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Correlated geminal wave function for molecules: An efficient resonating valence bond approach

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We show that a simple correlated wave function, obtained by applying a Jastrow correlation term to an antisymmetrized geminal power, based upon singlet pairs between electrons, is particularly suited for describing the electronic structure of molecules, yielding a large amount of the correlation energy. The remarkable feature of this approach is that, in principle, several resonating valence bonds can be dealt simultaneously with a single determinant, at a computational cost growing with the number of electrons similar to more conventional methods, such as Hartree-Fock or density functional theory. Moreover we describe an extension of the stochastic reconfiguration method, which was recently introduced for the energy minimization of simple atomic wave functions. Within this extension the atomic positions can be considered as further variational parameters, which can be optimized together with the remaining ones. The method is applied to several molecules from Li_2 to benzene by obtaining total energies, bond lengths and binding energies comparable with much more demanding multiconfiguration schemes. © *2004 American Institute of Physics.*
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I. INTRODUCTION

The comprehension of the nature of the chemical bond deeply lies on quantum mechanics; since the seminal work by Heitler and London,[1] very large steps have been made towards the possibility to predict the quantitative properties of the chemical compounds from a theoretical point of view. Mean field theories, such as Hartree-Fock (HF) have been successfully applied to a wide variety of interesting systems, although they fail in describing those in which the correlation is crucial to characterize correctly the chemical bonds. For instance, the molecular hydrogen H_2, the simplest and first studied molecule, is poorly described by a single Slater determinant in the large distance regime, which is the paradigm of a strongly correlated bond; indeed, in order to avoid expensive energy contributions—the so called ionic terms—that arise from two electrons of opposite spin surrounding the same hydrogen atom, one needs at least two Slater determinants to deal with a spin singlet wave function containing bonding and antibonding molecular orbitals. Moreover at the bond distance it turns out that the resonance between those two orbitals is important to yield accurate bond length and binding energy, as the correct rate between the ionic and covalent character is recovered. Another route that leads to the same result is to deal with an antisymmetrized geminal power (AGP) wave function, which includes the correlation in the geminal expansion; Barbiellini in Ref. 2 gave an illuminating example of the beauty of this approach solving merely the simple problem of the H_2 molecule.

On the other hand the variational methods based on the configuration interaction (CI) technique, which is able to take into account many Slater determinants, have been shown to be successful for small molecules [e.g., Be_2 Ref. 3]. In these cases it is indeed feasible to enlarge the variational basis up to the saturation, the electron correlation properties are well described and consequently all the chemical properties can be predicted with accuracy. However, for interesting systems with a large number of atoms this approach is impossible with a reasonable computational time. Coming back to the H_2 paradigm, it is straightforward to show that a gas with N H_2 molecules, in the dilute limit, can be dealt accurately only with 2^N Slater determinants, otherwise one is missing important correlations due to the antibonding molecular orbital contributions, referred to *each* of the N H_2 molecules. Therefore, if the accuracy in the total energy per atom is kept fixed, a CI-like approach does not scale polynomially with the number of atoms. Although the polynomial cost of these quantum chemistry algorithms—ranging from N^5 to N^7—is not prohibitive, a loss of accuracy, decreasing exponentially with the number of atoms is always implied, at least in their simplest variational formulations. This is related to the loss of size consistency of a truncated CI expansion. On the other hand, this problem can be overcome by coupled cluster methods, which however, in their practical realization are not variational.[4]

An alternative approach, not limited to small molecules, is based on density functional theory (DFT). This theory is in principle exact, but its practical implementation requires an approximation for the exchange and correlation functionals based on first principles, such the local density approximation (LDA) and its further gradient corrections (GGA), or on semiempirical approaches, such as BLYP and B3LYP. For this reason, even though much effort has been made so far to

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go beyond the standard functionals, DFT is not completely reliable in those cases in which the correlation plays a crucial role. Indeed it fails in describing HT_c superconductors and Mott insulators, and in predicting some transition metal compounds properties, whenever the outermost atomic d shell is near half-filled, as for instance, in the high potential iron proteins.[5] Also H_2 molecule in the large distance regime must be included in that list, since the large distance Born-Oppenheimer energy surface, depending on van der Waals forces, is not well reproduced by the standard functionals, although recently some progress has been made to include these important contributions.[6]

Quantum Monte Carlo (QMC) methods are alternative to the previous ones and until now they have been mainly used in two versions.

(i) Variational Monte Carlo (VMC) applied to a wave function with a Jastrow factor that fulfills the cusp conditions and optimizes the convergence of the CI basis.[7,8]

(ii) Diffusion Monte Carlo (DMC) algorithm used to improve, often by a large amount, the correlation energy of any given variational guess in an automatic manner.[9]

Hereafter we want to show that a large amount of the correlation energy can be obtained with a single determinant, using a size-consistent AGP-Jastrow (JAGP) wave function. Clearly our method is approximate and in some cases not yet satisfactory, but in a large number of interesting molecules we obtain results comparable and even better than multideterminants schemes based on few Slater determinants per atom that are affordable by QMC only for rather small molecules.

Moreover, we have extended the standard stochastic reconfiguration (SR) method to treat the atomic positions as further variational parameters. This improvement, together with the possibility to work with a single determinant, has allowed us to perform a structural optimization in a nontrivial molecule such as the benzene radical cation, reaching the chemical accuracy with an all-electron and feasible variational approach.

The paper is organized as follows: In Sec. II we introduce the variational wave function, which is expanded over a set of nonorthogonal atomic orbitals both in the determinantal AGP and the Jastrow part. This basis set is consistently optimized using the method described in Sec. III that, as mentioned before, allows also the geometry optimization. Results and discussions are presented in the remaining sections.

II. FUNCTIONAL FORM OF THE WAVE FUNCTION

In this paper we are going to extend the application of the JAGP wave function, already used to study some atomic systems.[10] We generalize its functional form in order to describe the electronic structure of a generic cluster containing several nuclei. With the aim to determine a variational wave function, suitable for a complex electronic system, it is important to satisfy, as we require in the forthcoming chapters, the "size consistency" property: if we smoothly increase the distance between two regions A and B each containing a given number of atoms, the many-electron wave function Ψ factorizes into the product of space-disjoint terms $\Psi = \Psi_A$ $\otimes \Psi_B$ as long as the interaction between the electrons coupling the different regions A and B can be neglected. In this limit the total energy of the wave function approaches the sum of the energies corresponding to the two space-disjoint regions. This property, which is obviously valid for the exact many-electron ground state, is not always fulfilled by a generic variational wave function.

Our variational wave function is defined by the product of two terms, namely, a Jastrow J and an antisymmetric part ($\Psi = J\Psi_{AGP}$). If the former is an explicit contribution to the dynamic electronic correlation, the latter is able to treat the nondynamic one arising from near degenerate orbitals through the geminal expansion. Therefore our wave function is highly correlated and it is expected to give accurate results especially for molecular systems. The Jastrow term is further split into a two-body and a three-body factors, $J = J_2 J_3$, described in the following sections after the AGP part.

A. Pairing determinant

As is well known, a simple Slater determinant provides the exact exchange electron interaction but neglects the electronic correlation, which is by definition the missing energy contribution. In the past different strategies were proposed to go beyond Hartree-Fock theory. In particular a sizable amount of the correlation energy is obtained by applying to a Slater determinant a so called Jastrow term, which explicitly takes into account the pairwise interaction between electrons. QMC allows to deal with this term in an efficient way.[11] On the other hand, within the quantum chemistry community AGP is a well known ansatz to improve the HF theory, because it implicitly includes most of the double excitations of a HF state.

Recently we proposed a trial function for atoms, which includes both the terms. Only the interplay between them yields in some cases, such as Be or Mg, an extremely accurate description of the correlation energy. In this work we extend this promising approach to a number of small molecular systems with known experimental properties, which are commonly used for testing new numerical techniques.

The major advantage of this approach is the inclusion of many CI expansion terms with the computational cost of a single determinant, which allow us to extend the calculation with a full structural optimization up to benzene, without a particularly heavy computational effort on a single processor machine. For an unpolarized system containing N electrons (the first $N/2$ coordinates are referred to the up spin electrons) the AGP wave function is a $N/2 \times N/2$ pairing matrix determinant, which reads

$$\Psi_{AGP}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \det[\Phi_{AGP}(\mathbf{r}_i, \mathbf{r}_{j+N/2})], \quad (1)$$

and the geminal function is expanded over an atomic basis

$$\Phi_{AGP}(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) = \sum_{l,m,a,b} \lambda_{a,b}^{l,m} \phi_{a,l}(\mathbf{r}^\uparrow) \phi_{b,m}(\mathbf{r}^\downarrow), \quad (2)$$

where indices l, m span different orbitals centered on atoms a, b, and i, j are coordinates of spin up and down electrons, respectively. The geminal functions may be viewed as an extension of the simple HF wave function, based on molecular orbitals, and in fact the geminal function coincide with

HF only when the number M of nonzero eigenvalues of the λ matrix is equal to $N/2$. Indeed the general function (2) can be written in diagonal form after an appropriate transformation

$$\Phi_{\mathrm{AGP}}(\mathbf{r}^{\uparrow},\mathbf{r}^{\downarrow})=\sum_{k}^{M}\lambda^{k}\tilde{\phi}_{k}(\mathbf{r}^{\uparrow})\tilde{\phi}_{k}(\mathbf{r}^{\downarrow}), \tag{3}$$

where $\tilde{\phi}_{k}(\mathbf{r})=\Sigma_{j,a}\mu_{k,j,a}\phi_{j,a}(\mathbf{r})$ are just the molecular orbitals of the HF theory whenever $M=N/2$. Notice that with respect to our previous pairing function formulation also off-diagonal elements are now included in the λ matrix, which must be symmetric in order to define a singlet spin orbital state. Moreover it allows one to easily fulfill other system symmetries by setting the appropriate equalities among different $\lambda_{l,m}$. For instance, in homo-nuclear diatomic molecules, the invariance under reflection in the plane perpendicular to the molecular axis yields the following relation:

$$\lambda_{m,n}^{a,b}=(-1)^{p_m+p_n}\lambda_{m,n}^{b,a}, \tag{4}$$

where p_m is the parity under reflection of the mth orbital.

Another important property of this formalism is the possibility to describe resonating bonds present in many structures, such as benzene. A $\lambda_{m,n}^{a,b}$ different from zero represents a chemical bond formed by the linear combination of the mth and nth orbitals belonging to ath and bth nuclei. It turns out that resonating bonds can be well described through the geminal expansion switching on the appropriate $\lambda_{m,n}^{a,b}$ coefficients: the relative weight of each bond is related to the amplitude of its λ.

Also the spin polarized molecules can be treated within this framework, by using the spin generalized version of the AGP, in which the unpaired orbitals are expanded as well as the paired ones over the same atomic basis employed in the geminal.[12] As already mentioned in the Introduction of this paper, the size consistency is an appealing feature of the AGP term. Strictly speaking, the AGP wave function is certainly size consistent when both the compound and the separated fragments have the minimum possible total spin, because the geminal expansion contains both bonding and antibonding contributions, which can mutually cancel the ionic term arising in the asymptotically separate regime. Moreover the size consistency of the AGP, as well as the one of the Hartree-Fock state, holds in all cases in which the spin of the compound is the sum of the spin of the fragments. However, similarly to other approaches,[4] for spin polarized systems the size consistency does not generally hold, and, in such cases, it may be important go beyond a single AGP wave function. Nevertheless we have experienced that a single reference AGP state is able to describe accurately the electronic structure of the compound around the Born-Oppenheimer minimum even in the mentioned polarized cases, such as in the oxygen dimer.

The last part of this section is devoted to the nuclear cusp condition implementation. A straightforward calculation shows that the AGP wave function fulfills the cusp conditions around the nucleus a if the following linear system is satisfied:

$$\sum_{j}^{(1s,2s)}\lambda_{a,b}^{j,j'}\hat{\phi}'_{a,j}(\mathbf{r}=\mathbf{R}_a)=-Z_a\sum_{c,j}\lambda_{c,b}^{j,j'}\phi_{c,j}(\mathbf{r}=\mathbf{R}_a), \tag{5}$$

for all b and j'; in the left-hand side the caret denotes the spherical average of the orbital gradient. The system can be solved iteratively during the optimization processes, but if we impose that the orbitals satisfy the single atomic cusp conditions, it reduces to

$$\sum_{c(\neq a),j}\lambda_{c,b}^{j,j'}\phi_{c,j}(\mathbf{R}_a)=0, \tag{6}$$

and because of the exponential orbital damping, if the nuclei are not close together, each term in the previous equations is very small, of the order of $\exp(-|\mathbf{R}_a-\mathbf{R}_c|)$. Therefore, with the aim of making the optimization faster, we have chosen to use $1s$ and $2s$ orbitals satisfying the atomic cusp conditions and to disregard the sum (6) in Eq. (5). In this way, once the energy minimum is reached, also the molecular cusp conditions (5) are rather well satisfied.

B. Two-body Jastrow term

As it is well known the Jastrow term plays a crucial role in treating many-body correlation effects. One of the most important correlation contributions arises from the electron-electron interaction. Therefore it is worth using at least a two-body Jastrow factor in the trial wave function. Indeed this term reduces the electron coalescence probability, and so decreases the average value of the repulsive interaction. The two-body Jastrow function reads

$$J_2(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\exp\left(\sum_{i<j}^{N}u(r_{ij})\right), \tag{7}$$

where $u(r_{ij})$ depends only on the relative distance $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ between two electrons and allows to fulfill the cusp conditions for opposite spin electrons as long as $u(r_{ij})\rightarrow r_{ij}/2$ for small electron-electron distance. The pair correlation function u can be parametrized successfully by few variational parameters. We have adopted two main functional forms. The first is similar to the one given by Ceperley,[13]

$$u(r)=\frac{F}{2}(1-e^{-r/F}), \tag{8}$$

with F being a free variational parameter. This form for u is particularly convenient whenever atoms are very far apart at distances much larger than F, as it allows to obtain good size consistent energies, approximately equal to the sum of the atomic contributions, without changing the other parts of the wave function with an expensive optimization. Within the functional form (8), it is assumed that the long range part of the Jastrow, decaying as a power of the distance between atoms, is included in the three-body Jastrow term described in the following section. The second form of the pair function u, particularly convenient at the chemical bond distance, where we performed most of the calculations, is the one used by Fahy, Wang, and Louie:[7]

$$u(r) = \frac{r}{2(1+br)}, \tag{9}$$

with a different variational parameter b.

In both functional forms the cusp condition for antiparallel spin electrons is satisfied, whereas the one for parallel spins is neglected in order to avoid the spin contamination. This allows to remove the singularities of the local energy due to the collision of two opposite spin electrons, yielding a smaller variance and a more efficient VMC calculation. Moreover, due to the Jastrow correlation, an exact property of the ground state wave function is recovered without using many Slater determinants, thus considerably simplifying the variational parametrization of a correlated wave function.

C. Three-body Jastrow term

In order to describe well the correlation between electrons the simple Jastrow factor is not sufficient. Indeed it takes into account only the electron-electron separation and not the individual electronic position $\mathbf{r}_i$ and $\mathbf{r}_j$. It is expected that close to nuclei the electron correlation is not accurately described by a translationally invariant Jastrow, as shown by different authors, see for instance, Ref. 14. For this reason we introduce a factor, often called three-body (electron-electron nucleus) Jastrow, which explicitly depends on both the electronic positions $\mathbf{r}_i$ and $\mathbf{r}_j$. The three-body Jastrow is chosen to satisfy the following requirements.

(A) The cusp conditions set up by the two-body Jastrow term and by the AGP are preserved.

(B) It does not distinguish the electronic spins otherwise causing spin contamination.

(C) Whenever the atomic distances are large it factorizes into a product of independent contributions located near each atom, an important requirement to satisfy the size consistency of the variational wave function.

Analogously to the pairing trial function in Eq. (2) we define a three-body factor as

$$J_3(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \exp\left(\sum_{i<j} \Phi_J(\mathbf{r}_i, \mathbf{r}_j) \right),$$

$$\Phi_J(\mathbf{r}_i, \mathbf{r}_j) = \sum_{l,m,a,b} g^{a,b}_{l,m} \psi_{a,l}(\mathbf{r}_i) \psi_{b,m}(\mathbf{r}_j), \tag{10}$$

where indices l and m indicate different orbitals located around the atoms a and b, respectively. Each Jastrow orbital $\psi_{a,l}(\mathbf{r})$ is centered on the corresponding atomic position $\mathbf{R}_a$. We have used Gaussian and exponential orbitals multiplied by appropriate polynomials of the electronic coordinates, related to different spherical harmonics with given angular momentum, as in the usual Slater basis. Analogously to the geminal function Φ_{AGP}, whenever the one particle basis set $\{\psi_{a,i}\}$ is complete the expansion (10) is also complete for the generic two particle function $\Phi_J(\mathbf{r}, \mathbf{r}')$. In the latter case, however, the one particle orbitals have to behave smoothly close to the corresponding nuclei, namely, as

$$\psi_{a,i}(\mathbf{r}) - \psi_{a,i}(\mathbf{R}_a) \simeq |\mathbf{r} - \mathbf{R}_a|^2, \tag{11}$$

or with larger power, in order to preserve the nuclear cusp conditions (5).

For the s-wave orbitals we have found energetically convenient to add a finite constant $c_l/(N-1)$. As shown in the Appendix B, a nonzero value of the constant c_l for such orbitals $\psi_{a,l}$ is equivalent to include in the wave function a size consistent one body term. As pointed out in Ref. 15, it is easier to optimize a one body term implicitly present in the three-body Jastrow factor, rather than including more orbitals in the determinantal basis set.

The chosen form for the three-body Jastrow (10) is similar to one used by Prendergast, Bevan, and Fahy[16] and has very appealing features: it easily allows including the symmetries of the system by imposing them on the matrix $g^{a,b}_{l,m}$ exactly as it is possible for the pairing part [e.g., by replacing $\lambda^{a,b}_{m,n}$ with $g^{a,b}_{m,n}$ in Eq. (4)]. It is size consistent, namely, the atomic limit can be smoothly recovered with the same trial function when the matrix terms $g^{a,b}_{l,m}$ for $a \neq b$ approach zero in this limit. Notice that a small nonzero value of $g^{a,b}_{l,m}$ for $a \neq b$ acting on p-wave orbitals can correctly describe a weak interaction between electrons such as the the van der Waals forces.

III. OPTIMIZATION METHOD

We have used the SR method already described in Ref. 17, which allows to minimize the energy expectation value of a variational wave function containing many variational parameters in an arbitrary functional form. The basic ingredient for the stochastic minimization of the wave function Ψ determined by p variational parameters $\{\alpha^0_k\}_{k=1,\ldots,p}$, is the solution of the linear system

$$\sum_{k=0}^{p} s_{j,k} \Delta \alpha_k = \langle \Psi | O_k (\Lambda I - H) | \Psi \rangle, \tag{12}$$

where the operators O_k are defined on each N electron configuration $x = \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$ as the logarithmic derivatives with respect to the parameters α_k:

$$O^k(x) = \frac{\partial}{\partial \alpha_k} \ln \Psi(x) \quad \text{for } k>0, \tag{13}$$

while for $k=0$ O_k is the identity operator equal to one on all the configurations. The $(p+1) \times (p+1)$ matrix $s_{k,j}$ is easily expressed in terms of these operators:

$$s_{j,k} = \frac{\langle \Psi | O_j O_k | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \tag{14}$$

and is calculated at each iteration through a standard variational Monte Carlo sampling; the single iteration constitutes a small simulation that will be referred in the following as "bin." After each bin the wave function parameters are iteratively updated ($\alpha_k \rightarrow \alpha_k + \Delta \alpha_k / \Delta \alpha_0$), and the method is convergent to an energy minimum for large enough Λ. Of course for particularly simple functional form of $\Psi(x)$, containing, e.g., only linear CI coefficients, much more efficients optimization schemes do exist.[18]

SR is similar to a standard steepest descent (SD) calculation, where the expectation value of the energy $E(\alpha_k) = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ is optimized by iteratively changing the parameters α_i according to the corresponding derivatives of the energy (generalized forces)

$$f_k = -\frac{\partial E}{\partial \alpha_k} = -\frac{\langle \Psi | O_k H + H O_k + (\partial_{\alpha_k} H) | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$
$$+ 2 \frac{\langle \Psi | O_k | \Psi \rangle \langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle^2}, \quad (15)$$

namely

$$\alpha_k \rightarrow \alpha_k + \Delta t f_k. \quad (16)$$

Δt is a suitable small time step, which can be taken fixed or determined at each iteration by minimizing the energy expectation value. Indeed the variation of the total energy ΔE at each step is easily shown to be negative for small enough Δt because, in this limit

$$\Delta E = -\Delta t \sum_i f_i^2 + O(\Delta t^2).$$

Thus the method certainly converges at the minimum when all the forces vanish. Notice that in the definition of the generalized forces (15) we have generally assumed that the variational parameters may appear also in the Hamiltonian. This is particularly important for the structural optimization since the atomic positions that minimize the energy enter both in the wave function and in the potential.

In the following we will show that similar considerations hold for the SR method, which can be therefore extended to the optimization of the geometry. Indeed, by eliminating the equation with index $k=0$ from the linear system (12), the SR iteration can be written in a form similar to the steepest descent:

$$\alpha_i \rightarrow \alpha_i + \Delta t \sum_k \bar{s}_{i,k}^{-1} f_k, \quad (17)$$

where the reduced $p \times p$ matrix $\bar{s}$ is

$$\bar{s}_{j,k} = s_{j,k} - s_{j,0} s_{0,k} \quad (18)$$

and the Δt value is given by

$$\Delta t = \frac{1}{2 \left(\Lambda - \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} - \Sigma_{k>0} \Delta \alpha_k s_{k,0} \right)}. \quad (19)$$

From the latter equation the value of Δt changes during the simulation and remains small for large enough energy shift Λ. However, using the analogy with the steepest descent, convergence to the energy minimum is reached also when the value of Δt is sufficiently small and is kept constant for each iteration. Indeed the energy variation for a small change of the parameters is

$$\Delta E = -\Delta t \sum_{i,j} \bar{s}_{i,j}^{-1} f_i f_j.$$

It is easily verified that the above term is always negative because the reduced matrix $\bar{s}$, as well as $\bar{s}^{-1}$, is positive definite, s being an overlap matrix with all positive eigenvalues.

For a stable iterative method, such as the SR or the SD one, a basic ingredient is that at each iteration the new parameters α' are close to the previous α according to a pre-

scribed distance. The fundamental difference between the SR minimization and the standard steepest descent is just related to the definition of this distance. For the SD it is the usual one defined by the Cartesian metric $\Delta_\alpha = \Sigma_k |\alpha'_k - \alpha_k|^2$, instead the SR works correctly in the physical Hilbert space metric of the wave function Ψ, yielding $\Delta_\alpha = \Sigma_{i,j} \bar{s}_{i,j} (\alpha'_i - \alpha_i)(\alpha'_j - \alpha_j)$, namely, the square distance between the two normalized wave functions corresponding to the two different sets of variational parameters $\{\alpha'\}$ and $\{\alpha_k\}$. Therefore, from the knowledge of the generalized forces f_k, the most convenient change of the variational parameters minimizes the functional $\Delta E + \bar{\Lambda} \Delta_\alpha$, where ΔE is the linear change in the energy $\Delta E = -\Sigma_i f_i (\alpha'_i - \alpha_i)$ and $\bar{\Lambda}$ is a Lagrange multiplier that allows a stable minimization with small change Δ_α of the wave function Ψ. The final iteration (17) is then easily obtained.

The advantage of SR compared with SD is obvious because sometimes a small change of the variational parameters correspond to a large change of the wave function, and the SR takes into account this effect through the Eq. (17). In particular, the method is useful when a nonorthogonal basis set is used as we have done in this work. Indeed by using the reduced matrix $\bar{s}$ it is also possible to remove from the calculation those parameters that imply some redundancy in the variational space. As shown in Appendix A, a more efficient change in the wave function can be obtained by updating only the variational parameters that remain independent within a prescribed tolerance, and therefore, by removing the parameters that linearly depend on the others. A more stable minimization is obtained without spoiling the accuracy of the calculation. A weak tolerance criterium $\epsilon \simeq 10^{-3}$, provides a very stable algorithm even when the dimension of the variational space is large. For a small atomic basis set, by an appropriate choice of the Jastrow and Slater orbitals, the reduced matrix $\bar{s}$ is always very well conditioned even for the largest system studied, and the above stabilization technique is not required. Instead the described method is particularly important for the extension of QMC to complex systems with large number of atoms and/or higher level of accuracy, because in this case it is very difficult to select—e.g., by trial and error—the relevant variational parameters, which allow a well conditioned matrix $\bar{s}$ for a stable inversion in Eq. (17).

A. Setting the SR parameters

In this work, instead of setting the constant Λ, we have equivalently chosen to determine Δt by verifying the stability and the convergence of the algorithm at fixed Δt value, which can be easily understood as an inverse energy scale. The simulation is stable whenever $1/\Delta t > \Lambda_{cut}$, where Λ_{cut} is an energy cutoff that is strongly dependent on the chosen wave function and is generally weakly dependent on the bin length. Whenever the wave function is too much detailed, namely, has a lot of variational freedom, especially for the high energy components of the core electrons, the value of Λ_{cut} becomes exceedingly large and too many iterations are required for obtaining a converged variational wave function. In fact a rough estimate of the corresponding number of iterations P is given by $P \Delta t \gg 1/G$, where G is the typical energy gap of the system, of the order of few electron volts
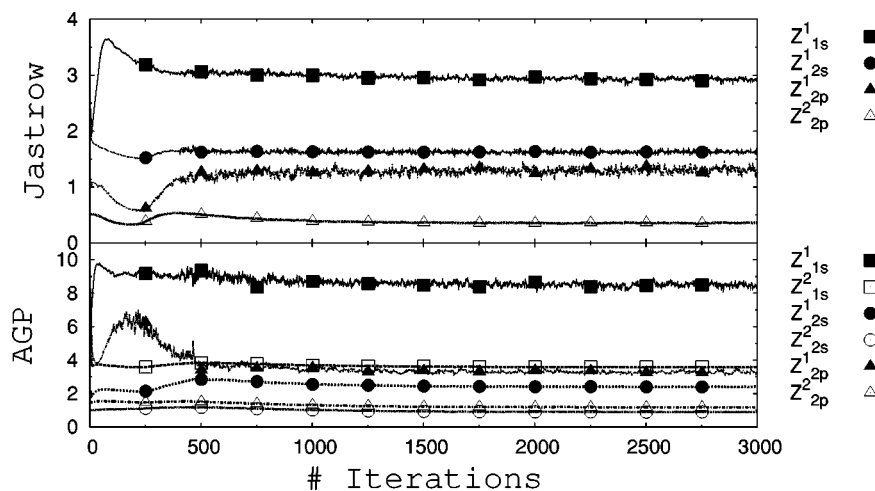
FIG. 1. Example of the convergence of the SR method for the variational parameters of the Be atom, as a function of the number of stochastic iterations. In the upper(lower) panel the Jastrow (geminal) parameters are shown. For each iteration, a variational Monte Carlo calculation is employed with a bin containing 15 000 samples of the energy, yielding at the equilibrium a standard deviation of $\simeq 0.0018H$. For the first 200 iteration $\Delta t = 0.00125H^{-1}$, for the further 200 iterations $\Delta t = 0.0025H^{-1}$, whereas for the remaining ones $\Delta t = 0.005H^{-1}$.

in small atoms and molecules. Within the SR method it is therefore extremely important to work with a bin length rather small, so that many iterations can be performed without much effort.

In a Monte Carlo optimization framework the forces f_k are always determined with some statistical noise η_k, and by iterating the procedure several times with a fixed bin length the variational parameters will fluctuate around their mean values. These statistical fluctuations are similar to the thermal noise of a standard Langevin equation

$$\partial_t \alpha_k = f_k + \eta_k, \qquad (20)$$

where

$$\langle \eta_k(t) \eta_{k'}(t') \rangle = 2 T_{\text{noise}} \delta(t-t') \delta_{k,k'}. \qquad (21)$$

The variational parameters α_k, averaged over the Langevin simulation time (as for instance, in Fig. 1 for $t > 2H^{-1}$), will be close to the true energy minimum, but the corresponding forces $f_k = -\partial_{\alpha_k} E$ will be affected by a bias that scales to zero with the thermal noise T_{noise}, due to the presence of nonquadratic terms in the energy landscape.

Within a QMC scheme, one needs to estimate T_{noise}, by increasing the bin length as clearly $T_{\text{noise}} \propto 1/$ bin length, because the statistical fluctuations of the forces, obviously decreasing by increasing the bin length, are related to the thermal noise by Eq. (21). Thus there is an optimal value for the bin length, which guarantees a fast convergence and avoid the forces to be biased within the statistical accuracy of the sampling.

An example is shown in Fig. 1 for the optimization of the Be atom, using a DZ basis both for the geminal and the three-body Jastrow part. The convergence is reached in about 1000 iteration with $\Delta t = 0.005H^{-1}$. However, in this case it is possible to use a small bin length, yielding a statistical accuracy in the energy much poorer than the final accuracy of about 0.05 mH. This is obtained by averaging the variational parameters in the last 1000 iterations, when they fluctuate around a mean value, allowing a very accurate determination of the energy minimum which satisfies the Euler conditions, namely, with $f_k = 0$ for all parameters. Those conditions have been tested by an independent Monte Carlo simulation about 600 times longer than the bin used during

the minimization. As shown in Fig. 2 the Euler conditions are fulfilled within statistical accuracy even when the bin used for the minimization is much smaller than the overall simulation. On the other hand, if the bin used is too small, as we have already pointed out, the averaging of the parameters is affected by a sizable bias.

Whenever it is possible to use a relatively small bin in the minimization, the apparently large number of iterations required for equilibration does not really matter, because a comparable amount of time has to be spent in the averaging of the variational parameters, as shown in Fig. 1. The comparison shown in Ref. 19 about the number of the iterations required, though is clearly relevant for a deterministic method, is certainly incomplete for a statistical method, because in the latter case an iteration can be performed in principle in a very short time, namely, with a rather small bin.

It is indeed possible that for high enough accuracy the number of iterations needed for the equilibration becomes negligible from the computational point of view. In fact in order to reduce, e.g., by a factor 10, the accuracy in the variational parameters, a bin ten times larger is required for decreasing the thermal noise T_{noise} by the same factor,
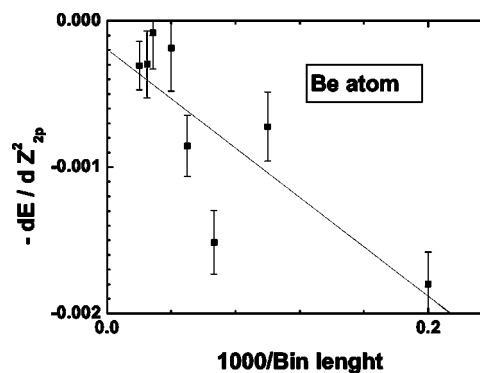
FIG. 2. Calculation of the derivative of the energy with respect to the second Z in the $2p$ orbital of the geminal function for the Be atom. The calculation of the force was obtained, at fixed variational parameters, by averaging over 10^7 samples, allowing, e.g., a statistical accuracy in the total energy of 0.07 mH. The variational parameters have been obtained by a SR minimization with fixed bin length shown in the x label. The parameter considered has the largest deviation from the Euler conditions.

whereas a statistical average 100 times longer is indeed necessary to reduce the statistical errors of the variational parameters by the same ratio. This means that the fraction of time spent for equilibration becomes ten times smaller compared with the less accurate simulation.

B. Structural optimization

In the last few years remarkable progresses have been made to develop QMC techniques which are able in principle to perform structural optimization of molecules and complex systems.[20–22] Within the Born-Oppenheimer approximation the nuclear positions R_i can be considered as further variational parameters included in the set $\{\alpha_i\}$ used for the SR minimization (17) of the energy expectation value. For clarity, in order to distinguish the conventional variational parameters from the ionic positions, in this section we indicate with $\{c_i\}$ the former ones, and with R_i the latter ones. It is understood that $R_i^\nu = \alpha_k$, where a particular index k of the whole set of parameters $\{\alpha_i\}$ corresponds to a given spatial component ($\nu = 1,2,3$) of the ith ion. Analogously the forces (15) acting on the ionic positions will be indicated by capital letters with the same index notations.

The purpose of the present section is to compute the forces F acting on each of the M nuclear positions $\{R_1,...,R_M\}$, being M the total number of nuclei in the system:

$$F(R_a) = -\nabla_{R_a} E(\{c_i\}, R_a), \qquad (22)$$

with a reasonable statistical accuracy, so that the iteration (17) can be effective for the structural optimization. In this work we have used a finite difference operator $\Delta/\Delta R_a$ for the evaluation of the force acting on a given nuclear position a

$$F(R_a) = -\frac{\Delta}{\Delta R_a} E = -\frac{E(R_a + \Delta R_a) - E(R_a - \Delta R_a)}{2\Delta R} + O(\Delta R^2), \qquad (23)$$

where ΔR_a is a three-dimensional vector. Its length ΔR is chosen to be 0.01 a.u., a value that is small enough for negligible finite difference errors. In order to evaluate the energy differences in Eq. (23) we have used the space-warp coordinate transformation[23,24] briefly summarized in the following paragraphs. According to this transformation also the electronic coordinates r will be translated in order to mimic the right displacement of the charge around the nucleus a

$$\bar{r}_i = r_i + \Delta R_a \omega_a(r_i), \qquad (24)$$

where

$$\omega_a(r) = \frac{F(|r - R_a|)}{\sum_{b=1}^{M} F(|r - R_b|)}. \qquad (25)$$

$F(r)$ is a function which must decay rapidly; here we used $F(r) = 1/r^4$ as suggested in Ref. 24.

The expectation value of the energy depends on ΔR, because both the Hamiltonian and the wave function depend

on the nuclear positions. Now let us apply the space-warp transformation to the integral involved in the calculation; the expectation value reads

$$E(R + \Delta R) = \frac{\int dr J_{\Delta R}(r)\Psi_{\Delta R}^2[\bar{r}(r)]E_L^{\Delta R}[\bar{r}(r)]}{\int dr J_{\Delta R}(r)\Psi_{\Delta R}^2[\bar{r}(r)]}, \qquad (26)$$

where J is the Jacobian of the transformation and here and henceforth we avoid for simplicity to use the atomic subindex a. The importance of the space warp in reducing the variance of the force is easily understood for the case of an isolated atom a. Here the force acting on the atom is obviously zero, but only after the space warp transformation with $\omega_a = 1$ the integrand of expression (26) will be independent of ΔR, providing an estimator of the force with zero variance.

Starting from Eq. (26), it is straightforward to explicitly derive a finite difference differential expression for the force estimator, which is related to the gradient of the previous quantity with respect to ΔR, in the limit of the displacement tending to zero:

$$F(R) = -\left\langle \lim_{|\Delta R| \to 0} \frac{\Delta}{\Delta R} E_L \right\rangle$$
$$+ 2\left(\langle H \rangle \left\langle \lim_{|\Delta R| \to 0} \frac{\Delta}{\Delta R} \ln(J^{1/2}\Psi) \right\rangle \right.$$
$$\left. - \left\langle H \lim_{|\Delta R| \to 0} \frac{\Delta}{\Delta R} \ln(J^{1/2}\Psi) \right\rangle \right), \qquad (27)$$

where the brackets indicate a Monte Carlo like average over the square modulus of the trial wave function, $\Delta/\Delta R$ is the finite difference derivative as defined in Eq. (23), and $E_L = \langle \Psi|H|x \rangle / \langle \Psi|x \rangle$ is the local energy on a configuration x where all electron positions and spins are given. In analogy with the general expression (15) of the forces, we can identify the operators O_k corresponding to the space-warp change of the variational wave function:

$$O_k = \frac{\Delta^\nu}{\Delta R} \ln(J_{\Delta R}^{1/2}\Psi_{\Delta R}). \qquad (28)$$

The above operators (28) are used also in the definition of the reduced matrix $\bar{s}$ for those elements depending on the variation with respect to a nuclear coordinate. In this way it is possible to optimize both the wave function and the ionic positions at the same time, in close analogy with the Car-Parrinello[25] method applied to the minimization problem. Also Tanaka[26] tried to perform Car-Parrinello like simulations via QMC, within the less efficient steepest descent framework.

An important source of systematic errors is the dependence of the variational parameters c_i on the ionic configuration R, because for the final equilibrium geometry all the forces f_i corresponding to c_i have to be zero, in order to guarantee that the true minimum of the potential energy surface is reached.[27] As shown clearly in the preceding section, within a QMC approach it is possible to control this condition by increasing systematically the bin length, when the thermal bias T_{noise} vanishes. In Fig. 3 we report the equilib-
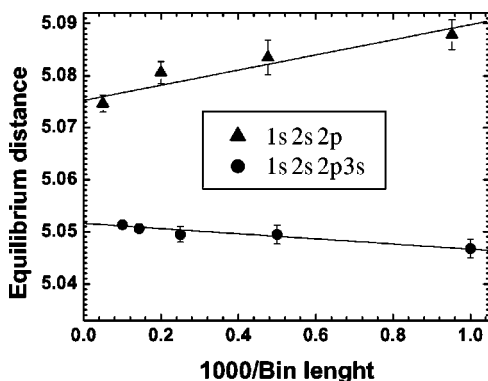
FIG. 3. Plot of the equilibrium distance of the Li_2 molecule as a function of the inverse bin length. The total energy and the binding energy are reported in Tables II and III, respectively. The triangles (full dots) refer to a simulation performed using 1000 (3000) iterations with $\Delta t = 0.015 H^{-1}$ ($\Delta t = 0.005 H^{-1}$) and averaging over the last 750 (2250) iterations. For all simulations the initial wavefunction is optimized at Li-Li distance 6 a.u.

rium distance of the Li molecule as a function of the inverse bin length, so that an accurate evaluation of such an important quantity is possible even when the number of variational parameters is rather large, by extrapolating the value to an infinite bin length. However, as it is seen in the picture, though the inclusion of the 3s orbital in the atomic AGP basis substantially improves the equilibrium distance and the total energy by $\simeq 1$ mH, this larger basis makes our simulation less efficient, as the time step Δt has to be reduced by a factor 3.

We have not attempted to extend the geometry optimization to the more accurate DMC, since there are technical difficulties,[28] and it is computationally much more demanding.

C. Stochastic versus deterministic minimization

In principle, within a stochastic approach, the exact minimum is never reached as the forces f_i are known only statistically with some error bar Δf_i. We have found that the method becomes efficient when all the forces are nonzero only within few tenths of standard deviations. Then for small enough constant Δt, and large enough bin compatible with the computer resources, the stochastic minimization, obtained with a statistical evaluation of $\bar{s}$ continues in a stable manner, and all the variational parameters fluctuate after several iterations around a mean value. After averaging these variational parameters, the corresponding mean values represent very good estimates satisfying the minimum energy condition. This can be verified by performing an independent Monte Carlo simulation much longer than the bin used for a single iteration of the stochastic minimization, and then by explicitly checking that all the forces f_i are zero within the statistical accuracy. An example is given in Fig. 2 and discussed in the preceding section.

On the other hand, whenever few variational parameters are clearly out of minimum, with $|f_i/\Delta f_i| > \sigma_{cut}$, with $\sigma_{cut} \simeq 10$, we have found a faster convergence with a much larger

Δt, by applying the minimization scheme only for those selected parameters such that $|f_i/\Delta f_i| > \sigma_{cut}$, until $|f_i/\Delta f_i| < \sigma_{cut}$. After this initialization it is then convenient to proceed with the global minimization with all parameters changed at each iteration, in order to explore the variational space in a much more effective way.

D. Different energy scales

The SR method performs generally very well, whenever there is only one energy scale in the variational wave function. However if there are several energy scales in the problem, some of the variational parameters, e.g. the ones defining the low energy valence orbitals, converge very slowly with respect to the others, and the number of iterations required for the equilibration becomes exceedingly large, considering also that the time step Δt necessary for a stable convergence depends on the high energy orbitals, whose dynamics cannot be accelerated beyond a certain threshold. It is easy to understand that SR technique not necessarily becomes inefficient for extensive systems with large number of atoms. Indeed suppose that we have N atoms very far apart so that we can neglect the interaction between electrons belonging to different atoms, than it is easy to see that the stochastic matrix Eq. (14) factorizes in N smaller matrices and the Δt necessary for the convergence is equal to the single atom case, simply because the variational parameters of each single atom can evolve independently form each other. This is due to the size consistency of our trial function that can be factorized as a product of N single atom trial functions in that limit. Anyway for system with a too large energy spread a way to overcome this difficulty was presented recently in Ref. 19. Unfortunately this method is limited to the optimization of the variational parameters in a super-CI basis, to which a Jastrow term is applied, which however cannot be optimized together with the CI coefficients.

In the present work, limited to a rather small atomic basis, the SR technique is efficient, and general enough to perform the simultaneous optimization of the Jastrow and the determinantal part of the wave function, a very important feature that allows to capture the most nontrivial correlations contained in our variational ansatz. Moreover, SR has been extended to deal with the structural optimization of a chemical system, which is another appealing characteristic of this method. The results presented in the following section show that in some nontrivial cases the chemical accuracy can be reached also within this framework.

However we feel that an improvement along the line described in Ref. 19 will be useful for realistic electronic simulations of complex systems with many atoms, or when a very high precision is required at the variational level and consequently a wide spread of energy scales has to be included in the atomic basis. We believe that the difficulty to work with a large basis set will be possibly alleviated by using pseudopotentials that allows to avoid the high energy components of the core electrons. However more work is necessary to clarify the efficiency of the SR minimization scheme described here.

TABLE I. Total energies in variational (E_{VMC}) and diffusion (E_{DMC}) Monte Carlo calculations; the percentages of correlation energy recovered in VMC [$E_c^{VMC}(\%)$] and DMC [$E_c^{DMC}(\%)$] have been evaluated using the "exact" (E_0) and Hartree-Fock (E_{HF}) energies from the references reported in the table. Here exact means the ground state energy of the nonrelativistic infinite nuclear mass Hamiltonian. The energies are in hartree.

	E_0	E_{HF}	E_{VMC}	$E_c^{VMC}(\%)$	E_{DMC}	$E_c^{DMC}(\%)$
Li	$-7.478\ 06^{a}$	$-7.432\ 727^{a}$	$-7.477\ 21(11)$	$98.12(24)$	$-7.477\ 91(12)$	$99.67(27)$
Li_2	-14.9954^{b}	$-14.871\ 52^{b}$	$-14.990\ 02(12)$	$95.7(1)$	$-14.994\ 72(17)$	$99.45(14)$
Be	$-14.667\ 36^{a}$	$-14.573\ 023^{a}$	$-14.663\ 28(19)$	$95.67(20)$	$-14.667\ 05(12)$	$99.67(13)$
Be_2	$-29.338\ 54(5)^{b}$	$-29.132\ 42^{b}$	$-29.3179(5)$	$89.99(24)$	$-29.333\ 41(25)$	$97.51(12)$
O	-75.0673^{a}	$-74.809\ 398^{a}$	$-75.0237(5)$	$83.09(19)$	$-75.0522(3)$	$94.14(11)$
H_2O	$-76.438(3)^{b}$	$-76.068(1)^{b}$	$-76.3803(4)$	$84.40(10)$	$-76.4175(4)$	$94.46(10)$
O_2	-150.3268^{b}	-149.6659^{b}	$-150.1992(5)$	$80.69(7)$	$-150.272(2)$	$91.7(3)$
C	-37.8450^{a}	$-37.688\ 619^{a}$	$-37.813\ 03(17)$	$79.55(11)$	$-37.8350(6)$	$93.6(4)$
C_2	$-75.923(5)^{b}$	$-75.406\ 20^{b}$	$-75.8273(4)$	$81.48(8)$	$-75.8826(7)$	$92.18(14)$
CH_4	-40.515^{d}	-40.219^{d}	$-40.4627(3)$	$82.33(10)$	$-40.5041(8)$	$96.3(3)$
C_6H_6	$-232.247(4)^{e}$	$-230.82(2)^{f}$	$-231.8084(15)$	$69.25(10)$	$-232.156(3)$	$93.60(21)$

[a]Exact and HF energies from Ref. 50.
[b]Reference 29.
[c]Reference 51.
[d]Reference 33.
[e]Estimated exact energy from Ref. 43.
[f]Reference 52.

IV. APPLICATION OF THE JAGP TO MOLECULES

In this work we study total, correlation, and atomization energies, accompanied with the determination of the ground state optimal structure for a restricted ensemble of molecules. For each of them we performed a full all-electron SR geometry optimization, starting from the experimental molecular structure. After the energy minimization, we carried out all-electron VMC and DMC simulations at the optimal geometry within the so called "fixed node approximation." The basis used here is a double zeta Slater set of atomic orbitals (STO-DZ) for the AGP part, while for parametrizing the three-body Jastrow geminal we used a double zeta Gaussian atomic set (GTO-DZ). In this way both the antisymmetric and the bosonic part are well described, preserving the right exponential behavior for the former and the strong localization properties for the latter. Sometimes, in order to improve the quality of the variational wave function we employed a mixed Gaussian and Slater basis set in the Jastrow part, which allows to avoid a too strong dependency in the variational parameters in a simple way. However, both in the AGP and in the Jastrow sector we never used a large basis set, in order to keep the wave function as simple as possible. The accuracy of our wave function can be obviously improved by an extension of the one particle basis set, but, as discussed in the preceding section, this is rather difficult for a stochastic minimization of the energy. Nevertheless, for most of the molecules studied with a simple JAGP wave function, a DMC calculation is able to reach the chemical accuracy in the binding energies and the SR optimization yields very precise geometries already at the VMC level.

In the first part of this section some results will be presented for a small set of widely studied molecules and belonging to the G1 database. In the second section we will treat the benzene and its radical cation $C_6H_6^+$, by taking into account its distortion due to the Jahn-Teller effect, which is well reproduced by our SR geometry optimization.

A. Small diatomic molecules, methane, and water

Except from Be_2 and C_2, all the molecules presented here belong to the standard G1 reference set; all their properties are well known and well reproduced by standard quantum chemistry methods, therefore they constitute a good case for testing new approaches and new wave functions.

The Li dimer is one of the easiest molecules to be studied after H_2, which is exact for any diffusion Monte Carlo calculation with a trial wave function that preserves the nodeless structure. Li_2 is less trivial due to the presence of core electrons that are only partially involved in the chemical bond and to the $2s$-$2p$ near degeneracy for the valence electrons. Therefore many authors have done benchmark calculation on this molecule to check the accuracy of the method or to determine the variance of the internuclear force calculated within a QMC framework. In this work we start from Li_2 to move toward a structural analysis of more complex compounds, thus showing that our QMC approach is able to handle relevant chemical problems. In the case of Li_2, a $3s$ $1p$ STO-DZ AGP basis and a $1s$ $1p$ GTO-DZ Jastrow basis turns out to be enough for the chemical accuracy (see Appendix C for a detailed description of the trial wave function). More than 99% of the correlation energy is recovered by a DMC simulation (Table I), and the atomization energy is exact within few thousand of eV (0.02 kcal mol^{-1}) (Table II). Similar accuracy have been previously reached within a DMC approach,[29] only by using a multireference CI like wave function, that before our work, was the usual way to improve the electronic nodal structure. As stressed before, the JAGP wave function includes many resonating configurations through the geminal expansion, beyond the $1s$ $2s$ HF ground state. The bond length has been calculated at the variational level through the fully optimized JAGP wave function: the resulting equilibrium geometry turns out to be highly accurate (Table III), with a discrepancy of only $0.001a_0$ from the exact result. For this molecule it is worth comparing our work with the one by Assaraf and Caffarel.[30]

TABLE II. Binding energies in eV obtained by variational (Δ_{VMC}) and diffusion (Δ_{DMC}) Monte Carlo calculations; Δ_0 is the exact result for the nonrelativistic infinite nuclear mass Hamiltonian. Also the percentages [$\Delta_{VMC}(\%)$ and $\Delta_{DMC}(\%)$] of the total binding energies are reported.

	Δ_0	Δ_{VMC}	$\Delta_{VMC}(\%)$	Δ_{DMC}	$\Delta_{DMC}(\%)$
Li_2	-1.069	$-0.967(3)$	$90.4(3)$	$-1.058(5)$	$99.0(5)$
O_2	-5.230	$-4.13(4)$	$78.9(8)$	$-4.56(5)$	$87.1(9)$
H_2O	-10.087	$-9.704(24)$	$96.2(1.0)$	$-9.940(19)$	$98.5(9)$
C_2	-6.340	$-5.476(11)$	$86.37(17)$	$-5.79(2)$	$91.3(3)$
CH_4	-18.232	$-17.678(9)$	$96.96(5)$	$-18.21(4)$	$99.86(22)$
C_6H_6	-59.25	$-52.53(4)$	$88.67(7)$	$-58.41(8)$	$98.60(13)$

Their zero-variance zero-bias principle has been proved to be effective in reducing the fluctuations related to the internuclear force; however they found that only the inclusion of the space warp transformation drastically lowers the force statistical error, which magnitude becomes equal or even lower than the energy statistical error, thus allowing a feasible molecular geometry optimization. Actually, our way of computing forces [see Eq. (27)] provides slightly larger variances, without explicitly invoking the zero-variance zero-bias principle.

The very good bond length, we obtained, is probably due to two main ingredients of our calculations: we have carried out a stable energy optimization that is often more effective than the variance one, as shown by different authors,[31] and we have used very accurate trial function as it is apparent from the good variational energy.

Indeed within our scheme we obtain good results without exploiting the computationally much more demanding DMC, thus highlighting the importance of the SR minimization described in Sec. III B.

Let us now consider larger molecules. Both C_2 and O_2 are poorly described by a single Slater determinant, since the presence of the nondynamic correlation is strong. Instead with a single geminal JAGP wave function, including implicitly many Slater determinants,[10] it is possible to obtain a quite good description of their molecular properties. For C_2, we used a $2s$ $1p$ STO-DZ basis in the geminal, and a $2s$ $1p$ DZ Gaussian Slater mixed basis in the Jastrow, for O_2 we employed a $3s$ $1p$ STO-DZ in the geminal and the same Jastrow basis as before. In both the cases, the variational energies recover more than 80% of the correlation energy, the DMC ones yield more than 90%, as shown in Table I. These results are of the same level of accuracy as those ob-

tained by Filippi and Umrigar[29] with a multireference wave function by using the same Slater basis for the antisymmetric part and a different Jastrow factor. From the Table II of the atomization energies, it is apparent that DMC considerably improves the binding energy with respect to the VMC values, although for these two molecules it is quite far from the chemical accuracy ($\simeq 0.1$ eV): for C_2 the error is 0.55(2) eV, for O_2 it amounts to 0.67(5) eV. Indeed, it is well known that the electronic structure of the atoms is described better than the corresponding molecules if the basis set remains the same, and the nodal error is not compensated by the energy difference between the separated atoms and the molecule. In a benchmark DMC calculation with pseudopotentials,[32] Grossman found an error of 0.27 eV in the atomization energy for O_2, by using a single determinant wave function; probably, pseudopotentials allow the error between the pseudoatoms and the pseudomolecule to compensate better, thus yielding more accurate energy differences. As a final remark on the O_2 and C_2 molecules, our bond lengths are in between the LDA and GGA precision, and still worse than the best CCSD calculations, but our results may be considerably improved by a larger atomic basis set, which we have not attempted so far.

Methane and water are very well described by the JAGP wave function. Also for these molecules we recover more than 80% of correlation energy at the VMC level, while DMC yields more than 90%, with the same level of accuracy reached in previous Monte Carlo studies.[33–36] Here the binding energy is almost exact, since in this case the nodal energy error arises essentially from only one atom (carbon or oxygen) and therefore it is exactly compensated when the atomization energy is calculated. Also the bond lengths are highly accurate, with an error lower then $0.005 a_0$.

For Be_2 we applied a 3s 1p STO-DZ basis set for the AGP part and a 2s 2p DZ Gaussian Slater mixed basis for the Jastrow factor. VMC calculations performed with this trial function at the experimental equilibrium geometry yield 90% of the total correlation energy, while DMC gives 97.5% of correlation, i.e., a total energy of $-29.33341(25)$ H. Although this value is better than that obtained by Filippi and Umrigar[29] ($-29.3301(2)$ H) with a smaller basis (3s atomic orbitals not included), it is not enough to bind the molecule, because the binding energy remains still positive [0.0069(37) H]. Instead, once the molecular geometry has been relaxed, the SR optimization finds a bond distance of $13.5(5) a_0$ at the VMC level; therefore the employed basis allows the mol-

TABLE III. Bond lengths (R) in atomic units; the subscript 0 refers to the exact results. For the water molecule R is the distance between O and H and θ is the angle HOH (in deg), for CH_4 R is the distance between C and H and θ is the HCH angle.

	R_0	R	θ_0	θ
Li_2	5.051	5.0516(2)		
O_2	2.282	2.3425(18)		
C_2	2.348	2.366(2)		
H_2O	1.809	1.8071(23)	104.52	104.74(17)
CH_4	2.041	2.049(1)	109.47	109.55(6)
	R_0^{CC}	R^{CC}	R_0^{CH}	R^{CH}
C_6H_6	2.640	2.662(4)	2.028	1.992(2)

TABLE IV. Binding energies in eV obtained by variational (Δ_{VMC}) and diffusion (Δ_{DMC}) Monte Carlo calculations with different trial wave functions for benzene. In order to calculate the binding energies yielded by the two-body Jastrow we used the atomic energies reported in Ref. 10. The percentages [$\Delta_{VMC}(\%)$ and $\Delta_{DMC}(\%)$] of the total binding energies are also reported.

	Δ_{VMC}	$\Delta_{VMC}(\%)$	Δ_{DMC}	$\Delta_{DMC}(\%)$
Kekulé+two-body	−30.57(5)	51.60(8)	⋯	⋯
Resonating Kekulé+two-body	−32.78(5)	55.33(8)	⋯	⋯
Resonating Dewar Kekulé+two-body	−34.75(5)	58.66(8)	−56.84(11)	95.95(18)
Kekulé+three-body	−49.20(4)	83.05(7)	−55.54(10)	93.75(17)
Resonating Kekulé+three-body	−51.33(4)	86.65(7)	−57.25(9)	96.64(15)
Resonating Dewar Kekulé+three-body	−52.53(4)	88.67(7)	−58.41(8)	98.60(13)
Full resonating+three-body	−52.65(4)	88.87(7)	−58.30(8)	98.40(13)

ecule to have a van der Waals like minimum, quite far from the experimental value. In order to have a reasonable description of the bond length and the atomization energy, one needs to include at least a $3s2p$ basis in the antisymmetric part, as pointed out in Ref. 37, and indeed an atomization energy compatible with the experimental result [0.11(1) eV] has been obtained within the extended geminal model[38] by using a much larger basis set $(9s,7p,4d,2f,1g)$.[39] This suggests that a complete basis set calculation with JAGP may describe also this molecule. However, as already mentioned in Sec. III D, our SR method cannot cope with a very large basis in a feasible computational time. Therefore we believe that at present the accuracy needed to describe correctly Be_2 is out of the possibilities of the approach.

B. Benzene and its radical cation

We studied the $^1A_{1g}$ ground state of the benzene molecule by using a very simple one particle basis set: for the AGP, a 2s1p DZ set centered on the carbon atoms and a 1s SZ on the hydrogen, instead for the three-body Jastrow, a 1s1p DZ-GTO set centered only on the carbon sites. C_6H_6 is a peculiar molecule, since its highly symmetric ground state, which belongs to the D_{6h} point group, is a resonance among different many-body states, each of them characterized by three double bonds between carbon atoms. This resonance is responsible for the stability of the structure and therefore for its aromatic properties. We started from a non resonating two-body Jastrow wave function, which dimerizes the ring and breaks the full rotational symmetry, leading to the Kekulé configuration. As we expected, the inclusion of the resonance between the two possible Kekulé states lowers the VMC energy by more than 2 eV. The wave function is further improved by adding another type of resonance, that includes also the Dewar contributions connecting third nearest neighbor carbons. As reported in Table IV, the gain with respect to the simplest Kekulé wave function amounts to 4.2 eV, but the main improvement arises from the further inclusion of the three-body Jastrow factor, which allows to recover the 89% of the total atomization energy at the VMC level. The main effect of the three-body term is to keep the total charge around the carbon sites to approximately six electrons, thus penalizing the double occupation of the p_z orbitals. The same important correlation ingredient is present in the well known Gutzwiller wave function already used for polyacetylene.[40] Within this scheme we have systematically

included in the three-body Jastrow part the same type of terms present in the AGP one, namely, both $g^{a,b}$ and $\lambda^{a,b}$ are nonzero for the same pairs of atoms. As expected, the terms connecting next nearest neighbor carbon sites are much less important than the remaining ones because the VMC energy does not significantly improve (see the full resonating +three-body wave function in Table IV). A more clear behavior is found by carrying out DMC simulations: the interplay between the resonance among different structures and the Gutzwiller-like correlation refines more and more the nodal surface topology, thus lowering the DMC energy by significant amounts. Therefore it is crucial to insert into the variational wave function all these ingredients in order to have an adequate description of the molecule. For instance, in Fig. 4 we report the density surface difference between the nonresonating three-body Jastrow wave function, which breaks the C_6 rotational invariance, and the resonating Kekulé structure, which preserves the correct A_{1g} symmetry:
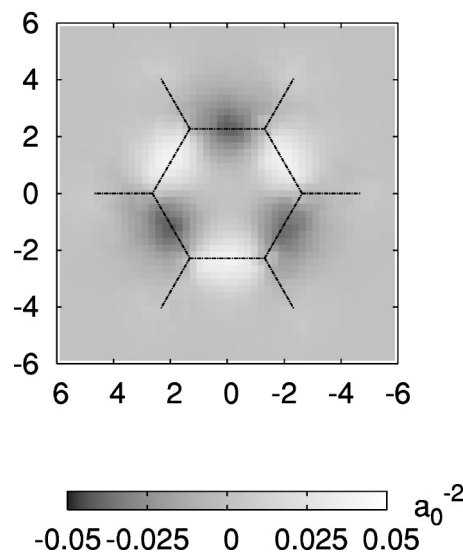
$\rho(r)$ resonating Kekule - $\rho(r)$ HF

FIG. 4. Surface plot of the charge density projected onto the molecular plane. The difference between the nonresonating (indicated as HF) and resonating Kekulé three-body Jastrow wave function densities is shown. Notice the corresponding change from a dimerized structure to a C_6 rotational invariant density profile.

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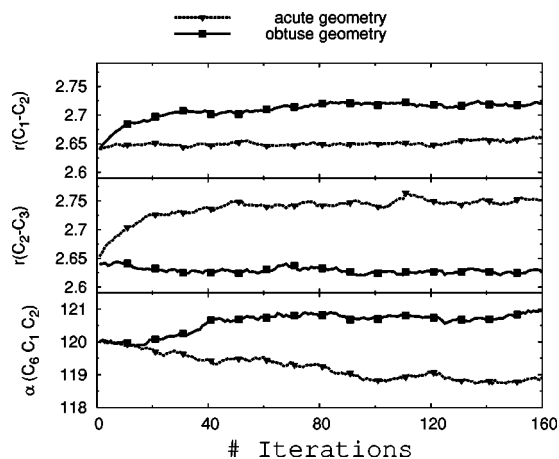
Correlated geminal wave function　　7121

FIG. 5. Plot of the convergence toward the equilibrium geometry for the $^2B_{2g}$ acute and the $^2B_{3g}$ obtuse benzene cation. Notice that both the simulations start from the ground state neutral benzene geometry and relax with a change both in the C-C bond lengths and in the angles. The symbols are the same of Table V.

TABLE V. Bond lengths (r) for the two lowest $^2B_{2g}$ and $^2B_{3g}$ states of the benzene radical cation. The angles α are expressed in degrees, the lengths in a_0. The carbon sites are numerated from 1 to 6.

	$^2B_{2g}$ acute	$^2B_{3g}$ obtuse	Computational method
$r(C_1-C_2)$	2.616	2.694	B3LYP/cc-pVTZ[a]
	2.649	2.725	BLYP/6-31G*[b]
	2.659(1)	2.733(4)	SR-VMC[c]
$r(C_2-C_3)$	2.735	2.579	B3LYP/cc-pVTZ[a]
	2.766	2.615	BLYP/6-31G*[b]
	2.764(2)	2.628(4)	SR-VMC[c]
$\alpha(C_6C_1C_2)$	118.4	121.6	B3LYP/cc-pVTZ[a]
	118.5	121.5	BLYP/6-31G*[b]
	118.95(6)	121.29(17)	SR-VMC[c]

[a]Reference 45.
[b]Reference 44.
[c]This work.

the change in the electronic structure is significant. The best result for the binding energy is obtained with the Kekulé Dewar resonating three-body wave function, which recovers 98.6% of the total atomization energy with an absolute error of 0.84(8) eV. As Pauling[41] first pointed out, benzene is a genuine RVB system, indeed it is well described by the JAGP wave function. Moreover Pauling gave an estimate for the resonance energy of 1.605 eV from thermochemical experiments in qualitative agreement with our results. A final remark about the error in the total atomization energy: the latest frozen core CCSD(T) calculations[42,43] are able to reach a precision of 0.1 eV, but only after the complete basis set extrapolation and the inclusion of the core valence effects to go beyond the pseudopotential approximation. Without the latter corrections, the error is quite large even in the CCSD approach, amounting to 0.65 eV.[42] In our case, such an error arises from the fixed node approximation, whose nodal error is not compensated by the difference between the atomic and the molecular energies, as already noticed in the previous subsection.

The radical cation $C_6H_6^+$ of the benzene molecule has been the subject of intense theoretical studies,[44,45] aimed to focus on the Jahn-Teller distorted ground state structure. Indeed the ionized $^2E_{1g}$ state, which is degenerate, breaks the symmetry and experiences a relaxation from the D_{6h} point group to two different states, $^2B_{2g}$ and $^2B_{3g}$, that belong to the lower D_{2h} point group. In practice, the former is the elongated acute deformation of the benzene hexagon, the latter is its compressed obtuse distortion. We applied the SR structural optimization, starting from the $^2E_{1g}$ state, and the minimization correctly yielded a deformation toward the acute structure for the $^2B_{2g}$ state and the obtuse for the $^2B_{3g}$ one; the first part of the evolution of the distances and the angles during those simulations is shown in Fig. 5. After this equilibration, average over 200 further iterations yields bond distances and angles with the same accuracy as the all-electron BLYP/6-31G* calculations reported in Ref. 44 (see Table V). As it appears from Table VI not only the structure

but also the DMC total energy is in perfect agreement with the BLYP/6-31G*, and much better than SVWN/6-31G* that does not contain semi empirical functionals, for which the comparison with our calculation is more appropriate, being fully *ab initio*.

The difference of the VMC and DMC energies between the two distorted cations are the same within the error bars; indeed, the determination of which structure is the real cation ground state is a challenging problem, since the experimental results give a difference of only few meV in favor of the obtuse state and also the most refined quantum chemistry methods are not in agreement among themselves.[44] A more affordable problem is the determination of the adiabatic ionization potential (AIP), calculated for the $^2B_{3g}$ state, following the experimental hint. Recently, very precise CCSD(T) calculations have been performed in order to establish a benchmark theoretical study for the ionization threshold of benzene;[45] the results are reported in Table VII. After the correction of the zero point energy due to the different structure of the cation with respect to the neutral molecule and taken from a B3LYP/cc-pVTZ calculation reported in Ref. 45, the agreement among our DMC result, the benchmark calculation and the experimental value is impressive. Notice that in this case there should be a perfect cancellation of nodal errors in order to obtain such an accurate value; however, we believe that it is not a fortuitous result, because in this case the underlying nodal structure does not change much by adding or removing a single electron. Therefore we expect that this property holds for all the affinity and ionization energy calculations with a particularly accurate variational wave function as the one we have proposed here. Nevertheless DMC is needed to reach the chemical accuracy,

TABLE VI. Total energies for the $^2B_{2g}$ and $^2B_{3g}$ states of the benzene radical cation after the geometry relaxation. A comparison with a BLYP/6-31G* and SVWN/6-31G* all-electron calculation (Ref. 44) is reported.

	VMC	DMC	BLYP/6-31G*	SVWN/6-31G*
$^2B_{2g}$	−231.4834(15)	−231.816(3)	−231.815495	−230.547931
$^2B_{3g}$	−231.4826(14)	−231.812(3)	−231.815538	−230.547751

since the VMC result is slightly off from the experimental one just by few tenths of eV. The AIP and the geometry determination for the $C_6H_6^+$ are encouraging to pursue this approach, with the aim to describe even much more interesting and challenging chemical systems.

V. CONCLUSION

In this work, we have tested the JAGP wave function on simple molecular systems where accurate results are known. As shown in the preceding section a large amount of the correlation energy is already recovered at the variational level with a computationally very efficient and feasible method, extended in this work to the nuclear geometry optimization. Indeed, much larger systems should be tractable because, within the JAGP ansatz, it is sufficient to sample a single determinant whose dimension scales only with the number of electrons. The presence of the Jastrow factor implies the evaluation of multidimensional integrals that, so far can be calculated efficiently only with the Monte Carlo method. Within this framework, it is difficult to reach the complete basis set limit, both in the Jastrow and the AGP terms, although some progress has been made recently.[19,46] Even if the dimension of the basis is limited by the difficulty to perform energy optimization with a very large number of variational parameters, we have obtained the chemical accuracy for most cases studied. From a general point of view the basis set convergence of the JAGP is expected to be faster than AGP considering that the electron-electron cusp condition is fulfilled exactly at each level of the expansion. Nevertheless, all results presented here can be systematically improved with larger basis set. In particular the Be_2 bonding distance should be substantially corrected by a more complete basis, that we have not attempted so far.[39]

The usefulness of the JAGP wave function is already well known in the study of strongly correlated systems defined on a lattice. For instance, in the widely studied Hubbard model, as well as in any model with electronic repulsion, it is not possible to obtain a superconducting ground state at the mean-field Hartree-Fock level. On the contrary, as soon as a correlated Jastrow term is applied to the BCS wave function (equivalent to the AGP wave function in momentum space[47]), the stabilization of a d-wave superconducting order parameter is possible, and is expected to be a realistic property of the model.[48] More interestingly the presence of the Jastrow factor can qualitatively change the wave function especially at one electron per site filling, by converting a BCS superconductor to a Mott insulator with a finite charge gap.[49]

The same effect is clearly seen for the gedanken experiment of a dilute gas of H_2 molecules, a clarifying test example already used in the introduction. The AGP wave function is essentially exact for a single molecule (at least with the complete basis set), but its obvious size consistent extension to the gas would lead to the unphysical result of superconductivity because the charge around each molecule would be free to fluctuate within the chosen set of geminal orbitals. Only the presence of the Jastrow term added to this wave function, allows the local conservation of the charge around

TABLE VII. Adiabatic ionization potential of the benzene molecule; our estimate is done for the $^2B_{3g}$ relaxed geometries of the benzene radical cation, with an inclusion of the zero point motion correction between the $^2B_{3g}$ state and the $^1A_{1g}$ neutral molecule ground state, calculated in Ref. 45 at the B3LYP/6-31G* level.

	VMC[a]	DMC[a]	CCSD(T)/cc-pV∞Z[b]	experiment[c]
AIP	8.86(6)	9.36(8)	9.29(4)	
ΔZPE_{ad}	-0.074	-0.074	-0.074	
best estimate	8.79(6)	9.29(8)	9.22(4)	9.2437(8)

[a]This work.
[b]Reference 45.
[c]Reference 53.

the molecule, by forbidding unphysical H_2 dimers with more than two electrons. Once the charge is locally conserved, the phase of the BCS-AGP wave function cannot have a definite value and phase coherence is correctly forbidden by the Jastrow factor. In the present work, the interplay between the Jastrow and the geminal part has been shown to be very effective in all cases studied and particularly in the nontrivial case of the benzene molecule, where we have shown systematically the various approximations. Only when *both* the Jastrow and the AGP terms are accurately optimized together, the AGP nodal structure of the wave function is considerably improved. For the above reasons and the size consistency of the JAGP we expect that this wave function should be generally accurate also in complex systems made by many molecules. The local conservation of the charge around each molecule is taken into account by the Jastrow factor, whereas the quality of each molecule is described also by the AGP geminal part exactly as in the H_2 gas example.

In the near future it is very appealing and promising to extend the JAGP study to the DNA nitrogenous bases, whose geometrical structure is very similar to the benzene ring. In particular, we plan to accurately evaluate the energetics (reduction potential, ionization energies, electron affinity, etc.) of DNA bases and base pairs, quantities of great importance to characterize excess electron and hole transfer which are involved in radiation damage as well as in the development of DNA technologies.

ACKNOWLEDGMENTS

APPENDIX A: STABILIZATION OF THE SR TECHNIQUE

Whenever the number of variational parameters increases, it often happens that the stochastic $(N+1)\times(N+1)$ matrix

$$s_{k,k'} = \frac{\langle \Psi | O_k O_{k'} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{A1}$$

TABLE VIII. Matrix of the λ coefficients of the geminal function expansion in the pairing determinant for the Li₂ molecule. The matrix is symmetric to have a spin singlet, therefore we show only the upper part of it.

	$1s_a$	$2s_a$	$2pz_a$	$2px_a$	$2py_a$	$3s_a$	$1s_b$	$2s_b$	$2pz_b$	$2px_b$	$2py_b$	$3s_b$
$1s_a$	1	-2.162×10^{-3}	-6.838×10^{-3}	0	0	-2.877×10^{-3}	0	0	0	0	0	0
$2s_a$	⋮	6.22×10^{-4}	-1.601×10^{-4}	0	0	2.031×10^{-3}	0	6.79×10^{-3}	-4.67×10^{-4}	0	0	1.790×10^{-3}
$2pz_a$	⋮	⋮	-4.25×10^{-4}	0	0	-1.132×10^{-3}	0	-4.67×10^{-4}	3.211×10^{-4}	0	0	7.67×10^{-4}
$2px_a$	⋮	⋮	⋮	-1.351×10^{-3}	0	0	0	0	0	-1.173×10^{-3}	0	0
$2py_a$	⋮	⋮	⋮	⋮	-1.351×10^{-3}	0	0	0	0	0	-1.173×10^{-3}	0
$3s_a$	⋮	⋮	⋮	⋮	⋮	-1.541×10^{-3}	0	1.790×10^{-3}	7.67×10^{-4}	0	0	-8.91×10^{-4}
$1s_b$	⋮	⋮	⋮	⋮	⋮	⋮	1	-2.162×10^{-3}	-6.838×10^{-3}	0	0	-2.877×10^{-3}
$2s_b$	⋮	⋮	⋮	⋮	⋮	⋮	⋮	6.22×10^{-4}	-1.601×10^{-4}	0	0	1.790×10^{-3}
$2pz_b$	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	-4.25×10^{-4}	0	0	-1.132×10^{-3}
$2px_b$	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	-1.351×10^{-3}	0	0
$2py_b$	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	-1.351×10^{-3}	0
$3s_b$	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	-1.541×10^{-3}

becomes singular, i.e., the condition number, defined as the ratio $\sigma = \lambda_N/\lambda_1$ between its maximum λ_N and minimum eigenvalue λ_1, is too large. In that case the inversion of this matrix generates clear numerical instabilities which are difficult to control especially within a statistical method. Here $O_k = d\ln\Psi(x)/d\alpha_k$ are the operators corresponding to the variational parameters α_k appearing in the wave function Ψ for $k=1,...,N$, whereas for $k=0$ the operator O_0 represents the identity one.

The first successful proposal to control this instability was to remove from the inversion problem (12), required for the minimization, those directions in the variational parameter space corresponding to exceedingly small eigenvalues λ_i.

In this Appendix we describe a better method. As a first step, we show that the reason of the large condition number σ is due to the existence of "redundant" variational parameters that do not make changes to the wave function within a prescribed tolerance ϵ. Indeed in practical calculations, we are interested in the minimization of the wave function within a reasonable accuracy. The tolerance ϵ may represent therefore the distance between the exact normalized variational wave function which minimizes the energy expectation value and the approximate acceptable one, for which we no longer iterate the minimization scheme. For instance, $\epsilon = 1/1000$ is by far acceptable for chemical and physical interest. A stable algorithm is then obtained by simply removing the parameters that do not change the wave function by less than ϵ from the minimization. An efficient scheme to remove the "redundant parameters" is also given.

Let us consider the N normalized states orthogonal to Ψ, but not orthogonal among each other

$$|e_i\rangle = \frac{(O_k - s_{k,0})|\Psi\rangle}{\sqrt{\langle\Psi|(O_k - s_{k,0})^2|\Psi\rangle}}, \qquad (A2)$$

where $s_{k,0}$ is defined in Eq. (A1). These normalized vectors define N directions in the N-dimensional variational parameter manifold, which are independent as long as the determinant S of the corresponding $N\times N$ overlap matrix

$$\bar{s}_{k,k'} = \langle e_k|e_{k'}\rangle \qquad (A3)$$

is nonzero. The number S is clearly positive and it assumes its maximum value 1 whenever all the directions e_i are mutually orthogonal. On the other hand, let us suppose that there exists an eigenvalue $\bar{\lambda}$ of $\bar{s}$ smaller than the square of the desired tolerance ϵ^2, then the corresponding eigenvector $|v\rangle = \Sigma_i a_i |e_i\rangle$ is such that

$$\langle v|v\rangle = \sum_{i,j} a_i a_j \bar{s}_{i,j} = \bar{\lambda}, \qquad (A4)$$

where the latter equation holds due to the normalization condition $\Sigma_i a_i^2 = 1$. We arrive therefore to the conclusion that it is possible to define a vector v with almost vanishing norm $|v| = \sqrt{\bar{\lambda}} \leqslant \epsilon$ as a linear combination of e_i, with at least some nonzero coefficient. This implies that the N directions e_k are linearly dependent within a tolerance ϵ and one can safely remove at least one parameter from the calculation.

TABLE IX. Matrix of the λ coefficients of the pairing function expansion in the three-body Jastrow for the Li_2 molecule. As in the previous table only the upper part is reported.

	sG_a	pGx_a	pGy_a	pGz_a	sG_b	pGx_b	pGy_b	pGz_b
sG_a	-0.2427	0	0	-2.713×10^{-4}	-5.136×10^{-4}	0	0	-1.202×10^{-5}
pGx_a	$\cdots$	-0.1772	0	0	0	-7.997×10^{-3}	0	0
pGy_a	$\cdots$	$\cdots$	-0.1772	0	0	0	-7.997×10^{-3}	0
pGz_a	$\cdots$	$\cdots$	$\cdots$	1.027×10^{-2}	1.202×10^{-5}	0	0	-8.749×10^{-3}
sG_b	$\cdots$	$\cdots$	$\cdots$	$\cdots$	-0.2427	0	0	-2.713×10^{-4}
pGx_b	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	-0.1772	0	0
pGy_b	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	-0.1772	0
pGz_b	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	1.027×10^{-2}

In general whenever there are p vectors v_i that are below the tolerance ϵ the optimal choice to stabilize the minimization procedure is to remove p rows and p columns from the matrix (A3), in such a way that the corresponding determinant of the $(N-p)\times(N-p)$ overlap matrix is maximum.

From practical purposes it is enough to consider an iterative scheme to find a large minor, but not necessarily the maximum one. This method is based on the inverse of $\bar{s}$. At each step we remove the ith row and column from $\bar{s}$ for which $\bar{s}_{i,i}^{-1}$ is maximum. We stop to remove rows and columns after p inversions. In this approach we exploit the fact that, by a consequence of the Laplace theorem on determinants, $\bar{s}_{k,k}^{-1}$ is the ratio between the described minor without the kth row and column and the determinant of the full $\bar{s}$ matrix. Since within a stochastic method it is certainly not possible to work with a machine precision tolerance, setting $\epsilon=0.001$ guarantees a stable algorithm, without affecting the accuracy of the calculation. The advantage of this scheme, compared with the previous one,[17] is that the less relevant parameters can be easily identified after few iterations and do not change further in the process of minimization.

APPENDIX B: SIZE CONSISTENCY OF THE THREE-BODY JASTROW FACTOR

In order to prove the size consistency property of the three-body Jastrow factor described in Sec. II C, let us take into account a system composed by two well separated subsystems A and B, which are distinguishable and whose dimensions are much smaller than the distance between themselves; in general they may contain more then one atom. In this case the Jastrow function J_3 (10) can be written as $J_3=e^U$ with

$$U=\frac{1}{2}\sum_{\substack{i,j\in A \\ i\neq j}}\phi(r_i,r_j)+\frac{1}{2}\sum_{\substack{i,j\in B \\ i\neq j}}\phi(r_i,r_j)$$

$$+\sum_{i\in A}\sum_{j\in B}\phi(r_i,r_j), \tag{B1}$$

where we have explicitly considered the sum over different subsystems. As usual, the two particle function $\phi(r_i,r_j)$ is expanded over a single particle basis ψ, centered on each nucleus of the system

$$\phi(r_i,r_j)=\sum_{m,n}\lambda^{m,n}\psi^m(r_i)\psi^n(r_j). \tag{B2}$$

The indices n and m refer not only to the basis elements but also to the nuclei which the orbitals are centered on.

The self consistency problem arises from the last term in Eq. (B1), i.e., when the electron r_i belongs to A and r_j to B. If the Jastrow is size consistent, whenever A and B are far apart from each other this term must vanish or at most generate a one-body term, that is, in turn size consistent, as we are going to show in the following. In the limit of large separation all the $\lambda^{m,n}$ off diagonal terms connecting any basis element of A to any basis element of B must vanish. The second requirement is a sufficiently fast decay of the basis set orbitals $\psi(r)$ whenever $r\rightarrow\infty$, except at most for a constant term C_n which may be present in the single particle orbitals, and is useful to improve the variational energy.

For the sake of generality, suppose that the system A contains M_A nuclei and N_A electrons. The first requirement implies that

$$\phi(r_i,r_j)=\sum_{m,n\in A}\lambda^{m,n}\psi^m(r_i)\psi^n(r_j)$$

$$+\sum_{m,n\in B}\lambda^{m,n}\psi^m(r_i)\psi^n(r_j), \tag{B3}$$

instead the second allows to write the following expression for the mixed term in Eq. (B1):

$$\sum_{i\in A}\sum_{j\in B}\phi(r_i,r_j)=N_B\sum_{n\in A}C_nP_n+N_A\sum_{m\in B}C_mP_m, \tag{B4}$$

where the factors P_n are one-body terms defined as

TABLE X. Orbital basis set parameters used for the Li_2 molecule. Since the molecule is homonuclear the parameters of the atom b are the same as the atom a.

	z_1	z_2	p
ϕ_{1s_a}	2.4485	4.2891	0.4278
ϕ_{2s_a}	0.5421	1.4143	-1.5500
ϕ_{2px_a}	0.6880	$\cdots$	$\cdots$
ϕ_{2py_a}	0.6880	$\cdots$	$\cdots$
ϕ_{2pz_a}	1.0528	$\cdots$	$\cdots$
ϕ_{3s_a}	0.6386	$\cdots$	$\cdots$
ϕ_{sG_a}	1.4356	$\cdots$	-0.2044
ϕ_{pGx_a}	0.7969	4.4217	-1.2689
ϕ_{pGy_a}	0.7969	4.4217	-1.2689
ϕ_{pGz_a}	8.98010^{-3}	-0.1924	0.3229

$$P_n = \begin{cases} \sum\limits_{m \in A} \lambda^{n,m} \sum\limits_{i \in A} \psi^m(r_i) & \text{if } n \in A \\ \sum\limits_{m \in B} \lambda^{n,m} \sum\limits_{i \in B} \psi^m(r_i) & \text{if } n \in B \end{cases}. \tag{B5}$$

Notice that if all the orbitals decay to zero, the size consistency is immediately recovered, since the sum in Eq. (B4) vanishes. Analogously to the derivation we have done to extract the one body contribution from the mixed term, the other two terms on the right-hand side of Eq. (B1) can be rearranged in the following form:

$$\frac{1}{2} \sum_{\substack{i,j \in A \\ i \neq j}} \phi(r_i, r_j) = (N_A - 1) \sum_{n \in A} C_n P_n$$

$$+ \text{two-body terms}, \tag{B6}$$

and the sum in Eq. (B1) can be rewritten as

$$U = (N-1) \sum_{n \in A} C_n P_n + (N-1) \sum_{n \in B} C_n P_n$$

$$+ \text{two-body size consistent terms}. \tag{B7}$$

Therefore the size consistency implies that the scaling of the C_n with the total number of particle N is

$$C_n = \frac{c_n}{N-1}, \tag{B8}$$

as mentioned in Sec. II C.

APPENDIX C: AN EXAMPLE CASE: JAGP WAVE FUNCTION FOR Li_2

We briefly describe the application of the JAGP to the Li_2 molecule. This example shows the beauty of our approach that allows to describe the chemical bond as resonance of many pairing functions whose importance is weighted by the λ coefficients. In the expansion of the geminal function for the determinant in Eq. (2) we used six orbitals for each atom:

$$\phi_{1s}, \phi_{2s} = C_{1s}(e^{-z_1 r} + p e^{-z_2 r}), \tag{C1}$$

$$\phi_{2p} = C_{2p} \vec{r} e^{-z_1 r}, \tag{C2}$$

$$\phi_{3s} = C_{3s} r^2 e^{-z_1 r}. \tag{C3}$$

The parameters p in $1s, 2s$ orbitals are fixed by the single atomic cusp conditions, and C_{1s}, C_{2p}, C_{3s} are the normalization constants. These orbitals are connected by different $\lambda_{m,n}^{a,b}$, which obey the constraints given by the symmetry of the system, and are reported in Table VIII. Since the trial function does not need to be normalized we set $\lambda_{1s,1s}^{a,a}$ equal to 1. The total number of nonzero λ is 58, but the constraints allow to reduce them to 18 variational parameters.

In the Jastrow part we used a two-body term that is a slightly modified version of the Eq. (9). In fact due to the simple symmetry of the system is possible to build a Jastrow more suitable for this diatomic molecule, namely

$$u(r,z) = \frac{r}{2[1 + \sqrt{a(x^2+y^2) + b z^2}]}, \tag{C4}$$

which distinguishes the different components of the two electrons distance. We found that this two-body Jastrow factor is particularly useful for Li_2, which is much more elongated than the other molecules studied here, for which the usual form in Eq. (9) has been employed. The optimal parameters obtained for the Jastrow are $a = 0.8796$, $b = 0.7600$. In the expansion of the pairing function for the three body Jastrow term [see Eq. (10)] we used the following orbitals:

$$\phi_{sG} = e^{-z_1 r^2} + p, \tag{C5}$$

$$\phi_{pG} = \vec{r}(e^{-z_1 r^2} + p e^{-z_2 r^2}). \tag{C6}$$

The λ matrix that connects these orbitals is given in Table IX; this matrix fulfills the same symmetry constraints as in the case of the paring determinant. In this case the total number of nonzero λ is 24 and the symmetry reduces the variational freedom to only eight parameters. The single particle orbitals are reported in Table X, and include other 15 parameters.

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