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Geminal wave functions with Jastrow correlation: A first application to atoms

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We introduce a simple generalization of the well-known geminal wave function already applied in quantum chemistry to atoms and small molecules. The main feature of the proposed wave function is the presence of the antisymmetric geminal part together with a Jastrow factor. Both the geminal and the Jastrow play a crucial role in determining the remarkable accuracy of the many-body state: the former permits the correct treatment of the nondynamic correlation effects; the latter allows the wave function to fulfill the cusp conditions and makes the geminal expansion rapidly converge to the lowest possible variational energies. This ansatz is expected to provide a substantial part of the correlation energy for general complex atomic and molecular systems. The antisymmetric geminal term can be written as a single determinant even in the polarized cases. In general, therefore, the computational effort to sample this correlated wave function is not very demanding, the scaling of the algorithm with the number of atoms being comparable with the simplest Hartree–Fock calculation. We applied this Jastrow-geminal approach to atoms up to $Z=14$, always getting good variational energies, by particularly improving those with a strong multiconfigurational nature. Our wave function is very useful for Monte Carlo techniques, such as fixed node. Indeed, the nodal surface obtained within this approach can be substantially improved through the geminal expansion. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1604379]

I. INTRODUCTION

One of the main goals in electronic structure calculations is to deal with a wave function both accurate enough to predict the physical properties of a quantum system and simple enough to allow feasible computations of them. In particular, although multideterminantal CI-like methods could be in principle very accurate, in practice the determinantal expansion becomes heavier and heavier from the computational point of view, as the number of determinants dramatically increases with the complexity of the electron system. On the other hand, a single determinantal wave function kernel of methods like Hartree–Fock (HF) and density functional theory (DFT), is sometimes not sufficient to describe strongly correlated systems, for instance the transition metal compounds and the near-degenerate shell structure of some atoms.

Since the 50's, the intensive efforts to explain the superconductivity theoretically have highlighted the role of pairing in the electronic structure. The BCS wave function belongs to an original ansatz in which the correlation is introduced through the product of pairing functions (in this context called Cooper pairs), already exploited in quantum chemistry by the pioneering work of Hurley *et al.*[1] to treat correlation effects in molecular properties. Their wave function was called *antisymmetrized geminal power* (AGP) that has been shown to be the particle–conserving version of the BCS ansatz.[2] It includes the single determinantal wave func-

tion, i.e., the uncorrelated state, as a special case and introduces correlation effects in a straightforward way, through the expansion of the pairing function (geminal): therefore, it was studied as a possible alternative to the other multideterminantal approaches. Although this ansatz seemed so appealing, it led to some expensive optimization procedures[3,4] with numerical problems,[5,6] in particular when applied to large systems, and so it turned out to be noncompetitive with respect to HF and CI.

We show in this paper that the use of Monte Carlo methods can overcome the previous difficulties in optimizing the AGP wave functions. Two of the most appealing features of these techniques are the possibility to tackle in a smart way the many-body interacting problem, having freedom in the choice of the functional form of the wave function, and to implement very efficient projection algorithms, like diffusion Monte Carlo (DMC) and Green's function Monte Carlo (GFMC). The trial wave function used in these methods is obtained by multiplying an antisymmetric term (usually called the Slater term) to a Jastrow factor, which correlates the electrons and takes into account the interelectron cusp conditions the true wave function must fulfill. The Slater term can be either HF- or CI- or AGP-like. As already pointed out by Umrigar,[7] the rate of convergence of CI expansion is increased by the Jastrow factor, just because it allows the wave function to have the correct cusps, otherwise present only asymptotically in the linear combination of determinants.

In this paper we study the AGP–Jastrow (AGP+J) wave function, applied to the atomic problem. The wave function we consider is actually a resonating valence bond

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(RVB) state, first investigated in 1973 by Anderson[8,9] to study the high–temperature superconductivity, and later applied by Bouchaud and Lhuillier[10] in Monte Carlo calculations of liquid ^{3}He. It is remarkable that this kind of wave function can describe well the ground state of all the atoms studied here, in particular those light atoms affected by non-dynamic correlation. Moreover, the Jastrow part is crucial not only in reducing the pairing expansion but also in inducing a significant improvement of the nodal surfaces of the wave function, once we optimize both the Jastrow and the determinantal part at the same time. The minimization of the total energy can be efficiently performed by using an optimization procedure based upon the stochastic reconfiguration (SR) method,[11] which allows us to determine a large number of variational parameters, both for the Jastrow and the determinantal part. Due to the simplicity of the AGP+J wave function and its capability to take into account resonating Slater configurations, this wave function is expected to be appropriate also for molecules and more complex systems.

The paper is organized as follows: in Sec. II we define the wave function, in Sec. III we describe the energy minimization method, and finally in Secs. IV and V we present detailed results and conclusions.

II. FUNCTIONAL FORM OF THE WAVE FUNCTION

The wave function we used in our QMC calculations is the antisymmetrized product of geminals (AGP), multiplied by a simple symmetric Jastrow factor

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \Psi_{AGP}(\mathbf{r}_1, \ldots, \mathbf{r}_N) J(\mathbf{r}_1, \ldots, \mathbf{r}_N), \qquad (1)$$

where the origin of the reference frame is the nuclear position. The two parts of the wave function (1) will be described in detail below.

A. The determinantal part

Let Φ be the pairing function (geminal) which takes into account the correlation between two electrons with opposite spin. If the system is unpolarized ($N^\uparrow = N^\downarrow = N/2$) and the state is a spin singlet, the AGP wave function is

$$\Psi_{AGP}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$
$$= \hat{A}[\Phi(\mathbf{r}_1^\uparrow, \mathbf{r}_1^\downarrow)\Phi(\mathbf{r}_2^\uparrow, \mathbf{r}_2^\downarrow)\cdots\Phi(\mathbf{r}_{N/2}^\uparrow, \mathbf{r}_{N/2}^\downarrow)], \qquad (2)$$

where $\hat{A}$ is an operator that antisymmetrizes the product in the square brackets and the geminal is a singlet

$$\Phi(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) = \phi(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \qquad (3)$$

implying that $\phi(\mathbf{r}, \mathbf{r}')$ is symmetric under a permutation of its variables. Given this conditions, one can prove[12] that the spatial part of the Ψ_{AGP} can be written in a very compact form

$$\Psi_{AGP}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \det(A_{ij}), \qquad (4)$$

where A_{ij} is an $(N/2) \times (N/2)$ matrix defined as

$$A_{ij} = \phi(\mathbf{r}_i^\uparrow, \mathbf{r}_j^\downarrow). \qquad (5)$$

We are going to extend the definition of the geminal wave function to a polarized system, i.e., a system with a different number of electrons for each spin. This generalization of the geminal model was first proposed by Coleman[13] and called GAGP. Without loss of generality, one can assume that the number of up particles ($N^\uparrow$) is greater than the down ones ($N^\downarrow$). In order to write the many-body wave function with the geminals, one needs to introduce $N^\uparrow - N^\downarrow$ single particle spin orbitals $\bar{\Phi}_j$ not associated with any geminal and holding unpaired electrons. Once again, one recovers the compact notation (4) for the spatial part of Ψ_{AGP} (see the Appendix), but this time A_{ij} is an $N^\uparrow \times N^\uparrow$ matrix defined in the following way:

$$A_{ij} = \begin{cases} \phi(\mathbf{r}_i^\uparrow, \mathbf{r}_j^\downarrow) & \text{for } j = 1, N^\downarrow \\ \bar{\phi}_j(\mathbf{r}_i^\uparrow) & \text{for } j = N^\downarrow + 1, N^\uparrow, \end{cases} \qquad (6)$$

where the index i ranges from 1 to $N^\uparrow$.

The pairing function can be expanded over a basis of single particle orbitals[14]

$$\phi(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) = \sum_{i=1}^{M} \lambda_i \psi_i(\mathbf{r}^\uparrow) \psi_i^*(\mathbf{r}^\downarrow), \qquad (7)$$

where ψ_i are general real or complex normalized functions and λ_i are variational parameters that may depend on the chosen spatial symmetry of the geminal. Hereafter, for simplicity, we do not assume that the orbitals are mutually orthogonal.

For the application to atoms, in order that the wave function Ψ has a definite angular momentum, it is convenient that the geminal is rotationally invariant around the nucleus. This requirement is achieved by taking the generic orbital ψ_i to be an eigenfunction of the single particle angular momentum operators l^2 and l_z; hence, the orbital will be denoted by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi), \qquad (8)$$

where Y_{lm} are spherical harmonics with standard notations and the radial part R_{nl} depends on the principal quantum number n. In this way, the atomic geminal function takes the form

$$\phi(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) = \sum_{nl} \sum_{m=-l}^{l} \lambda_{nl}(-1)^m \psi_{nlm}(\mathbf{r}^\uparrow) \psi_{nlm}^*(\mathbf{r}^\downarrow). \qquad (9)$$

In the polarized case, the remaining orbitals $\bar{\psi}_j$ may change the total angular momentum and spin quantum numbers with the same rules valid for Slater-type wave functions. Within our ansatz it is therefore possible to have definite total spin and angular momenta, at least in all cases when the conventional Slater determinant does. On the other hand, whenever a linear combination of Slater determinants is required to have a definite symmetry, e.g., with Clebsch–Gordon coefficients, the same holds for the GAGP wave function. Indeed, each GAGP can be obtained by antisymmetrizing the product of Slater orbitals (that determine the quantum numbers) and a singlet zero angular momentum term built with the remaining electron pairs. In this way, as far as the quantum numbers

of the many-body wave function are concerned, the expansion is similar to the conventional one with simple Slater determinants.

The minimal geminal expansion is for $M = N^{\downarrow}$, then the AGP wave function is reduced to the HF one; instead, if M is greater than $N^{\downarrow}$, one can prove that the AGP is equivalent to a linear combination of many Slater determinants (see Appendix B). Therefore, within this functional form, one is able to introduce the correlation in the determinantal part of the wave function just by adding some terms in the geminal expansion. For a two–electron closed–shell system, like helium atom, or an ensemble of such noninteracting systems, this wave function is exact in the $M = \infty$ limit. For the other atoms we will show that the AGP+J wave function can lead to very good variational energies even in the cases where the HF approximation is rather poor, especially for light elements.

In order to optimize the radial part R_{nl} of the the single particle orbitals, we expand these radial functions in a Slater basis, in close analogy with Roothaan–Hartree–Fock calculations,[15] namely using functions of the type

$$r^{n-1}e^{-z_k r}, \tag{10}$$

with $n \geq 1$, taking in principle as many different z_k's as required for convergence.

In the Roothaan–Hartree–Fock the coefficients of the linear combinations are more involved, since the orthogonality among all single particle states is required. In the Monte Carlo approach we have found that it is much simpler and more efficient to deal with nonorthogonal orbitals, without spoiling the accuracy of the calculation. In fact, for light elements with $Z \leq 15$, studied here, it is possible to obtain almost converged results by using only two exponentials for each radial component (double zeta).

Hence, our single particle orbitals read in general

$$R_{nl}(r) = C r^{n-1}(e^{-z_1 r} + p e^{-z_2 r}), \tag{11}$$

where p is another variational parameter and C is the normalization factor for the radial part R_{nl}

$$C = \frac{1}{\sqrt{(2n)!}}((2z_1)^{-(2n+1)} + 2p(z_1 + z_2)^{-(2n+1)}$$
$$+ p^2(2z_2)^{-(2n+1)})^{-1/2}. \tag{12}$$

Actually, p is not free for all the orbitals: indeed, for a more accurate variational wave function, we impose the electron–nucleus cusp condition,[16,17] which is satisfied by the exact many-body ground state and implies that each orbital must fulfill the following relation:

$$\frac{\partial \hat{\psi}}{\partial r} = -Z\psi \tag{13}$$

at $r = 0$ (the caret denotes the spherical average). That condition is automatically obeyed by all but $1s$ and $2s$ orbitals of the type given in Eq. (11). Instead, the parameter p of $1s$ orbital must be

$$p = \frac{z_1 - Z}{Z - z_2}, \tag{14}$$

and for the $2s$ state, in order to fulfill Eq. (13), we choose a functional form of the type

$$\psi_{2s}(r) = e^{-z_1 r} + (p + \alpha r)e^{-z_2 r}, \tag{15}$$

where α is a further variational parameter and p is given by

$$p = \frac{z_1 - \alpha - Z}{Z - z_2}. \tag{16}$$

In our study, we found that the presence of the α term leads to a very marginal improvement of the variational wave function; therefore, we set $\alpha = 0$ and we kept the $1s$ and $2s$ orbitals to have the same functional form, in order to reduce the total number of parameters.

B. The Jastrow factor

The Jastrow factor in our wave function is very simple and has been widely used in previous Monte Carlo electronic structure calculations

$$J(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \prod_{i < j} \exp(f(\mathbf{r}_i, \mathbf{r}_j)), \tag{17}$$

where the product is over all pairs of electrons and for simplicity the function f depends only on their relative distance r_{ij} and their spins σ_i and σ_j, namely

$$f_{\text{two body}}(r_{ij}) = \frac{a_{\sigma_i \sigma_j} r_{ij}}{1 + b_{\sigma_i \sigma_j} r_{ij}}. \tag{18}$$

The value of $a_{\sigma_i \sigma_j}$ is fixed by the cusp condition at the coalescence points of two electrons and $b_{\sigma_i \sigma_j}$ contains at most three free variational parameters, as $b_{\uparrow\downarrow} = b_{\downarrow\uparrow}$ is implied by the spatial symmetry of the Jastrow factor. The cusp conditions for parallel and antiparallel spin electrons are different and yield two different values of $a_{\sigma_i \sigma_j}$

$$a = \tfrac{1}{4} \quad \text{for} \quad \sigma_i = \sigma_j \tag{19a}$$

$$a = \tfrac{1}{2} \quad \text{for} \quad \sigma_i \neq \sigma_j. \tag{19b}$$

As pointed out in Ref. 18, whenever $a_{\sigma_i \sigma_j}$ or $b_{\sigma_i \sigma_j}$ depend on the electron spins $\sigma_i \sigma_j$, the wave function will be *spin contaminated*, i.e., it will not be an eigenstate of the total spin operator S^2. We have chosen to preserve the correct spin symmetry of the total wave function, by keeping $a_{\sigma_i \sigma_j} = 1/2$ and $b_{\sigma_i \sigma_j} = b$, hence fulfilling only the second condition (19b). Indeed, the cusp condition for electrons with parallel spins is much less important because their probability to get close is clearly small, due to the Pauli principle.

For the nitrogen atom, we checked the quality of this wave function with respect to a spin-contaminated one with two variational parameters, $b_{\uparrow\uparrow} = b_{\downarrow\downarrow} = b_1$ and $b_{\uparrow\downarrow} = b_2$, both of them reported in Table II, listed with the other atoms. In both the cases, we kept the geminal expansion to be minimal (HF+J-type wave function). As reported in Table I, the improvement in energy obtained by contaminating the spin wave function is rather negligible, and disappears when the FN DMC simulation is carried out. This implies that it is

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 Ref. 26. M is the number of terms in the pairing expansion. The energies are in hartree.

	M	E_0	E_{HF}	E_{VMC}	$E_c^{VMC}(\%)$	E_{DMC}	$E_c^{DMC}(\%)$
Li	1	−7.478 06	−7.432 727	−7.474 15(10)	91.4(2)	−7.478 06(5)	100.0(1)
	5			−7.475 82(2)	95.06(5)	−7.478 01(5)	99.9(1)
Be	2	−14.667 36	−14.573 023	−14.631 45(5)	61.9(5)	−14.656 5(4)	88.5(4)
	5			−14.661 695(10)	93.995(11)	−14.667 11(3)	99.73(3)
	5[a]			−14.665 04(5)	97.54(5)	−14.667 26(1)	99.894(11)
B	2	−24.653 91	−24.529 061	−24.604 2(3)	60.3(2)	−24.638 5(5)	87.7(4)
	5			−24.628 01(4)	79.25(4)	−24.649 3(3)	96.3(3)
C	2	−37.845 0	−37.688 619	−37.784 8(6)	61.5(4)	−37.829 6(8)	90.2(5)
	5			−37.798 5(7)	70.3(4)	−37.835 9(8)	94.2(5)
N	2	−54.589 2	−54.400 934	−54.521 80(15)	64.20(8)	−54.575 5(5)	92.7(3)
	2[b]			−54.525 65(15)	66.20(8)	−54.575 3(4)	92.6(2)
	14			−54.526 3(2)	66.62(11)	−54.576 9(2)	93.47(10)
O	3	−75.067 3	−74.809 398	−74.975 0(7)	64.2(3)	−75.047 7(8)	92.4(3)
	14			−74.983 8(6)	67.6(2)	−75.051 6(9)	93.9(3)
F	4	−99.733 9	−99.409 349	−99.619 0(8)	64.6(3)	−99.714 5(15)	94.0(5)
	14			−99.631 5(7)	68.4(2)	−99.714 1(6)	93.91(18)
Ne	5	−128.937 6	−128.547 098	−128.807 0(10)	66.6(3)	−128.920 4(8)	95.6(2)
	14			−128.815 9(6)	68.83(17)	−128.919 9(7)	95.47(18)
Na	5	−162.254 6	−161.858 912	−162.133 4(7)	69.37(19)	−162.232 5(10)	94.4(2)
	9			−162.143 4(7)	71.91(16)	−162.237 0(10)	95.5(2)
Mg	6	−200.053	−199.614 636	−199.911 3(8)	67.67(19)	−200.032 7(9)	95.4(2)
	9			−199.936 3(8)	73.38(19)	−200.037 5(10)	96.5(2)
	9[a]			−200.000 2(5)	87.95(12)	−200.038 9(5)	96.79(11)
Al	6	−242.346	−241.876 707	−242.190 0(9)	66.77(19)	−242.321 5(10)	94.8(2)
	9			−242.212 4(9)	71.53(19)	−242.326 5(10)	95.8(2)
Si	6	−289.359	−288.854 363	−283.187 5(10)	66.0(2)	−289.327 5(10)	93.8(2)
	9			−289.197 0(10)	67.9(2)	−289.328 5(10)	94.0(2)
P	6	−341.259	−340.718 781	−341.070 0(10)	65.0(2)	−341.222 0(15)	93.2(3)

[a]Wave function with a three-body Jastrow factor.
[b]Wave function with a two-body Jastrow factor spin contaminated.

possible to obtain almost optimal nodes, without spoiling the spin symmetry and by using only one variational parameter for the Jastrow factor.

In order to study the effectiveness of the Jastrow for a more accurate determination of the nodal surface, we have implemented a more involved Jastrow factor, including three-body correlation terms, and we have applied it to a few atoms (Be and Mg). Indeed, the Jastrow term f in Eq. (17) is a general function of the positions of two electrons and it has been parametrized similarly to the geminal function (7), but truncated up to the $l=1$ angular momentum

$$f(\mathbf{r}_i,\mathbf{r}_j)=f_{\text{two body}}(r_{ij})+\psi_0(\mathbf{r}_i)\psi_0(\mathbf{r}_j)+\vec{\psi}_1(\mathbf{r}_i)\cdot\vec{\psi}_1(\mathbf{r}_j). \tag{20}$$

The functional form for the s-wave (ψ_0) and p-wave ($\vec{\psi}_1$) components can be chosen among different types; the most widely used in the literature are the polynomial[19,20] and the Gaussian–polynomial mixed form.[21] In this work, we have selected the expansion over a Gaussian basis, as reported in Table V. This parametrization of the Jastrow factor, though certainly less general compared with the best possible ones,[22] includes the most significant part of the three-body correlation,[23] which involves two electrons and the nuclei. Our purpose, in fact, is to check whether it is possible to lower significantly the energy of the AGP+J wave function,

whenever the Jastrow part of the wave function is systematically improved together with the determinantal part.

III. METHOD

A. Minimization method

We have performed the wave function optimization by using the *stochastic minimization* of the total energy based upon the stochastic reconfiguration (SR) technique, already exploited for lattice systems.[11] Let $\Psi_T(\alpha^0)$ be the wave function depending on an initial set of p variational parameters $\{\alpha_k^0\}_{k=1,\dots,p}$. Consider now a small variation of the parameters $\alpha_k=\alpha_k^0+\delta\alpha_k$. The corresponding wave function $\Psi_T(\alpha)$ is equal, within the validity of the linear expansion, to the following one:

$$\Psi_T'(\alpha)=\left(\Psi_T(\alpha^0)+\sum_{k=1}^{p}\delta\alpha_k\frac{\partial}{\partial\alpha_k}\Psi_T(\alpha^0)\right). \tag{21}$$

Therefore, by introducing local operators defined on each configuration $x=\{\mathbf{r}_1,\dots,\mathbf{r}_N\}$ as the logarithmic derivatives with respect to the variational parameters

$$O^k(x)=\frac{\partial}{\partial\alpha_k}\ln\Psi_T(x), \tag{22}$$

and for convenience the identity operator $O^0 = 1$, we can write Ψ'_T in a more compact form

$$|\Psi'_T(\alpha)\rangle = \sum_{k=0}^{p} \delta\alpha_k O^k |\Psi_T\rangle, \qquad (23)$$

where $|\Psi_T\rangle = |\Psi_T(\alpha_0)\rangle$ and $\delta\alpha_0 = 1$. In general, $\delta\alpha_0 \neq 1$; in that case the variation of the parameters will be scaled

$$\delta\alpha_k \rightarrow \frac{\delta\alpha_k}{\delta\alpha_0}, \qquad (24)$$

and Ψ'_T will be proportional to $\Psi_T(\alpha)$ for small $\delta\alpha_k/\delta\alpha_0$.

Our purpose is to set up an iterative scheme to reach the minimum possible energy for the parameters α, exploiting the linear approximation for $\Psi_T(\alpha)$, which will become more and more accurate close to the convergence, when the variation of the parameters is smaller and smaller. We follow the stochastic reconfiguration method and define

$$|\Psi'_T\rangle = P_{SR}(\Lambda - H)|\Psi_T\rangle, \qquad (25)$$

where Λ is a suitable large shift, allowing Ψ'_T to have a lower energy than Ψ_T,[11] and P_{SR} is a projection operator over the $(p+1)$–dimensional subspace, spanned by the basis $\{O_k|\Psi_T\rangle\}_{k=0,...,p}$, over which the function $|\Psi'_T\rangle$ has been expanded [Eq. (23)]. Indeed, in order to determine the coefficients $\{\delta\alpha_k\}_{k=1,...,p}$ corresponding to Ψ'_T defined in Eq. (25), one needs to solve the SR conditions

$$\langle\Psi_T|O^k(\Lambda - H)|\Psi_T\rangle = \langle\Psi_T|O^k|\Psi'_T\rangle \quad \text{for } k=0,...,p, \qquad (26)$$

that can be rewritten in a linear system

$$\sum_l \delta\alpha_l \, s^{lk} = f^k, \qquad (27)$$

where $s^{lk} = \langle\Psi_T|O^lO^k|\Psi_T\rangle$ is the covariance matrix and $f^k = \langle\Psi_T|O^k(\Lambda - H)|\Psi_T\rangle$ is the known term; both s^{lk} and f^k are computed stochastically by a Monte Carlo integration. These linear equations (27) are very similar to the ones introduced by Filippi and Fahy[24] for the energy minimization of the Slater part. In our formulation, there is no difficulty to optimize the Jastrow and the Slater part of the wave function at the same time. The present scheme is also much simpler because it does not require dealing with an effective one-body Hamiltonian. However, a systematic comparison of the performances achieved by the two methods is still missing.

After the system (27) has been solved, we update the variational parameters

$$\alpha_k = \alpha_k^{(0)} + \frac{\delta\alpha_k}{\delta\alpha_0} \quad \text{for } k=1,...,p, \qquad (28)$$

and we obtain a new trial wave function $\Psi_T(\alpha)$. By repeating this iteration scheme several times, one approaches the convergence when $\delta\alpha_k/\delta\alpha_0 \rightarrow 0$ for $k \neq 0$, and in this limit the SR conditions (26) implies the Euler equations of the minimum energy. Obviously, the solution of the linear system (27) is affected by statistical errors, yielding statistical fluctuations of the final variational parameters α_k even when convergence has been reached, namely when the $\{\alpha_k\}_{k=1,...,p}$ fluctuate without drift around an average value. We perform

several iterations in that regime; in this way, the variational parameters can be determined more accurately by averaging them over all these iterations and by evaluating also the corresponding statistical error bars.

It is worth noting that the solution of the linear system (27) depends on Λ only through the $\delta\alpha_0$ variable. Therefore, the constant Λ indirectly controls the rate of change in the parameters at each step, i.e., the speed of the algorithm for convergence and the stability at equilibrium: a too small value will produce uncontrolled fluctuations for the variational parameters, a too large one will allow convergence in an exceedingly large number of iterations. The choice of Λ can be controlled by evaluating the change of the wave function at each step as

$$\frac{|\Psi'_T - \Psi_T|^2}{|\Psi_T|^2} = \sum_{k,k'>0} \delta\alpha_k \, \delta\alpha_{k'} \, s^{kk'}. \qquad (29)$$

By keeping this value small enough during the optimization procedure, one can easily obtain a steady and stable convergence.

Finally, we mention that the stochastic procedure is able in principle to perform a global optimization, as discussed in Ref. 11 for the SR and in Ref. 25 for the stochastic gradient approximation (SGA), because the noise in the sampling can avoid the dynamics of the parameters to get stuck into local minima.

B. Variational and diffusion Monte Carlo

We performed standard variational (VMC) and diffusion Monte Carlo (DMC), the latter within the so-called fixed node (FN) approximation, which allows us to obtain the lowest energy state with the same nodes of a trial wave function. As trial state for FN, we have used the VMC wave function optimized with the SR method described in the previous section.

IV. RESULTS

We have carried out quantum Monte Carlo calculations for atoms from Li to P, using the antisymmetrized geminal power times the Jastrow factor (AGP+J) to describe the atomic electronic structure. We performed the optimization of both the geminal and the Jastrow part minimizing the energy with the method described in Sec. III. For all the atoms, we considered the minimal geminal expansion, corresponding to the HF single determinant, and the simplest Jastrow factor with a single parameter (18), reported in Table II. To improve the antisymmetric part, we increased the number of orbitals in the geminal expansion, and for Be and Mg atoms we also systematically considered an improved Jastrow term, such as the three-body one described above (see Tables IV and V). As one can notice from the tables, our wave function parametrization is very compact, even in the case of the most correlated states, since it always contains a relatively small number of parameters for each atom.

In order to judge the outcome of our calculations, we computed the correlation energies and in particular its fraction with respect to the exact ground-state energy for the nonrelativistic infinite nuclear mass Hamiltonian, estimated

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TABLE II. **HF+J (two body) wave functions**. Parameters of the Jastrow and the pairing function with the notation described in the text. "#" means that the corresponding parameter has to be evaluated from the cusp condition in Eq. (15). The line over the orbitals label refers to the unpaired ones. The values are given with the statistic error due to the stochastic approach in the minimization.

	b	Orbital	Z_1	Z_2	p	λ
Li	0.731(3)	$1s$	3.556(2)	2.374 1(15)	#	1.0
		$\overline{2s}$	1.4289(12)	0.538 0(2)	#	
Be	0.773(2)	$1s$	4.569(6)	3.289(5)	#	1.0
		$2s$	2.602(3)	0.785 0(8)	#	1.0
B	0.877(2)	$1s$	5.569(5)	4.195(4)	#	1.0
		$2s$	3.527(2)	1.078 8(2)	#	1.0
		$\overline{2p}$	2.437(4)	1.100 1(5)	0.266 4(3)	
C	0.990(2)	$1s$	6.533(6)	5.075(8)	#	1.0
		$2s$	4.475(3)	1.355 2(3)	#	1.0
		$\overline{2p}$	2.9835(12)	1.388 6(5)	0.237 4(4)	
N	1.110(3)	$1s$	7.461(8)	5.901(15)	#	1.0
		$2s$	5.387(3)	1.632 3(1)	#	1.0
		$\overline{2p}$	3.4908(9)	1.637 3(4)	0.203 6(3)	
N	contaminated	$1s$	7.2738(17)	5.522(7)	#	1.0
	$b_{\uparrow\downarrow}=0.940(3)$	$2s$	5.254(2)	1.669 2(15)	#	1.0
	$b_{\uparrow\uparrow}=0.624(4)$	$\overline{2p}$	3.4544(4)	1.665 59(13)	0.215 93(9)	
O	1.152(2)	$1s$	8.303(5)	6.53(3)	#	1.0
		$2s$	6.428(2)	1.936 2(5)	#	1.0
		$2p$	3.9921(7)	1.849 32(15)	0.164 8(2)	1.0
		$\overline{2p}$	3.9921(7)	1.849 32(15)	0.164 8(2)	
F	1.226(9)	$1s$	9.171(3)	6.82(2)	#	1.0
		$2s$	7.380(2)	2.240 2(4)	#	1.0
		$2p$	4.5025(2)	2.075 8(2)	0.145 1(10)	1.0
		$\overline{2p}$	4.5025(2)	2.075 8(2)	0.145 1(10)	
Ne	1.321(3)	$1s$	10.103(4)	7.01(4)	#	1.0
		$2s$	8.341(10)	2.531 9(5)	#	1.0
		$2p$	5.0273(10)	2.315 5(4)	0.135 8(2)	1.0
Na	1.514(7)	$1s$	11.102(2)	7.58(5)	#	1.0
		$2s$	8.823(2)	2.879 5(4)	#	1.0
		$2p$	5.7178(9)	2.809 2(8)	0.180 27(18)	1.0
		$\overline{3s}$	1.540(3)	0.734(2)	0.126 5(2)	
Mg	1.654(6)	$1s$	12.0855(15)	7.96(5)	#	1.0
		$2s$	9.349(4)	3.261 1(16)	#	1.0
		$2p$	6.3795(10)	3.290 5(5)	0.215 69(17)	1.0
		$3s$	1.9288(10)	1.022 14(13)	0.144 9(2)	1.0
Al	1.812(8)	$1s$	13.0791(17)	8.43(7)	#	1.0
		$2s$	9.846(8)	3.646(2)	#	1.0
		$2p$	7.0560(15)	3.787 3(7)	0.259 7(3)	1.0
		$3s$	2.24(8)	1.262 7(2)	0.144 5(2)	1.0
		$\overline{3p}$	1.83(2)	0.886 6(2)	0.101 2(7)	
Si	1.961(7)	$1s$	14.072(2)	8.77(8)	#	1.0
		$2s$	10.40(5)	4.027 5(8)	#	1.0
		$2p$	7.703(10)	4.261(5)	0.294 4(12)	1.0
		$3s$	2.468(5)	1.46(2)	0.124 1(2)	1.0
		$\overline{3p}$	2.274(2)	1.16(2)	0.122 7(3)	
P	2.074(9)	$1s$	15.053(4)	9.10(15)	#	1.0
		$2s$	10.997(5)	4.426 9(5)	#	1.0
		$2p$	8.346(2)	4.751 9(12)	0.327 3(17)	1.0
		$3s$	2.7386(5)	1.62(2)	0.112 9(3)	1.0
		$\overline{3p}$	2.5918(18)	1.347 9(7)	0.112 5(2)	

in Ref. 26. The quality of the variational wave function can be seen by computing the expectation value of the energy by means of the VMC calculations. Furthermore, we carried out DMC simulations within the FN approximation, which allow us to optimize the amplitude of the wave function inside each nodal volume, where its sign is given and fixed by the variational state. Therefore, the DMC energy depends on the quality of the nodal structure of the variational wave function and the capability of improving the nodes during the optimi-

zation is crucial to obtain almost exact DMC energy values. To that purpose, it is very important to have a variational functional form appropriate to reproduce the correct nodes. We show that the AGP+J wave function satisfies this requirement well, yielding in all the atoms studied here very good DMC results. The VMC and DMC energies are listed in Table I; in Figs. 1 and 2 we plot the percentage of the correlation energy recovered, respectively, by VMC and DMC calculations for different atoms and wave functions.
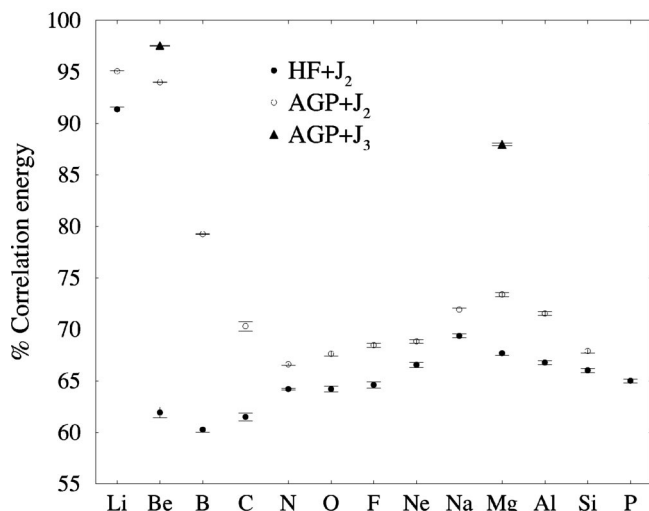
Variational Monte Carlo

FIG. 1. VMC correlation energies for HF+J_2 (minimal geminal expansion with a two-body Jastrow factor), AGP+J_2 (best geminal expansion) and AGP+J_3 (best geminal with a three-body Jastrow factor).

The VMC calculations with the minimal geminal expansion and the two-body Jastrow factor yield from 60 to 68% of the total correlation energy, with the exception of the Li atom, where 91.4% of the correlation energy is obtained. Therefore, there is a sizable loss of accuracy in going from Li to Be, the worst case being the boron atom. The corresponding DMC simulations get a large amount of the energy missing in the VMC calculations, recovering from 87.7% to 99.9% of the total correlation energy, but the dependence on the atomic number shows the same behavior found in VMC: the worst results are obtained for Be, B, and C atoms, due to the strong multiconfigurational nature of their ground states. As is well known, one can improve substantially the variational state of those atoms including not only the $1s^2 2s^2$ configuration but also the $2s^2 2p^2$, because of the near-
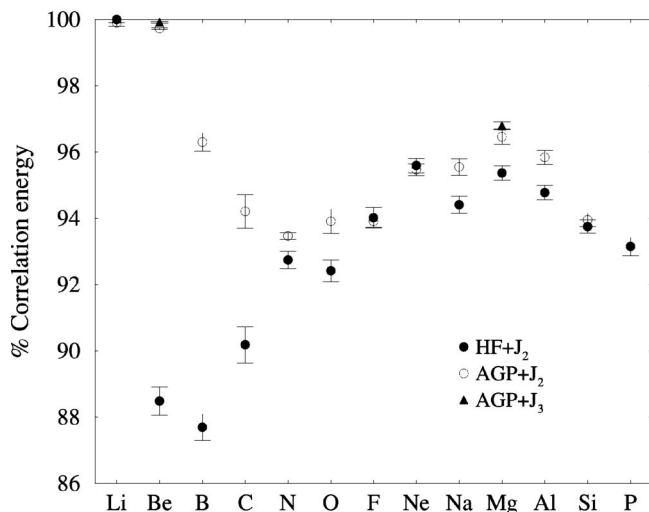
Diffusion Monte Carlo

FIG. 2. DMC correlation energies obtained by HF+J_2, AGP+J_2, and AGP+J_3 wave functions.

TABLE III. Comparison of the energies obtained by various authors for Be.

	Basis	Jastrow	VMC	DMC
Present work	$2s1p$	Two body	$-14.661\,695(10)$	$-14.667\,11(3)$
Huang et al. (Ref. 22)	$2s1p$	Two body	$-14.660\,88(5)$	$-14.666\,89(4)$
Present work	$2s1p$	Three body	$-14.665\,04(4)$	$-14.667\,26(1)$
Huang et al. (Ref. 22)	$2s1p$	Three body	$-14.666\,62(1)$	$-14.667\,23(1)$
Sarsa et al. (Ref. 20)	$2s1p$	Three body	$-14.652\,3(1)$	
Kurtz et al. (Ref. 27)	$6s3p2d$	None	$-14.617\,1$	

degeneracy of $2s$ and $2p$ orbitals. In this case the AGP+J ansatz is particularly efficient: by adding just one term in the geminal expansion, we are able to remove this loss of accuracy in the correlation energy both in the VMC and the DMC calculations.

In Table III, we summarize some results obtained for Be in previous works and compare them with ours. AGP calculations of atoms have been performed only a few times so far; the best one for Be is reported in the last row of Table III. Kurtz et al.[27] were able to recover 84% of correlation energy using a geminal expansion with a very large basis; our variational AGP+J wave function reaches 94% with a much smaller basis ($1s$, $2s$, and $2p$ orbitals). By including a three-body Jastrow factor, 97.5% of the correlation energy is finally obtained, which is comparable with the best multiconfiguration wave functions previously studied.[22]

This outcome highlights the importance of the Jastrow in reducing the geminal expansion and yielding a better energy. The nodal surface can be substantially improved with the present approach, because the pairing expansion contains implicitly not only the four determinants $1s^2 2s^2$ and $1s^2 2p^2$, but also the other three $2s^2 2p^2$ and three $2p^2 2p^2$, which can further improve the wave function. Indeed, the geminal expansion reduces exactly to four determinants in the limit $\lambda_{2s} \to 0$ and $\lambda_{2p} \to 0$ with constant ratio $\lambda_{2s}/\lambda_{2p}$. The fact that the minimum energy is obtained for $\lambda_{2s} \neq 0$ and $\lambda_{2p} \neq 0$ (see Tables IV and V) clearly shows that the energy can be lowered by considering the remaining configurations described above. Indeed, our DMC energies are more than two standard deviations lower than the ones by Huang et al.,[22] to our knowledge the best available ones obtained with the four determinants: one $1s^2 2s^2$ and three $1s^2 2p^2$. In order to determine accurate nodes for the corresponding DMC calculation they used the two-body Jastrow factor similar to the one (18) we used or a highly involved three-body term much more complete than ours (for this reason our corresponding VMC energy is slightly worse in this case). We also verified, therefore, that a more accurate description of the Jastrow factor (which does not affect directly the nodes) is crucial to obtain better nodes, provided the variational parameters, belonging to both the Jastrow and the determinantal part, are optimized altogether. For instance, in Ref. 20 the authors optimized only the coefficients in front of the four determinants $1s2s-1s2p$ and not the orbitals, obtaining for Be

TABLE IV. **AGP+J (two body) wave functions**. The notations are the same as in Table II.

	b	Orbital	Z_1	Z_2	p	λ
Li	0.8342(4)	$1s$	2.867(4)	4.64(2)	#	1.0
		$2s$	2.353(6)	$Z_2 \to Z_1$	#[a]	$-2.20(6)\ 10^{-1}$
		$\underline{2p}$	2.41(2)		0.0	$-2.20(9)\ 10^{-3}$
		$\underline{2s}$	0.533 4(2)	1.347(2)	#	
Be	1.009(5)	$1s$	4.713 9(6)	3.311 8(3)	#	1.0
		$2s$	2.275 61(16)	0.789 55(2)	#	$-1.95(8)\ 10^{-3}$
		$2p$	3.389(2)	1.064 95(4)	0.887 8(18)	$3.49(15)\ 10^{-4}$
B	1.005(7)	$1s$	5.650 9(8)	4.204 1(7)	#	1.0
		$2s$	3.355 45(19)	1.072 94(2)	#	$-4.41(7)\ 10^{-3}$
		$\underline{2p}$	3.701(7)	1.462 98(13)	0.827(2)	$6.92(10)\ 10^{-4}$
		$\underline{2p}$	2.409 3(3)	1.071 97(4)	0.281 02(8)	
C	1.036(5)	$1s$	6.542 0(6)	5.049 4(8)	#	1.0
		$2s$	4.409 4(3)	1.353 943(18)	#	$-5.40(10)\ 10^{-3}$
		$\underline{2p}$	4.289(3)	1.881 7(2)	0.776 9(8)	$7.53(14)\ 10^{-4}$
		$\underline{2p}$	2.957 58(8)	1.362 88(2)	0.232 76(2)	
N	1.124(5)	$1s$	7.455 3(11)	5.866(2)	#	1.0
		$2s$	5.503 1(12)	1.613 05(8)	#	$-2.345(9)\ 10^{-2}$
		$2p$	5.708(9)	2.548 8(8)	0.983 4(14)	$2.538(9)\ 10^{-3}$
		$3s$	3.415(2)		0.0^b	$-7.521(4)\ 10^{-4}$
		$3p$	2.191 4(6)		0.0^b	$3.454(13)\ 10^{-4}$
		$\underline{3d}$	2.649 8(6)		0.0^b	$1.881(4)\ 10^{-4}$
		$\underline{2p}$	3.489 77(11)	1.635 02(2)	0.205 373(12)	
O	1.2073(10)	$1s$	8.335 9(4)	6.551 4(15)	#	1.0
		$2s$	6.424 8(3)	1.941 27(5)	#	$-9.54(6)\ 10^{-3}$
		$2p$	3.974 18(5)	1.779 90(4)	0.168 724(8)	$-5.73(4)\ 10^{-3}$
		$3s$	5.333 7(16)		0.0^b	$3.09(2)\ 10^{-4}$
		$3p$	2.008 49(8)		0.0^b	$2.156(13)\ 10^{-4}$
		$\underline{3d}$	2.859 8(5)		0.0^b	$5.02(3)\ 10^{-5}$
		$\underline{2p}$	3.989 28(8)	1.859 65(3)	0.172 589(8)	
F	1.310(3)	$1s$	9.232(2)	7.037(14)	#	1.0
		$2s$	7.090 1(19)	2.152 0(2)	#	$-1.30(6)\ 10^{-2}$
		$2p$	4.485 7(4)	2.009 46(14)	0.153 08(6)	$-9.15(19)\ 10^{-3}$
		$3s$	3.000 7(7)		0.0^b	$7.92(15)\ 10^{-4}$
		$3p$	2.296 6(5)		0.0^b	$3.25(13)\ 10^{-4}$
		$\underline{3d}$	3.250 0(10)		0.0^b	$6.51(18)\ 10^{-5}$
		$\underline{2p}$	4.503 4(5)	2.092 41(15)	0.155 89(4)	
Ne	1.3500(10)	$1s$	10.123 3(3)	7.319(4)	#	1.0
		$2s$	8.086 8(2)	2.470 46(2)	#	$4.650(18)\ 10^{-2}$
		$2p$	5.007 52(4)	2.288 73(2)	0.133 639(5)	$3.028(13)\ 10^{-2}$
		$3s$	3.657 36(11)		0.0^b	$-2.668(11)\ 10^{-3}$
		$3p$	1.745 05(5)		0.0^b	$-1.379(7)\ 10^{-4}$
		$3d$	2.742 43(12)		0.0^b	$-1.102(7)\ 10^{-4}$
Na	1.5469(11)	$1s$	11.121 4(11)	7.807(19)	#	1.0
		$2s$	8.663 8(18)	2.824 30(13)	#	$-8.43(19)\ 10^{-3}$
		$2p$	5.730 8(3)	2.788 83(12)	0.190 53(5)	$-5.69(17)\ 10^{-3}$
		$3s$	3.858 5(14)		0.0^b	$2.86(12)\ 10^{-4}$
		$\underline{3p}$	3.169 3(8)		0.0^b	$1.26(8)\ 10^{-4}$
		$\underline{3s}$	1.538 32(2)	0.753 6(16)	0.135 076(3)	
Mg	1.692(6)	$1s$	12.098 3(14)	8.12(4)	#	1.0
		$2s$	9.310 3(19)	3.252 5(3)	#	1.0^c
		$2p$	6.386 2(5)	3.288 64(16)	0.220 40(7)	1.0^c
		$3s$	1.757 1(2)	0.963 73(13)	0.112 95(7)	$1.986(10)\ 10^{-4}$
		$3p$	3.417(15)	1.228 4(2)	0.439(11)	$-2.825(15)\ 10^{-5}$
Al	1.840(8)	$1s$	13.084(2)	8.47(9)	#	1.0
		$2s$	9.826(8)	3.634 4(12)	#	1.0^c
		$2p$	7.053 2(16)	3.778 0(8)	0.259 7(3)	1.0^c
		$3s$	2.190(3)	1.256 8(11)	0.148 7(6)	$7.781(13)\ 10^{-4}$
		$\underline{3p}$	5.58(2)	1.553 1(7)	0.141 6(7)	$-1.004(10)\ 10^{-4}$
		$\underline{3p}$	1.916(3)	0.937 4(6)	0.128 2(5)	
Si	1.968(3)	$1s$	14.069 7(7)	8.68(4)	#	1.0
		$2s$	10.407 7(18)	4.024 9(4)	#	1.0^c
		$2p$	7.703 0(7)	4.261 4(3)	0.294 44(12)	1.0^c
		$3s$	2.443 7(3)	1.427 85(13)	0.120 38(3)	$7.327(16)\ 10^{-4}$
		$\underline{3p}$	6.110(12)	1.847 1(3)	0.196 70(14)	$-8.961(18)\ 10^{-5}$
		$\underline{3p}$	2.261 4(8)	1.16(1)	0.123 7(2)	

[a]In the $Z_2 \to Z_1$ limit the orbital becomes $(1 + \alpha r)\exp(-z_1 r)$, with $\alpha = Z_1 - Z$.

[b]In the case of dynamic correlation, we used single zeta orbitals beyond the HF ones.

[c]For Mg, Al, and Si, we optimized only the λs related to the $3s-3p$ shells, whose contribution is the most important in describing the resonance in that multiconfigurational ground states.

TABLE V. **AGP+J (three body) wave functions**. The notations are the same as in Table II. The parametrization for the three-body Jastrow factor is also reported.

			Be		
Geminal	Z_1	Z_2	p	λ	
$1s$	7.48(8)	3.545(2)	#	1.0	
$2s$	2.403(3)	0.818 1(3)	#	$3.95(9)\ 10^{-3}$	
$2p$	2.86(5)	1.106 4(9)	1.245(9)	$-6.27(9)\ 10^{-4}$	
Jastrow 2 body	b				
	0.7935(19)				
Jastrow 3 body	Z_1	Z_2	a_0	a_1	a_2
$\psi_0(r)^{\mathrm{a}}$	2.238(4)	15.9(2)	$-0.349\ 1(4)$	0.112 2(4)	$-0.606\ 7(12)$
$\bar{\psi}_1(\mathbf{r})^{\mathrm{b}}$	0.19775(14)	6.060(10)	0.165 35(9)	1.907(2)	

			Mg		
Geminal	Z_1	Z_2	p	λ	
$1s$	12.0	0.0	#	1.0	
$2s$	10.784(2)	3.168 5(4)	#	$2.40(18)\ 10^{-1}$	
$2p$	6.6199(4)	3.252 96(19)	0.192 85(9)	$8.56(2)\ 10^{-1}$	
$3s$	1.9220(3)	1.012 49(15)	0.083 12(8)	$1.674(13)\ 10^{-4}$	
$3p$	2.599(12)	1.273 8(3)	0.535(14)	$-2.152(17)\ 10^{-5}$	
Jastrow 2 body	b				
	1.191(5)				
Jastrow 3 body	Z_1	Z_2	a_0	a_1	a_2
$\psi_0(r)^{\mathrm{c}}$	1.465(6)		$-0.391\ 9(5)$	1.386 7(9)	$-0.891(2)$
$\bar{\psi}_1(\mathbf{r})^{\mathrm{b}}$	13.03(3)	1.074(10)	0.878 9(2)	0.298 22(5)	

[a] $\psi_0(r) = a_0(\exp(-Z_1 r^2) + a_1 \exp(-Z_2 r^2) + a_2)$.
[b] $\bar{\psi}_1(\mathbf{r}) = \mathbf{r}\, a_0(\exp(-Z_1 r^2) + a_1 \exp(-Z_2 r^2))$.
[c] $\psi_0(r) = a_0((1 + a_1 r^2)\exp(-Z_1 r^2) + a_2)$.

energy not comparable with the best possible ones. The AGP+J is simple enough to allow a feasible parametrization of the variational state, by capturing the most important correlation.

We found that also Mg, Al, and Si, the second row atoms corresponding to Be, B, and C in the first row, have quite a strong multiconfigurational character, involving here $3s$ and $3p$ orbitals. Analogously to the beryllium case, for Mg we have optimized both the two-body and the three-body Jastrow factor, together with the AGP wave function containing $3s-3p$ resonance. In this case, although at the variational level the three-body wave function is much better than the two-body one (see Fig. 1), that difference disappears almost completely in the DMC results. This shows that the correction of the nodal surface allowed by the more accurate three-body Jastrow does not seem to be crucial as in the Be atom. On the other hand, the effect of the AGP expansion is significant in further improving the DMC calculation, which already yields good FN energies even with a simple HF+J trial wave function for atoms heavier than C (percentage of correlation energy always greater than 92%). By adding the $3p$ contribution to the geminal we were able to recover 96.8% of the correlation energy of Mg (see Fig. 2). Also, for Al the presence of the $3p$ orbital is significant in reducing the DMC energy, and for Si it seems important only in the VMC value. As clearly shown in Fig. 2 the amount of non-

dynamic correlation is expected to be negligible for large Z: for this reason we have not carried out the geminal optimization for $Z > 14$.

Finally, by using the AGP+J wave function, we optimized some atoms (from N to Na) not affected by nondynamic correlation; here, in order to obtain an improvement in the VMC and in the DMC energies, we needed a bigger basis ($3s2p1d$) to be used in the geminal expansion.

V. CONCLUSIONS AND PERSPECTIVES

In this work we have introduced a variational wave function which contains the main ingredients of electron correlations: The Jastrow factor, that allows us to satisfy the electron–electron cusp condition, and the geminal expansion, that allows us to consider a correlated multiconfiguration state, with a numerically feasible scheme, namely by evaluating only a single but appropriately defined determinant.

The application to atoms is particularly successful for low atomic number, where Hartree–Fock is particularly poor, due to the almost degenerate $2s-2p$ shells. The case of beryllium is an interesting benchmark. Indeed, by considering the change of the geminal part altogether with the Jastrow term, we obtained an excellent representation of this correlated atom. Our results, presented in Table III, are not

only comparable but appear even better than the best multideterminantal schemes (using, e.g., four Slater determinants), showing that it is possible to represent nontrivial correlated states by properly taking into account the interplay of the Jastrow term and the determinantal part of the wave function. Our variational energies for the other atoms (see Table I) can be substantially lowered because we have considered, in this first application, a wave function with the two-body Jastrow factor.

As is well known, the variational energy of the Hartree–Fock wave function cannot be improved by extending the variational calculation to a larger basis including all particle–hole excitations applied to the Hartree–Fock state. Analogously, the geminal wave function is not only stable with respect to these particle–hole configurations, but also to all possible states obtained by destroying a singlet pair on some orbital and creating another one on another orbital. Though this wave function can take into account a big number of configurations which may allow an energy improvement, obviously it cannot include everything within a single geminal, otherwise the wave function would be exact. Indeed, there exist multiconfiguration states that are known to be important for atoms like C or those with larger Z,[28] and that involve complicated multiparticle excitations to the Hartree–Fock state. These cannot be reduced to creation/destruction of singlet pairs and therefore cannot be handled with a single geminal function. However, in our study we have found that the single geminal function with the proper Jastrow factor already provides satisfactory results for all atoms, yielding more than 93% of the correlation energy in all cases studied by carrying out DMC simulations.

The extension of this approach to molecules or more complex electronic systems is straightforward, and is indeed particularly promising. As pointed out in Ref. 29, the geminal wave function for a diatomic system can correctly describe the interatomic Born–Oppenheimer potential from small to large distances, where, in this limit, the wave function of isolated atoms can be smoothly recovered. This important property cannot be satisfied within the Hartree–Fock theory, even for the simplest H_2 molecule (without contaminating the singlet ground-state wave function).

For an electronic system with many atoms, the geminal expansion together with the Jastrow term is very similar to the so called resonating valence bond (RVB) expansion, introduced by Pauling (see, e.g., Ref. 30) a long time ago, and revived recently by Anderson to consider the properties of strongly correlated electronic systems. The geminal part, when expanded in terms of Slater determinants, yields a very large and nontrivial number of configurations, which increases exponentially with the number of atoms considered. The Jastrow factor in this case suppresses the weight of those configurations with two electrons close to the same atomic orbital, correctly describing the effect of the strong Coulomb repulsion. We see therefore the remarkable advantage of this approach. Just for complex systems with many atoms, an RVB wave function corresponding to an exponentially large number of configurations can be efficiently used for a more accurate description of electron correlation. It is appealing, not only from the computational point of view, that these properties can be obtained by sampling a single determinant wave function within the quantum Monte Carlo techniques.

APPENDIX A: SPIN-POLARIZED GEMINAL WAVE FUNCTION

In this Appendix, we consider the most general geminal wave function with definite spin $S = (N_\uparrow - N_\downarrow)/2$, where $N_\uparrow$ ($N_\downarrow$) is the number of spin–up (spin–down) electrons and $N_\uparrow > N_\downarrow$ is assumed. To this purpose we introduce second quantized fermionic fields (see, e.g., Fetter and Walecka[31]) $\psi^\dagger(\mathbf{r},\sigma)$ and $\psi(\mathbf{r},\sigma)$, where $\mathbf{r}$ is the electron position and $\sigma = \pm 1/2$ is its spin projection along the z axis. These fields satisfy the canonical anticommutation rules

$$\{\psi(\mathbf{r},\sigma),\psi^\dagger(\mathbf{r}',\sigma')\} = \delta_{\sigma\sigma'}\delta(\mathbf{r}-\mathbf{r}'). \tag{A1}$$

In these notations, the most general wave function with definite spin can be formally written in the following way:

$$|\Psi\rangle = P_N \prod_{i=N_\downarrow+1}^{N_\uparrow} \psi_{i,\uparrow}^\dagger \exp(\Phi^\dagger)|0\rangle, \tag{A2}$$

where P_N is the projection on the given number of particles $N = N_\uparrow + N_\downarrow$, $|0\rangle$ denotes the vacuum of electrons, and $\psi_{i,\uparrow}^\dagger$ is the most generic (Bogoliubov) orbital with spin $S = 1/2$

$$\psi_{i,\uparrow}^\dagger = \int d\mathbf{r} \ (\phi_i^<(\mathbf{r})\psi(\mathbf{r},\downarrow) + \phi_i^>(\mathbf{r})\psi^\dagger(\mathbf{r},\uparrow)), \tag{A3}$$

which is defined by the orbital functions $\phi_i^>$ for the creation of a particle with spin up and $\phi_i^<$ for the annihilation of a particle with spin down. For instance, a conventional Slater determinant of spin-up particles can be written as $\Pi_i \psi_{i,\uparrow}^\dagger|0\rangle$, where $\phi_i^< = 0$. It is clear, therefore that this representation is more general and may provide a wave function Ψ with more variational freedom than the conventional Slater determinants.

Finally, the pairing creation operator $\Phi^\dagger$ is a singlet, namely $\exp(\Phi^\dagger)|0\rangle$ has spin zero, and is defined by a generic symmetric function $\Phi(\mathbf{r},\mathbf{r}') = \Phi(\mathbf{r}',\mathbf{r})$

$$\Phi^\dagger = \int d\mathbf{r} \int d\mathbf{r}' \ \Phi(\mathbf{r}',\mathbf{r})\psi^\dagger(\mathbf{r},\downarrow)\psi^\dagger(\mathbf{r}',\uparrow). \tag{A4}$$

Our purpose is to show here that the value of the wave function Ψ can be simply computed, similarly to a conventional Slater determinant, on each configuration $x = \{\mathbf{r}_{1,\uparrow},\ldots,\mathbf{r}_{N_\downarrow,\downarrow}\}$, where $\mathbf{r}_{i,\uparrow}$ are the positions of spin–up particles and $\mathbf{r}_{i,\downarrow}$ are the spin–down ones. These configurations can be generally written as

$$\langle x| = \langle 0| \prod_{i=1}^{N_\uparrow} \psi(\mathbf{r}_i,\uparrow) \prod_{j=1}^{N_\downarrow} \psi(\mathbf{r}_j,\downarrow). \tag{A5}$$

Indeed, the value F of the wave function on $\langle x|$ is

$$F = \langle x|\Psi\rangle$$

$$= \langle 0|\prod_i \psi(\mathbf{r}_i,\uparrow)\prod_j \psi(\mathbf{r}_j,\downarrow)\prod_{k=N_\downarrow+1}^{N_\uparrow} \psi_{k,\uparrow}^\dagger \exp(\Phi^\dagger)|0\rangle.$$
(A6)

Now, we insert the identity $\exp(-\Phi^\dagger)\exp(\Phi^\dagger)$ between each fermionic field in the above equation (A6)

$$F = \langle 0|\exp(\Phi^\dagger)\exp(-\Phi^\dagger)\psi(\mathbf{r}_1,\uparrow)$$
$$\times \exp(\Phi^\dagger)\cdots\exp(-\Phi^\dagger)\psi(\mathbf{r}_{N_\downarrow},\downarrow)$$
$$\times \exp(\Phi^\dagger)\cdots\exp(-\Phi^\dagger)\psi_{N_\uparrow,\uparrow}^\dagger \exp(\Phi^\dagger)|0\rangle. \quad (A7)$$

Exploiting the relation valid for generic operators A and B

$$\exp(-A)\ B\exp(A) = B - [A,B] + \tfrac{1}{2}[A,[A,B]] + \ldots,$$
(A8)

one is able to evaluate the following terms:

$$\exp(-\Phi^\dagger)\psi(\mathbf{r}_i,\uparrow)\exp(\Phi^\dagger)$$

$$= \psi(\mathbf{r}_i,\uparrow) - \int d\mathbf{r}\ \Phi(\mathbf{r}_{i,\uparrow},\mathbf{r})\psi^\dagger(\mathbf{r},\downarrow),$$

$$\exp(-\Phi^\dagger)\psi(\mathbf{r}_i,\downarrow)\exp(\Phi^\dagger)$$

$$= \psi(\mathbf{r}_i,\downarrow) + \int d\mathbf{r}\ \Phi(\mathbf{r},\mathbf{r}_{i,\downarrow})\psi^\dagger(\mathbf{r},\uparrow), \quad (A9)$$

$$\exp(-\Phi^\dagger)\psi^\dagger i,\uparrow \exp(\Phi^\dagger)$$

$$= \psi_{i,\uparrow}^\dagger + \int d\mathbf{r}\int d\mathbf{r}'\ \Phi(\mathbf{r},\mathbf{r}')\phi_i^<(\mathbf{r}')\psi^\dagger(\mathbf{r},\uparrow).$$

In order to derive the above relations, notice that all the terms in the right-hand side of Eq. (A8) are always zero beyond the first two. After substituting the expressions in Eq. (A7) and by using $\langle 0|\exp(\Phi^\dagger) = \langle 0|$, $\psi(\mathbf{r},\sigma)|0\rangle = 0$ and $\langle 0|\psi^\dagger(\mathbf{r},\sigma) = 0$, one can iteratively apply the canonical commutation rules (A1) and a simplified result for F is obtained

$$F = \langle 0|\prod_{i=1}^{N_\uparrow} \psi(\mathbf{r}_i,\uparrow)\prod_{i=1}^{N_\uparrow} \tilde{\psi}_{i,\uparrow}^\dagger|0\rangle, \quad (A10)$$

where $\tilde{\psi}_{i,\uparrow}^\dagger$ is the creator of an orbital function of the type (A3), with transformed orbitals

$$\phi_i(\mathbf{r}) = \Phi(\mathbf{r},\mathbf{r}_{i,\downarrow}) \quad \text{for } i = 1,\ldots,N_\downarrow,$$

$$\bar{\phi}_i(\mathbf{r}) = \phi_i^>(\mathbf{r}) + \int d\mathbf{r}'\ \Phi(\mathbf{r},\mathbf{r}')\phi_i^<(\mathbf{r}')$$
(A11)

$$\text{for } i = N_\downarrow + 1\cdots N_\uparrow.$$

Then, the final value of F can be simply computed by a *single* determinant, as it represents just the value of an $N_\uparrow \times N_\uparrow$ Slater determinant with orbitals given in (A11) on the spin-up configurations, yielding the final expression (6) reported in the text.

APPENDIX B: GEMINAL AS A MULTICONFIGURATION WAVE FUNCTION

As pointed out in Sec. II A, for the minimal geminal expansion, i.e., $M = N^\downarrow$, the AGP wave function is reduced to the HF one. Otherwise, if $M > N^\downarrow$, it becomes a multiconfiguration wave function. We prove this property by starting with the expression for an antisymmetrized geminal wave function written in the second quantized form

$$|\Psi\rangle = P_N \exp(\Phi^\dagger)|0\rangle = (\Phi^\dagger)^{N^\downarrow}|0\rangle. \quad (B1)$$

Here, for the sake of simplicity, we assume that the system is unpolarized, but the proof can be easily extended to the polarized case. As reported in Eq. (7), the expansion for the geminal is

$$\phi(\mathbf{r}^\uparrow,\mathbf{r}^\downarrow) = \sum_{i=1}^M \lambda_i \phi_i(\mathbf{r}^\uparrow)\phi_i^*(\mathbf{r}^\downarrow). \quad (B2)$$

We define the creation operator for a particle in the ith state with spin σ as

$$\hat{\psi}_{i\sigma}^\dagger = \int d\mathbf{r}\ \phi_i(\mathbf{r})\psi^\dagger(\mathbf{r},\sigma), \quad (B3)$$

where $\{\phi_i\}$ are the orbitals defining the states, which we do not assume to be orthogonal among each other. Then, we can rewrite the geminal creation operator in Eq. (A4) in terms of the single particle operators

$$\Phi^\dagger = \sum_{i=1}^M \lambda_i \hat{\psi}_{i\uparrow}^\dagger \hat{\psi}_{i\downarrow}^\dagger. \quad (B4)$$

Therefore, if we put this expression in Eq. (B1) and use the anticommutation rules, the AGP wave function reads

$$|\Psi\rangle = \sum_{\substack{i_1,\ldots,i_{N^\downarrow} \in M \\ i_1 \neq i_2 \neq \cdots \neq i_{N^\downarrow}}} \lambda_{i_1}\cdots\lambda_{i_{N^\downarrow}}\ \hat{\psi}_{i_1\uparrow}^\dagger \hat{\psi}_{i_1\downarrow}^\dagger \cdots \hat{\psi}_{i_{N^\downarrow}\uparrow}^\dagger \hat{\psi}_{i_{N^\downarrow}\downarrow}^\dagger|0\rangle.$$
(B5)

Each term in the above sum is a Slater determinant with orbitals $\phi_{i_1},\ldots,\phi_{i_{N^\downarrow}}$. Hence, the antisymmetrized geminal product is equivalent to a linear combination of them, with coefficients given by the product of those λs selected by the configuration present in each Slater determinant. If $M = N^\downarrow$, the summation has only one term, related to the unique possible configuration of $N^\downarrow$ single particle orbitals: this is the HF case. Otherwise, if $M > N^\downarrow$, one deals with a multiconfiguration wave function. Let us consider, for instance, the geminal for Be. The HF case corresponds to the following geminal expansion:

$$\Phi_{\text{Be}}(\mathbf{r},\mathbf{r}') = \phi_{1s}(\mathbf{r})\phi_{1s}(\mathbf{r}') + \phi_{2s}(\mathbf{r})\phi_{2s}(\mathbf{r}'), \quad (B6)$$

where all the λ have been set to 1, because they affect only the multiplicative constant in front of the total wave function. The correlated case just beyond the minimal geminal expansion is

$$\Phi_{\text{Be}}(\mathbf{r},\mathbf{r}') = \lambda_{1s}\phi_{1s}(\mathbf{r})\phi_{1s}(\mathbf{r}') + \lambda_{2s}\phi_{2s}(\mathbf{r})\phi_{2s}(\mathbf{r}')$$

$$+ \lambda_{2p}\sum_{\mu \in \{x,y,z\}} \phi_{2p_\mu}(\mathbf{r})\phi_{2p_\mu}(\mathbf{r}'), \quad (B7)$$

where we used the real basis representation. The corresponding configuration interaction wave function is

$$|\Psi\rangle = \lambda_{1s}\lambda_{2s}|1s^2 2s^2| + \lambda_{1s}\lambda_{2p}\sum_{\mu}|1s^2 2p_{\mu}^2|$$

$$+ \lambda_{2s}\lambda_{2p}\sum_{\mu}|2s^2 2p_{\mu}^2| + \lambda_{2p}\lambda_{2p}\sum_{\mu \neq \nu}|2p_{\mu}^2 2p_{\nu}^2|.$$

(B8)

Here, the λ's amplitude sets the relative weight of the corresponding configurations, playing a crucial role in curing nondynamic correlation effects and improving the electronic nodal structure of the wave function, with the computational cost of a single determinant.

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