The fate of the resonating valence bond in graphene

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We apply a variational wave function capable of describing qualitatively and quantitatively the so called "resonating valence bond" in realistic materials, by improving standard ab initio calculations by means of quantum Monte Carlo methods. In this framework we clearly identify the Kekulé and Dewar contributions to the chemical bond of the benzene molecule, and we establish the corresponding resonating valence bond energy of these well known structures (≈ 0.01eV/atom). We apply this method to unveil the nature of the chemical bond in undoped graphene and show that this picture remains only within a small "resonance length" of few atomic units.

Since the recent experimental isolation of 2D graphene layers\cite{1}, there has been a renewed interest in the electronic properties of graphene. On the other hand the resonating valence bond (RVB) theory was proposed several years ago by Linus Pauling\cite{2} and its successful application to aromatic compounds containing the benzene ring, has immediately raised the question whether this fascinating theory remains meaningful in graphene, which can be viewed as a two dimensional realization of Carbon rings in a honeycomb lattice.

Graphene is a subject of intense studies, also because its peculiar band structure implies a vanishing density of states at the Fermi energy with Dirac cones and non conventional semimetallic behavior\cite{3}. We also mention that the photoemission properties, and a possible opening of a gap around the Dirac cones have not been fully understood neither experimentally\cite{4} nor theoretically\cite{5,6}, and recently it has been speculated that electron correlation may play a crucial role in this material\cite{7}, and could lead not only to the explanation of this effect but also to a rather speculative $d + id$ (room)-high-temperature superconductivity upon doping. Generally speaking the role of electron correlation in graphene remains highly controversial\cite{8}, and the attention in the field has been renewed by a recent numerical simulation of the Hubbard model on the honeycomb lattice\cite{9}. In that work, by using an unbiased numerical method, it was shown that the ground state of the model could be highly non trivial: an insulator, with neither magnetic nor whatsoever broken symmetry, namely a RVB spin liquid state.

In this Letter we clarify the role of RVB correlations in graphene and other Carbon compounds by using a tool\cite{10} for ab-initio calculations based on quantum Monte Carlo (MC) methods, capable of describing rather well the electron correlation in several challenging molecules, up to the quantitative description of the weak binding in graphite\cite{11}. With this technique we can visualize the RVB character of the chemical bond, and describe realistically an RVB spin liquid state, with the same type of variational wave function that has been shown to be rather accurate in model systems, especially in spin ones\cite{12}. Since in realistic models that allow charge fluctuations, like e.g. the Hubbard model, it is not possible to work with a complex wave function without breaking time reversal symmetry, we restrict our variational freedom to real wave functions, which nevertheless allow a very wide class of spin-liquid states.

We shortly describe the wave function used in this Letter, as more details have been published elsewhere (see e.g. \cite{13,14} and refs. therein). The RVB ansatz\cite{15}

\[ | \text{RVB} \rangle = J| \text{AGP} \rangle \]

(JAGP) is made of a product of a Jastrow factor $J$, which takes into account the short range strong Coulomb repulsion, and the so called antisymmetrized geminal power (AGP). A singlet valence bond between two electrons of opposite spin is determined by a geminal function $f$. At variance with the usual Slater Determinant (SD), where no correlation between opposite spin electrons is considered, in the AGP all the electrons are paired with the same geminal. The resulting wave function is then antisymmetrized. We parametrize $f$ by using a given number $n^+$ of molecular orbitals (MOs) as $f(\mathbf{r}_0, \mathbf{r}_1) = \sum_{n_k^+} n_k \psi_k(r_1) \psi_k(r_1')$, where $n_k$ are variational parameters. The MOs $\psi_k$ are expanded in an atomic basis set and fully optimized by minimizing the variational MC (VMC) energy expectation value of the full electron-ion Hamiltonian within the Born-Oppenheimer approximation\cite{14}. In all the calculations of this work, we have replaced the 1s core electrons of
the Carbon atom with appropriate pseudopotentials, which also account for scalar relativistic effects. When \( n^* > N/2 \), with \( N \) denoting the number of electrons, the wave function has a larger variational freedom with respect to the best (lowest in energy) Jastrow SD wavefunction (JSD), and is able to improve the description of the electron correlation, especially when the AGP is used in combination with the Jastrow factor. The latter is particularly important for the description of a spin liquid state and is represented by a weight factor \( J(R) = \exp(\sum_{i<j} u(\vec{r}_i, \vec{r}_j)) \) over the \( 3N \)-dimensional configuration \( R \) of the electron positions \( \vec{r}_i \). For the explicit form of \( J \), see e.g. Ref. [14]. Provided the two-electron function \( u(\vec{r}_i, \vec{r}_j) \) decays slow enough with the distance between the electrons \( |\vec{r}_i - \vec{r}_j| \), it is possible to describe rather well a spin liquid insulator, even when, in absence of \( J(R) \), the AGP pairing function describes a semimetal (for \( n^* = N/2 \)) or a superconductor (for \( n^* > n \)). As discussed in Ref. [14], an appropriate choice of \( n^* \) is crucial to improve the accuracy in the description of the chemical bond with the JAGP ansatz: \( n^* \) is the minimum number of MO’s that can be used for describing a product of independent Hartree-Fock (HF) wave functions for isolated atoms. Within this choice of \( n^* \), both the two-electron functions \( f \) and \( u \) are expanded in a basis of localized gaussian atomic orbitals, with a method that in principle converges to the complete basis set limit (CBS), yielding the lowest possible energy state compatible with the given ansatz.

We test our variational ansatz on small Carbon compounds. We consider the atomization energy of the Carbon dimer and of benzene, computed as the difference between the JAGP energy for the entire molecule and of the C\(_n\)H\(_8\) molecule (AGP primitive basis: 5x5p) and C\(_6\)H\(_6\) (C primitive basis: 24x22p10d6f; H: 3s2p).

To get a deeper insight into our variational calculation with the JAGP wave function, we introduce also a “valence-projected pairing function” (VPPF), defined as \( f_{\text{VPPF}}(r_\uparrow, r_\downarrow) = \sum_{k>N/2} n_k \psi_k(\vec{r}_\uparrow) \psi_k(\vec{r}_\downarrow) \). In the HF case of a single SD, \( f_{\text{VPPF}}(r_\uparrow, r_\downarrow) = 0 \). Hence, when singlet valence bond pairing occurs and \( n_k \) is non zero even for \( k > N/2 \), we can visualize and characterize, in real space, the genuine RVB contribution to the chemical bond. We can also plot the VPPF restricted to the \( \pi \)-band as a function of \( r_\downarrow \) as done for benzene in Fig. 4. Kekulé nearest neighbor and Dewar further neighbor correlations are manifest. Fig. 4 proves the JAGP wave function to be a powerful tool for the description of the fundamental features of the RVB chemical bond.

We now discuss the case of undoped graphene. We consider rectangular supercells \( L_x \times L_y \), with \( L_x = 3n_a \) and \( L_y = m\sqrt{3}a \) where \( a = 1.42 \) \( \text{Å} \) is the nearest neighbor Carbon distance and \( n, m \) are integers. We use an increasing number \( 4nm \) of C atoms (8, 16, 24, and 48, with \( n, m \) such that \( L_x/L_y \approx 1 \)). These supercells do not satisfy the \( \pi/3 \) rotation symmetry of the infinite lattice.

| Molecule | C\(_6\)H\(_6\) | 8 C | 16 C | 48 C |
|----------|---------------|----|------|------|
| All      | 0.118(2)      | 0.159(7) | 0.207(4) | 0.181(1) |
| \( \pi \) | 0.101(2)      | 0.116(5) | 0.147(8) | 0.15(1)   |

TABLE II: VMC contribution (in eV) of all (All) the occupied bands and of the \( \pi \) band to the binding energy of C\(_6\)H\(_6\) and graphene layers of 8 C, 16 C, and 48 C atoms (AGP primitive basis: 11s9p7d).

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Table I: VMC (V) and LRDMC (LR) atomization energy (in eV) of C\(_2\) (AGP primitive basis: 5x5p) and C\(_6\)H\(_8\) (C primitive basis: 24s22p10d6f; H: 3s2p).

| Molecule | C\(_2\) | C\(_6\)H\(_8\) | 8 C | 16 C | 48 C |
|----------|---------|---------------|----|------|------|
| C\(_2\)   | 5.54(2) | 6.33(2)       | 5.76(2) | 6.30(2) | 6.30(2) |
| C\(_6\)H\(_8\) | 56.98(1) | 57.11(3)   | 57.11(1) | 57.14(1) | 56.62(3) |

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\( a \) Ref. 23, \( b \) Ref. 24

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TABLE I: VMC (V) and LRDMC (LR) atomization energy (in eV) of C\(_2\) (AGP primitive basis: 5x5p) and C\(_6\)H\(_8\) (C primitive basis: 24s22p10d6f; H: 3s2p).
FIG. 1: (Colors online) Two dimensional plot of the AGP pairing function restricted to the molecular orbitals above the HOMO. The arrow indicates the reference position \( r \) fixed on an atom, colored in red for the sake of clarity.

FIG. 2: (Colors online) Two dimensional plot of the AGP pairing function for a graphene layer of 48 C atoms restricted to the molecular orbitals above the HOMO (VPPF). The arrow indicates the reference atom.

This helps the system to break rotational symmetries, such as \( d_{xy} \) or \( d_{x^2-y^2} \) for a real pairing function, that are energetically favored when the expected \( d + id \) pairing symmetry\(^{20}\) characterizes the ground state wave function. For each system size, we optimize the JAGP wave function, find the VMC energy and the VMC RVB energy (by means of correlated–sampling simulations). As reported in Table III we have also checked the contribution of the \( \pi \)–band orbitals to the RVB energy gain. In Fig. 2 we show the VPPF (restricted to the \( \pi \)–band) for the largest supercell considered here. Despite the small number of atoms, we already see an almost perfect rotational symmetry of the VPPF, that is not compatible with \( d \)–wave pairing. To prove that our method is capable of tackling with pairing functions with \( d \)–wave symmetry we apply our scheme to the CaCuO\(_2\) parent compound of cuprate high-temperature superconductors. As shown in Fig. 3 in less than 3000 iterations we melt the \( s \)–wave pairing and are able to detect the correct \( d \)–wave symmetry of the pairing function. We can conclude, therefore, that the RVB chemical bond in graphene is characterized by a pairing function with a clear \( s \)–wave symmetry.

Finally, in order to understand the thermodynamic properties of graphene, we consider a finite size scaling of our results. In Fig. 4 we show the energy gain due to the \( s \)–wave RVB (upper panel) and the ratio \( R = n_{N/2+1}/n_{N/2} \) of the LUMO/HOMO weights \( n_k \) as a function of the inverse number of C atoms in the supercell. Before discussing this result, we recall what happens to the above–mentioned quantities in the absence of correlation, i.e. when there is no Jastrow factor in our variational ansatz. In such a case, if the ratio \( R \) converges to a finite quantity in the thermodynamic limit, the AGP wave function describes an \( s \)–wave superconductor with true off diagonal long range order. Besides, the thermodynamic–limit RVB energy per atom remains finite and represents just the condensation energy of the \( s \)–wave superconductor. In the presence of \( J \) instead, a different scenario is possible. Indeed, a ratio \( R > 0 \) in the thermodynamic limit and a finite RVB energy/atom denote a spin liquid state with a spin and a charge gap in its spectrum. This possibility is compatible with the recent Hubbard model results\(^{9}\), and may explain also the existence of a small gap in the photoemission experiments, genuine and determined only by the RVB character of the ground state. Due to the computational cost increase for larger supercells, it is difficult to obtain an accurate thermodynamic limit with our VMC method.
However, clear trends are evident from Fig. In the upper panel, we see that the energy gain of the RVB wave function systematically decreases as the system size increases, apart for the negligible value found for the 24 C supercell. The anomaly of the 24 C cluster can be easily explained as a shell–effect. Indeed, this cluster should be closer to the thermodynamic limit, since it contains the so-called K point, the gapless Dirac point in graphene. This shell effect does not affect the eigenvalues of the pairing function, which instead decrease monotonically as the system size increases and reach a very small value in the thermodynamic limit (lower panel). If we extrapolate the upper–panel results, omitting the 24 C cluster, also the RVB energy per C atom becomes extremely small in the thermodynamic limit (smaller than the accuracy of the present data). Both panels thus suggest that the semimetal character of graphene should be stable in the thermodynamic limit. A small gap could appear in the excitation spectrum only if its value was extremely small \( \approx 0.01 \text{eV} \). We have estimated this value by matching our results for the \( n_k \) with the ones obtained within the Hartree Fock theory, namely \( f(|r - r'|) \propto |r - r'|^{-2} \).

In particular our parametrization allows us to represent also slowly decaying pairing functions, as for instance the one obtained within the Hartree Fock theory, namely \( f(|r - r'|) \propto |r - r'|^{-2} \).

In conclusion we have systematically studied Carbon–based compounds from the simplest C\(_2\) molecule to graphene layers. We have shown that the RVB character of the chemical bond can be depicted in terms of a very powerful and accurate wave function that not only improves the description of the chemical bond but it is also capable to show qualitatively new effects induced by the electron correlation. We have found clear numerical evidence that singlet s–wave pairing in graphene be quite robust and sizeable up to a small length scale of few atomic units. This feature might remain in the thermodynamic limit leading to a very small gap in the photoemission spectrum or to s–wave superconductivity upon doping, effects that can be in principle verified experimentally.

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