The nature of the quadruple chemical bond in the dicarbon molecule

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The molecular dissociation energy has often been explained and discussed in terms of singlet bonds, formed by a number of 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. Recently, in order to explain the excitation spectrum of the carbon dimer, an unusual quadruple bond has been proposed, that remains highly debated and controversial. With our ansatz, we are able to probe a sizeable spin fluctuation energy gain also in this simple molecule, that provides a natural and much simpler explanation of the fourth bond. Spin fluctuations are indeed extremely important to reproduce the $C_2$ binding energy, while restoring almost exactly the zero spin value of the ground state.

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 neighbouring 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, it is difficult to detect this effect, and therefore we adopt the Resonating Valence Bond (RVB) paradigm, that has been successfully applied even when standard single reference molecular orbital theory fails. Our approach generalises 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 first consider a very small molecule, but nevertheless very important and challenging: the carbon dimer. Its ground state is a perfect singlet, while the isolated atoms have two spin projected onto a given number of particles and total spin projection $S_{tot} = \sum_i \sigma_i$ along the $z$-quantization axis. This wave function is known as the Antisymmetrised Geminal Product (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 are omitted (namely the last line in Eq. (1)), the wave function 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; 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 by dramatically improving the accuracy of this wave function, 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 compact and accurate ansatz, that is as easy to visualise and understand as a mean field ansatz. We consider first the most general two electron pairing function:

$$g(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2) = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) \phi_+ (\vec{r}_1, \vec{r}_2)$$

$$+ \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) \phi_- (\vec{r}_1, \vec{r}_2)$$

$$+ |\uparrow\uparrow\rangle \phi_+ (\vec{r}_1, \vec{r}_2) + |\down\down\rangle \phi_- (\vec{r}_1, \vec{r}_2)$$ (1)

where, 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 $\phi_+ (\vec{r}_1, \vec{r}_2) = \pm \phi_+ (\vec{r}_2, \vec{r}_1)$ and $\phi_\sigma (\vec{r}_2, \vec{r}_1) = \mp \phi_\sigma (\vec{r}_1, \vec{r}_2)$ for $\sigma = \uparrow, \downarrow$. When considering a generic (even) number $N$ of electrons of given spin $\sigma_i$ and positions $\vec{r}_i \ (i = 1, \cdots, N)$, we antisymmetrise the product over all the electron pairs that, by definition, occupy the same pairing function. The corresponding wave function 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 $S_{tot} = \sum_i \sigma_i$ along the $z$-quantization axis.
Coulomb repulsion. In this simplified picture, introduced by P.W. Anderson long time ago [19], one can consider with a single pairing function all the valence bond (VB) configurations (see Figure 1), in practice with almost optimal weights. This has been shown for instance in strongly correlated lattice models [20]. A remarkable advantage of this approach is that an exponentially large number of VBs can be considered at a cost of a mean field, with the price of relying on a statistical approach, namely this mean field has to be evaluated several times, a large but not prohibitive number. Therefore its computational cost remains basically the one of a single mean field, times a large prefactor.

The Jastrow factor is an explicitly symmetric function of the $N$ coordinates and spins:

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

(2)

where $f$, at variance of $g$, is the most general two-particle bosonic (and positive) wave function. 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. Though this feature is obviously approximate, it generalises in a rather convenient way the so called “symmetry restoring after projection” [21,22]. As shown in Figure 1, a simple way to understand this effect is to consider two atoms with opposite spins. If the spins are oriented in the direction of the electronic basis, defining our Jastrow in Eq. 2, the latter one cannot have any effect in the total wave function. Conversely, it turns out energetically convenient to orient the spins of the atoms in a direction perpendicular to previous one. In this way (see Figure 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, even for a finite (as is our case) number of atoms [23].

Before going in more details we summarise in Figure 2-3 the physical picture of our wave function 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 wave function, 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 [19], the important role of fluctuating triplet bonds has not been appreciated, so far.

![Figure 1](image1.png)

**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 degrees 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 wave functions used in this work limited to only singlet bonds (JAGPs defined in main text) and (3) containing both singlet and triplet bonds (JAGP). The balls indicate the electrons, singlet and triplet bonds are displayed with cyan and orange colours, 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.

![Figure 2](image2.png)

**FIG. 2.** Energy and spin $S^2$ for different WFs.

I. RESULTS

In the following we report detailed calculations by using the setup and the methodology described in the Methods and in the supplementary information (SI). As it is shown in Table I in the broken symmetry ansatz JsAGP the total spin value is rather large, showing a large spin contamination, that is not present in the atom. By turning on the triplet correlations only in the pairing function $g$ the situation is even worse, as only with an appropriate spin-dependent Jastrow factor $J$ one is able to recover almost the exact result. This confirms the picture that the C$_2$ molecule can be considered as the simplest...
FIG. 3. Size consistency of carbon and nitrogen dimers: both the systems at large distance recover the energy and the expectation value of the $S^2$ operator of two isolated atoms. At bond distance however the carbon atoms maintain a large localised $S^2$, while the nitrogen atoms have an $S^2$ value much smaller than the ones of independent atoms. Lines are guides to the eye.

\[
\begin{array}{cccc}
\text{Energy [H]} & \text{Binding [eV]} & \text{Gap [eV]} \\
\hline
JAGP & -75.9045(2) & 6.31(1) & - \\
Estimated Exact & -75.9265 & 6.44 & - \\
Experiment & - & 6.30 & 2.5 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Energy [H]} & \text{Binding [eV]} & \text{Gap [eV]} \\
\hline
JAGP & -75.8961(2) & 6.08(1) & - \\
Experiment & - & 6.30 & 2.5 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Energy [H]} & \text{Binding [eV]} & \text{Gap [eV]} \\
\hline
JAGP & -75.8680(3) & 5.30(2) & 0.99(2) \\
Experiment & - & 6.08 & 2.5 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Energy [H]} & \text{Binding [eV]} & \text{Gap [eV]} \\
\hline
JAGP & -75.8658(1) & 5.26(1) & 1.05(1) \\
Experiment & - & 5.30 & 2.5 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Energy [H]} & \text{Binding [eV]} & \text{Gap [eV]} \\
\hline
JAGP & -75.8737(2) & 5.47(1) & 0.84(1) \\
Experiment & - & 6.30 & 2.5 \\
\end{array}
\]

\section{II. DISCUSSION}

We have presented a new paradigm for state of the art quantum chemistry calculations, and discovered a new root to the chemical bond, where a key role is played by the implicit spin coupling between electron pairs. We have studied in details the simple C$_2$ molecule and found, rather unexpectedly over previous expectations, that a large fraction of the chemi-

\begin{table}[h]
\centering
\caption{Spin measures with the different WFs.}
\begin{tabular}{cccc}
\hline
Atom & Molecule & Half Molecule & $2\mu_B$ \\
\hline
JsAGPs & 2.00 & 0.00 & 1.529(4) & 0.0005(4) \\
JAGPu & 2.00534(3) & 0.1743(5) & 1.760(2) & 0.5833(4) \\
JsAGP & 2.00418(5) & 0.2880(4) & 2.0185(5) & 0.7194(4) \\
JAGP & 2.00542(1) & 0.0327(1) & 2.0649(3) & 0.0013(5) \\
Exact & 2.00 & 0.00 & - & - \\
\hline
\end{tabular}
\end{table}

$\delta = 1$ antiferromagnet. Indeed, when we go from the broken symmetry ansatz and include correctly the quantum fluctuations in JAGP the wave function becomes almost exact, because, as it is shown in Figure 2, it is not only an almost perfect singlet but recovers almost all the molecular binding. We also see in this picture that the energy gain, due to spin fluctuations, is consistent with the estimated energy to break the fourth bond in Ref. [8].

That the two atoms have to be oriented with antiparallel spins is not surprising when we go at large distance. What is really surprising in this small molecule, is that (see Figure 3) the spin $S^2(\Lambda)$ (see Methods) around a single atom remains almost the same ($S^2(\Lambda) = 2$) even when we arrive at bond distance, showing that the local spin moment is large even in this regime. This effect is very robust and in Figure 3 it is also evident that almost all the atomic spin is extremely localised around the nuclear positions, and its value can be measured with no ambiguities. This is a special feature of the C$_2$ molecule, and contrasts with the behaviour of other molecules. For comparison we report in Figure 3 also the corresponding JAGP results 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, recovered correctly only at large distance. Note that also the N$_2$ molecule is very well represented by our ansatz, e.g. with an estimated well depth of 229.2(5) kcal/mol in very good agreement with the estimated exact one of 228.48(6) kcal/mol [24].

As shown in the supplementary information, our variational estimate is essentially the state of the art for an all-electron calculation. Moreover, we also report in Table II 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 in Ref. [8] 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.
cal bond can be attributed to spin fluctuations. Indeed, when we allow our wave function for triplet correlations both in the Jastrow and in the mean field part, we obtain a remarkable improvement in the description of the bond, in this way explaining the highly debated nature of the quadruple bond in this molecule. In order to show that the corresponding energy gain is mostly due to spin fluctuations we report in Figure 4.1-2 the density and spin components of the HOMO orbital within our mean-field ansatz. It is clear that the bonding 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, by means of our Jastrow factor, the evaluation of the spin-wave zero point energy of a quantum antiferromagnet. Experiments can validate or falsify our picture by simply measuring the value of the local spin moment; in the C\textsubscript{2} molecule the local moment of the atoms should be almost equal to their free value.

\begin{equation}
\hat{S}_i^2(\Lambda) = \left[ \int_{\Lambda} d^3x \sum_{i=1}^{N} \hat{S}_i(\vec{x} - \vec{r}_i) \right]^2,
\end{equation}

by extending the calculation described in SI only within the region \(\Lambda\). Here \(\hat{S}_i\) is the spin operator acting on the electron at the position \(\vec{r}_i\). We divide the space into two regions separated by a plane cutting the molecule into two equivalent ones containing only one atom.

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AUTHOR CONTRIBUTIONS

C.G. and S.S. developed the code used for all the calculations and interpreted the data that C.G. produced for the paper. T.S. dealt with some algorithmic issues of the pfaffian algebra. S.S. proposed the research project that led to this paper.