Fate of the Resonating Valence Bond in Graphene

Mariapia Marchi

SISSA, Via Bonomea 265, 34136 Trieste, Italy and Dipartimento di Fisica,
Università di Trieste, strada Costiera 11, 34151 Trieste, Italy

Sam Azadi

Institute of Physical Chemistry and Center for Computational Sciences,
Johannes Gutenberg University Mainz, Staudinger Weg 9, 55128 Mainz, Germany

Sandro Sorella*

SISSA, Via Bonomea 265, 34136 Trieste, Italy and Democritos Simulation Center CNR-IOM Istituto Officina dei Materiali,
34151 Trieste, Italy

We apply a variational wave function capable of describing qualitatively and quantitatively the so-called "resonating valence bond" (RVB) 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 establish the corresponding RVB energy of these structures ($\simeq 0.01$ eV/atom). We apply this method to unveil the nature of the chemical bond in undoped graphene, providing an estimate of the RVB energy gain, and show that this picture remains only within a small "resonance length" of a few atomic units.

Since the recent experimental isolation of two-dimensional (2D) graphene layers [1], there has been a renovated 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 [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 2D realization of carbon (C) rings in a honeycomb lattice.

Graphene is the subject of intense study, also because its peculiar band structure implies a vanishing density of states at the Fermi energy with Dirac cones and nonconventional semimetallic behavior [3]. We also mention that the photoemission properties, and a possible opening of a gap around the Dirac cones, have not been fully understood either experimentally [4] or theoretically [5,6], and recently it has been speculated that electron correlation may play a crucial role in this material [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 [8], and attention in the field has been renewed by a recent numerical simulation of the Hubbard model on the honeycomb lattice [9]. In that work, by using an unbiased numerical method, it was shown that the ground state of the model could be highly nontrivial: 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 C compounds by using a tool [10] for *ab initio* calculations based on quantum Monte Carlo (MC) methods, capable of describing rather well several challenging molecules, up to the quantitative description of the weak binding in graphite [11]. The major advance offered by this technique is the possibility to describe, with a fully *ab initio* method, a RVB spin-liquid state with the same type of highly correlated many-body wave function (WF), so far applied successfully only in the simplest model Hamiltonians [12].

Since in realistic models that allow charge fluctuations it is not possible to work with a complex WF without breaking time reversal symmetry, we restrict our variational freedom to real wave functions, which nevertheless allow a very wide class of spin-liquid ground states.

We shortly describe the WF used in this Letter (for more details see [13,14] and references therein). The RVB ansatz [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. One can show that AGP can be rewritten in terms of a single determinant of the pairing functions f (see, e.g., [13]), whereas with the usual Slater determinant (SD) no correlation between opposite spin electrons is considered. We parametrize f by using a given number n^* of molecular orbitals (MOs) as $f(\vec{r}^\uparrow, \vec{r}^\downarrow) = \sum_k^{n^*} n_k \psi_k(r_\uparrow) \psi_k(r_\downarrow)$, with n_k variational parameters. The

MOs ψ_k are expanded in an atomic basis set and fully optimized with variational MC (VMC) simulations minimizing the expectation value of the full electron-ion Hamiltonian within the Born-Oppenheimer approximation [14]. In all the calculations, we have replaced the C atom $1s$ core electrons with appropriate pseudopotentials [16], which also account for scalar relativistic effects. When $n^* > N/2$ (N being the number of electrons) the WF has a larger variational freedom with respect to the best (lowest in energy) Jastrow SD wave function (JSD) [17], 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 $J(\mathbf{R}) = \exp[\sum_{i<j} u(\vec{r}_i, \vec{r}_j)]$ over the $3N$-dimensional configuration $\mathbf{R}$ of the electron positions $\vec{r}_i$. Provided the two-electron function $u(\vec{r}_i, \vec{r}_j)$ decays slowly enough with the electron distance $|\vec{r}_i - \vec{r}_j|$, it is possible to describe rather well a spin-liquid insulator, even when, in absence of $J(\mathbf{R})$, the AGP pairing function describes a semimetal (for $n^* = N/2$) or a superconductor (for $n^* > n$) [18]. An appropriate choice of n^* is crucial [14] for improving the JAGP accuracy in the chemical bond description: n^* is the minimum number of MOs 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, yielding the lowest possible energy state compatible with the given ansatz [19].

First we test our variational ansatz on small C compounds. We consider the C dimer and benzene atomization energy, computed as the difference between the JAGP energy for the entire molecule and the JSD energy of the isolated atoms [14]. To compare our results with the experimental binding energies we also include inner shell correlations and relativistic effects and we subtract the zero-point energy. The simulations for C_2 were performed in Ref. [14] ($n^* = 7$). Both for C_2 and for C_6H_6 (for which $n^* = 24$) we have used basis sets converged within 0.01 eV/atom (for more technical details see Refs. [14,19]). We evaluate C_2 inner shell correlations by comparing the all-electron energy found in Ref. [20] with the energy found in Ref. [21], using the same pseudopotential [16] adopted in this Letter. We take spin orbit effects and benzene inner shell correlations from Refs. [22,23]. Table I shows our VMC and lattice-regularized diffusion MC (LRDMC) [24] results.

One of the main achievements of our calculation is represented by the sizeable energy gain obtained by using a large number of MOs in the WF AGP part. This energy gain is particularly important to get a quantitative description of the C_2 chemical bond. For benzene, all the atomization energies we have computed apparently

TABLE I. C_2 and C_6H_6 VMC (V) and LRDMC (LR) atomization energy (in eV).

Molecule	(V)JSD	(V)JAGP	(LR)JSD	(LR)JAGP	Exp.
C_2	5.54(2)	6.33(2)	5.76(2)	6.30(2)	6.30(2)[a]
C_6H_6	56.98(1)	57.11(3)	57.11(1)	57.14(1)	56.62(3)[b]

[a]Ref. [22].
[b]Ref. [23].

overestimate the reported experimental value. This slight overestimation does not depend on the accuracy of our total energy estimates, because one has to add several corrections that come from other methods and experiments. In our opinion the most direct way to judge the accuracy of the variational calculation of the atomization energy is to make the same calculation with a much more accurate method. Indeed we see in Table I that the LRDMC result provides the same answer independent of the variational guess and coincident with the JAGP VMC result. Thus, our variational ansatz appears to be adequate and encourages us to quantify the RVB energy, which, in the present formulation, can be defined as the energy difference between the best variational energy found with $N/2$ MOs (JSD) and the one with $n^* > N/2$, both obtained in presence of J. In Table II, we report the contribution of the π-band orbitals to the RVB energy of benzene and graphene. The π orbitals yield approximately 80% of the pairing and represent in general the most important contribution, as expected.

To get a deeper insight into our variational calculation with the JAGP WF, we also introduce a "valence-projected pairing function" (VPPF), defined as $f_{VPPF}(r_\uparrow, r_\downarrow) = \sum_{k>N/2} n_k \psi_k(r_\uparrow)\psi_k(r_\downarrow)$. In the HF case of a single SD, $f_{VPPF}(r_\uparrow, r_\downarrow) = 0$. Hence, when singlet valence bond pairing occurs and n_k is nonzero 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 π band as a function of $r_\downarrow$ as done for benzene in Fig. 1. Despite a residual atomic resonance around $\vec{r}_0$, true Kekulé and Dewar valence bonds are manifest. Figure 1 proves the JAGP WF 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 $L_x = 3na$

TABLE II. VMC contribution (in eV) of all (All) the occupied bands and of the π band to the binding energy of C_6H_6 and graphene layers of 8C, 16C, and 48C atoms (graphene AGP primitive basis: $11s9p7d$).

Molecule	C_6H_6	8C	16C	48C
All	0.118(2)	0.159(7)	0.207(4)	0.18(1)
π	0.101(2)	0.116(5)	0.147(8)	0.15(1)
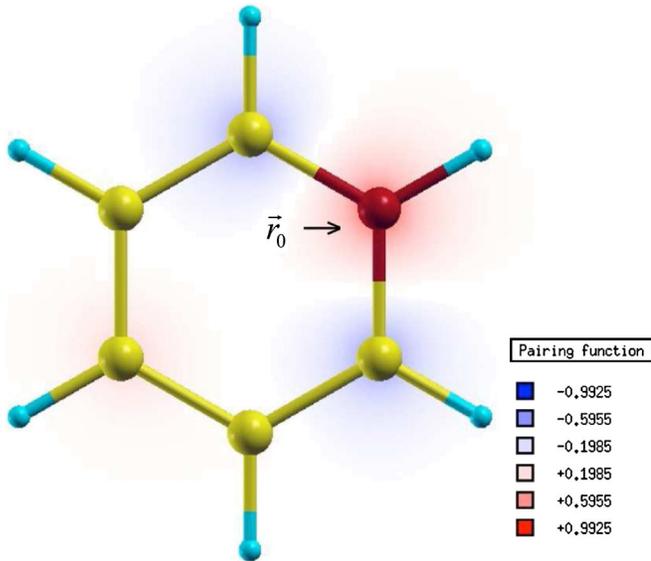
FIG. 1 (color online). 2D plot of the AGP pairing function restricted to the molecular orbitals above the HOMO. Color scale in arbitrary units. The arrow indicates the reference position $r_\uparrow$ fixed on an atom, colored in red for the sake of clarity.

and $L_y = m\sqrt{3}a$ where $a = 1.42$ Å is the nearest neighbor C distance and n, m are integers. We use an increasing number of C atoms ($4nm = 8$, 16, 24, and 48, with n, m such that $L_x/L_y \simeq 1$). These supercells do not satisfy the $\pi/3$ rotation symmetry of the infinite lattice [25]. 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 [26] characterizes the ground state WF. For each system size, we optimize the JAGP WF, find the VMC energy and the VMC RVB energy (by means of correlated-sampling simulations) and check the contribution of the π-band orbitals to the RVB energy gain (see Table II). In Fig. 2
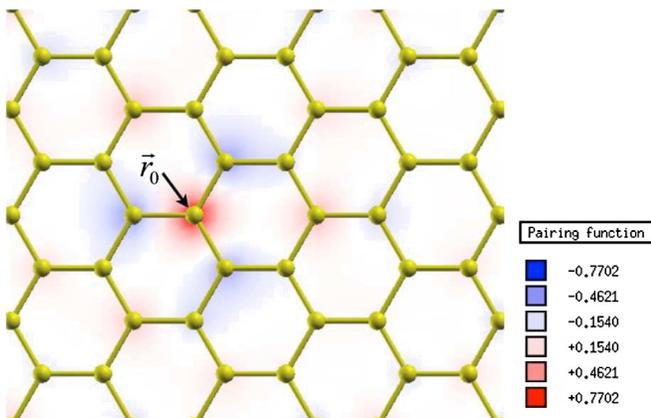
we show the VPPF (restricted to the π band) for the largest supercell considered here. We believe that the alternating signs of the pairing function in the two different sublattices reflect the stability of Marshall's sign rule in a strongly correlated wave function [12]. Despite the small number of atoms, we already see an almost perfect rotational symmetry of the VPPF, that is not compatible with d-wave pairing.

Moreover, in order to prove that our method is capable of tackling 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 WF describes an s-wave superconductor with true off-diagonal long-range order and the 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 also explain the existence of a small gap in the

FIG. 2 (color online). 2D plot of the AGP pairing function for a graphene layer of 48 C atoms restricted to the molecular orbitals above the HOMO (VPPF). Color scale in arbitrary units. The arrow indicates the reference atom.
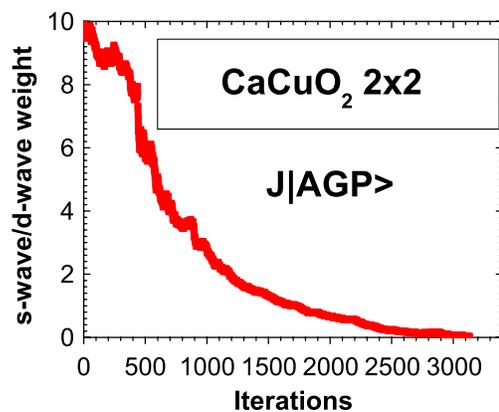
FIG. 3 (color online). Ratio between the s-wave and the d-wave weight in the JAGP WF for the $CaCuO_2$ parent compound of the high-temperature cuprate superconductor (2×2 supercell).
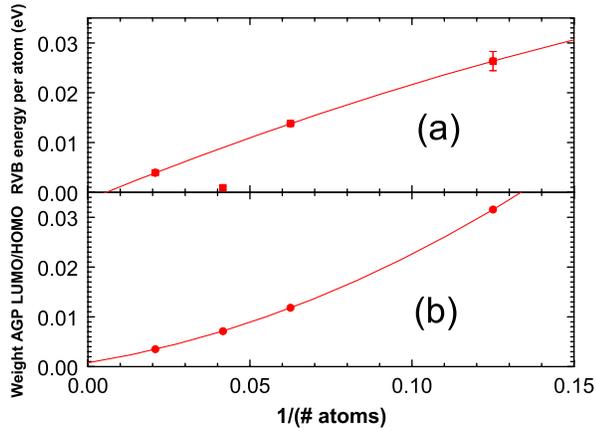
FIG. 4 (color online).   (a) RVB energy per atom for the graphene layer, as a function of the number of atoms in the supercell (Γ point). (b) Ratio of the LUMO/HOMO weight in the AGP, a measure of the RVB character of the bond. Lines are guides to the eye.

photoemission experiments, a genuine effect determined only by the RVB character of the ground state.

Because of the big computational cost for large supercells, it is difficult to obtain an accurate thermodynamic limit with our VMC method. However, clear trends are evident from Fig. 4. In the upper panel, we see that the energy gain of the RVB WF 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 R which instead decreases monotonically as the system size increases and reaches a very small value in the thermodynamic limit (lower panel). If we extrapolate the upper-panel results, omitting the 24 C cluster, the RVB energy per C atom also 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 $\simeq 0.01$ eV. We have estimated this value by matching our results for the n_k with the ones obtained with an s-wave BCS Hamiltonian with nearest and next-nearest neighbor coupling, describing a Z_2 gapped spin liquid [5] when correlation is included by means of an appropriate Jastrow.

In conclusion we have systematically studied C-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 WF that not only improves the description of the chemical bond but is also able to show qualitatively new effects induced by the electron correlation. We have found numerical evidence that singlet s-wave pairing in

graphene is 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 small doping, effects that can be in principle verified experimentally.

*sorella@sissa.it
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