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ABSTRACT

The molecular dissociation energy has often been explained and discussed in terms of singlet bonds, formed by bounded pairs of valence electrons. In this work, we use a highly correlated resonating valence bond ansatz, providing a consistent paradigm for the chemical bond, where spin fluctuations are shown to play a crucial role. Spin fluctuations are known to be important in magnetic systems and correspond to the zero point motion of the spin waves emerging from a magnetic broken symmetry state. Within our ansatz, a satisfactory description of the carbon dimer is determined by the magnetic interaction of two carbon atoms with antiferromagnetically ordered $S = 1$ magnetic moments. This is a first step that, thanks to the highly scalable and efficient quantum Monte Carlo techniques, may open the door for understanding challenging complex systems containing atoms with large spins (e.g., transition metals).

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I. INTRODUCTION

In a non-relativistic Hamiltonian that do not contain explicit spin interactions, the chemical interaction is, in a conventional picture, mostly determined by covalent bonds where electrons prefer to form singlet pairs across neighboring atoms, in this way preserving the total spin of the molecule. In this work, we will show that, rather unexpectedly, the spin interaction plays a crucial role and a faithful description of the chemical bond can be obtained by allowing local spin triplet excitations in some of the electron pairs. With standard techniques based on molecular orbitals,¹ it is difficult to detect this effect, and therefore, we adopt the Resonating Valence Bond (RVB) paradigm² that has been successfully applied even when standard single reference molecular orbital theory fails. Our approach generalizes the standard “frozen singlet” RVB picture, thus leading to a compact and accurate description of the electron correlation, at the prize of a very small spin contamination.

We consider a very small molecule, but nevertheless very important: the carbon dimer. Its ground state is a perfect singlet, while the isolated atoms have two unpaired electrons, and any type of mean field approach, such as HF or density functional theory

(DFT), is completely off with errors of the order of eV. In addition, highly correlated methods, such as coupled cluster,^{3–5} face severe difficulties in describing its ground state properties so that the highly involved multi-configuration expansions^{5–7} are often adopted.

In a recent study, based on a correlated valence bond approach,⁸ Shaik *et al.* proposed that a fourth bond is necessary to explain the C_2 spectrum at low energy. Within a correlated resonating valence bond approach, they have found that the 2σ and 3σ molecular orbitals, after $s-p$ hybridization, change their nature as compared to standard molecular orbital theory and show a corresponding bonding character. By taking into account the remaining two π orbitals, obviously bonding, they argued that an unexpected quadruple bond should be a more appropriate description of the C_2 molecule. This result was rather surprising, especially considering that quadruple bonds should very rarely occur.^{9–13}

In this work, we also adopt a RVB approach, but with the help of a powerful statistical technique, named quantum Monte Carlo (QMC),^{14,15} we are able to work with a very compact and accurate ansatz that is as easy to visualize and understand as a mean field ansatz. We consider first the most general two-electron pairing function

$$\begin{aligned}
 g(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2) = & \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)g_+(\vec{r}_1, \vec{r}_2) \\
 & + \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)g_-(\vec{r}_1, \vec{r}_2) \\
 & + |\uparrow\uparrow\rangle g_{\uparrow}(\vec{r}_1, \vec{r}_2) + |\downarrow\downarrow\rangle g_{\downarrow}(\vec{r}_1, \vec{r}_2) \quad (1)
 \end{aligned}$$

in order to satisfy the Pauli principle $g(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2) = -g(\vec{r}_2\sigma_2, \vec{r}_1\sigma_1)$, yielding $g_{\pm}(\vec{r}_1, \vec{r}_2) = \pm g_{\pm}(\vec{r}_2, \vec{r}_1)$ and $g_{\sigma}(\vec{r}_2, \vec{r}_1) = -g_{\sigma}(\vec{r}_1, \vec{r}_2)$ for $\sigma = \uparrow, \downarrow$. When considering a generic (even) number N of electrons of given spin σ_i and positions \vec{r}_i ($i = 1, \dots, N$), we antisymmetrize the power over all the electron pairs that are determined by the same pairing function. The corresponding wave function (WF) represents the most general mean-field state, namely, the ground state of a mean-field Hamiltonian containing also BCS anomalous terms, projected onto a given number N of particles and total spin projection $S_{tot}^z = \sum_{i=1}^N \sigma_i$ along the z -quantization axis. This WF is known as the Antisymmetrized Geminal Power (AGP). There are three important cases: (i) when no triplet correlations are allowed, we have a perfect singlet and we denote it by AGPs; (ii) when only the parallel spin term of the triplet component is omitted [namely, the last line in Eq. (1)], the WF can break the spin symmetry, but the magnetic order parameter can be directed only in the z -quantization axis, and in this case, we will refer to AGPu; and (iii) the most important case is the most general one that contains all triplet contributions. Henceforth, it will be indicated with AGP, as we believe it represents the most powerful description of the chemical bond within the paradigm developed in this work. Its practical implementation requires the use of Pfaffian's algebra, as already described in Ref. 16.

Originally, the AGPs was found to be very poor, violating size consistency even in cases where the HF was size consistent. The important ingredient, solving the above issues,^{17,18} by dramatically improving the accuracy of this WF, is the introduction of a correlated term named Jastrow factor that can weight the energetically too expensive configurations where electrons are too close and feel the large Coulomb repulsion. In this simplified picture, introduced by Anderson long time ago,¹⁹ one can consider with a *single pairing function* all the valence bond (VB) configurations [see Fig. 1(1)], in practice, with almost optimal weights. This has been shown, for instance, in strongly correlated lattice models.²⁰

The Jastrow Factor (JF) is an explicitly symmetric function of the N coordinates and spins,

$$J(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \dots, \vec{r}_N\sigma_N) = \prod_{i \neq j} [f_{\sigma_i, \sigma_j}(\vec{r}_i, \vec{r}_j)], \quad (2)$$

where f , at variance of g , is the most general two-particle bosonic (and positive) WF. This form of the Jastrow is more general than the conventional one because, usually, a simplified or even absent spin dependency in the f function is adopted, denoted in the following with the symbol J_s . Without including spin dependency, a perfect singlet remains such after multiplication of the Jastrow. However, the spin dependency is necessary if we want to recover the singlet from a spin contaminated broken symmetry ansatz. Although this feature is obviously approximate, it generalizes in a rather convenient way, the so-called "symmetry restoring after projection."^{21,22} As shown in Fig. 1(1), a simple way to understand this effect is to consider two atoms with opposite spins. If the spins are oriented in

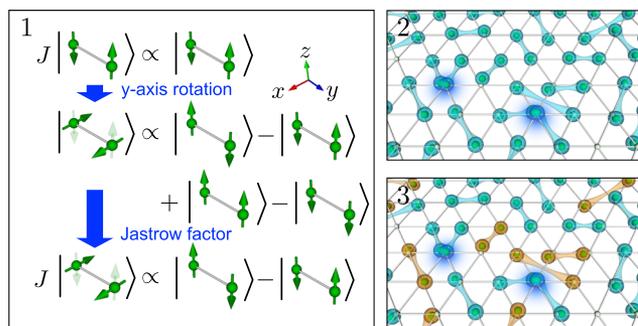


FIG. 1. (1) Restoring the singlet state for the Jastrow correlated broken symmetry ansatz. The Jastrow factor cannot change the broken symmetry ansatz if it is oriented in the same quantization axis (z -axis) of the electron basis. If we rotate the spins of the broken symmetry ansatz by 90° around the y -axis, the state becomes a quite general linear combination of spin configurations in the original basis. By carefully tuning the weights of each configuration with an appropriate spin-dependent Jastrow factor, we can recover the exact expansion of the singlet state in this basis. (2) Cartoon picture of a typical valence bond generated by the Jastrow correlated AGP WFs used in this work limited to only singlet bonds (JAGPs defined in the main text) and (3) containing both singlet and triplet bonds (JAGP). The balls indicate the electrons, and singlet and triplet bonds are displayed with cyan and orange, respectively. The main effect of the Jastrow factor is to reduce the probability that different electron bond pairs overlap on the same atom, in this way avoiding the effect of the strong Coulomb repulsion and dramatically improving the quality of the simpler AGP ansatz.

the direction of the electronic basis, defining our Jastrow in Eq. (2), the latter one cannot have any effect in the total WF. Conversely, it turns out energetically convenient to orient the spins of the atoms in a direction perpendicular to the previous one. In this way [see Fig. 1(1)], the Jastrow can suppress the unfavored triplet configurations with parallel spins. This optimal spin-orientation is rigorously valid within the well-known spin-wave theory of a quantum antiferromagnet, and the Jastrow in this case allows the description of the quantum fluctuations and the corresponding zero point energy gain, even for a finite (as is our case) number of atoms.²³

Before going into further details, we summarize in Figs. 1(2) and 1(3) the physical picture of our WF in the realistic case when the Coulomb repulsion is strong, and in a given atom, it is unlikely to have doubly occupied orbitals. In this way, the expansion of the many body WF can be seen as a liquid "soup" of mainly non-overlapping singlet and triplet bonds. Our findings indicate that, despite this picture was introduced long time ago, the important role of fluctuating triplet bonds has not been fully appreciated so far.

II. METHOD

After optimization, we have computed not only the total energy but also the total spin square,²⁴ which can be efficiently evaluated by QMC. The first quantity can be further improved by the so-called Fixed Node (FN) projection that basically allows the lowest possible energy with a Jastrow J not limited only to the two-electron correlation. In order to avoid too cumbersome tables, in the following, we report only FN energy results obtained with this very accurate

technique, whereas all the other quantities refer just to the bare variational WF with the explicit Jastrow written in Eq. (2). Within this technique, it is also possible to consider the spin square value restricted in a given region of space Λ , namely,

$$\bar{S}^2(\Lambda) = \left[\int_{x \in \Lambda} d^3x \sum_{i=1}^N \bar{S}_i \delta(\vec{x} - \vec{r}_i) \right]^2, \quad (3)$$

by extending the calculation described in Ref. 25 only within the region Λ . Here, \bar{S}_i is the spin operator acting on the electron at the position \vec{r}_i . Unless otherwise specified, in all molecular diatomic calculations, Λ is determined by dividing the whole space into two regions separated by a plane cutting the molecule into two equivalent ones containing only one atom.

III. WAVE FUNCTION

In this section, we will show how to define and calculate the WF power of the general Antisymmetrized Geminal Power (AGP), or its restricted formulation (AGPs and AGPu), and the JF for a given configuration of electronic positions and spins $\mathbf{X} = \{(\mathbf{r}_1 \uparrow), \dots, (\mathbf{r}_{N_\uparrow} \uparrow), (\mathbf{r}_{N_\uparrow+1} \downarrow), \dots, (\mathbf{r}_N \downarrow)\}$.

A. The basis set

The electronic coordinates are expanded in a set of localized Gaussian orbitals $\{\phi_{I,\nu}(\mathbf{r})\}$, where I and ν indicate the ν -th orbital centered on the I th atom at the position \mathbf{R}_I in the form

$$\phi_{I,\nu}(\mathbf{r}) = e^{-\frac{|\mathbf{r}-\mathbf{R}_I|^2}{Z_\nu}} [Y_{l_\nu, m_\nu} \pm Y_{l_\nu, -m_\nu}], \quad (4)$$

where Z_ν is a numerical coefficient that describes how diffuse the atomic orbital is around the atom, while Y_{l_ν, m_ν} is the spherical harmonic function with angular quantum numbers l_ν and m_ν . The sign of the combination $[Y_{l_\nu, m_\nu} \pm Y_{l_\nu, -m_\nu}]$ is chosen to ensure the orbital type ν to be real. This basis set has been used without further contractions for the description of the JF, but we had to use a different solution in order to consider a large Gaussian basis set for the AGP, AGPs, and AGPu with a reasonable computational cost. Indeed, for this study, we used hybrid atomic orbitals (HOs)^{26,27} obtained as linear combinations of elements of the Gaussian basis set,

$$\bar{\phi}_{I,\omega}(\mathbf{r}) = \sum_\nu \mu_{\omega,\nu} \phi_{I,\nu}(\mathbf{r}). \quad (5)$$

Our choice is to use HO to describe the atomic orbitals that physically play a role. By taking into account that the atoms considered here can be obtained by the occupation of at most two s -wave and three p -wave orbitals, we decided to use five HOs both for the carbon and nitrogen atoms, and one HO for the Hydrogen atom. For the sake of compactness, we indicate the basis as $\{\phi_k(\mathbf{r})\}$ combining the indices ω and I in a single index k for a lighter notation. The use of the HO basis set allows us to expand the wave function in a large set of atomic Gaussian orbitals while remaining with a reasonably small number of variational parameters.

B. The AGP

The AGP is the most general WF that can be built using the pairing function and contains the AGPs and the AGPu as particular cases. In the following, we will explain how to calculate the full AGP including all the terms from Eq. (1). The algebra used for the AGP applies also to AGPs and AGPu exactly in the same way, but in the latter case, a further simplification leads to the canonical determinant form for their evaluation as shown in the literature.^{17,28–31}

The building block of the AGP in a given basis set $\phi(\mathbf{r})$ is, as mentioned, the pairing function whose general parametrization is

$$g(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2) = \sum_{k,l} \lambda_{k,l}^{\sigma_1 \sigma_2} \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2), \quad (6)$$

where λ is a matrix representing g with a finite number of variational parameters. For simplicity, we will enumerate the spin up electrons from one to N_\uparrow and the spin down ones from $N_\uparrow + 1$ to N . To build the AGP, we consider a generic number N of electrons of given spin $\sigma_i = \pm 1/2$ and positions \vec{r}_i ($i = 1, \dots, N$). We then antisymmetrize the power over all the electron pairs that, by definition, occupy the *same* pairing function. Considering for the moment an even number of electrons, we can build the matrix that contains all the pairs as

$$W = \begin{pmatrix} 0 & g(\mathbf{r}_1 \uparrow, \mathbf{r}_2 \uparrow) & \dots & g(\mathbf{r}_1 \uparrow, \mathbf{r}_N \downarrow) \\ g(\mathbf{r}_2 \uparrow, \mathbf{r}_1 \uparrow) & 0 & \dots & g(\mathbf{r}_2 \uparrow, \mathbf{r}_N \downarrow) \\ \vdots & \vdots & \ddots & \vdots \\ g(\mathbf{r}_{N-1} \downarrow, \mathbf{r}_1 \uparrow) & g(\mathbf{r}_{N-1} \downarrow, \mathbf{r}_2 \uparrow) & \dots & g(\mathbf{r}_{N-1} \downarrow, \mathbf{r}_N \downarrow) \\ g(\mathbf{r}_N \downarrow, \mathbf{r}_1 \uparrow) & g(\mathbf{r}_N \downarrow, \mathbf{r}_2 \uparrow) & \dots & 0 \end{pmatrix}. \quad (7)$$

It is a $N \times N$ matrix where to each row and to each column corresponds an electron. We can distinguish four different blocks of this matrix depending on the spin of the pairs. We can write the matrix W as

$$W = \begin{pmatrix} W_{\uparrow\uparrow} & W_{\uparrow\downarrow} \\ W_{\downarrow\uparrow} & W_{\downarrow\downarrow} \end{pmatrix}, \quad (8)$$

where $W_{\uparrow\uparrow}$ and $W_{\downarrow\downarrow}$ are a $N_\uparrow \times N_\uparrow$ and a $N_\downarrow \times N_\downarrow$ antisymmetric matrix, respectively, which take into account the parallel spin terms of the triplet, while $W_{\uparrow\downarrow}$ is a $N_\uparrow \times N_\downarrow$ matrix such that $W_{\uparrow\downarrow} = -W_{\downarrow\uparrow}^T$, describing the remaining triplet and singlet contribution.

The extension to an odd number of electrons requires the use of an unpaired orbital that is added as a last row and column of the matrix W . Being Θ_\uparrow the vector containing the value of $\Theta(\mathbf{r})$ calculated at the \uparrow electronic positions and Θ_\downarrow the one calculated for the \downarrow electronic positions, we modify the matrix in Eq. (8) as

$$W = \begin{pmatrix} W_{\uparrow\uparrow} & W_{\uparrow\downarrow} & \Theta_\uparrow \\ W_{\downarrow\uparrow} & W_{\downarrow\downarrow} & \Theta_\downarrow \\ -\Theta_\uparrow^T & -\Theta_\downarrow^T & 0 \end{pmatrix}. \quad (9)$$

In theory, it is possible to further add an arbitrary number of pairs of unpaired orbitals in the same way. In this case, Θ_\uparrow and Θ_\downarrow are defined as matrices of size $N_\uparrow \times N_{unpaired}$ and $N_\downarrow \times N_{unpaired}$, respectively.

As suggested by the name antisymmetrized geminal power, our goal is to define a WF that is literally the antisymmetrized power of the geminals and the unpaired orbitals (if present), namely,

$$\Phi(\mathbf{X}) = \sum_{\alpha} \text{Sgn}(\alpha) (g(\mathbf{r}_{1_{\alpha}} \sigma_{1_{\alpha}}, \mathbf{r}_{2_{\alpha}} \sigma_{2_{\alpha}}) g(\mathbf{r}_{3_{\alpha}} \sigma_{3_{\alpha}}, \mathbf{r}_{4_{\alpha}} \sigma_{4_{\alpha}}) \cdots \\ \times g(\mathbf{r}_{p-1_{\alpha}} \sigma_{p-1_{\alpha}}, \mathbf{r}_{p_{\alpha}} \sigma_{p_{\alpha}}) \Theta_1(\mathbf{r}_{p+1_{\alpha}}) \cdots \Theta_{N-p}(\mathbf{r}_{N_{\alpha}})), \quad (10)$$

where α is one of the possible ways of distributing the N electrons between the $N/2$ pairs and the N_{unpaired} unpaired orbitals Θ , and $\text{Sgn}(\alpha)$ is the sign of the corresponding permutation of the particles that is required to ensure the fermionic behavior. The Pfaffian is the algebraic operation that performs this task,^{16,32} yielding

$$\Psi_{AGP}(\mathbf{X}) = \text{Pf}(W). \quad (11)$$

1. Pfaffian definition

The Pfaffian is an algebraic operation defined for the antisymmetric square matrix with an even number of rows and columns. This is always compatible with our matrix W that is antisymmetric and has always an even number of rows and columns for each value of N . Before introducing the Pfaffian, we define a partition of the matrix W as

$$A(\alpha) = \text{sign}(\alpha) \prod_{k=1}^M W_{i_k j_k}, \quad (12)$$

where all i_k and j_k are different, $i_k < j_k$ for each k , and $i_1 < i_2 < \cdots < i_N$. The $\text{sign}(\alpha)$ is given by the permutation of the vector of the indices $\{i_1, j_1, i_2, j_2, \dots, i_M, j_M\}$. The Pfaffian is then defined as

$$\text{Pf}(W) = \sum_{\alpha} A(\alpha), \quad (13)$$

where the sum over α is extended over all the possible partitions. The result is such that $\text{Pf}(W)^2 = \det(W)$. To better clarify the correspondence to Eq. (10), an alternative definition³³ of the Pfaffian can be adopted. It can indeed be defined alternatively as

$$\text{Pf}(W) = \left[(N/2)! 2^{N/2} \right]^{-1} \sum_P \text{sign}(P) \prod_{k_p=1}^{N/2} W_{i_{k_p} j_{k_p}}, \quad (14)$$

where P now represents a generic permutation of the possible row and column indices of the matrix without any constraints and the $\text{sign}(P)$ is the parity of the permutation. It is easy to recognize the antisymmetrized sum corresponding to Eq. (10) in this definition. Let us introduce now a further property of the Pfaffian that will be useful for the definition of the AGPs and AGPu. In the following, we will indicate with 0 a $m \times m$ matrix with all vanishing elements and B a generic $m \times m$ matrix, and we have that

$$\text{Pf} \begin{bmatrix} 0 & B \\ -B^T & 0 \end{bmatrix} = (-1)^{m(m-1)/2} \det(B). \quad (15)$$

C. AGPs and AGPu

In the case of AGPs and AGPu, the matrices $W_{\uparrow\uparrow}$ and $W_{\downarrow\downarrow}$ are identically zero, and specifically, for the AGPs, the matrix $W_{\uparrow\downarrow}$ is symmetric. Moreover, it is necessary to add $N_{\text{unpaired}} = |N_{\uparrow} - N_{\downarrow}|$ unpaired orbitals with a single spin component \uparrow or \downarrow depending on the polarization. Supposing, for simplicity, $N_{\uparrow} > N_{\downarrow}$, under these constraints, Eq. (9) can be simplified as

$$W = \begin{pmatrix} 0 & W_{\uparrow\downarrow} & \Theta_{\uparrow} \\ -W_{\uparrow\downarrow}^T & 0 & 0 \\ -\Theta_{\uparrow}^T & 0 & 0 \end{pmatrix}. \quad (16)$$

With this definition, we can calculate the value of the AGPs and AGPu directly using Eq. (11). However, we can further simplify the calculation for AGPs and AGPu by noting that Eq. (16) is consistent with Eq. (15) upon substitution of $B = (W_{\uparrow\downarrow} \Theta_{\uparrow})$, yielding a determinant of a smaller matrix containing only $W_{\uparrow\downarrow}$ and Θ_{\uparrow} .

D. Jastrow factor

A common strategy within QMC is to multiply the WF with an exponential JF to improve the ground state description. By means of the exponential modulation provided by the JF, we can take into account the electron correlation by also speeding up the convergence to the complete basis set limit. Indeed, with an appropriate choice, the JF can also satisfy exactly the electron–electron and electron–ion cusp conditions of the many-body WF, consequences of the Coulomb $1/r$ singularity. Our JF has two main contributions,

$$J(\mathbf{X}) = e^{U_{ei} + U_{ee}}, \quad (17)$$

where U_{ei} is a single body term that treats explicitly the electron–ion interaction and U_{ee} is a many-body term to take into account the electronic correlation. The single body term is in the form

$$U_{ei} = \sum_{i=1}^N u_{ei}(\mathbf{r}_i), \quad (18)$$

with u_{ei} being

$$u_{ei}(\mathbf{r}_i) = - \sum_{I=1}^{\#ions} Z_I \frac{1 - \exp(b_{ei} |\mathbf{r}_i - \mathbf{R}_I|)}{b_{ei}}, \quad (19)$$

where Z_I is the atomic number of the atom I and b_{ei} is a variational parameter. The electron–electron term is instead written as

$$U_{ee} = \sum_{i < j} u_{ee}(\mathbf{r}_i \sigma_i, \mathbf{r}_j \sigma_j), \quad (20)$$

where the sum is extended over the pairs of different electrons and where

$$u_{ee}(\mathbf{r}_i \sigma_i, \mathbf{r}_j \sigma_j) = k_{\sigma_i \sigma_j} \frac{|\mathbf{r}_i - \mathbf{r}_j|}{1 + b_{\sigma_i \sigma_j}^{ee} |\mathbf{r}_i - \mathbf{r}_j|} + b(\mathbf{r}_i \sigma_i, \mathbf{r}_j \sigma_j), \quad (21)$$

with the 2×2 matrix $b_{\sigma_i \sigma_j}^{ee}$ described by one $b_{\sigma_i \sigma_j}^{ee} = b^{ee}$ or two variational parameters for $\sigma_i = \sigma_j$ when $k_{\sigma_i \sigma_j} = 1/4$ and $b_{\sigma_i \sigma_j}^{ee} = b_{\parallel}^{ee}$ and

for $\sigma_i \neq \sigma_j$ when $k_{\sigma_i, \sigma_j} = 1/2$ and $b_{\sigma_i, \sigma'}^{ee} = b_{\perp}^{ee}$. The conventional expression for the JF can be obtained by removing all spin dependency in the previous expressions and remaining only with the variational parameters corresponding to the opposite spin case $k_{\sigma_i, \sigma_j} = 1/2$ and $b_{\sigma_i, \sigma'}^{ee} = b^{ee}$.

As already anticipated, thanks to the first term in Eq. (21) and the chosen form of u_{ei} , we can explicitly deal with the cusp conditions of the electron–electron and electron–ion potentials, respectively. This highly increases the convergence to the basis set limit without considering too much sharp (with large exponents) Gaussian orbitals. The second term in Eq. (21) instead is a bosonic pairing function b that has the same definition of Eq. (6) but without the symmetry constraints required by the fermions. The use of this term highly improves the description of the charge and spin correlations of the system, as opposed to the very common choice to adopt a simplified or even absent spin dependency in the function b , describing only the charge correlation. In the following, we have indicated the JF without spin dependency as J_s .

IV. RESULTS

In the following, we report detailed calculations by using the setup and the methodology described in Secs. I–III. As shown in Table I, in the broken symmetry ansatz JsAGPu, the total spin value is rather large, implying a large spin contamination that is not present in the atom. By turning on the triplet correlations in the pairing function g and restricting the Jastrow factor to depend only on the electronic densities, i.e., the JsAGP case in Table I, the contamination is even worse with an increase in the total spin. Remarkably, by using the proposed spin-dependent Jastrow factor J in Eq. (2), it is possible to recover an almost exact singlet WF. This confirms the picture that the C_2 molecule can be considered as the smallest antiferromagnet made of two atoms with opposite spins. Indeed, when we go from the broken symmetry ansatz and include correctly the quantum fluctuations in JAGP, the WF becomes almost exact because, as shown in Fig. 2, it is not only an almost perfect singlet but recovers almost all the molecular binding. The energy associated with spin fluctuations can be quantified in analogy with the simple model of two $S = 1$ spins interacting with an Heisenberg antiferromagnetic coupling $J\vec{S}_1 \cdot \vec{S}_2$.³⁴ Here, the singlet ground state with energy $-2J$ is below the classical energy $-J$ of two antiparallel spins along a chosen direction. Analogously, the JAGP ansatz has a spin fluctuation energy gain referenced to the corresponding JAGPu one [see Fig. 1(1)]. As shown in Fig. 2, the Appendix, and

TABLE I. Spin measures with the different WFs.

	S^2			$2 \mu_B$
	Atom	Molecule	Half molecule	Moment $\parallel z$
JsAGPs	2.00	0.00	1.529(4)	0.0005(4)
JAGPu	2.005 34(3)	0.1743(5)	1.760(2)	0.5833(4)
JsAGP	2.004 18(5)	0.2880(4)	2.0185(5)	0.7194(4)
JAGP	2.005 42(1)	0.0327(1)	2.0649(3)	0.0013(5)
Exact	2.00	0.00

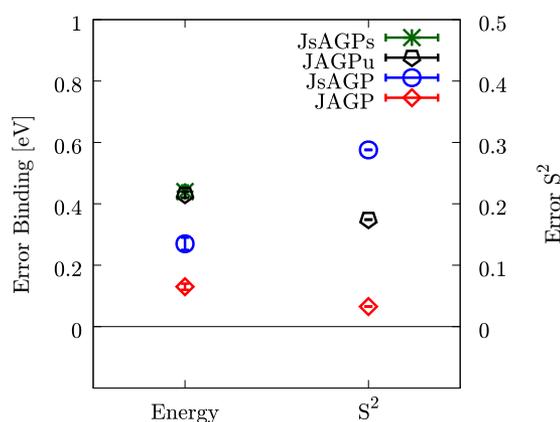


FIG. 2. Energy and spin S^2 for the different WFs.

Table II, this energy gain represents a large fraction of the estimated energy ($\approx 0.5 \text{ eV}^8$) to break the previously proposed fourth bond, i.e., $\approx 0.30 \text{ eV}$.

When the two atoms are placed at a large distance, it is clear that their spins have to be equal to the corresponding isolated $S = 1$ atomic value. What is really surprising in this small molecule is that (see Fig. 3) the spin $S^2(\Lambda)$ around a single atom is almost the same [$S^2(\Lambda) = 2$] when we are at the bond distance, showing that the local spin moment is large even in this regime. This effect is very robust (see the inset in Fig. 3) as we have found that almost all the atomic spins are extremely localized around the nuclear positions, and their values can be measured with no ambiguities. This is a special feature of the C_2 molecule and contrasts with the behavior of other molecules. For instance, there exists an ongoing debate on why the chemical bond in C_2 is stronger than in acetylene, which has a triple bond, but C_2 has a longer bond and a smaller force constant than the C–C bond of HCCH. In our picture, the simple answer is that the C_2 chemical bond is increased by a sizable “long distance” magnetic contribution because the atomic spin moment is basically unscreened as opposed to a standard triple bond molecule, a triple bond that is obviously more effective to reduce the bond length, dominated by the electrostatic charge. Indeed, in Table II, it is evident that in the triple bond N_2 and HCCH dimers, the total spin square S_{half}^2 calculated for each monomer is much smaller than the one expected for an independent N atom or a CH group, suggesting

TABLE II. Expectation value of the total spin square S^2 for different systems. An evaluation of the local moment S_{half}^2 is shown, which is defined here by the expectation value of the spin square operator, measured in the two semi-infinite regions, each one containing half the molecule, specularly symmetric with respect to a plane perpendicular to the molecular axis.

	S^2	S_{half}^2
C_2	0.0327(1)	2.0649(3)
N_2	0.0061(1)	1.3760(3)
HCCH	0.0045(1)	1.3889(2)

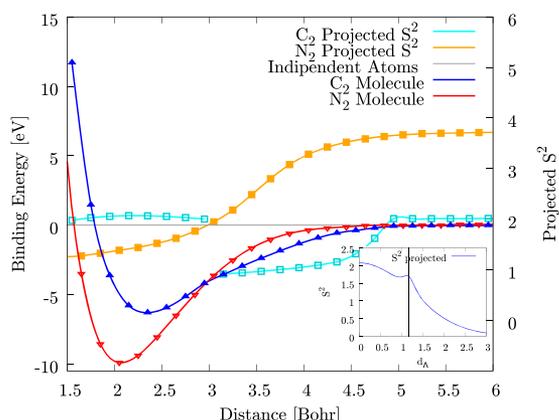


FIG. 3. Size consistency of carbon and nitrogen dimers: both the systems at a large distance recover the energy and the expectation value of the S^2 operator of two isolated atoms. At the bond distance, however, the carbon atoms maintain a large localized S^2 , while the spin of the nitrogen atoms is much smaller than the corresponding atomic value. The lines are guides to the eye. In the carbon dimer, the sharp change of the projected S^2 at around 3 $a.u.$ is probably a consequence of an avoided crossing between two energy levels with the same $^1\Sigma_g^+$ symmetry that has been shown in an accurate and detailed DMRG calculation.³⁵ In the inset, the projected spin square [Eq. (3)] of the C_2 molecule at equilibrium is computed as a function of the distance d_A . The semi-infinite region contains one or no atom as a function of the distance between the plane perpendicular to the molecular axis, defining this region, and the center of the molecule.

that the high value of S_{half}^2 for the carbon dimer is a peculiar feature of this system. Moreover, in Fig. 3, we report the JAGP dispersion curve for the N_2 molecule: in a standard triple bond, the spin around each atom is substantially screened and therefore much below the free atomic value, fully recovered only at large distances. Note that also the N_2 molecule is very well represented by our ansatz, e.g., with an estimated well depth of 229.1(1) kcal/mol in very good agreement with the estimated exact one of 228.48(6) kcal/mol.³⁶

As shown in the Appendix, our variational estimate is essentially the state of the art for an all-electron calculation.

V. CONCLUSION

We have studied in detail the simple C_2 molecule and found, rather unexpectedly over previous expectations, that a large fraction of the chemical bond can be attributed to spin fluctuations. Indeed, when we allow our WF for triplet correlations both in the Jastrow and in the mean field part, we obtain a remarkable improvement in the description of the bond.

It is particularly instructive to see the role of correlation in modifying the molecular orbitals, by taking as a reference the ones corresponding to a simple DFT double bond picture. The AGP part of our WF, after full optimization of the energy in the presence of the Jastrow factor, can be also recasted in terms of molecular orbitals by an almost standard diagonalization.²⁵ The spin character of the resulting orbitals is displayed in Fig. 4, where it is shown that (i) at variance of the DFT mean-field ansatz, the $3\sigma_g$ bonding orbital is

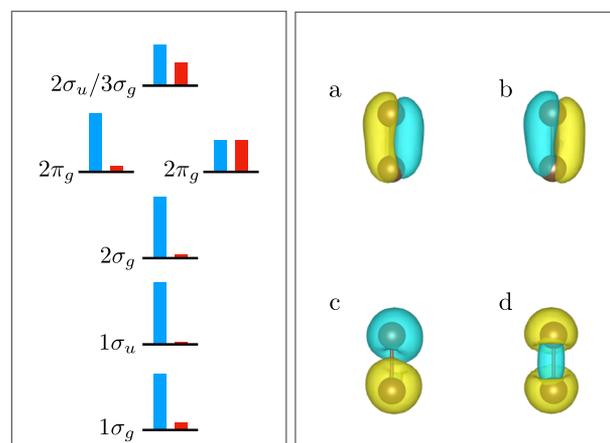


FIG. 4. (Left) After breaking the spin symmetry, each spin-independent orbital of an unrestricted Slater determinant ansatz splits into a pair of single occupied ones with no definite spin projection. The histograms represent the corresponding spin component weights: the height of the blue (red) rectangle indicates the percentage of the majority (minority) spin. Note that the occupation order is different in DFT calculations where the order is $1\sigma_g/1\sigma_u/2\sigma_g/2\sigma_u/2 \times (2\pi_g)$ and where the orbitals have a single spin component. (Right) Majority and minority spin orbitals with the most relevant spin contamination. The orbitals (a) and (b) come from the $2\pi_g$ and have the same weight, and the orbitals (c) and (d) are the last occupied ones (indicated as $2\sigma_u/3\sigma_g$); in this case, the (c) orbital has a 65% and the (d) one has a 35% weight.

eventually present as the minority spin component of the HOMO, in partial agreement with the quadruple bond picture. (ii) In our ansatz, however, the main effect that mostly determines the chemical bond is the spin contamination of the most important occupied orbitals $2\sigma_u$, $3\sigma_g$, and $2\pi_g$. In this way, they can contribute to the bonding by means of the corresponding spin-fluctuation energy gain that is instead vanishing for the inner core orbitals [this is because they have a definite spin in the same quantization axis chosen for the Jastrow factor, see the explanation in Fig. 1(1)].

We have shown therefore that the bonding in C_2 cannot be explained with charge electrostatic, and instead, the large atomic spin value confirms that the energy is intimately due to correlation, the same that allows, by means of our Jastrow factor, the evaluation of the spin-wave zero point energy gain of a quantum antiferromagnet.

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APPENDIX: TOTAL ENERGY AND EXCITATIONS

In Table III, we compare the FN energies of our JAGP WF with the ones obtained with other state of the art variational methods.

TABLE III. Total energy comparison between different variational methods and WFs.

WF	Total Energy (H)
JsAGPs	−75.893 8(2)
JAGPu	−75.893 5(2)
JSD ^a	−75.867 2(1)
JAGP	−75.904 5(2)
JFVCAS ^a	−75.910 6(1)
FCIQMC ^b	−75.802 51(8)

^aReference 6.^bReference 7.

TABLE IV. Carbon dimer excitations.

	Energy (H)	Binding (eV)	Gap (eV)
		$X^1\Sigma^+$	
JAGP	−75.9045(2)	6.31(1)	...
Estimated exact ^a	−75.9265	6.44	...
Experiment ^b	...	6.30	...
		$a^3\Pi$	
JAGP	−75.8961(2)	6.08(1)	0.23(1)
Experiment ^c	0.09
		$b^3\Sigma^+$	
JAGP	−75.8680(3)	5.30(2)	0.99(2)
Experiment ^c	0.80
		$b^3\Sigma^+$ vertical	
JAGP	−75.8658(1)	5.26(1)	1.05(1)
Experiment ^d	1.14
		$c^3\Sigma^-$	
JAGP	−75.8737(2)	5.47(1)	0.84(1)
Experiment ^c	1.04

^aReference 36.^bReference 37.^cReference 38.^dReference 39.

Moreover, we also report in Table IV the direct and adiabatic triplet excitations of the molecule, obtained within the JAGP. We recover very well the small energy gap to the $^3\Pi$ excitation that is highly challenging. Another important excitation is the vertical $^3\Sigma^+$ state that was used by Shaik *et al.* to estimate the binding energy of the quadruple bond. This is also correctly estimated by our ansatz and represents the lowest energy “spin-wave” in this simple antiferromagnetic system.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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