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Multiconfiguration wavefunctions for Quantum Monte Carlo calculations of first-row diatomic molecules

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We use the variance minimization method to determine accurate wavefunctions for first-row homonuclear diatomic molecules. The form of the wavefunction 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 wavefunction are optimized. The optimized wavefunctions recover 77-94% of the correlation energy in variational Monte Carlo and 91-99% of the correlation energy in diffusion Monte Carlo.

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 wavefunction. It is possible to construct a compact and accurate wavefunction if its functional form incorporates the analytical features of the true wavefunction. CI, for example, uses an expansion in determinants of single-particle orbitals that is slowly convergent because it cannot reproduce the cusp in the wavefunction at the electron-electron coalescence [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 wavefunction with 50-100 free parameters can be found that yields energies comparable to a CI wavefunction with millions of determinants.

In QMC methods, the inter-electron cusp is built into the wavefunction 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 inter-electron distances so that it directly correlates electrons with each other. 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 multi-center systems. The other component of the wavefunction is the determinantal part. Although a single determinant wavefunction has often been employed, it is well known that the non-dynamic 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 wavefunctions for molecules and leads to accurate results when combined with a generalized Jastrow 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 wavefunctions increase with atomic number, some of the more interesting QMC calculations of finite and extended systems have been valence-only calculations [4]. However, there is some evidence that the errors introduced in QMC by using pseudopotentials calculated within the local density approximation [5] or HF [6] 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 [7] and [8]) but the only attempt to systematically study the performance of QMC methods for first row molecules [9] does not provide encouraging results. The authors use a simple form of the Jastrow factor and a single determinant wavefunction and they recover a progressively smaller fraction of the correlation energy for molecules of increasing size, N_2 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 multi-configuration 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/mole = 0.0016 Hartree/molecule). Since our wavefunctions are the result of a non linear 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 wavefunctions. Nevertheless, our results provide a benchmark to which future molecular QMC calculations can be compared.

In section II, the functional form of the trial wavefunction is described. In section III, we briefly present the variance optimization method used to determine the parameters that enter in the molecular wavefunctions, the variational Monte Carlo (VMC) and the diffusion Monte Carlo (DMC) methods. In section IV, we report the ground state energies we obtained for the first row diatomic molecules with our trial wavefunctions 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 list the parameters that enter in the most accurate wavefunction for each molecule and, in Appendix B, we briefly discuss two more general forms of the wavefunction than the one used in the rest of the paper.

II. FUNCTIONAL FORM OF THE WAVEFUNCTION

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

$$\Psi = \left(\sum_n d_n \mathrm{D}_n^{\uparrow} \mathrm{D}_n^{\downarrow} \right) \mathrm{J}(r_{ij}) \tag{1}$$

$\mathrm{D}_n^{\uparrow}$ and $\mathrm{D}_n^{\downarrow}$ 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:

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

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_α} is the normalization of the radial part of the basis function and is equal to $((2\,\zeta_{k_\alpha})^{2\,n_{k_\alpha}+1}/(2\,n_{k_\alpha})!)^{1/2}$. 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 wavefunction 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 wavefunction was used with the orbitals frozen to be the HF orbitals. We believe that in order to obtain wavefunctions 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 $\{d_i\}$. 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 $\{d_i\}$. As a consequence, there is a considerable reduction in the number of free parameters.

A simple, commonly used Jastrow factor is:

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

where the product is over all pairs of electrons. Imposing the electron-electron cusp condition ($\partial \mathrm{J}/\partial r_{ij} = \mathrm{J}/2$ for unlike spin and $\mathrm{J}/4$ 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 non-symmetrical Jastrow yields a wavefunction 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 wavefunction that is not an eigenstate of S^2 or violating the cusp conditions for parallel spin electrons by correlating them with the same Jastrow 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 non-symmetrical Jastrow, with the understanding that we are breaking the spin symmetry and that our wavefunctions will be contaminated by other spin components. This choice is motivated by the fact that the non-symmetrical Jastrow yields wavefunctions 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 inter-electron coordinates and is therefore completely symmetric under spatial rotations and reflections.

The generalized Jastrow factor $\mathrm{J}(r_i, r_j, r_{ij})$ we use is a modification of the form introduced by Umrigar *et al.* [2] which yields good wavefunctions for atoms by explicitly introducing electron-electron-nucleus correlation. This form is a generalization of the Boys and Handy [15] form. Subsequently, other authors [10,16], using arguments based on backflow wavefunctions, 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, $A_{\alpha i}$, the electron-electron correlation, B_{ij}, and the electron-electron-nucleus correlation, $C_{\alpha ij}$:

$$\mathrm{J}(r_i, r_j, r_{ij}) = \prod_{\alpha i} \exp\left(A_{\alpha i}\right) \prod_{ij} \exp\left(B_{ij}\right) \prod_{\alpha ij} \exp\left(C_{\alpha ij}\right). \tag{4}$$

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 [17]. We express the generalized Jastrow in terms of scaled interparticle distances:

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

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

$$A_{\alpha i} = \frac{a\, R_{i\alpha}}{1 + a'\, R_{i\alpha}}, \tag{6}$$

$$B_{ij} = \frac{b\, U}{1 + b'\, U}, \tag{7}$$

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

P and P' are complete polynomials in U, S and T. F and F' contain non-analytic terms in U, S, T and the hyperradius $R = (R_{i\alpha}^2 + R_{j\alpha}^2)^{1/2}$:

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

where 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. These non-analytic terms 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]. The ground state wavefunction of helium cannot be expanded in an analytic series of the interparticle coordinates but there exists an expansion in powers of the hyperradius and its logarithm [19]:

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

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. Ermolaev [20] 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. [21]; 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 Maslen [22] 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 $\phi_{3,1}$ is given in Eq. 74 of Ref. [21].

One problem with the inclusion in a trial wavefunction 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 wavefunction that satisfies the cusp conditions given that all the other terms are cuspless, so it cures the divergence of the local energy at the nucleus and at the 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 discontinuity 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 [18]. Since we know the lowest order terms of the Fock expansion, we can simply include them in the wavefunction 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 [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 wavefunction. 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 wavefunction by setting b to 1/2 for antiparallel spin electrons and to 1/4 for parallel spin electrons. The electron-nucleus cusp condition ($\partial \widehat{\Psi}/\partial r_{i\alpha} = -Z\,\Psi$ at $r_{i\alpha} = 0$, where the hat denotes a spherical average) relates the coefficient a of the Jastrow to the parameters of the determinantal part through the equations

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

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

The electron-electron-nucleus term in the wavefunction (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 wavefunctions [2,3] and now we investigate it within molecular systems. For all the first row homonuclear molecules, we generated a set of wavefunctions by using a ratio of two $4^{\rm th}$ order polynomials and another set with a simple $5^{\rm th}$ 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 wavefunction in (Eq. 8) with P being a $5^{\rm th}$ order polynomial and $P' = 0$.

In the most general case, the terms $A_{\alpha i}$, B_{ij} and $C_{\alpha ij}$ 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 inter-electron coordinates to yield a wavefunction 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 inter-electron cusp conditions but we limit the asymmetry of the Jastrow to the b term with the hope that, the less asymmetric the Jastrow 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. We summarize the constraints in our wavefunction:

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

Observe that we introduce the non-analytic 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 ^{1}S 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 non-analytic 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 antiparallel 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 B, we discuss the form of two spin unrestricted wavefunctions that can be obtained when some of the above constraints in the Jastrow and in the determinantal part are relaxed.

A $5^{\rm th}$ 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 5 electron-electron and 5 electron-nucleus cusp conditions are imposed, the number of free parameters reduces to 23. There are in addition 6 $\Phi_{2,0}$-like and 6 $\Phi_{3,1}$-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 10. The wavefunctions presented in this paper include only 3 of these 10 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 wavefunction.

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 wavefunction 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 principal quantum number does not exceed those occurring in the HF configuration. To select these additional configurations, we obtain a MCSCF wavefunction using GAMESS and we add the configurations with a large weight in the GAMESS output to our best single configuration wavefunction. 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 wavefunction presented in the previous section has a large number of parameters, of the order of 60. To optimize such a complicated wavefunction, the variance minimization method has been shown to be a stable method [2,23] as opposed to total energy minimization which is feasible only for wavefunctions 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 wavefunction available before we start the optimization, Ψ_0:

$$\sigma^2_{\rm opt}[\Psi] = \sum_i^{N_c} \left[\frac{\mathcal{H}\Psi(R_i)}{\Psi(R_i)} - E_{\rm guess}\right]^2 w(R_i)/\sum_i^{N_c} w(R_i). \tag{12}$$

$E_{\rm guess}$ 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 wavefunction 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 $\sigma_{\rm opt}$ by having a few configurations gain a very large weight and a local energy that is very close to $E_{\rm guess}$. 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 wavefunction 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 wavefunction being the true wavefunction. However, setting the guessed energy lower than the variational energy in the above scheme is equivalent to a simultaneous minimization of the variance and of the energy [24].

B. Variational/Metropolis Monte Carlo

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

$$\mathrm{E}_{\rm VMC} = \frac{1}{N}\sum_i^N \frac{\mathcal{H}\Psi(R_i)}{\Psi(R_i)}. \tag{13}$$

We use a very efficient accelerated Metropolis method [25] that allows us to simultaneously make large Monte Carlo moves and have a high acceptance. Consequently, the auto-correlation time for the expectation values calculated is small.

C. Diffusion Monte Carlo

The imaginary-time evolution operator $\exp(-\mathcal{H}\tau)$ is used to project out the ground state from the trial wavefunction within the fixed-node and the short-time approximations [26]. 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.

IV. RESULTS AND CONCLUSIONS

We have calculated both single and multi-configuration wavefunctions 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 multi-configuration wavefunctions are listed in appendix A. All trial wavefunctions are optimized at the experimental bond length. The experimental bond lengths are those quoted in Ref. [27] with the exception that the bond length of Be_2 is taken from Ref. [28]. In order to calculate the correlation energy recovered by our wavefunctions in VMC and DMC, we need the HF energies and the exact non-relativistic, infinite nuclear mass energies. We used the HF energies calculated by Cade and Wahl at the experimental bond length [27]. 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 [29] and at 4.00 a_0 [27]. We estimated the exact energies as the sum of the accurate non-relativistic, infinite nuclear mass atomic energies by Davidson *et al.* [30] and the experimental dissociation energies corrected for the zero point motion as given in [31]. For B_2, we use a theoretical estimate of the dissociation energy [32] because the experimental value has only been determined with an uncertainty of 14 kcal/mole [31]. For Be_2, the dissociation energy is from [29] and for Li_2 from [33].

We use three measures of goodness to judge the quality of a wavefunction: the standard deviation of the local energy in VMC, $\sigma_{\rm VMC}$, the VMC energy, $E_{\rm VMC}$, and the DMC energy, $E_{\rm DMC}$. 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 $\sigma_{\rm VMC}$ by more than a factor of two. Consequently, the single configuration wavefunction gives mediocre energies, 76% and 90% of the correlation energy in VMC and DMC respectively, but the two-configuration wavefunction recovers 99.2% and 99.9% of the correlation energy in VMC and DMC [3] respectively.

TABLE I. Total energies of Li_2 in VMC and DMC with increasing number of configuration state functions (CSF). We list the configurations omitting the core doubly occupied molecular orbital $1\sigma_g$. $E_c^{\rm VMC}$ and $E_c^{\rm DMC}$ are the percentages of correlation energy in VMC and DMC. $\sigma_{\rm VMC}$ 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	$E_{\rm VMC}$	$E_{\rm DMC}$	$E_c^{\rm VMC}$ (%)	$E_c^{\rm DMC}$ (%)	$\sigma_{\rm VMC}$
$2\sigma_g^2$	-14.97343(7)	-14.9911(1)	82.26(5)	96.5(1)	.112
$2\sigma_u^2$	-14.97745(6)	-14.9909(1)	85.51(4)	96.4(1)	.098
$1\pi_{ux}^2 + 1\pi_{uy}^2$	-14.98404(5)	-14.9923(1)	90.83(4)	97.5(1)	.086
$3\sigma_g^2$	-14.98850(4)	-14.9938(1)	94.43(4)	98.7(1)	.086

TABLE II. Total energies in VMC ($E_{\rm VMC}$) and DMC ($E_{\rm DMC}$) for our best single and multi-configuration state function wavefunctions. $E_c^{\rm VMC}$ and $E_c^{\rm DMC}$ are the percentages of correlation energy recovered in VMC and DMC. $\sigma_{\rm VMC}$ is the root mean square fluctuation of the local energy in VMC and $T_{\rm corr}$ 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 wavefunction. R_0 is the experimental bond length, $E_{\rm HF}$ the HF energy and E_0 the exact, non-relativistic, infinite nuclear mass energy. Bond lengths are in Bohrs and energies are in Hartree atomic units.

molecule	CSF,D	R_0	$E_{\rm HF}$	E_0	$E_{\rm VMC}$	$E_{\rm DMC}$	$E_c^{\rm VMC}$ (%)	$E_c^{\rm DMC}$ (%)	$\sigma_{\rm VMC}$	$T_{\rm corr}$
Li_2	1,1	5.051	-14.87152	-14.9954	-14.97343(7)	-14.9911(1)	82.26(5)	96.5(1)	.112	1.39
	4,5				-14.98850(4)	-14.9938(1)	94.43(4)	98.7(1)	.086	1.06
Be_2	1,1	4.63	-29.13242	-29.33854(5)	-29.2782 (1)	-29.3176(4)	70.70(7)	89.8(2)	.242	1.45
	2,2				-29.2979 (1)	-29.3231(3)	80.28(6)	92.5(1)	.228	1.19
B_2	1,1	3.005	-49.09088	-49.415(2)	-49.3115 (3)	-49.3778(8)	68.06(8)	88.5(2)	.432	1.60
	6,11				-49.3602 (2)	-49.3979(6)	83.10(7)	94.7(2)	.408	1.15
C_2	1,1	2.3481	-75.40620	-75.923(5)	-75.7567 (5)	-75.8613(8)	67.82(9)	88.1(2)	.707	1.71
	4,16				-75.8282 (4)	-75.8901(7)	81.66(7)	93.6(1)	.641	1.27
N_2	1,1	2.068	-108.9928	-109.5423	-109.3756 (6)	-109.487 (1)	69.7 (1)	89.9(2)	.935	1.46
	4,17				-109.4148 (5)	-109.4932(8)	76.80(8)	91.1(1)	.891	1.09
O_2	1,1	2.282	-149.6659	-150.3268	-150.1507 (6)	-150.268 (1)	73.4 (1)	91.0(2)	1.09	1.40
	4,7				-150.1846 (6)	-150.272 (1)	78.48(8)	91.7(2)	1.06	1.09
F_2	1,1	2.68	-198.7701	-199.5299	-199.3647 (7)	-199.478 (2)	78.26(9)	93.2(2)	1.23	1.22
	2,2				-199.4101 (6)	-199.487 (1)	84.23(8)	94.3(1)	1.19	0.97

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, $\sigma_{\rm VMC}$, $E_{\rm VMC}$ and $E_{\rm DMC}$ (except that the one- and two-configuration $E_{\rm DMC}$ and the three- and four-configuration $\sigma_{\rm VMC}$ 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 wavefunction.

In table II, we list the total energies obtained in VMC and DMC and $\sigma_{\rm VMC}$ obtained with our best single-determinant and multi-determinant wavefunctions. In figure IV, we plot the percentage of correlation energy recovered. The use of an efficient accelerated Metropolis algorithm [25] and a small time step error DMC algorithm [3] 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 76.8-94.4% for multi-configuration wavefunctions in VMC. The corresponding numbers are 88.1-96.5% and 91.1-98.7% in DMC. The smallest percentage of correlation energy recovered is not for the heaviest molecules but rather for the molecules in the middle of the row for which many configuration state functions make small but non-negligible contributions. There is considerable resemblance in the shapes of the VMC and DMC curves and the multi-configuration 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 $\sigma_{\rm VMC}$ and $E_{\rm VMC}$ 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, $\sigma_{\rm VMC}$, increases by more than a factor of 10 for both the single and the multi-configuration wavefunctions. The dependence of $\sigma_{\rm VMC}$ 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 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 figure IV, we show the autocorrelation time of the local energy in VMC, $T_{\rm corr}$, calculated as explained in Ref. [25]. The quantities shown in figure IV depend on the wavefunction alone whereas $T_{\rm corr}$ has also a strong dependence on the particular form of Metropolis algorithm used. We used the single-electron accelerated Metropolis algorithm described in Ref. [25] 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 $T_{\rm corr}$ 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, $T_{\rm corr}$ 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. Therefore, for the simple algorithm, an extra factor of Z^2 should be included in estimating the scaling of the computational cost with atomic number.

For all the molecules, the value of $T_{\rm corr}$ is smaller for the multi-configuration wavefunctions than the single-configuration ones. This is a consequence of the more rapid variation of the local energy for the multi-configuration wavefunctions: adding more configurations not only reduces the magnitude of the fluctuations of the local energy, $\sigma_{\rm VMC}$, 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 $T_{\rm corr}$ 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.

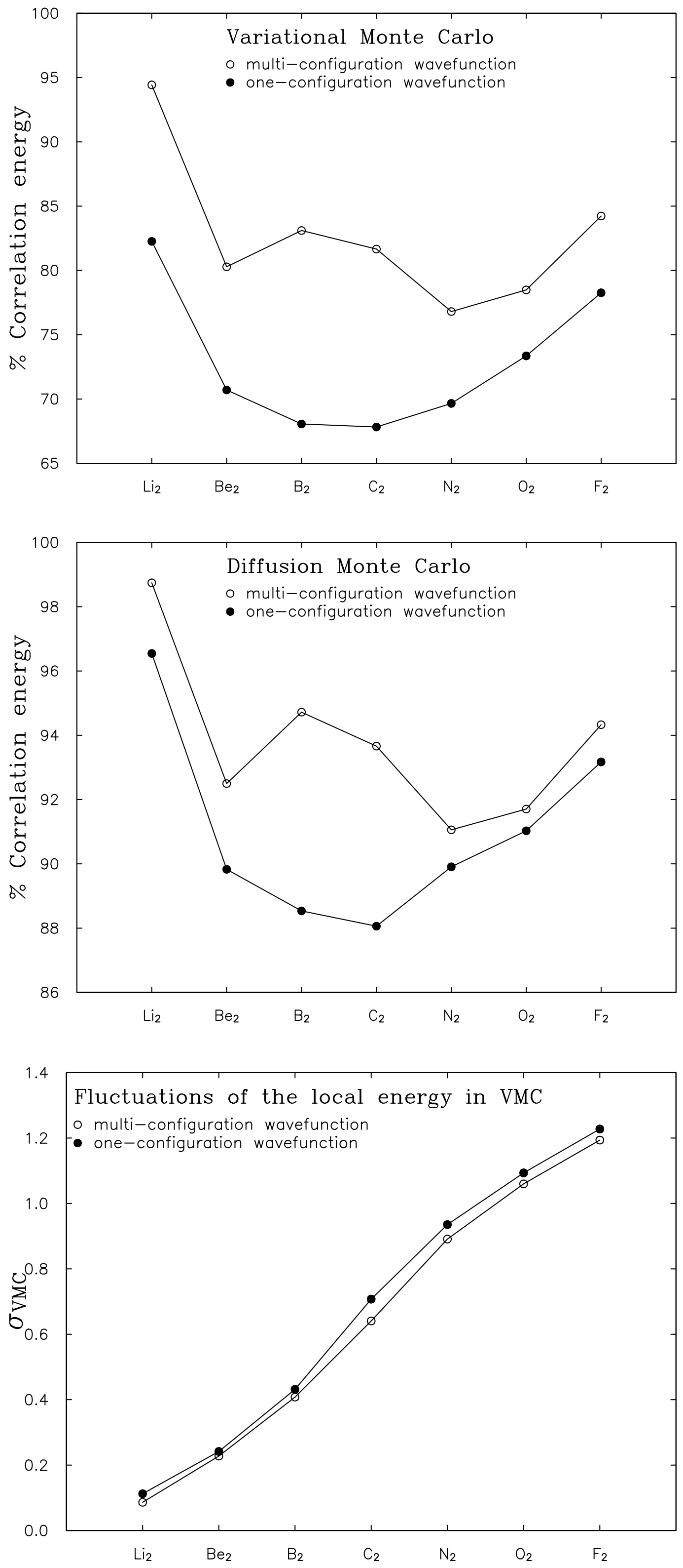

FIG. 1. Percentage of correlation energy in VMC (upper plot) and DMC (middle plot) and root mean square fluctuation $\sigma_{\rm VMC}$ (lower plot) with one-configuration (full circle) and multi-configuration (empty circle) wavefunctions.

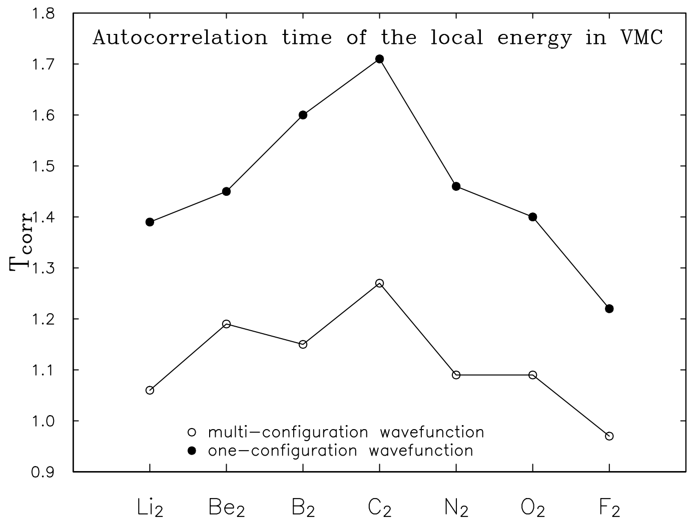

FIG. 2. Autocorrelation time of the local energy in VMC, T_{corr}, using the accelerated Metropolis algorithm of Ref. [25], for one-configuration (full circle) and multi-configuration (empty circle) wavefunctions.

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 wavefunction 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 wavefunction, so they do better than Schmidt *et al.* in spite of using a simple Jastrow. For completeness, we also compare with the results obtained by conventional quantum chemistry methods. Peterson *et al.* [31] 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 diffuse functions for each angular momentum.

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 *et al.* [9]	Schmidt *et al.* [10]	Sun *et al.* [13]	Peterson *et al.* [31]
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	76.80(8)	14(9)	55	–	74.8
O_2	78.48(8)	–	–	–	75.3
F_2	84.23(8)	–	–	–	76.2

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 Li_2, B_2, C_2 and N_2 but the statistical errors they report are so large (ranging from 5% for Li_2 to 14% for N_2) that it is not possible to make a meaningful comparison with our DMC results. For N_2, Reynolds *et al.* [11] obtain 89.3% of the correlation energy in DMC energy for a single configuration wavefunction. For Li_2, Sun *al.* [13] present DMC energies for both single configuration and three-configuration wavefunctions. For their optimized multi-configuration wavefunction, 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 wavefunction to the introduction of spurious nodes upon optimization. Since they do not give the parameters of the unoptimized wavefunction, 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 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 Li_2) are better than those in the literature. However, due to the nature of non-linear optimization, it is quite possible that further optimization could result in somewhat better wavefunctions. There is a near redundancy in the wavefunctions. Consequently, we can often find several wavefunctions with very different parameters that are nearly equivalent by all three measures of goodness, $\sigma_{\rm VMC}$, $E_{\rm VMC}$ and $E_{\rm DMC}$. 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 wavefunction.

The wavefunctions presented in Appendix A 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 incorporate this information into the wavefunction 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: MOLECULAR WAVEFUNCTIONS

We list the parameters entering in the molecular wavefunctions 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 "x" 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 one if the coefficients of 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 wavefunction has additional nodes. We tested our wavefunctions for additional nodes as follows. We selected random Monte Carlo configurations, 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 wavefunctions. One wavefunction was a single-configuration wavefunction whereas the other two were four-configuration wavefunctions, the suspect one of Table IV and another with nodeless $1\pi_u$ orbitals. We found no instances where the suspect wavefunction had additional nodes compared to the other two wavefunctions. Moreover in all cases the nodes of the two four-configuration wavefunction were closer to each other than to the nodes of the one-configuration wavefunction. Hence, we have no reason to discard the wavefunction 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 wavefunction with nodeless $1\pi_u$ orbitals.

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

	1s	1s	2s	2s	$2p_x$	$2p_x$	$2p_x$	$2p_z$	$2p_z$	3s
Li_2										
ζ	3.27995989	2.28831206	2.73880540	0.68577832	0.96258600	0.76444397	x	0.93704020	0.81001556	x
$1\sigma_g$	0.49668036	1.	0.68620629	-0.01084861	–	–	x	0.00381859	0.00273488	x
$1\sigma_u$	0.48879639	1.	0.67736088	0.00884097	–	–	x	0.01826701	-0.00000015	x
$2\sigma_g$	-0.52654417	0.	-0.60723826	1.	–	–	x	0.24461758	-0.34075401	x
$2\sigma_u$	0.01070161	0.	-0.00849443	1.	–	–	x	-0.20808381	0.26792925	x
$3\sigma_g$	0.03505375	0.	0.00152570	1.	–	–	x	0.38483371	-0.64664614	x
$1\pi_{ux}$	–	–	–	–	-0.41939565	1.	x	–	–	x
Be_2										
ζ	4.62189968	2.77264728	1.50225214	1.06823041	x	x	x	3.81191899	0.75123077	x
$1\sigma_g$	0.12199787	1.	-0.02900878	0.	x	x	x	-0.01985985	-0.00245281	x
$1\sigma_u$	0.12048334	1.	-0.06760440	0.06422096	x	x	x	-0.01644462	0.00938380	x
$2\sigma_g$	0.01242556	0.	-0.37842047	1.	x	x	x	0.00045121	0.18393314	x
$2\sigma_u$	0.00993392	0.	-0.33032906	1.	x	x	x	-0.00129038	-0.24395693	x
$3\sigma_g$	0.00140379	0.	-0.12408559	0.	x	x	x	-0.00190129	1.	x
B_2										
ζ	5.25858882	3.89858548	1.42212201	0.71047897	2.39724031	1.01837309	x	5.14563330	1.49472396	x
$1\sigma_g$	0.52804833	1.	0.	0.00435852	–	–	x	-0.03976780	0.00153091	x
$1\sigma_u$	0.53078079	1.	0.02500648	-0.00188813	–	–	x	-0.03757349	-0.00000243	x

$2\sigma_g$	0.19543628	0.	1.	0.03305034	–	–	x	0.00000088	0.18785475	x
$2\sigma_u$	0.13171980	0.	1.	0.70366078	–	–	x	-0.00912632	-0.38011972	x
$3\sigma_g$	0.04293544	0.	0.	-0.04621885	–	–	x	0.01013171	1.	x
$1\pi_{ux}$	–	–	–	–	0.21438715	1.	x	–	–	x
$1\pi_{gx}$	–	–	–	–	0.09022142	1.	x	–	–	x
C_2										
ζ	5.42573879	5.17211876	2.06725862	1.14222937	2.90510768	1.28599459	x	6.25972337	1.99411433	x
$1\sigma_g$	1.	0.	0.36898660	0.17458458	–	–	–	-0.02109262	0.18297338	x
$1\sigma_u$	0.76156641	1.	0.02649275	0.01114166	–	–	–	-0.04444475	-0.00000005	x
$2\sigma_g$	0.	1.	-0.26057513	-0.13104673	–	–	–	-0.02720989	-0.13469311	x
$2\sigma_u$	1.	0.	0.47357451	0.82774540	–	–	–	-0.02873624	-0.30292132	x
$3\sigma_g$	0.	0.	-0.12905685	-0.09583920	–	–	–	0.01352243	1.	x
$1\pi_{ux}$	–	–	–	–	0.29354104	1.	x	–	–	x
$1\pi_{gx}$	–	–	–	–	0.10503847	1.	x	–	–	x
N_2										
ζ	7.161651	5.30023927	1.99687020	1.15726712	4.59920878	1.90354196	1.06441579	6.73669933	2.05834355	x
$1\sigma_g$	0.81034563	1.	0.	0.01403989	–	–	–	-0.05496485	0.	x
$1\sigma_u$	0.80790955	1.	0.	0.01451722	–	–	–	-0.05595389	0.00674596	x
$2\sigma_g$	0.26637979	0.	1.	0.13484759	–	–	–	-0.00261276	0.	x
$2\sigma_u$	0.18172135	0.	1.	0.57382056	–	–	–	-0.01235877	-0.33950701	x
$3\sigma_g$	0.03864951	0.	0.	-0.28564034	–	–	–	0.02143523	1.	x
$3\sigma_u$	-0.07664487	0.	0.	0.45529379	–	–	–	0.02528901	1.	x
$1\pi_{ux}$	–	–	–	–	0.09306429	1.	0.43320847	–	–	x
$1\pi_{gx}$	–	–	–	–	0.06930760	0.74748175	1.	–	–	x
O_2										
ζ	8.37893035	5.83585377	2.03227845	1.11720107	5.47490240	2.01321122	1.22750443	6.17389874	2.04162265	x
$1\sigma_g$	0.85695328	1.	0.	0.01052597	–	–	–	-0.02538046	0.00162249	x
$1\sigma_u$	0.85507523	1.	0.	0.06369849	–	–	–	-0.02386335	0.01208177	x
$2\sigma_g$	0.15447439	0.	1.	-0.01064917	–	–	–	-0.00171337	-0.08414297	x
$2\sigma_u$	0.12035307	0.	1.	0.11753080	–	–	–	-0.00935689	-0.19254401	x
$3\sigma_g$	0.02032235	0.	0.	-0.24994105	–	–	–	0.04370540	1.	x
$3\sigma_u$	-0.03622421	0.	0.	-0.18279976	–	–	–	0.04864800	1.	x
$1\pi_{ux}$	–	–	–	–	0.07552323	1.	0.42381936	–	–	x
$1\pi_{gx}$	–	–	–	–	0.06672498	1.	0.52580598	–	–	x
F_2										
ζ	9.40563159	4.60915507	6.86646767	2.28915412	6.34292263	1.82409885	1.03869593	6.40563026	1.85836113	1.63631116
$1\sigma_g$	1.	-0.23912988	0.40653328	0.	–	–	–	-0.00511000	0.00824867	0.00003617
$1\sigma_u$	1.	-0.15013942	0.35571137	0.	–	–	–	-0.00611289	0.00260979	0.00365379
$2\sigma_g$	0.	-0.55814609	0.25264481	1.	–	–	–	-0.00000063	-0.05454680	0.02116684
$2\sigma_u$	0.	-0.57120235	0.26718304	1.	–	–	–	-0.00331032	-0.08307265	0.13441697
$3\sigma_g$	0.	-0.10099309	0.04784263	0.	–	–	–	0.05795116	1.	-0.04663035
$3\sigma_u$	0.	0.23337598	-0.11916628	0.	–	–	–	0.04660448	1.	0.30213344
$1\pi_{ux}$	–	–	–	–	0.05965082	1.	0.06278323	–	–	–
$1\pi_{gx}$	–	–	–	–	0.05907112	1.	0.17809041	–	–	–

In table V, we list the configuration state functions in the determinantal part of the wavefunctions 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 that the wavefunction belongs to a certain multiplet. The configuration state functions are not constructed to be orthonormal. The normalization of the whole wavefunction 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.

TABLE V. Configuration state functions in the determinantal part of the wavefunction. 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.	
	$2\sigma_g^2 \to 2\sigma_u^2$	-0.25819838	
	$2\sigma_g^2 \to 1\pi_u^2$	-0.16300208	$\pi_{ux}^2 + \pi_{uy}^2$
	$2\sigma_g^2 \to 3\sigma_u^2$	-0.63663264	
Be_2	$(2\sigma_g^2,\ 2\sigma_u^2)$	1.	
	$2\sigma_u^2 \to 3\sigma_g^2$	-0.18082768	
B_2	$(2\sigma_g^2,\ 2\sigma_u^2,\ 1\pi_{ux},\ 1\pi_{uy})$	1.	
	$2\sigma_u^2 \to 3\sigma_g^2$	-0.46020891	
	$1\pi_{ux}1\pi_{uy} \to 1\pi_{gx}1\pi_{gy}$	-0.24315278	
	$2\sigma_g \to 3\sigma_g$	0.20302269	$2\sigma_g^+ 3\sigma_g^- - 2\sigma_g^- 3\sigma_g^+$
	$2\sigma_u \pi_u \to 3\sigma_g \pi_g$	0.18234951	$\sigma_u^+ \pi_{ux}^+ \sigma_g^+ \pi_{gy}^- - \sigma_u^+ \pi_{ux}^+ \sigma_g^- \pi_{gy}^+ - \sigma_u^+ \pi_{uy}^+ \sigma_g^+ \pi_{gx}^- + \sigma_u^+ \pi_{uy}^+ \sigma_g^- \pi_{gx}^+$
		0.06868304	$\sigma_u^- \pi_{ux}^+ \sigma_g^+ \pi_{gy}^+ - \frac{1}{2}(\sigma_u^+ \pi_{ux}^+ \sigma_g^+ \pi_{gy}^- + \sigma_u^+ \pi_{ux}^+ \sigma_g^- \pi_{gy}^+)$
			$-(\sigma_u^- \pi_{uy}^+ \sigma_g^+ \pi_{gx}^+ - \frac{1}{2}(\sigma_u^+ \pi_{uy}^+ \sigma_g^+ \pi_{gx}^- + \sigma_u^+ \pi_{uy}^+ \sigma_g^- \pi_{gx}^+))$
C_2	$(2\sigma_g^2,\ 2\sigma_u^2,\ 1\pi_{ux}^2,\ 1\pi_{uy}^2)$	1.	
	$2\sigma_u^2 \to 3\sigma_g^2$	-0.19809465	
	$2\sigma_u\ 1\pi_u \to 3\sigma_g\ 1\pi_g$	-0.10749697	$\sigma_u^+ \pi_{ux}^- \pi_{gx}^+ \sigma_g^- - \sigma_u^+ \pi_{ux}^- \pi_{gx}^- \sigma_g^+ - \sigma_u^- \pi_{ux}^+ \pi_{gx}^+ \sigma_g^- + \sigma_u^- \pi_{ux}^+ \pi_{gx}^- \sigma_g^+$
			$+ \sigma_u^+ \pi_{uy}^- \pi_{gy}^+ \sigma_g^- - \sigma_u^+ \pi_{uy}^- \pi_{gy}^- \sigma_g^+ - \sigma_u^- \pi_{uy}^+ \pi_{gy}^+ \sigma_g^- + \sigma_u^- \pi_{uy}^+ \pi_{gy}^- \sigma_g^+$
	$1\pi_u^2 \to 1\pi_g^2$	-0.41731580	$\pi_{ux}^2 \pi_{gy}^2 + \pi_{uy}^2 \pi_{gx}^2$
			$-\frac{1}{2}(\pi_{ux}^+ \pi_{uy}^- \pi_{gx}^+ \pi_{gy}^- - \pi_{ux}^+ \pi_{uy}^- \pi_{gx}^- \pi_{gy}^+ - \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^+ \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^- \pi_{gy}^+)$
N_2	$(2\sigma_g^2,\ 2\sigma_u^2,\ 3\sigma_g^2,\ 1\pi_{ux}^2,\ 1\pi_{uy}^2)$	1.	
	$1\pi_u^2 \to 1\pi_g^2$	-0.22531590	$\pi_{ux}^2 \pi_{gy}^2 + \pi_{uy}^2 \pi_{gx}^2$
			$-\frac{1}{2}(\pi_{ux}^+ \pi_{uy}^- \pi_{gx}^+ \pi_{gy}^- - \pi_{ux}^+ \pi_{uy}^- \pi_{gx}^- \pi_{gy}^+ - \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^+ \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^- \pi_{gy}^+)$
		-0.05069832	$\pi_{ux}^+ \pi_{uy}^- \pi_{gx}^+ \pi_{gy}^- + \pi_{ux}^+ \pi_{uy}^- \pi_{gx}^- \pi_{gy}^+ + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^+ \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^+ \pi_{gx}^- \pi_{gy}^+$
			$-2(\pi_{ux}^+ \pi_{uy}^+ \pi_{gx}^- \pi_{gy}^- + \pi_{ux}^- \pi_{uy}^- \pi_{gx}^+ \pi_{gy}^+)$
	$3\sigma_g 1\pi_u \to 3\sigma_u 1\pi_g$	0.04268351	$\sigma_g^+ \pi_{ux}^- \sigma_u^+ \pi_{gx}^- - \sigma_g^+ \pi_{ux}^- \sigma_u^- \pi_{gx}^+ - \sigma_g^- \pi_{ux}^+ \sigma_u^+ \pi_{gx}^- + \sigma_g^- \pi_{ux}^+ \sigma_u^- \pi_{gx}^+$
			$+ \sigma_g^+ \pi_{uy}^- \sigma_u^+ \pi_{gy}^- - \sigma_g^+ \pi_{uy}^- \sigma_u^- \pi_{gy}^+ - \sigma_g^- \pi_{uy}^+ \sigma_u^+ \pi_{gy}^- + \sigma_g^- \pi_{uy}^+ \sigma_u^- \pi_{gy}^+$
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.	

	$1\pi_{ux}1\pi_{uy} \rightarrow 1\pi_{gx}1\pi_{gy}$	-0.31571961	
	$3\sigma_g^2 \rightarrow 3\sigma_u^2$	-0.16137915	
	$3\sigma_g 1\pi_u \rightarrow 3\sigma_u 1\pi_g$	0.08582248	$\sigma_g^+\sigma_u^-\pi_{ux}^+\pi_{gy}^+ - \sigma_g^-\sigma_u^+\pi_{ux}^+\pi_{gy}^+ - \sigma_g^+\sigma_u^-\pi_{uy}^+\pi_{gx}^+ + \sigma_g^-\sigma_u^+\pi_{uy}^+\pi_{gx}^+$
F_2	$(2\sigma_g^2, 2\sigma_u^2, 3\sigma_g^2, 1\pi_{ux}^2, 1\pi_{uy}^2, 1\pi_{gx}^2, 1\pi_{gy}^2)$	1.	
	$3\sigma_g^2 \rightarrow 3\sigma_u^2$	-0.40839532	

In table VI, we list the coefficients in the Jastrow part of the wavefunction. 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 non-analytic 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.

TABLE VI. Coefficients in the generalized Jastrow factor.

	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2
κ	0.82538	0.65218	0.72910	0.94149	1.08053	1.26394	1.1693
a	-1.02201620	-0.83463132	-0.48597970	-0.71775746	-0.65833061	-0.64944858	-0.26109075
a'	1.15947946	0.00483375	0.13536768	-0.06369385	-0.8341518	-0.02515861	0.22306985
b	0.5	0.5	0.5	0.5	0.5	0.5	0.5
b'	0.61203730	0.94714228	1.49781969	1.82602291	1.69788097	2.43371077	2.32732819
U	0.	0.	0.	0.	0.	0.	0.
S	0.	0.	0.	0.	0.	0.	0.
U^2	0.11671020	0.62605245	0.89691338	1.19368109	1.23628493	2.28887621	2.41241296
US	0.71190615	0.83511837	1.06009555	1.43966292	1.32420315	1.65446132	2.04155229
S^2	-0.43145485	-0.01549994	-0.24781333	-0.43184051	-0.18078037	-0.42695989	-0.75904085
T^2	0.04235669	0.27515513	0.24100338	0.28149456	0.17593975	0.11775923	0.08538426
U^3	0.53175346	-0.00813873	-0.01170476	-0.15460480	0.62962070	-0.11888607	-1.71248873
U^2S	-0.38959387	-0.59811395	-0.92657104	-1.35379215	-1.71559267	-3.74181658	-2.98378548
US^2	0.	0.	0.	0.	0.	0.	0.
UT^2	0.05626528	-0.25235141	-0.32485334	-0.34822646	-0.70345769	-1.31867407	-0.09042590
S^3	0.25708077	0.11908369	0.20030146	0.31882697	0.61105623	0.86831364	1.06786237
ST^2	0.26911788	0.26383993	0.32404003	0.29914168	1.52449140	1.50047247	0.40065342
U^4	-0.34015910	-0.08822773	0.08069458	0.05440071	-0.44139963	0.63548249	1.56566911
U^3S	-0.04282564	0.02536724	-0.30753481	-0.40960050	-0.96302156	-1.01364514	-0.15313797
U^2S^2	0.29884409	0.30961549	0.67393674	1.20472966	1.76466598	3.93860848	3.00314709
U^2T^2	0.12661773	0.66303859	0.60858542	1.55020409	1.98306644	1.19485769	1.35874335
US^3	0.	0.	0.	0.	0.	0.	0.
UST^2	-0.44648370	-0.58362447	-0.40604987	-1.23659955	-2.30865134	0.26977921	-0.12352564
S^4	-0.13977320	-0.06387960	-0.10810296	-0.18917845	-0.42864023	-0.68378332	-0.80287742
S^2T^2	0.33669601	0.12862034	-0.03147302	0.20755968	-0.52625266	-0.90163871	0.09855252
T^4	0.04725450	-0.08834322	-0.05079853	-0.15516591	-0.20143302	0.36723599	0.01192137
U^5	-0.06532812	-0.01605750	-0.16704457	-0.31623882	-1.13308576	-1.10544771	-0.40074736
U^4S	0.29915696	0.06612945	0.19920785	0.44442045	1.83305175	0.87513234	-0.55842472
U^3S^2	-0.20342959	-0.04115217	-0.00470850	-0.04999229	-0.47942695	0.07300354	0.42868125
U^3T^2	-0.22561317	-0.40311179	-0.26883990	-1.08992909	-1.00945458	-0.53860911	-1.29844118
U^2S^3	-0.01486689	-0.04181306	-0.13166720	-0.29610563	-0.42090475	-1.26319605	-1.02211341
U^2ST^2	0.90078820	0.59173115	0.43707444	1.57083704	2.34329290	3.20194158	2.63684851
US^4	0.	0.	0.	0.	0.	0.	0.
US^2T^2	-0.91632739	-0.34800977	-0.22538952	-0.74724497	-0.86318352	-3.22193971	-2.84866061
UT^4	-0.02150624	0.06463542	0.04015009	0.15149973	0.15484092	-0.28038197	-0.05595671
S^5	0.02450736	0.01089318	0.02054542	0.04312620	0.12017336	0.20186174	0.22822277
S^3T^2	0.17004344	0.06251642	0.03804675	0.06604226	0.41304672	0.97904379	0.70815439
ST^4	-0.07441985	-0.02289367	-0.04147728	-0.08639517	-0.10611676	-0.59443058	-0.24475784
$\Phi_{2,1}$	1.	1.	1.	1.	1.	1.	1.
RU	-1.00678734	-1.18103572	-1.49920150	-2.03599083	-1.87270605	-2.33976164	-2.88719093
RS	0.23571694	-0.25380822	-0.08246212	-0.01299280	-0.61076291	-0.56502308	-0.35270207
U^3/R	0.07633340	0.09080912	0.13088796	0.19507867	0.18303702	0.08604029	0.27877810

APPENDIX B: GENERAL SPIN UNRESTRICTED WAVEFUNCTIONS

As explained in section II, we use a restricted form of the Jastrow factor where only the b coefficients are different for antiparallel and parallel spin electrons. Consequently, the electron-electron cusp conditions are satisfied while the degree of asymmetry is small ensuring little admixture of higher spin components. An alternative approach could be to relax the constraints on the Jastrow.

The first wavefunction we present represents the most general wavefunction we can construct. It corresponds to the wavefunction 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 need no longer vanish. As far as the determinantal wavefunction is concerned, we no longer have to construct it to be an eigenstate of S^2. As a consequence, up and down orbitals, $\phi_i^\uparrow$ and $\phi_i^\downarrow$ can now be different. The second wavefunction corresponds to a wavefunction 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 wavefunctions, 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. $b^{\uparrow\downarrow} = 1/2 \qquad b^{\uparrow\uparrow} = b^{\downarrow\downarrow} = 1/4$.
2. $a^\uparrow = a^\downarrow \qquad a'^\uparrow = a'^\downarrow \qquad b^{\uparrow\downarrow} = 1/2 \qquad b^{\uparrow\uparrow} = b^{\downarrow\downarrow} = 1/4 \qquad b'^{\uparrow\uparrow} = b'^{\downarrow\downarrow} \qquad c^{\uparrow\uparrow} = c^{\downarrow\downarrow} \qquad \phi_i^\uparrow = \phi_i^\downarrow$,

For the lightest molecules, after generating an optimal restricted wavefunction, we tried relaxing some constraints allowing the antiparallel spin electron coefficients to differ from the parallel ones. We still kept the non-analytic 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 wavefunctions of significantly better quality than the minimally unrestricted ones described in the rest of the paper.

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