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# Resonating valence bond wave function with molecular orbitals: Application to first-row molecules

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We introduce a method for accurate quantum chemical calculations based on a simple variational wave function, defined by a single geminal that couples all the electrons into singlet pairs, combined with a real space correlation factor. The method uses a constrained variational optimization, based on an expansion of the geminal in terms of molecular orbitals. It is shown that the most relevant nondynamical correlations are correctly reproduced once an appropriate number  $n$  of molecular orbitals is considered. The value of  $n$  is determined by requiring that, in the atomization limit, the atoms are described by Hartree–Fock Slater determinants with Jastrow correlations. The energetics, as well as other physical and chemical properties, are then given by an efficient variational approach based on standard quantum Monte Carlo techniques. We test this method on a set of homonuclear ( $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{F}_2$ ) and heteronuclear ( $\text{LiF}$  and  $\text{CN}$ ) dimers for which strong nondynamical correlations and/or weak van der Waals interactions are present. © 2009 American Institute of Physics. [doi:10.1063/1.3249966]

## I. INTRODUCTION

Already in the early stages of quantum mechanics, Pauling<sup>1</sup> introduced the so-called resonating valence bond (RVB) theory of the chemical bond, starting from the simple consideration that a spin singlet can be formed between any two valence electrons belonging to neighboring atoms. In this scheme, the ground state wave function of a molecule, such as benzene, can lower the energy by allowing the resonance among all possible valence bond configurations that can be drawn by linking the positions of two atoms (e.g., the Kekulé and Dewar configurations in the benzene molecule). However, its application was limited, since the number of bonds were growing exponentially with the number of atoms. As a consequence, the powerful language of molecular orbitals (MOs) applied to Hartree–Fock (HF) and post-HF methods became popular. Nonetheless, quite recently, the interest in RVB wave functions has been strongly revived. Indeed, soon after the discovery of the high- $T_c$  superconductors, Fazekas and Anderson<sup>2</sup> realized that a single determinant wave function combined with a suitable real space correlation term—henceforth referred to as “the Jastrow factor”—could be used to represent a complex RVB state. In this new ansatz a crucial ingredient is the form of the determinantal part of the wave function, that is required to be a singlet state with total spin  $S=0$ . This picture, aimed at explaining the high- $T_c$  superconductivity, represents also a very efficient numerical implementation of the original RVB idea, soon reconsidered in this form for lattice models,<sup>3–7</sup> and then in

realistic simulations of atoms and small molecules.<sup>8–11</sup> Although the Anderson’s RVB wave function has been originally defined just for singlet states, the same concept can be applied to electronic systems with arbitrary spin  $S>0$ , with the inclusion of unpaired orbitals. This is a very important generalization in order to describe polarized compounds, like the transition element compounds which show high-spin configurations in their low-lying energy states. In the actual RVB description of realistic systems, it is necessary to resort to standard quantum Monte Carlo (QMC) methods<sup>12</sup> in order to compute the variational expectation values of the energy and correlation functions.<sup>8,9,13</sup>

In this article, we propose an extension of the RVB picture that is based on a MO expansion of the singlet valence bond pairs defining the wave function. This ansatz yields a correlation consistent RVB representation by means of a constrained energy minimization which keeps the number of MOs fixed while stretching the bond. By setting this number to a value such that a Jastrow correlated HF wave function is recovered in the atomization limit, we obtain, with a single determinant, a remarkably accurate description of the bond, even when strong nondynamical correlations are present in the system. In this paper we illustrate the method and test it on a set of dimers composed by first-row atoms and on selected small molecules belonging to the so-called G1 set (see Ref. 14), often used to test new theoretical methods. The approach described in this work has also been applied to the study of the controversial ground state of the iron dimer.<sup>15</sup>

In the following, we describe the RVB wave function and our extension, and we show test results on various homonuclear and heteronuclear dimers ( $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{F}_2$ ,  $\text{LiF}$ , and  $\text{CN}$ ). In Appendix A we describe the constrained minimization of the MO expansion of the trial wave func-

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tion. In Appendix B, we present a systematic study of the variational energies obtained with the RVB wave function, as a function of the number of MOs (Appendix B 1) and the size of the atomic basis set used (Appendix B 2).

## II. VARIATIONAL METHOD

### A. General description of the wave function

The fundamental ingredient of our variational method is an  $N$ -electron RVB wave function, called JAGP since it is the product of a Jastrow factor  $J$ , and a determinantal part which is an antisymmetrized geminal power (AGP), previously introduced in Refs. 8 and 9 ( $\Psi_{\text{JAGP}} = J \Phi_N$ ). Below we shall describe this wave function.

In the case of  $N$  electrons with  $N_\uparrow$  up spins ( $N_\downarrow$  down spins), where for simplicity we take  $N_\uparrow \geq N_\downarrow$ , we can describe a pure spin state with total spin  $S = |N_\uparrow - N_\downarrow|/2$  and maximum spin projection  $S_z^{\text{tot}} = S$  by means of the antisymmetrized product of  $N_\downarrow$  singlet pairs and  $2S$  unpaired orbitals corresponding to the remaining spin-up electrons. Hence the determinantal part reads

$$\Phi_N(\vec{R}) = \mathcal{A} \prod_{i=1}^{N_\downarrow} \phi(\vec{r}_i^\uparrow, \vec{r}_i^\downarrow) \prod_{j=N_\downarrow+1}^{N_\uparrow} \phi_j(\vec{r}_j^\uparrow), \quad (1)$$

with  $\mathcal{A}$  the antisymmetrization operator,  $\vec{R} = \{\vec{r}_1^\uparrow, \dots, \vec{r}_{N_\uparrow}^\uparrow, \vec{r}_1^\downarrow, \dots, \vec{r}_{N_\downarrow}^\downarrow\}$  the  $3N$ -dimensional vector of coordinates,  $\phi(\vec{r}, \vec{r}') = \phi(\vec{r}', \vec{r})$  a symmetric orbital function describing the singlet pairs, and  $\phi_j(\vec{r})$  the unpaired orbitals. It can be shown that the wave function in Eq. (1) can be rewritten in terms of a single determinant (see Ref. 8 and references therein).

$\Phi_N(\vec{R})$  has definite total spin. We also impose all possible symmetries to be satisfied by Eq. (1), such as angular momentum and spatial reflections.

Similar constructions with definite spin can be done, by allowing also triplet pairing between the  $2S$  unpaired electrons. Since this involves a bit more complicated algebra like the use of Pfaffians,<sup>10,11</sup> we do not consider it here.

The Jastrow factor takes into account the electronic correlation between two electrons and is conventionally split into a homogeneous interaction  $J_2$  depending on the relative distance between two electrons (i.e., a two-body term), and a non homogeneous contribution depending also on the electron-ion distance, included in the one-body  $J_1$ , three-body  $J_3$ , and four-body  $J_4$  terms.  $J_1$  is a single-particle function which is important to compensate the change in the one particle density induced by  $J_2$ ,  $J_3$ , and  $J_4$ , as well as to satisfy the electron-ion cusp conditions. The one- and two-body terms  $J_1$  and  $J_2$  are defined by the following equations:

$$J_1 = \exp \left[ \sum_{ia} - (2Z_a)^{3/4} u(Z_a^{1/4} r_{ia}) + \sum_{ial} g_l^a \chi_{al}^J(\vec{r}_i) \right] \quad (2)$$

and

$$J_2 = \exp \left[ \sum_{i<j} u(r_{ij}) \right], \quad (3)$$

where  $i, j$  are indexes running over the electrons and  $l$  runs over different single-particle orbitals  $\chi_{al}^J$  centered on the

atomic center  $a$ .  $r_{ia}$  and  $r_{ij}$  denote electron-ion and electron-electron distances, respectively. The corresponding cusp conditions are fixed by the function  $u(r) = F[1 - \exp(-r/F)]/2$  (see, e.g., Ref. 13).  $g_l^a$  and  $F$  are optimizable variational parameters.

The three- and four-body Jastrow  $J_3 J_4$  are given by

$$J_3 J_4(\vec{R}) = \exp \left( \sum_{i<j} f(\vec{r}_i, \vec{r}_j) \right), \quad (4)$$

with  $f(\vec{r}, \vec{r}')$ , being a two-electron coordinate function that can be expanded into the same single-particle basis used for  $J_1$ ,

$$f(\vec{r}_i, \vec{r}_j) = \sum_{ablm} g_{lm}^{ab} \chi_{al}^J(\vec{r}_i) \chi_{bm}^J(\vec{r}_j), \quad (5)$$

with  $g_{lm}^{ab}$  optimizable parameters. Three-body (electron ion electron) correlations are described by the diagonal matrix elements  $g^{aa}$ , whereas four-body correlations (electron ion electron ion) are described by matrix elements with  $a \neq b$ .

The exhaustive and complete expression of the Jastrow factor  $J(\vec{R}) = J_1(\vec{R}) J_2(\vec{R}) J_3(\vec{R}) J_4(\vec{R})$  that we adopt in this work allows to take into account not only weak electron-electron interactions of the van der Waals (vdW) type, but it is also extremely effective for suppressing higher energy configurations with overlapping valence bonds, which otherwise lead to a too large electron density around an atom.

As any functions of two coordinates, also the pairing function  $\phi$  in Eq. (1) can be expanded in terms of single-particle orbitals. We can thus write

$$\phi(\vec{r}, \vec{r}') = \sum_{j=1}^{n-2S} \lambda_j \phi_j(\vec{r}) \phi_j(\vec{r}'), \quad (6)$$

where  $n$  is large enough and  $\{\phi_j\}$  is an orthogonal single-particle basis set, which reaches its complete basis set (CBS) limit for  $n \rightarrow \infty$ . Notice that, in these notations, we assume that the  $2S$  unpaired orbitals  $\phi_j$  of Eq. (1) correspond to the indexes  $n - 2S + 1 \leq j \leq n$  in Eq. (6).

The single-particle orbitals  $\phi_j$  can be conveniently chosen as the MOs obtained with a conventional restricted HF (RHF) calculation. The MO basis allows us to write Eq. (6) in a diagonal form equivalent to a more involved matrix form when the MOs are developed in an atomic basis set<sup>9</sup> of orbitals  $\varphi_{a,j}$  where  $a$  indicates the atomic center and  $j$  the type:  $\phi_i(\vec{r}) = \sum_{a,j} \zeta_{a,j}^i \varphi_{a,j}(\vec{r})$ . The coefficients  $\zeta_{a,j}^i$ , as well as the weights  $\lambda_j$ , can be used as variational parameters defining the geminal in Eq. (6). By truncating the expansion in Eq. (6) to a number of MOs  $n$  equal to the number of electron pairs plus the unpaired orbitals, namely,  $n = N_\uparrow$ , one recovers the usual RHF theory, because the antisymmetrization operator  $\mathcal{A}$  singles out only one Slater determinant. Moreover, the MO weights  $\lambda_j$  affect only an overall prefactor of this Slater determinant, so that their actual values are irrelevant in this case. However, the pairing function is generally not limited to have only  $N_\uparrow$  nonvanishing eigenvalues  $\lambda_j$ . Therefore, the RVB wave function represents a clear extension of the RHF theory, not only for the presence of the Jastrow factor, which considerably improves the dynamical correlations, but mainly because its determinantal part goes

TABLE I. Atomic energies for Li, Be, B, C, N, O, and F: comparison between RHF benchmarks, estimated exact values, VMC and LRDMC JHF data, and the percentage of recovered correlation energy (%) (evaluated using the estimated exact value and the Hartree-Fock energy). For Li and Be all-electron results are shown. For all the other atoms, results were obtained with a pseudopotential (Ref. 16).

Atom	RHF	Est. exact	JHF VMC	JHF LRDMC	%
Li	-7.432 727 <sup>a</sup>	-7.478 06 <sup>a</sup>	-7.477 07(6)	-7.478 07(3)	100
Be	-14.573 023 <sup>a</sup>	-14.667 36 <sup>a</sup>	-14.647 47(9)	-14.657 5(1)	89.5
B	-2.543 75616 <sup>b</sup>	-2.619 40948 <sup>b</sup>	-2.603 1(1)	-2.611 0(1)	88.9
C	-5.329 03005 <sup>b</sup>	-5.432 49352 <sup>b</sup>	-5.410 5(1)	-5.421 6(1)	89.5
N	-9.668 37630 <sup>b</sup>	-9.799 73109 <sup>b</sup>	-9.777 1(3)	-9.789 8(1)	92.4
O	-15.708 44748 <sup>b</sup>	-15.901 65954 <sup>b</sup>	-15.875 4(1)	-15.892 33(8)	95.2
F	-23.938 49161 <sup>b</sup>	-24.192 90003 <sup>b</sup>	-24.168 0(3)	-24.186 0(2)	97.3

<sup>a</sup>From Ref. 17.

<sup>b</sup>From Ref. 16.

beyond RHF when  $n > N_{\uparrow}$ , by including also nondynamical correlations. Quite generally, a gain in energy and a more accurate calculation are expected whenever  $n > N_{\uparrow}$ .

## B. Valence bond energy consistent number of MOs in the AGP

The main property used in the following derivation relies on the fact that the atoms are well described by a Jastrow correlated RHF (JHF) wave function. Indeed, the application of the Jastrow factor  $J$  on a simple HF Slater determinant provides at least  $\approx 90\%$  of the correlation energy in all the atoms (see Refs. 8 and 12 and Table I). Here we show that it is possible to extend and remarkably improve the correlated HF approximation for the chemical bond, by means of a RVB wave function with an *appropriate* number  $n$  of MOs appearing in Eq. (6). These MOs are chosen to minimize the energy expectation value in the presence of the Jastrow factor, while an upper bound on the number  $n$  is univocally determined by imposing that, when the atoms are at large distance, we cannot obtain an energy below the sum of the JHF atomic energies.

The above mentioned criteria are based on the assumption that the large intra-atomic correlations do not affect the chemical properties of the bond, which are instead extremely sensitive to the usually much weaker interatomic correlations. Moreover, electrons close to the atomic centers are chemically inert because they are far away from the region where the bond is formed. Hence, an improvement in the description of the atoms with many determinants<sup>18</sup> would lead in this case only to a rigid shift of the total energy. The above assumption is a quite generally accepted idea that has been exploited in different ways by a large variety of approaches. For instance, it validates the use of pseudopotentials, the configuration interaction (CI) with the frozen core approximation,<sup>19</sup> and is the basis for other quantum chemistry methods such as the symmetry-adapted perturbation theory (Ref. 20) and the Morokuma analysis (see Ref. 21 and references therein).

In the following we shall denote the aforementioned appropriate number  $n$  of MOs with  $n^*$ . Let us denote with  $M$  a molecule composed by atoms  $A_1, A_2$ , etc. The optimal value of  $n^*$  is most generally obtained by saturating a simple upper bound value  $\tilde{n}$ ,

$$n^* \leq \tilde{n} = \sum_i N_{\uparrow}(A_i), \quad (7)$$

where  $i$  is an index running over the atoms composing the molecule  $M$ . Since in some cases convergence in the energy for the JAGP can be obtained even for  $n^* < \tilde{n}$ , we have used the inequality to define  $n^*$  and the corresponding wave function will be denoted by  $JAGPn^*$ . If the sum of the number of spin-up electrons in the atoms equals the number of the MOs required by a RHF calculation  $n_{\text{HF}}(M)$  for the molecule, then  $n^* = n_{\text{HF}}(M)$  and the  $JAGPn^*$  wave function reduces to a JHF description of the molecule. This is the case, e.g., for  $\text{Be}_2$  and  $\text{B}_2$ . In all the other cases we have  $n_{\text{HF}}(M) < \tilde{n}$ , and, in this work, we have found that there is a substantial energy gain in increasing the number of MOs with respect to the RHF value. This happens, for instance, for  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{F}_2$ , and  $\text{CN}$ , whereas for  $\text{LiF}$ , though  $\tilde{n} > n_{\text{HF}}$ , accurate results can be obtained even with  $n^* = n_{\text{HF}}$ .

The upper bound in Eq. (7) can be slightly improved, as it will be shown in the following. This is particularly important when some degenerate multiplets of orbitals are not completely occupied, as for the  $\text{C}_2$  molecule where, by using  $\tilde{n}$  MOs in the AGP expansion, one of the two antibonding  $\pi^*$  orbitals remains empty, and therefore it is not possible to satisfy the orbital symmetry of the  $^1\Sigma_g^+$   $\text{C}_2$  wave function. In the general case the highest MO included in the AGP has degeneration  $D$  and it may occur that only  $\tilde{D} < D$  orbitals of the multiplet are included in the AGP expansion by the upper bound in Eq. (7). For this reason it is important to improve the upper bound (7) for  $n^*$ , in particular cases when the chemical compound is spatially symmetric, namely, for reflections, rotations, translations, of the atomic positions. In fact, let us suppose that the molecule is composed by several atoms. Some spatial symmetry operations can make equivalent  $n_A \geq 1$  identical atoms of type  $A$ . Assuming that these symmetries remain valid up to the atomization limit, we denote by  $m$  the minimum value of  $n_A$  among all atomic species. Then if  $m > 1$  it is possible to improve the upper bound (7) by

$$n^* \leq \tilde{n} + m - 1. \quad (8)$$

For instance, for  $\text{C}_2$ , according to Eq. (8) we have  $m=2$  due to the reflection symmetry of the molecule and  $n^* \leq \tilde{n} + 1$ .

Indeed  $n^* = \tilde{n} + 1$  not only allows to fulfill the  ${}^1\Sigma_g^+$  symmetry but also provides a substantial improvement of the binding with respect to  $n^* = \tilde{n}$  (see Fig. 3 in Appendix B 1). The one extra MO added cannot have any effect at large distance in a fully symmetric calculation that connects the compound at rest to  $m=2$  equivalent carbon atoms at large distance. Indeed, in this case, the presence of the extra orbital could improve only the energy of one of the two JHF atoms, thus violating their equivalence. Therefore the eigenvalue  $\lambda_j$  of Eq. (6) corresponding to the extra MO must vanish in the atomization limit.

Generally speaking a value for  $n$  larger than the upper bound (8) certainly leads to a lower value of the total energy, but may improve much more the atomic energies, rather than the bonding. Actually, we have seen that, in all cases so far considered, the accuracy in describing the chemical bond improves systematically by increasing the number of MOs, provided it remains smaller than the upper bound. Clearly, whenever Eq. (7) or Eq. (8) is satisfied, the atomization energy has to be referred to the JHF calculation, even if lower energies could be achieved with a JAGP wave function for the atoms.<sup>8</sup> Remarkably, in the limit of large number of MOs, when the lowest JAGP total energies are obtained both for the atom and the molecule, the binding energy becomes always worse than the corresponding JAGP $n^*$ .

The JAGP $n^*$  wave function can be used also to describe bulk systems by applying the upper bound of Eq. (7) and of Eq. (8) to the supercell containing a finite number of atoms, so that the values of  $\tilde{n}$  and  $m$  easily follow exactly as in the case of a finite open system. The upper bound computed in this way may exceed by a large amount the number  $n_{\text{HF}}$  of MOs necessary to define a single Slater determinant in the supercell. Thus, convergence in the energy is expected in this case for  $n^* \ll \tilde{n}$ . For instance, in the case of graphene for a typical supercell of 48 atoms,  $\tilde{n} = 4 \times 48 = 192$ , whereas  $n_{\text{HF}} = 3 \times 48 = 144 \ll 192$ .

The constrained optimization of the JAGP wave function with a given number of MOs is a generalization of the standard QMC optimization<sup>18</sup> which minimizes the total energy and will be described in Appendix A.

### III. RESULTS

In this section we shall describe the results that we have obtained for a set of molecules composed of first-row atoms, where strong nondynamical correlation and/or weak vdW interactions are present. These molecules are used as a test case for our method.

Our study has been carried out by means of QMC simulations. We started from the constrained optimization of the variational wave function described in Sec. II, which was initialized by taking density functional theory orbitals in the local density approximation, and then we performed variational Monte Carlo (VMC) or lattice regularized diffusion Monte Carlo (LRDMC) simulations.<sup>22</sup>

For the determinantal part of the wave function we have used a Slater (for Be<sub>2</sub>, and the Li atom in the LiF molecule) or mixed Slater/Gaussian (for B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>, CN, and the F atom in the LiF molecule) basis, large enough for an

accuracy of 1 mH in the total energies. This quantity sets the tolerance for our CBS limit extrapolation. In particular, for Be<sub>2</sub> the basis set is 6s4p2d, for B<sub>2</sub> 5s4p1d, for C<sub>2</sub> 5s5p, for N<sub>2</sub> 5s3p2d, for O<sub>2</sub> 6s5p2d, for F<sub>2</sub> 5s5p2d, for the Li atom in the LiF molecule 5s4p, whereas for the F atom, as well as for the C and N atoms composing the CN molecule, we used the same basis adopted for the corresponding dimers. In the mixed Slater/Gaussian cases we have used one Slater orbital for each angular momentum, except for  $d$  orbitals, which have been chosen of a purely Gaussian form. Thus, by fully optimizing all the coefficients and the exponents of the primitive basis set, we have verified that the dimension of the basis is sufficient to achieve the desired accuracy. In Appendix B 2 we show, as an example, selected studies of convergence in the basis set.

A much smaller basis was used for the Jastrow factor because this allows for a more efficient energy optimization. On the other hand, the essentially exact contribution of Jastrow-type dynamical correlations, which do not change the phases of the wave function, can be very accurately obtained with the well established DMC technique,<sup>12</sup> within the recent LRDMC implementation.<sup>22</sup> LRDMC is equivalent to standard DMC for all-electron calculations and represents an improvement of the older technique because it allows to obtain a rigorous upper bound of the total energy even when pseudopotentials are used in the calculation. The DMC/LRDMC approach can be seen as a stochastic optimization of the Jastrow factor which keeps fixed the phases of the RVB wave function. In some test cases (see Appendix B 2), we have also verified that a larger basis in the Jastrow does not provide significant changes in the physical and chemical quantities here considered because total energy differences are much less sensitive to the extension of the Jastrow basis set.

We have used a helium-core pseudopotential<sup>16</sup> for all but Be and Li atoms. In some test cases without pseudopotentials (e.g., Be<sub>2</sub>) we have explicitly verified that the DMC and the LRDMC energies are consistent, but we have adopted the latter method for the sake of generality. In the C<sub>2</sub> case we have also checked that the effects of the pseudopotential on the total energy differences are negligible.<sup>23</sup>

In Table II, we compare with estimated exact results, bond lengths, and well depths obtained by means of VMC and LRDMC simulations performed with JHF or JAGP $n^*$  wave functions for the various molecules considered in this paper. We optimized each wave function for a bunch of different interatomic distances. The energy and interatomic distance at the minimum were found by interpolating the energy close to its minimum value with a cubic polynomial. We also report binding energies found in Ref. 18 with DMC calculations for a fully optimized all-electron Jastrow-correlated single determinant wave function (in our table denoted with J $\times$ SD DMC). Finally, we compare the JAGP $n^*$  zero point energy (ZPE) with available experimental data. This quantity was computed by standard first order perturbation theory in the anharmonic cubic term. For this property, the agreement between both VMC and LRDMC results and experimental

TABLE II. Bond lengths (in a.u.), well depths (in eV), and ZPE (in mH) for a set of first-row diatomic molecules. We report VMC and LRDMC values for both JHF and JAGP $n^*$  trial wave functions and experimental results or estimated exact values. The well-depth exact estimates are given by the experimental binding energies subtracted by the spin-orbit energies when accessible (i.e., for all atoms but B<sub>2</sub> and Be<sub>2</sub>) and the ZPE. We also report the J $\times$ SD DMC well depths of Ref. 18 when available. For Be<sub>2</sub> (all electron calculations) and B<sub>2</sub> (calculations with the pseudopotential in Ref. 16),  $n^*=N_{\uparrow}=4$ , hence the JHF and JAGP $n^*$  results coincide.

	Bond length (a.u.)							
	Be <sub>2</sub> (all el.)	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	LiF	CN
JHF VMC	4.85(5)	3.041(6)	2.367(2)	2.048(1)	2.27(1)	2.66(1)	2.95(4)	2.185(6)
JAGP $n^*$ VMC	4.85(5)	3.041(6)	2.334(6)	2.075(2)	2.268(7)	2.661(5)	2.92(2)	2.200(6)
JHF LRDMC	4.65(7)	3.021(9)	2.369(3)	2.051(1)	2.270(4)	2.665(9)	2.949(8)	2.201(3)
JAGP $n^*$ LRDMC	4.65(7)	3.021(9)	2.337(6)	2.075(1)	2.277(4)	2.663(3)	2.950(7)	2.202(2)
Exact estim.	4.63 <sup>a</sup>	3.005 <sup>b</sup>	2.3481 <sup>c</sup>	2.075 <sup>b</sup>	2.283 <sup>b</sup>	2.668 <sup>b</sup>	2.955 <sup>b</sup>	2.214 <sup>b</sup>
	Well depth (eV)							
	Be <sub>2</sub> (all el.)	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	LiF	CN
JHF VMC	0.120(5)	2.754(3)	5.538(9)	9.662(3)	4.976(8)	1.124(4)	5.93(2)	7.52(1)
JAGP $n^*$ VMC	0.120(5)	2.754(3)	6.327(9)	9.874(2)	5.060(7)	1.671(2)	5.96(2)	7.68(1)
J $\times$ SD DMC	0.125(1)	2.798(3)	5.656(3)	9.583(3)	4.992(7)	1.349(6)	...	...
JHF LRDMC	0.143(6)	2.797(2)	5.763(9)	9.665(2)	5.070(5)	1.452(3)	6.049(6)	7.661(5)
JAGP $n^*$ LRDMC	0.143(6)	2.797(2)	6.297(8)	9.882(1)	5.126(5)	1.688(2)	6.056(6)	7.744(5)
Exact estim.	0.1153(3) <sup>a</sup>	2.91(6) <sup>d</sup>	6.43(2) <sup>e</sup>	9.902(3) <sup>e</sup>	5.233(3) <sup>e</sup>	1.693(5) <sup>e</sup>	6.03(9) <sup>f</sup>	7.86(9) <sup>f</sup>
	ZPE (mH)							
	Be <sub>2</sub> (all el.)	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	LiF	CN
JHF VMC	0.56(5)	2.49(5)	4.3(1)	6.38(6)	3.8(1)	2.20(3)	2.3(2)	4.9(1)
JAGP $n^*$ VMC	0.56(5)	2.49(5)	4.2(1)	5.48(3)	3.85(9)	2.20(3)	2.1(2)	4.87(8)
JHF LRDMC	0.61(9)	2.51(7)	4.38(3)	5.83(6)	3.77(5)	2.16(3)	2.18(8)	4.81(3)
JAGP $n^*$ LRDMC	0.61(9)	2.51(7)	4.3(1)	5.51(2)	3.70(9)	2.22(2)	2.10(6)	4.82(4)
Expt.	0.56 <sup>a</sup>	2.4 <sup>b</sup>	4.2 <sup>c</sup>	5.4 <sup>c</sup>	3.6 <sup>c</sup>	2.1 <sup>c</sup>	2.07 <sup>b</sup>	4.71 <sup>b</sup>

<sup>a</sup>From Ref. 24.

<sup>b</sup>From Ref. 25.

<sup>c</sup>From Ref. 26.

<sup>d</sup>From Ref. 27.

<sup>e</sup>From Ref. 28.

<sup>f</sup>From Ref. 29.

findings is satisfactory in most of the cases. The accuracy in the ZPE can probably be improved by doing a more careful fit around the minimum.

Below we comment all the different cases.

### A. Beryllium and boron dimers

Although the beryllium dimer does not belong to the so-called G1-set of molecules (see, e.g., Ref. 14), this dimer is a very important test case for the variational method proposed in this paper. Indeed, several computational methods (see, e.g., Ref. 30), including previous QMC simulations,<sup>9</sup> have failed in the attempt of reproducing the binding of this molecule. Moreover, until the 1980s Be<sub>2</sub> represented a technical challenge for the experimentalists, and even later the value of its binding energy was not well established. A review on the experimental and theoretical investigations of Be<sub>2</sub> has recently appeared,<sup>24</sup> containing also new reference experimental data for its binding energy.

In Fig. 1 we provide the energy dispersion curve for the Be<sub>2</sub> molecule. The main plot shows a comparison between standard RHF calculations,<sup>30</sup> VMC data obtained with the

JAGP $n^*$  wave function, VMC, and LRDMC results for a JAGP with  $n > n^*$ . We also show an expanded Morse oscillator (EMO) fit of the recent experimental data of Ref. 24.

As mentioned before, in this case it turns out that  $n^* \leq n_{\text{HF}}(\text{Be}_2) + 1$ . In particular, by using the upper bound of Eq. (7) our JAGP $n^*$  reduces to a simple JHF wave function with  $n^*=4$  [the upper bound  $n^*=5$  of Eq. (8) does not provide significant improvements in a fully symmetric calculation]. Within the  $n=n^*$  constraint, bond features such as binding energy and bond length are reproduced fairly accurately, whereas a trial wave function with  $n > n_{\text{HF}}(\text{Be}_2) + 1$  fails to bind the molecule at the expected distance, even though the total VMC (LRDMC) energy  $E = -29.322\,95(8)\text{H}$  ( $E = -29.333\,85(7)\text{H}$ ) is much below the constrained minimization by about 24 mH (14 mH) at  $R=5$  a.u.. This total energy is very accurate from an absolute point of view and compares well with state of the art QMC calculations.<sup>18</sup> However, the variational wave function with the lowest variational energy, i.e., the JAGP with  $n=10$ , behaves similarly to an uncorrelated RHF, and both provide a very poor description of this chemical bond.<sup>31</sup> More in detail, the VMC JAGP $n=10$  energy dispersion curve presents one minimum at an inter-

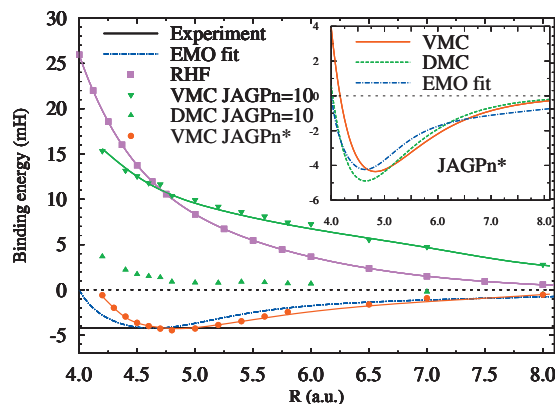


FIG. 1.  $\text{Be}_2$  binding energy (in millihartree) vs the nuclei distance  $R$  (in atomic units). Comparison of RHF (Ref. 30) outcomes,  $\text{JAGPn}^*$  results (in this case  $n^*=4$ ), and VMC and LRDMC results obtained with a JAGP wave function with  $n=10$  (squares, dots, downward, and upward triangles, respectively), while lines are a guide to the eye). In the figure, the experimental binding energy subtracted by the ZPE (Ref. 24) (solid line) and an EMO fit of the experimental data (Ref. 24) (dash-dotted line) are also plotted. The reference atomization limit for the  $\text{JAGPn}^*$  results is given by atomic calculations with a JHF wave function. For  $n=10$ , the atomization reference is given by an atomic JAGP wave function with the same primitive basis set as the JAGP wave function for the dimer. In the inset: comparison of fits to VMC and LRDMC data (solid and dashed lines, respectively) for the  $\text{JAGPn}^*$  wave function and the EMO fit of experimental data from Ref. 24 (dash-dotted line). Labels for the inset axes are the same as in the main frame. All curves are shifted with respect to their own atomization limit.

atomic distance  $R > 8$  a.u., while LRDMC  $\text{JAGPn}=10$  displays an additional swallower minimum close to the expected bond length. On the other hand, the quite accurate dispersion curve obtained by the full optimization of the JHF wave function shows, for the first time to our knowledge, that the key missing ingredients in the HF for  $\text{Be}_2$  are just the dynamical correlations carried out by our Jastrow factor. Although very simple, our Jastrow factor includes many-body correlations (up to two-ion two-electron interactions), that allow to take into account effective attractions between atoms given by vdW forces<sup>13</sup> and other polarization-polarization contributions.<sup>32</sup> Indeed, the dynamical interactions are extremely important to bind the molecule and it is crucial that the Jastrow factor includes this effect. For instance, the different parametrization of the Jastrow factor used in Ref. 18 does not allow to bind  $\text{Be}_2$  at a variational level, at variance with this work. On the other hand, the DMC binding energies of Ref. 18 are much closer to our VMC and DMC results, further suggesting the importance of the dynamical correlations in the bond.

In the inset of Fig. 1, we compare the VMC and LRDMC  $\text{JAGPn}^*$  energy dispersion curves shifted by their asymptotic limits. Despite some slight differences, the agreement between the two QMC techniques within the  $n=n^*$  constraint and the most recent experimental findings<sup>24</sup> can be considered fairly good in this case due to the very weak binding of the molecule.

Also the  $\text{JAGPn}^*$  description for  $\text{B}_2$  reduces to a JHF wave function. Both bond length and binding energy agree within two standard deviations with the estimated exact data.

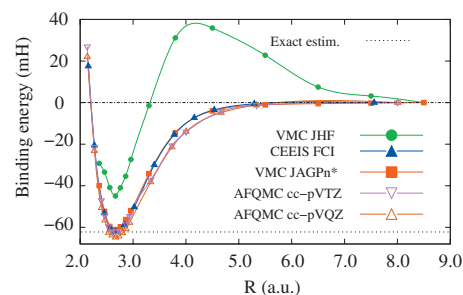


FIG. 2. Energy dispersion curve for the  $\text{F}_2$  molecule obtained with several computational techniques. The zero reference energy (dashed line) is twice the JHF atomic total energy for the  $\text{JAGPn}^*$  and the JHF molecules, whereas it is the large distance energy of the dimer for the remaining data. The slash-dotted line indicates the experimental binding energy (Ref. 28) subtracted by the zero point and spin-orbit energies. Lines are a guide to the eye. The CEEIS-FCI data are taken from Ref. 35, whereas AFQMC data are taken from Ref. 33.

## B. Fluorine dimer

A remarkable example of the accuracy of our technique is provided by the energy dispersion curve of the fluorine dimer reported in Fig. 2, where we show the results obtained with various QMC methods (and different wave functions), and other *ab initio* results. More in detail, we compare our JHF and  $\text{JAGPn}^*$  VMC data (see also Table III, where, for comparison, we also report our LRDMC results) with two energy dispersion curves obtained with auxiliary-field QMC (AFQMC) simulations for an unrestricted HF reference wave function spin projected to eliminate spin contamination<sup>33</sup> and an *ab initio* study based on full CI (FCI) calculations combined with the correlation energy extrapolation by intrinsic scaling (CEEIS) technique<sup>34</sup> plus core-electron correlations and scalar relativistic corrections.<sup>35</sup>

One can observe the dramatic improvements of the  $\text{JAGPn}^*$  wave function with respect to JHF simulations (see also Tables II and III). According to Eq. (7), we have used  $n^*=n_{\text{HF}}(\text{F}_2)+1$  because the upper bound of Eq. (8),  $n^*=n_{\text{HF}}(\text{F}_2)+2$ , does not lead to significant differences within

TABLE III.  $\text{F}_2$  binding energies (in mH) as a function of the internuclear distance  $R$  in a.u. (see also Fig. 2): VMC and LRDMC results (energy of the molecule at distance  $R$  minus two times the JHF atomic energy) for a JHF and the  $\text{JAGPn}^*$  wave functions.

$R$ (a.u.)	VMC JHF	VMC $\text{JAGPn}^*$	LRDMC JHF	LRDMC $\text{JAGPn}^*$
2.36	-23.9(4)	-39.9(4)	-32.4(4)	-39.6(4)
2.46	-28.1(6)	-52.3(5)	-42.1(5)	-53.2(4)
2.56	-35.5(5)	-59.5(5)	-48.2(5)	-59.7(4)
2.668	-39.6(5)	-61.0(4)	-49.7(4)	-60.9(4)
2.76	-35.6(5)	-59.7(5)	-49.1(4)	-60.6(4)
2.86	-30.1(4)	-56.2(4)	-44.1(4)	-57.1(4)
2.96	-22.0(5)	-51.9(4)	-38.1(5)	-52.1(4)
3.3	3.9(5)	-34.2(5)		-34.6(4)
3.8	36.5(6)	-14.4(5)		-13.4(4)
4.5	41.2(6)	-4.0(4)		-2.5(4)
5.5	28.1(5)	-1.0(4)		
6.5	12.8(5)	-0.1(5)		
7.5	8.5(5)	0.5(5)		
8.5	5.4(5)	0.2(5)		

our energy accuracy. We remark here instead the importance of adding just one MO to the HF theory because this allows to consider all bonding and antibonding MOs in the AGP, thus leading to a fully size consistent result which benchmarks the energy dispersion curve from the bond length to the atomization limit. The agreement of the JAGP $n^*$  with the *ab initio* CEEIS-FCI calculations is remarkably good already at a VMC level. In fact, the VMC binding is 1.671(2) eV against 1.6867 eV of FCI calculations (without spin-orbit corrections). The LRDMC binding is 1.688(2) eV. Instead the AFQMC curves seem to be shifted of approximately 2–3 mH with respect to our JAGP $n^*$  data in the bond and intermediate length regions. This is due to an underestimation of the energy at large distance caused by the use of a simple unrestricted HF wave function (see the discussion in Sec. IV of Ref. 33 and Figs. 4 and 6 therein). Indeed the AFQMC well depths are 1.70(2) and 1.77(1) eV for the cc-pVTZ and the cc-pVQZ wave functions, respectively, when the reference at large distance is the molecular energy, whereas it is 1.60(1) and 1.70(1) eV, respectively, when the large distance reference is twice the energy of the separated atoms.

The results we have presented so far, reported in Table II, represent an astonishing example of the importance of constraining the variational wave function to an appropriate form during the optimization of the energy. Indeed, a brute force optimization of a correlated wave function, which is a rather demanding computation especially within QMC, would lead to an upper bound of the total energy which is almost meaningless, particularly in the Be<sub>2</sub> case. The rationale behind this effect is that an unconstrained optimization may not satisfy the requirement for the wave function to be a fair representation of the ground state of a physical Hamiltonian. While in lattice models it is possible to constrain the determinantal part of the RVB wave function to be the ground state of a short-range Bardeen–Cooper–Schrieffer (BCS) Hamiltonian—a quite sensible and accepted choice in strongly correlated models—this is much harder in continuous-type calculations. The constraint that we propose, very simple to implement in practice, just mimics the effect of computing the ground state of a HF Hamiltonian with an additional sufficiently weak BCS coupling between electrons. In fact, in this limit one obtains the complete or partial occupation—via the  $\lambda_j$  in Eq. (6)—of a number of MOs  $n^*$  not necessarily equal to the RHF prediction. In this context, the BCS coupling represents the effective interaction between electrons, which pairs them into the chemical bond. For instance, it is well known that the ground state of the H<sub>2</sub> dimer at large distance is very well described by the singlet entangled state obtained with the AGP,<sup>36</sup> only when the bonding and antibonding orbitals are taken into account. This state can be considered the ground state of a BCS Hamiltonian that in the atomization limit simply splits into a sum of two atomic HF Hamiltonians, with vanishingly small pairing. This coupling is, however, important to lift the degeneracy between the singlet and the triplet states. The same physics happens in the F<sub>2</sub> molecule studied in this work.

TABLE IV. Well depths for C<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>: comparison between pfaffian results (Refs. 10 and 11) and JAGP $n^*$  results. The VMC and LRDMC findings are compared with the exact estimates previously reported in Table II.

Method	WF	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
VMC	STU	5.94(2)	9.42(3)	4.94(3)
VMC	JAGP $n^*$	6.327(9)	9.874(2)	5.060(7)
DMC	STU	6.26(2)	9.84(2)	4.93(2)
LRDMC	JAGP $n^*$	6.297(8)	9.882(1)	5.125(5)
Exact estim.		6.44(2)	9.908(3)	5.241(3)

### C. Carbon, nitrogen, and oxygen dimers

The C<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> molecules represent challenging cases for our correlation consistent AGP approach. Indeed, when  $0 \leq S < S_{\max}$  and  $S_{\max} > 1$ , the lack of size-consistency in the AGP poses a fundamental limitation in order to reach the JHF limit in the dissociation. Note that  $S=0$  and  $S_{\max}=1$  is a nontrivial case when the JAGP is size consistent and the JHF is not (e.g., the simplest H<sub>2</sub> molecule or the F<sub>2</sub> described in the previous section). Strictly speaking, the restriction of the number of MOs to  $n^*$  does not guarantee a size consistent JHF result, even for the JAGP wave function. In the general case, the total JAGP energy in the atomization limit is an upper bound of  $\sum_A E_{\text{JHF}}(A)$  evaluated in the CBS limit. A generalization of the JAGP, based on the Pfaffian algebra, which includes also triplet pairing for electrons with the same spin, allows to have JHF size consistent results also in the cases with  $S=S_{\max}-1$  ( $S_{\max} > 1$ ), e.g., in O<sub>2</sub>. Despite we have not implemented this generalization, triplet pairing seems to provide a rather negligible effect at bond length, as very good results can already be obtained with the present JAGP ansatz.

The constrained minimization of the JAGP $n^*$  wave function leads to very significant improvements with respect to JHF results in both the binding energy and the bond length for C<sub>2</sub> and N<sub>2</sub>, if compared with the exact estimates coming from the experimental values. In O<sub>2</sub> the situation is quite different, since  $n^*=n_{\text{HF}}(\text{O}_2)+1$  and the MO missing in the HF scheme is quite high in energy, compared to all the paired MOs included in Eq. (6) according to our constraint. Therefore, it is not surprising that, in this case, the improvement upon JHF findings is smaller. The comparison with the exact estimates is nevertheless quite satisfactory.

By comparing the results in Table II for N<sub>2</sub>, O<sub>2</sub>, and F<sub>2</sub> with the single-determinant DMC well depths of Ref. 18, we note improvements already at the JHF level, and even bigger improvements are obtained upon Grossman’s benchmarks<sup>14</sup> (to which one should add the ZPE). We should mention that in Ref. 14, the basis used for the determinantal part is not optimized. Other differences could be due to either the different pseudopotentials used or the calculations not fully converged in the CBS limit.

As a further evidence of the accuracy of our method, in Table IV we compare the well depths found for C<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> with results obtained by using a singlet-triplet-unpaired (STU) Pfaffian wave function<sup>10,11</sup> and taking as a reference at large distance the JHF atomic limit, i.e., the binding energy is computed as  $E_{\text{molecule}}(\text{STU}) - 2E_{\text{atom}}(\text{JHF})$ . As shown



in Table IV, we find a rather good agreement for the well depth even in the challenging  $C_2$  molecule, when  $S=S_{\max}-2$  and an exact size consistent result is not possible even within the more general pairing function containing triplet correlations. In principle, the Pfaffian wave function, being a generalization of the JAGP, should have a larger binding energy by taking the corresponding JHF atomic energy as a reference, provided the CBS limit is reached and the pseudopotentials are accurate enough. Instead, in all the cases shown in Table IV, the STU and the  $JAGPn^*$  binding energy are very close, at least at the DMC level. The fact that our binding energy is always larger and more accurate comes probably from the use of a more complete basis, fully optimized in both the coefficients and the exponents, whereas in Refs. 10 and 11 the atomic basis is not optimized.

These comparisons show that our  $JAGPn^*$  ansatz provides quite generally a very accurate description of the chemical bond. This emphasizes the role of singlet electron pairs in the chemical bond and is consistent with the RVB theory. Thus, the present variational wave function can be considered the cheap but nevertheless accurate realization of the RVB idea, since only a single determinant and standard VMC are needed.

#### D. Heteronuclear dimers

We further carried out calculations for a couple of heteronuclear diatomic molecules belonging to the G1 set (namely, LiF and CN), selected on the basis of the quite big discrepancy between the binding energy found in Ref. 14 and the reported experimental values. Bond lengths, dissociation energies, and ZPEs for these two molecules are reported in Table II. We compare our well depths with the exact estimates obtained by correcting the experimental dissociation energies with the experimental ZPE and spin-orbit energies reported in Ref. 29.

As mentioned in Sec. II B, LiF is one of the cases in which  $n^*=\tilde{n}$  does not yield significant improvements with respect to the JHF wave function, even though  $\tilde{n}>n_{\text{HF}}$ . Instead, for CN the  $JAGPn^*$  wave function improves the description of the bond with respect to the JHF one, giving a bond length in fairly good agreement with the experimental value, although the binding energy is underestimated by  $\approx 0.1$  eV with respect to the exact estimate reported in Ref. 29. As for the homonuclear dimers shown in the previous sections, also in the heteronuclear cases here considered, our method provides binding energies in closer agreement with the experimental values<sup>29</sup> than those of Ref. 14. In particular, for LiF the agreement is very good already at the JHF level, as anticipated above.

#### IV. CONCLUSIONS

In conventional QMC variational techniques, based on the use of the Jastrow factor, it is not possible to consider a finite basis set and to exploit the huge cancellation between atomic energies and molecular energies within the same basis set. Indeed, after the introduction of the Jastrow factor, the wave function is unavoidably defined on an infinite

dimensional Hilbert space. As a consequence, it is more difficult to achieve the chemical accuracy on the energy differences and obtain a good description of the chemical bond, as we have shown, for instance, in the  $Be_2$  case. Here, a very accurate variational energy obtained by applying the DMC technique to our lowest energy JAGP wave function completely misses the correct features of the bond. In this case, with an unconstrained variational approach, qualitatively correct results can be obtained probably only by reaching the chemical accuracy on the total energy, that is clearly a very difficult task for any approximate variational technique. In fact, this target was so far achieved within QMC only by using several determinants in small molecules.<sup>18</sup>

In this paper we propose a simple constraint which allows to exploit the above mentioned cancellation between atomic and molecular energies even in QMC calculations based on a single determinant wave function. In fact, instead of imposing a constraint on the dimension of the atomic Hilbert space, we change a bit this point of view by constraining the number of MOs to an appropriate value that allows to take JHF results for the isolated fragments as a reference for the dissociation energy of the molecule. With this constraint we have shown that it is possible to obtain much more accurate results in both variational and LRDMC calculations.

Although we have not carried out a systematic study of all the G1 set considered in Ref. 14, in several cases where the discrepancy was sizable we obtain an almost exact description of the bond (e.g., in  $F_2$ ). Surprisingly the LRDMC calculation provides only small improvements upon the simple and much cheaper VMC calculation, which turns out to be remarkably accurate in our approach. Also in cases where we do not improve upon the JHF results (e.g., LiF), we nonetheless obtain accurate binding energies, within a precision of about 0.1 eV. The latter achievement could be due to the accurate basis set we have considered in our work, together with the state-of-the-art optimization technique,<sup>37</sup> which is able to handle the large number of parameters in an extended basis set.

In conclusion, we have introduced a new and general approach to perform electronic structure calculations of quantum chemistry compounds based on a variational RVB wave function. In this formulation, we have shown that a substantial improvement in the description of the chemical bond is possible by extending the standard correlated single determinant theory with the JAGP wave function. In the original formulation of the RVB theory, the gain in energy obtained by the resonance of several valence bond configurations was just named the “resonance valence bond energy.” Within this new formulation we propose that this energy gain can be achieved by increasing the number of MOs of the JAGP from its HF value and without exceeding a value  $n^*$  of MOs. This value can be determined by requiring a correlation consistent property from the bond length to the atomization limit, realized via a constrained energy minimization.

## ACKNOWLEDGMENTS

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## APPENDIX A: CONSTRAINED OPTIMIZATION OF THE AGP WAVE FUNCTION

### 1. MO expansion of the AGP

In this appendix we expand the pairing function  $\Phi$  in atomic orbitals  $\xi_j(\vec{r})$  located at atomic positions  $\vec{R}_j$ ,

$$\Phi(\vec{r}, \vec{r}') = \sum_{j,j'} \lambda_{j,j'} \xi_j(\vec{r}) \xi_{j'}(\vec{r}'), \quad (\text{A1})$$

where  $\lambda$  is the pairing matrix and  $j, j'$  label the considered atomic orbitals on the corresponding atomic positions  $\vec{R}_j, \vec{R}_{j'}$ . Obviously, in order to define a singlet state the pairing matrix should be symmetric  $\lambda_{j,j'} = \lambda_{j',j}$ . Hereafter, both for simplicity and for the sake of generality we do not assume this symmetry because it can be easily satisfied during the optimization scheme, when necessary. Therefore, in the general case we are left with  $N_L = L \times L - 1$  independent variational constants, where  $L$  is the linear size of the matrix  $\lambda$ , namely, the dimension of the atomic basis. There is only one linear dependence between the  $L \times L$  entries of the matrix  $\lambda$  because the multiplication of  $\Phi$  by an overall constant does not change the AGP apart for its normalization. This constraint is usually satisfied by keeping fixed an arbitrary matrix element to the unit value.

Usually, the number  $N_L$  is very large, and in the following we determine a systematic way to work with much less variational parameters, being nevertheless efficient in determining the lowest energy MOs of the chosen variational ansatz.

For simplicity we do not consider unpaired orbitals, because for them no constraint is applied, therefore we set  $N_\uparrow = N_\downarrow$ . Moreover, in the following we can assume that the original orbitals  $\xi_j$  have been orthogonalized by a suitable transformation depending on the overlap matrix,

$$S_{i,j} = \langle \xi_i | \xi_j \rangle, \quad (\text{A2})$$

Namely, we implicitly assume the following change in the definition of the orbitals and the corresponding matrix  $\lambda$  in Eq. (A1),

$$\begin{aligned} \xi_j(\vec{r}) &\rightarrow \sum_k (S^{-1/2})_{j,k} \xi_k(\vec{r}), \\ \lambda_{i,j} &\rightarrow \sum_{k,l} (S^{1/2})_{i,k} \lambda_{k,l} (S^{1/2})_{l,j}. \end{aligned} \quad (\text{A3})$$

This greatly simplifies the forthcoming analysis without loss of generality.

Then, for the resulting square matrix we can use the well known singular value decomposition,

$$\lambda_{i,j} = \sum_{k=1}^r \alpha_k \psi_i^k \bar{\psi}_j^k, \quad (\text{A4})$$

where  $\alpha_k \geq 0$  and  $\psi^k$  ( $\bar{\psi}^k$ ) are a set of  $r \leq L$  MOs for the spin-up (spin-down) electrons that are orthonormal, i.e.,  $\sum_i \psi_i^j \psi_i^j = \delta_{i,j}$ . Formally the spin-up MOs and the spin-down ones are the eigenvectors of the  $2L \times 2L$  symmetric matrix,

$$H = \begin{vmatrix} 0 & \lambda \\ \lambda^\dagger & 0 \end{vmatrix}, \quad (\text{A5})$$

which has pair of eigenvectors with eigenvalues  $\pm \sqrt{\alpha_k}$  given by

$$\begin{vmatrix} \psi^k \\ \pm \bar{\psi}^k \end{vmatrix}. \quad (\text{A6})$$

A simple way to reduce the number of parameters is to require that the matrix has rank  $r < L$  so that all the eigenvalues  $\alpha_k$  for  $k > r$  are assumed to be zero or negligible. For instance, if  $r = N/2$  we obtain the standard Slater determinant with  $N_\uparrow = N_\downarrow = N/2$  MOs for each spin component.

This projection scheme can be made general, and this leads to a remarkable extension of the Slater determinant, within the AGP wave function expanded in MOs, as discussed in Appendix A 2.

### 2. Projection on a rank- $r$ geminal

If the rank  $r$  of a geminal matrix  $\lambda_{i,j}$  is equal to half the number of electrons  $N/2$ , then the AGP represents a Slater determinant. Even if  $N/2$  is usually much smaller than the dimension of the atomic basis  $L$ , Fermi statistics at zero temperature favors the occupation of the lowest possible energy levels, so that  $r \approx N/2$  turns out to be a reasonably accurate guess for the AGP wave function. In principle this wave function may have much larger rank up to  $r = L$ , but one may expect that most of the singular values will have negligible weight. Therefore, from a general point of view, and not only for reducing the number of variational parameters, it is important to optimize in an efficient way a full  $L \times L$  matrix of rank  $N/2 \leq r \leq L$  given by Eq. (A4).

To this purpose we propose the following scheme of constrained optimization, where  $r$  is chosen and fixed to a reasonable value  $n^* \approx N/2$  during the optimization.

Given  $\lambda^0$  a rank- $r$  matrix, in order to simplify the notations, we write the corresponding singular value decomposition (A4) in a matrix form,

$$\lambda^0 = \psi^0 \alpha^0 \bar{\psi}_T^0, \quad (\text{A7})$$

where  $\psi^0$  and  $\bar{\psi}^0$  are  $L \times r$  matrices, the subscript  $T$  indicates the transpose of a matrix, and the nonzero singular values  $\alpha_k^0$ ,  $k = 1 \cdots r$  are denoted by a diagonal matrix  $\alpha^0$ .

Then we change this matrix  $\lambda^0$  by adding to it a general first order contribution,

$$\lambda' = \lambda^0 + \lambda^1(\epsilon),$$

where henceforth the superscript indicates the order of the expansion in  $\epsilon$ . This new matrix will be constrained to have

rank  $r$ . Therefore all the terms in Eq. (A4) can be expanded within first order in perturbation,

$$\lambda^1 = \epsilon(\psi^0 \alpha^0 \bar{\psi}_T^1 + \psi^1 \alpha^0 \bar{\psi}_T^0) + \epsilon \psi^0 \alpha^1 \bar{\psi}_T^0. \quad (\text{A8})$$

In order to satisfy the constraint on the rank in the matrix  $\lambda^1$ , it is much simpler to work with an unconstrained matrix  $\bar{\lambda}$ , and left and right projection matrices,

$$P^R = \bar{\psi}_T^0 \bar{\psi}^0, \quad (\text{A9})$$

$$P^L = \psi_T^0 \psi^0. \quad (\text{A10})$$

The two matrices above are projection matrices ( $P=P_T$  and  $P^2=P$ ) as they project vectors in the  $r$  dimensional subspaces corresponding to the nonzero values of the singular value decomposition (A4).

Indeed it is very simple to show that if the matrix  $\lambda^0 + \lambda^1$  satisfies the constraint of a singular value decomposition with rank  $r$ ,  $\lambda^1$  has to satisfy the simple relation,

$$(I - P^L)\lambda^1(I - P^R) = 0, \quad (\text{A11})$$

because in the expression (A8)  $(I - P^L)\psi^0 = 0$  and  $\bar{\psi}_T^0(I - P^R) = 0$ .

Thus an unconstrained variation in the matrix  $\bar{\lambda}$  can be projected onto the constrained one by using the above projection matrices,

$$\lambda^1 = \bar{\lambda} - (I - P^L)\bar{\lambda}(I - P^R), \quad (\text{A12})$$

in the sense that, after the above projection, the matrix  $\lambda^0 + \lambda^1$  is suitable and can be considered to satisfy the constraint of a rank- $r$  matrix at first order in the perturbation (the matrix  $\lambda^1$  being sufficiently small).

Indeed, by simple inspection, the right hand side of Eq. (A12) immediately satisfies the condition (A11), that is, so far considered a necessary condition. It is also possible to show with a lengthy but straightforward calculation using first order perturbation theory of the symmetric matrix  $H$  given in Eq. (A5), that relation (A11) is also a sufficient condition for a perturbation that does not change the rank of a singular value decomposition.

### 3. Application to QMC

In the actual application of the recent QMC scheme for minimization of the energy, it is important to evaluate derivatives of a function with respect to the unconstrained parameters  $\bar{\lambda}$ . This function  $E(x)$  can be either the logarithm of the wave function or the local energy on a particular electronic configuration  $x$  sampled by the MC technique.<sup>8,9,18</sup>

Given the matrix  $D_{i,j} = \partial E / \partial \lambda_{i,j}$  of the unconstrained derivatives with respect to  $\lambda_{i,j}$ , by using Eq. (A12) and the chain rule for derivatives, then the corresponding matrix of constrained derivatives  $\bar{D}_{i,j} = \partial E / \partial \bar{\lambda}_{i,j}$  can be computed by simple matrix manipulation in the following way:

$$\bar{D} = D - (I - P_T^L)D(I - P_T^R). \quad (\text{A13})$$

In order to work with the original matrices we have to replace in Eqs. (A12) and (A13) the ones obtained by applying the inverse of the transformation (A3),

$$P^R \rightarrow S^{1/2} P^R S^{-1/2}, \quad (\text{A14})$$

$$P^L \rightarrow S^{-1/2} P^L S^{1/2}. \quad (\text{A15})$$

Notice also that after this transformation  $P_T^R$  and  $P_T^L$  are no longer equal to  $P^R$  and  $P^L$  in Eq. (A13).

The scheme therefore can be summarized in the following steps.

- (1) Compute the unconstrained derivatives  $D$  that, with some algebra, can be casted into a product of much smaller rectangular matrices  $U, V$  such that  $D = U_T V$  of dimension  $L \times N/2$ . Notice that also the projection matrices can be written in this convenient form, as in Eq. (A9).
- (2) Apply the projection (A13) by using the current MOs. By exploiting the fact that all the matrices involved are written in terms of much smaller rectangular matrices, a very convenient computation can be achieved scaling like  $N^2 L$  instead of  $L^3$  as in the straightforward implementation of the projection.
- (3) Apply the recent optimization schemes<sup>8,9,18</sup> and change the unconstrained parameters  $\bar{\lambda}$ . Then apply the projection, by diagonalizing the matrix  $\bar{\lambda}$ , and taking only the right and left eigenvectors corresponding to the largest singular values. New MOs are then defined after this diagonalization.
- (4) Repeat the above-described steps until convergence in the energy is achieved.

## APPENDIX B: AGP AND BASIS SET EXPANSION EFFECTS

### 1. Effect of the improved upper bound for $n^*$ : The $C_2$ case

As explained in Sec. II B,  $C_2$  is one of the exceptions to the rule of Eq. (7). In this case, we have  $\tilde{n} = 6$ , but the more

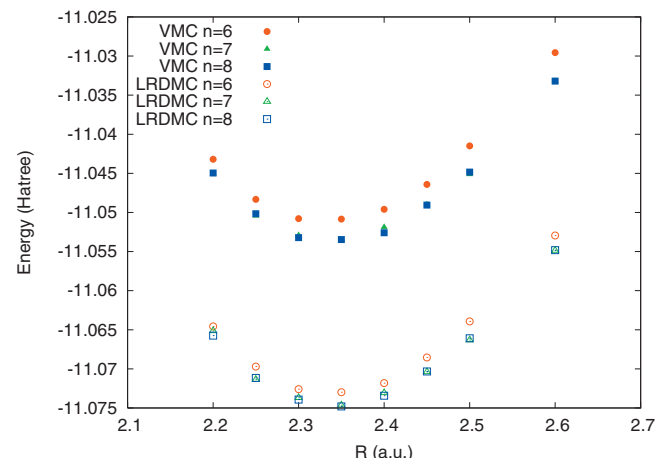


FIG. 3. Energy dispersion curve for  $C_2$  dimer with  $n=6$  (circles),  $n=7$  (squares),  $n=8$  (triangles) MOs. VMC and LRDMC results are represented by filled and empty symbols, respectively.

TABLE V. Total energies from all electron calculations for  $C_2$  with a JAGP expanded on a different number of MOs  $n$  are shown.  $n=9$  corresponds to the  $n^*$  upper bound of Eq. (8). The estimated exact total energy  $E_0$  is reported for comparison.

$n$	VMC	LRDMC
9	-75.8439(7)	-75.8934(4)
10	-75.8453(7)	-75.8930(4)
15	-75.8473(8)	-75.8928(4)
$E_0$	-75.9265 <sup>a</sup>	

<sup>a</sup>From Ref. 28.

accurate upper bound in Eq. (8) allows to work with  $n^*=7$ . Indeed, by following strictly Eq. (7) one would include a single antibonding orbital  $\pi^*$  in the AGP, while that orbital is double degenerate, due to the rotational symmetry of the molecule. Therefore, in order to fulfill the symmetry of the dimer, it is particularly important to fill the degenerate levels in the AGP by setting  $n^*=7$ . In Fig. 3 we show the VMC and LRDMC energies at various internuclear distances found with a JAGP wave function expanded in  $\tilde{n}$  and  $n^*$  MOs. In this case, the improved upper bound for  $n^*$  yields a gain of  $\approx 2.7$  mH in the VMC energies and of  $\approx 1.5$  mH in the LRDMC ones. Incidentally, the  $n=n^*=7$  energies agree within the error bars with the data resulting from a JAGP with  $n=8$  MOs.

An analogous check was done with all electron simulations at a fixed interatomic distance  $R=2.35$  a.u.. Results are reported in Table V. We note a saturation of LRDMC total energies for  $n > n^*$ .

## 2. Convergence in the basis set of the AGP and the Jastrow parts

Below we report the convergence in the basis set for selected molecules.

TABLE VI. JHF and JAGP $n^*$  VMC and LRDMC total energies (in Hartree) for the  $N_2$  pseudomolecule. Energies were computed at the experimental bond length using different basis sets for both the determinantal part and the three and four-body Jastrow term (34BJ).

Det.	JHF		
	34BJ	VMC	LRDMC
5s5p	2s2p	-19.9031(5)	-19.9338(2)
5s5p	3s3p	-19.9071(3)	-19.9346(2)
5s5p	4s4p	-19.9076(4)	-19.9349(2)
4s4p	3s3p	-19.9071(3)	-19.9344(2)
6s6p	3s3p	-19.9080(3)	-19.9348(2)
5s3p2d	2s2p	-19.9074(3)	-19.9339(1)
5s5p2d	3s3p	-19.9086(4)	-19.9349(2)
Det.	JAGP $n^*$		
	34BJ	VMC	LRDMC
5s5p	2s2p	-19.9159(5)	-19.9422(2)
5s5p	3s3p	-19.9204(3)	-19.9433(2)
5s5p	4s4p	-19.9200(3)	-19.9423(2)
4s4p	3s3p	-19.9185(3)	-19.9418(2)
6s6p	3s3p	-19.9205(3)	-19.9430(2)
5s3p2d	2s2p	-19.9208(3)	-19.9430(2)
5s5p2d	3s3p	-19.9213(3)	-19.9430(2)

TABLE VII. JHF and JAGP $n=8$  total energies (in Hartree) for the  $C_2$  pseudomolecule. Energies were computed at the experimental bond length using three different basis set for the three-four-body Jastrow term.

		VMC	LRDMC
JHF	(34BJ 2s2p)	-11.0239(3)	-11.0539(3)
JHF	(34BJ 3s2p)	-11.0245(2)	-11.0543(2)
JHF	(34BJ 3s3p)	-11.0250(2)	-11.0550(3)
JAGP $n=8$	(34BJ 2s2p)	-11.0535(1)	-11.0748(2)
JAGP $n=8$	(34BJ 3s2p)	-11.0536(2)	-11.0745(1)
JAGP $n=8$	(34BJ 3s3p)	-11.0544(1)	-11.0745(2)

### a. $N_2$ convergence in the basis set

For  $N_2$  we checked the convergence in the basis set by means of VMC and LRDMC simulations at the experimental internuclear distance. Total energies are reported in Table VI.

### b. $C_2$ convergence in the Jastrow basis set

We further checked the effects of a larger three and four-body Jastrow factor (34BJ) in the case of  $C_2$ . We performed simulations at the experimental bond length with the JHF wave function and the JAGP with  $n=8$  MOs (whose results agrees with the JAGP $n^*$  as shown in Appendix B 1) with the 2s2p Jastrow used for all the other cases and for two larger basis sets (namely, 3s2p, and 3s3p). Results are shown in Table VII. As expected, effects on the molecular total energy of a larger three- and four-body Jastrow are negligible in the LRDMC at least for the RVB wave function. For all the other cases, the largest Jastrow basis provides an energy gain of at most 1 mH with respect to the smaller basis.

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