indicate the excitations from the orbitals of the HF configuration. In general, configuration state functions consist of more than one determinant as shown in the fourth column of the table. The coefficients of the determinants in a given configuration are fixed by the requirement

TABLE VI. Coefficients in the generalized Jastrow factor.

	Li ₂	Be ₂	B ₂	C ₂	N ₂	O ₂	F ₂
κ	0.825 38	0.652 18	0.729 10	0.941 49	1.080 53	1.263 94	1.169 3
a	-1.022 016 20	-0.834 631 32	-0.485 979 70	-0.717 757 46	-0.588 566 65	-0.661 255 75	-0.261 090 75
a'	1.159 479 46	0.004 833 75	0.135 367 68	-0.063 693 85	-0.863 173 16	-0.064 512 34	0.223 069 85
b	0.5	0.5	0.5	0.5	0.5	0.5	0.5
b'	0.612 037 30	0.947 142 28	1.497 819 69	1.826 022 91	1.704 541 24	2.445 423 90	2.327 328 19
U	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0
U^2	0.116 710 20	0.626 052 45	0.896 913 38	1.193 681 09	1.236 284 93	2.288 876 21	2.412 412 96
US	0.711 906 15	0.835 118 37	1.060 095 55	1.439 662 92	1.324 203 15	1.654 461 32	2.041 552 29
S^2	-0.431 454 85	-0.015 499 94	-0.247 813 33	-0.431 840 51	-0.180 780 37	-0.426 959 89	-0.729 040 85
T^2	0.042 356 69	0.275 155 13	0.241 003 38	0.281 494 56	0.175 939 75	0.117 759 23	0.085 384 26
U^3	0.531 753 46	-0.008 138 73	-0.011 704 76	-0.154 604 80	0.629 620 70	-0.118 886 07	-1.712 488 73
U^2S	-0.389 593 87	-0.598 113 95	-0.926 571 04	-1.353 792 15	-1.715 592 67	-3.741 816 58	-2.983 785 48
US^2	0	0	0	0	0	0	0
UT^2	0.056 265 28	-0.252 351 41	-0.324 853 34	-0.348 226 46	-0.703 457 69	-1.318 674 07	-0.090 425 90
S^3	0.257 080 77	0.119 083 69	0.200 301 46	0.318 826 97	0.611 056 23	0.868 313 64	1.067 862 37
ST^2	0.269 117 88	0.263 839 93	0.324 040 03	0.299 141 68	1.524 491 40	1.500 472 47	0.400 653 42
U^4	-0.340 159 10	-0.088 227 73	0.080 694 58	0.054 400 71	-0.441 399 63	0.635 482 49	1.565 669 11
U^3S	-0.042 825 64	0.025 367 24	-0.307 534 81	-0.409 600 50	-0.963 021 56	-1.013 645 14	-0.153 137 97
U^2S^2	0.298 844 09	0.309 615 49	0.673 936 74	1.204 729 66	1.764 665 98	3.938 608 48	3.003 147 09
U^2T^2	0.126 617 73	0.663 038 59	0.608 585 42	1.550 204 09	1.983 066 44	1.194 857 69	1.358 743 35
US^3	0	0	0	0	0	0	0
UST^2	-0.446 483 70	-0.583 624 47	-0.406 049 87	-1.236 599 55	-2.308 651 34	0.269 779 21	-0.123 525 64
S^4	-0.139 773 20	-0.063 879 60	-0.108 102 96	-0.189 178 45	-0.428 640 23	-0.683 783 32	-0.802 877 42
S^2T^2	0.336 696 01	0.128 620 34	-0.031 473 02	0.207 559 68	-0.526 252 66	-0.901 638 71	0.098 552 52
T^4	0.047 254 50	-0.088 343 22	-0.050 798 53	-0.155 165 91	-0.201 433 02	0.367 235 99	0.011 921 37
U^5	-0.065 328 12	-0.016 057 50	-0.167 044 57	-0.316 238 82	-1.133 085 76	-1.105 447 71	-0.400 747 36
U^4S	0.299 156 96	0.066 129 45	0.199 207 85	0.444 420 45	1.833 051 75	0.875 132 34	-0.558 424 72
U^3S^2	-0.203 429 59	-0.041 152 17	-0.004 708 50	-0.049 992 29	-0.479 426 95	0.073 003 54	0.428 681 25
U^3T^2	-0.225 613 17	-0.403 111 79	-0.268 839 90	-1.089 929 09	-1.009 454 58	-0.538 609 11	-1.298 441 18
U^2S^3	-0.014 866 89	-0.041 813 06	-0.131 667 20	-0.296 105 63	-0.420 904 75	-1.263 196 05	-1.022 113 41
U^2ST^2	0.900 788 20	0.591 731 15	0.437 074 40	1.570 837 04	2.343 292 90	3.201 941 58	2.636 848 51
US^4	0	0	0	0	0	0	0
US^2T^2	-0.916 327 39	-0.348 009 77	-0.225 389 52	-0.747 244 97	-0.863 183 52	-3.221 939 71	-2.848 660 61
UT^4	-0.021 506 24	0.064 635 42	0.040 150 09	0.151 499 73	0.154 840 92	-0.280 381 97	-0.055 956 71
S^5	0.024 507 36	0.010 893 18	0.020 545 42	0.043 126 20	0.120 173 36	0.201 861 74	0.228 222 77
S^3T^2	0.170 043 44	0.062 516 42	0.038 046 75	0.066 042 26	0.413 046 72	0.979 043 79	0.708 154 39
ST^4	-0.074 419 85	-0.022 893 67	-0.041 477 28	-0.086 395 17	-0.106 116 76	-0.594 430 58	-0.244 757 84
$\Phi_{2,1}$	1	1	1	1	1	1	1
RU	-1.006 787 34	-1.181 035 72	-1.499 201 50	-2.035 990 83	-1.872 706 05	-2.339 761 64	-2.887 190 93
RS	0.235 716 94	-0.253 808 22	-0.082 462 12	-0.012 992 80	-0.610 762 91	-0.565 023 08	-0.352 702 07
U^3/R	0.076 333 40	0.090 809 12	0.130 887 96	0.195 078 67	0.183 037 02	0.086 040 29	0.278 778 10

that the wave function belongs to a certain multiplet. The configuration state functions are not constructed to be orthonormal. The normalization of the whole wave function is also arbitrary, so we are free to set the largest coefficient to “1” if we properly rescale the other coefficients. Consequently, the determinantal coefficients cannot be directly compared to those from a configuration interaction or an MCSCF calculation.

In Table VI, we list the coefficients in the Jastrow part of the wave function. The coefficients of the odd powers in T are zero and are not listed in the table. These coefficients are used both for like and unlike spin electrons, with the exception that b is set to 1/4 for like spin electrons. Algebraic relations exist among the coefficients due to the imposition of the cusp conditions: the coefficients of U , S , US , S^2 , US^2 , S^3 , US^3 , S^4 , US^4 , and S^5 are chosen as dependent parameters. As far as the nonanalytic terms, we decided on an

empirical basis to include only $\Phi_{2,1}$ and three $\Phi_{2,0}$ -like terms. The coefficient of $\Phi_{2,1}$ is fixed to one.

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