The new Resonating Valence Bond Method for ab-initio Electronic Simulations

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The Resonating Valence Bond theory of the chemical bond was introduced soon after the discovery of quantum mechanics and has contributed to explain the role of electron correlation within a particularly simple and intuitive approach where the chemical bond between two nearby atoms is described by one or more singlet electron pairs. In this chapter Pauling’s resonating valence bond theory of the chemical bond is revisited within a new formulation, introduced by P.W. Anderson after the discovery of High-Tc superconductivity. It is shown that this intuitive picture of electron correlation becomes now practical and efficient, since it allows us to faithfully exploit the locality of the electron correlation, and to describe several new phases of matter, such as Mott insulators, High-Tc superconductors, and spin liquid phases.

I. INTRODUCTION

Soon after the discovery of quantum mechanics Linus Pauling introduced the so called “Resonating Valence Bond” (RVB) theory of the chemical bond, an innovative point of view that soon became popular and certainly had a tremendous impact in chemical and physical sciences. Until now this theory remains extremely useful to explain the role of electron correlation within a particularly simple and intuitive approach, where the chemical bond is described by a main ingredient: the singlet formed by electron pairs belonging to different atoms, when they become sufficiently close. It was soon realized however that this beautiful description was not practical simply because the number of resonating chemical bonds increases exponentially with the number of atoms. Thus, the molecular orbital approach, the basic ingredient of Hartree-Fock, DFT and post Hartree-Fock methods, became the standard recipe for the electronic simulation as it is discussed in several chapters of this book (see in particular Chap. “Tensor Product Approximation (DMRG) and Coupled Cluster Method in Quantum Chemistry” by Legeza et al., “Computational Techniques for Density Functional-based Molecular Dynamics Calculations in Plane-Wave and Localized Basis Sets” by Tzanov and Tuckerman, and Chap. “Application of (Kohn-Sham) Density Functional Theory to Real Materials” by Ghiringhelli). We show in this chapter that a new resonating valence bond scheme is possible. This new formulation of the resonating valence bond theory is borrowed by the fascinating theory of High-Tc superconductivity proposed by Anderson, right after its discovery in the 90’s. By means of quantum Monte Carlo computations and the increasing power of modern supercomputers this intuitive picture of electron correlation becomes practical and efficient, since it allows us to exploit the short range nature of the chemical bond, as well as, to describe several new phases of matter, such as Mott insulators and High-Tc superconductors.

When two atoms are close their valence electrons interact with each other, forming the chemical bond. In the most simplified picture of two single valence electrons (e.g., in the $H_2$ molecule) the singlet pairing allows us to minimize the Coulomb energy and satisfy the antisymmetry of the wave function by acting only on its spin part $\frac{1}{\sqrt{2}}(|\uparrow\downarrow|-|\downarrow\uparrow|)$, whereas its orbital part $f$ is symmetric and is a generic function of the two valence electron coordinates:

$$f(\vec{r},\vec{r}') = f(\vec{r}',\vec{r})$$

being non-zero even in the interatomic region where the chemical bond is formed. As a matter of fact, a wave function of the above form is exact for two electrons in a singlet ground state and allows us to describe, for instance, the $H_2$ molecule at all interatomic distances, a well-known case where a restricted Hartree-Fock wave function

$$\Phi_H(\vec{r},\vec{r}') = \phi(\vec{r})\phi(\vec{r}')$$

is not the correct one.
miserably fails at large distances, because it is not able to reproduce the Heitler-London solution (HLS):

\[ f_{HL}(\vec{r}, \vec{r}') = \phi_A(\vec{r})\phi_B(\vec{r}') + \phi_B(\vec{r})\phi_A(\vec{r}') \]

(3)

where \( \phi \) indicates an Hartree-Fock molecular orbital, with \( \phi_A (\phi_B) \) an atomic one localized around the atom \( A (B) \).

The simple extension of this simple singlet valence bond of two electrons was originally formulated in terms of simple Slater determinants, e.g. two determinants for the single bond in \( H_2 \). Indeed the simple superposition of the bonding \( \phi_+ = \phi_A + \phi_B \) and the antibonding \( \phi_- = \phi_A - \phi_B \) orbitals in the pairing function

\[ f(\vec{r}, \vec{r}') = \phi_+(\vec{r})\phi_+(\vec{r}') + \lambda\phi_-(\vec{r})\phi_-(\vec{r}) \]

(4)

allows us to recover the HLS for \( \lambda = -1 \) at large distance.

Suppose to extend this picture to a more complex molecule like benzene, a planar molecule made of six Hydrogen atoms and six Carbon atoms (chemical formula \( C_6H_6 \)), placed at the vertices of an ideal hexagon. In this molecule there is only one \( p_z \) orbital per Carbon atom pointing in the \( z \) direction perpendicular to the molecular plane. This single particle state can be occupied only by one valence electron per Carbon as, in first approximation, all the remaining 36 electrons of the molecule are well described by a single Slater determinant. A first success of the original RVB theory was to identify the most important two-electrons singlet bonds in this molecule, that are shown in Fig.(1). Each structure is obtained by joining two-electrons singlet bonds among neighboring atoms in the hexagon, indicated here by bold lines. Bold lines cannot superpose, because otherwise two valence electrons with opposite spins have to occupy the same \( p_z \) orbital on the same atom, implying an high energetic cost due to the strong Coulomb repulsion. Therefore, only by the superposition of inequivalent structures the electronic wave function can be symmetric under rotation by 60 degrees, and the corresponding energy gain is called the “resonance valence bond energy”. In Fig.(1), for each valence bond structure, represented by an hexagon, we can expand the corresponding three singlet bonds in terms of orbital functions. We thus obtain a different Slater determinant for any of the possible \( 2^3 = 8 \) spin configurations obtained in each hexagon. Then if we count the total number of determinants, corresponding to the five Kekule’ and Dewar structures, we conclude that already in this simple molecule we need forty determinants to represent this RVB wave function. It is easy to realize that in a complex system containing several atoms, the number of such determinants grows exponentially with the number of atoms \( N_A \), at least because a single valence bond, where singlets between different atoms are drawn in the same way as for a single hexagon in Fig.(1), requires at least \( 2^{N_A/2} \) determinants, and the method cannot be effectively applied to realistic systems containing several atoms. Basically for this simple reason the Pauling RVB approach was soon abandoned, and the single-determinant technique based on molecular orbitals became popular for its simplicity and effectiveness.

\[
\frac{1}{\sqrt{2}} \left( |\uparrow \downarrow \rangle - |\downarrow \uparrow \rangle \right) \left[ \psi_A(r)\psi_B(r') + \psi_B(r)\psi_A(r') \right]
\]

Figure 1: Kekulé and Dewar contributions to the resonance valence bond energy in the benzene molecule. Bold lines schematically indicate a two electron singlet joining the corresponding Carbon atoms located at the vertices of the hexagon.
After several decades the RVB theory for High-temperature superconductors was introduced by Anderson in 1987 [1]. The key ingredient in this theory is that the singlet pairing function \( f \) describing a superconductor, when expressed in real space, is exactly equivalent to the function \( f \) already introduced for a chemical bond. Indeed the wave function of a superconductor for a system with fixed number \( N \) of electrons can be described by the so-called antisymmetrized geminal product (AGP) wave function:

\[
F(x) = F(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2; \cdots ; \vec{r}_N, \sigma_N) = Af(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2)f(\vec{r}_3, \sigma_3; \vec{r}_4, \sigma_4) \cdots f(\vec{r}_{N-1}, \sigma_{N-1}; \vec{r}_N, \sigma_N) \tag{5}
\]

where \( A \) is the antisymmetrization operator over all particle permutations, and \( x \) indicate conventionally a real space configuration, where all \( N \) electrons have definite positions and spins \( \sigma_i \) along the \( z \) spin quantization axis. If, for instance, we take a pairing function for the benzene molecule localized in a given Kekule’ structure, by applying the above antisymmetryzation we obtain almost all valence bonds, but unfortunately something more. Indeed there is nothing that forbid the above expansion to generate a diagram like the one in Fig.(2), namely the bonds can superpose, violating the simple and most important constraint of the RVB theory, that two electrons cannot occupy the same valence \( p_z \) orbital due to the strong Coulomb repulsion. Anderson’s idea is basically that an explicit, correlated factor \( J(x) > 0 \) can avoid these energetically expensive configurations, and achieves the target of an RVB wave function, built by a superconducting, namely an AGP function:

\[
\Psi_{\text{NewRVB}} = J(x)F(x) \tag{6}
\]

What have we gained with this new definition?

The most important achievement was to understand a possible mechanism of superconductivity. High-\( T_c \) superconductors are close to Mott insulators well-described by an RVB wave function where the pairing function \( f \) has \( d^- \) wave symmetry and the phase coherence implied by the \( F(x) \) alone is instead suppressed by the correlation factor \( J(x) \). As it is shown in Fig.(3), by a small amount of doping these preformed pairs allow charge propagation and lead to a faithful description of an High-temperature superconductor with a finite \( d^- \) wave off-diagonal long range order.

In the following instead we use the wave function paradigm given in Eq.(6) just as a convenient numerical ansatz to represent a RVB wave function. Indeed, as it will be shown in the following, in a given electronic configuration \( x \), both the AGP \( F(x) \) and the Jastrow factor \( J(x) \) can be computed with a reasonable number of operations, namely scaling at most as the third power of the number of electrons.

It is important here to emphasize that, once the Jastrow factor is taken to satisfy the constraint of no doubly-occupied valence states, we need only one pairing function to describe all the Kekule’ and Dewar structures because \( f \) can be taken as the sum over all the six nearest-neighbor (for Kekule’) Carbon-Carbon bonds plus a small weight of the six largest distance ones (for representing the Dewar structures). As anticipated this means that correlation is localized in space, and its overall effect in a complex structure is obtained by simply summing up in \( f \) all these space independent contributions. After that we need only the computation of a single determinant \( F(x) \) and a simple Jastrow factor \( J(x) \), for evaluating a wave function described in principle by an exponentially large number of Slater determinants.

Figure 2: An example of a valence bond configuration in benzene that is forbidden by the Jastrow factor \( J(x) \sim 0 \) because two pairs of electrons occupy the same valence orbitals in the two Carbon sites connected by the long bond.
II. THE WAVE FUNCTION

The wave function $\Psi_{NewRVB}$, that we have considered in this work, is written as the product of an antisymmetric (fermionic) function $F(x)$, and a symmetric (bosonic) exponential function $J(x) = e^u$: where both $F$ and the Jastrow factor $J$ depend on the spatial and spin coordinates $x_i = (r_i, \sigma_i)$ of the $N$ electrons in the system, $x = \{x_i\}_{i=1,...,N}$. Once the pairing function $f$ and the correlation factor $u$ are defined, the value of the total wave function $\Psi_{NewRVB}(x)$ can be computed efficiently on a given configuration containing $N/2$ electron pairs of opposite spin electrons $\vec{r}_i^\uparrow, \vec{r}_j^\downarrow$:

$$\Psi_{NewRVB}(x) = \exp(\sum_{i<j} u(\vec{r}_i, \vec{r}_j)) \text{Det} f(\vec{r}_i^\uparrow, \vec{r}_j^\downarrow) \quad (7)$$

After that, a standard variational quantum Monte Carlo approach is possible in order to compute the expectation value of the energy and correlation functions, with a reasonable computational time, scaling very well with the number of electrons, i.e. $N^3$. This is described later in more detail. For a complementary view on constructing correlated wave functions for quantum chemistry, see the Chap. “Tensor Product Approximation (DMRG) and Coupled Cluster Method in Quantum Chemistry” by Legeza et al. For the time being it is important to emphasize that, as described in the introduction, the Jastrow term is chosen as to employ the local projection of no doubly-occupied valence electrons, that should be a consequence of an accurate energy minimization. On the other hand, for the same reason, the parametrization of the pairing function $f$, the basic ingredient of $F(x)$, has to be described in detail in real space, in order to represent each correlated singlet bond. The two pairing functions $u$ and $f$ can be conveniently expanded by using two different set of atomic orbitals. To this purpose, we consider an atomic basis $\{\phi_\mu(\vec{r})\}$, where each element $\phi_\mu$ is localized around an atomic center $\vec{R}_\mu$ (obviously several elements may refer to the same atomic center). Then the pairing function $f$ can generally be written as:

$$f(\vec{r}, \vec{r}') = \sum_{\mu,\nu} f_{\mu\nu} \phi_\mu(\vec{r}) \phi_\nu(\vec{r}') \quad (8)$$

where $f_{\mu\nu}$ is now a symmetric finite matrix, satisfying the following important properties:

1. if the atomic basis is large enough and reaches completeness, it is possible to represent also the two particle functions $f$ and $u$ in a complete way.

\begin{figure}[h]
\centering
\includegraphics[scale=0.5]{figure3.png}
\caption{Schematic example of the mechanism of High-temperature superconductivity (HTc) within the Resonating Valence Bond theory. In the insulator each valence bond structure covers all valence orbital sites and charge cannot propagate in the insulator. Upon small doping empty sites appear in the lattice (connected here by a dashed line). Such holes can freely move in this soup of preformed electron pairs, leading to HTc supercurrent flow. For clarity the two antiferromagnetic sublattices are indicated by green and red circles.}
\end{figure}
2. the atomic basis $\phi_{\mu}$ is not necessarily orthonormal. Actually, for practical purposes, it is convenient to choose simple, e.g., Gaussian or Slater, localized orbitals, without any orthogonalization constraint.

Analogously, also the correlation term $u$ can be expanded in a different set of atomic orbitals. However, in order to speed up the convergence to the complete basis set (CBS) limit, or in other words to parametrize satisfactorily this Jastrow term within a small basis, it is important to fulfill the so called cusp conditions, so that all the singular behavior of the function $u$ when $r \to 0$ (electron-electron) or when $r \to R_a$ (electron-ion) are satisfied exactly, namely $u(r, r^2) \sim 1/2 |r^2 - r^2|$ and $u(r, r^2) \sim -Z_a |r^2 - R_a|^2$, respectively. Here $R_a$ and $Z_a$ indicate the atomic positions and the corresponding atomic number $Z_a$ of the electronic system considered, respectively. The general form of the Jastrow correlation $u$ is therefore written in the following form:

$$u(r, r') = u_{ee}(|r^2 - r'^2|) + (u_{ci}(r) + u_{ei}(r')) + \sum_{\mu, \nu} u_{\mu \nu} \chi_{\mu}(r) \chi_{\nu}(r')$$

(9)

where $u_{ee}$ and $u_{ci}$ are simple functions satisfying the electron-electron and electron-ion cusp conditions and are reported elsewhere[11]. In order to allow a general and complete description of the latter one-body term, it is also assumed that one orbital in the above expansion is just constant and identically one, say for $\mu, \nu = 0$. Then, it is simple to realize that this term just renormalize $u_{ci}$ by:

$$u_{ci}(r) \to u_{ci}(r) + 2 \sum_{\nu \neq 0} u_{0\nu} \chi_{\nu}(r)$$

(10)

so that, for a sufficiently large basis set, both the single-body and the two-body dependency of the Jastrow factor can be represented with an arbitrary degree of accuracy and detail.

$\{\chi_{\mu}(r)\}$ is also a localized basis set, exactly of the same form as $\phi_{\mu}$ used for expanding the pairing function $f$. In this case, however, it is convenient to use a different set of orbitals, and usually a much smaller basis dimension is necessary to obtain converged results, at least in the energy differences and for the relevant chemical properties.

In the following we will provide a synthetic description of the atomic orbitals that are used to write both the determinantal and the Jastrow parts of the wave function.

### A. Atomic Orbitals

A generic atomic orbital $\phi_{\mu}$ centered at the position $R_{\mu}$ is written in terms of the radial vector $r - R_{\mu}$ connecting the position $R_{\mu} = R_a$ of nucleus $a$ to the position $r$ of an electron. Hereafter the atomic index $a$ will be neglected in order to simplify the notation. Of coarse there are several atomic orbitals used to describe each atom.

In this work we consider the most general atomic orbital centered around the atomic position $R_{\mu}$ that can be expanded in terms of simple elementary atomic orbitals. These elementary orbitals are determined by a radial part given by a simple Gaussian or Slater form, whereas their angular part is characterized by an angular momentum $l$ and its projection $m$ along a given axis:

$$\phi_{l,m}^{\text{STO}}(r; \zeta) \propto ||r - R_{\mu}|| e^{-\zeta ||r - R_{\mu}||} Y_{l,m}(\Omega)$$

(11)

and the Gaussian type orbitals (GTO):

$$\phi_{l,m}^{\text{GTO}}(r; \zeta) \propto ||r - R_{\mu}|| e^{-\zeta ||r - R_{\mu}||^2} Y_{l,m}(\Omega)$$

(12)

where $Y_{l,m}(\Omega)$ is a real spherical harmonic centered around $R_{\mu}$. The proportionality constant is fixed by the normalization and depends on the parameter $\zeta$. Other parametric forms for the atomic orbitals exist, see for instance [14], but have not been used in this work.

As discussed previously, the electron-ion cusp condition is satisfied by the term $u_{ci}$ included in the Jastrow term. For this reason we need smooth atomic orbitals with no cusps at the nuclear positions. This is automatically satisfied by all the GTO and STO orbitals described here, with the exception of the $s$-orbital STO (i.e., $l = m = 0$), that is smoothed as follows:

$$\phi_{0,0}^{\text{STO}}(r; \zeta) \propto (1 + \zeta ||r - R_{\mu}||) e^{-\zeta ||r - R_{\mu}||} Y_{0,0}(\Omega)$$

(13)
Observe that each elementary orbital described here depends parametrically only on the exponent $\zeta$.

The most general atomic orbital $\phi_{\mu}(\vec{r})$ can be expanded in terms of elementary orbitals as follows:

$$
\phi_{\mu}(\vec{r}) = \sum_{l,k,m} c_{l,m}^{k} \phi_{l,m}^{X,k,l}(\vec{r}, \zeta_{k,l}),
$$

namely it may contain elementary functions corresponding to different angular momenta, different types Slater ($X_{k,l} = STO$) or Gaussian ($X_{k,l} = GTO$), and different exponents $\zeta_{k,l}$. Usually in quantum chemistry methods, this type of operation is called contraction and is often adopted to reduce the atomic basis dimension for the description of strongly bound atomic orbitals (e.g., 1s). Therefore, it is not common to hybridize different angular momenta.

In our approach instead, in order to describe the wave function with an affordable number of variational parameters, it is crucial to reduce the atomic basis dimension $D$ as much as possible, because the number of variational parameters (mostly given by the number of matrix elements $f_{\mu\nu}, u_{\mu\nu}$ in Eqs.8,9) is proportional to the basis dimension square, namely, $D(D + 1)/2$, only for $f$. It is therefore extremely important to reduce this number $D$ by optimizing the independent atomic orbitals in a large primitive basis of elementary functions. In this way a very small number of contracted orbitals – referred to as “hybrid” orbitals here – are necessary to reach converged variational results.

B. Molecular Orbitals

A generic orbital of a Slater Determinant, for instance, within Hartree-Fock theory, can be expanded in terms of atomic orbitals, namely, it has components spread over all the atoms of the system considered. These orbitals are usually called molecular orbitals (MO).

In the following sections we consider other functional forms for the determinantal part of the wave function. The relation between the AGP and those other wave functions can be easily understood by rewriting the pairing function $f(r_i, r_j)$ in the following equivalent way. First of all we diagonalize the matrix $f$, whose elements are the $f_{\mu\nu}$, by taking into account that the atomic orbitals are not necessarily orthogonal each other, namely the matrix $S$ has elements $S_{\mu,\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle \neq \delta_{\mu\nu}$. This can be done by using a standard generalized diagonalization:

$$
\text{fSP} = \text{PA}.
$$

where the generalized eigenvectors of $f$ define each column of the matrix $P$, whereas $\Lambda$ is a diagonal matrix containing the corresponding generalized eigenvalues $\lambda_{\alpha}$. Here, for notational convenience, the non-vanishing eigenvalues $\lambda_{\alpha}$ are sorted in ascending order, according to their absolute values: $|\lambda_1| \leq |\lambda_2| \leq \ldots \leq |\lambda_n|$. Thus, from $\text{P}^T \text{SP} = \text{I}$, by right-multiplying both sides of Eq.15 for the matrix $\text{P}^T = (\text{SP})^{-1}$ we obtain $f = \text{P} \Lambda \text{P}^T$. Then, by substituting it in 8, we finally obtain that the pairing function can be also written as

$$
\Phi_{\alpha}(\vec{r}) = \sum_{i} c_{\alpha,i} \phi_{i}(\vec{r}).
$$

Notice that, if the number of non-zero eigenvalues $\lambda_{\alpha}$ is exactly equal to the number of pairs $N/2$, the antisymmetrization in Eq.[5] projects out only a single Slater determinant, and the molecular orbitals coincide in this case with the standard ones. From this point of view it is transparent that this wave function can improve the Hartee-Fock single-determinant picture, especially when, as discussed in the introduction, it is combined with the Jastrow factor.

We remark here, that, even when the AGP is exactly equivalent to a Slater determinant ($n = N/2$), the combined optimization of the Jastrow factor and the molecular orbitals may lead to a qualitatively different wave function, namely with different chemical and physical properties. In such case it is fair to consider this kind of wave function as an RVB and therefore it will be also indicated in the following with the nRVB acronym.
C. New RVB Wave Function

It has been proved \cite{12, 18} that a Jastrow correlated AGP function, the new RVB (nRVB), satisfies the size-consistency of singlet fragments, namely the energy of the system is equal to the sum of the energies of the fragments, when the fragments are at very large distance. This property holds provided that the Jastrow term is flexible enough.

The fully optimized wave function with \( n = N/2 \), that will be denoted hereafter by JHF, corresponds to a Jastrow correlated Hartree-Fock wave function, and it provides an accurate description of atoms\cite{8, 11}, with more than 90% of the correlation energy. The idea here is to use the larger variational freedom given by the nRVB ansatz for \( n > N/2 \), only to improve the chemical bond, without requiring an irrelevant improvement of the isolated atoms. A natural criterion for restricting the number \( n \) of MOs to a minimal number in a molecule or any electronic system, is to require that, when the atoms are at large distances, we cannot obtain an energy below the sum of the JHF atomic energies. The number \( n^* \) of MOs defined in this way is therefore determined by the obvious requirement that:

\[
n^* \geq \sum_a \text{Max}(N_a^\uparrow, N_a^\downarrow) \tag{18}
\]

as we need at least one atomic orbital for each pair with opposite spin electrons and each unpaired electron, where \( N_a^\uparrow (N_a^\downarrow) \) is the maximum number of spin-up (spin-down) electrons contained in the atom \( a \). A rank \( n \) of the nRVB larger than \( n^* \) or equal to \( n^* \) will be sufficient to build uncoupled atomic wave functions at large distance by means of a factorized \( f_{\mu\nu} \) in terms of block-diagonal atomic contribution. For further details and for a discussion of polarized systems see Ref. \cite{11}.

This constraint on the number \( n \) of molecular orbitals is not only useful to reduce the number of variational parameters but it is extremely important to improve the description of the chemical bond. In fact, we have reported a number of cases \cite{11} where, by increasing \( n \) to a value much larger than \( n^* \), the accuracy in the description of equilibrium properties and chemical properties drastically deteriorates. A larger value of \( n \) guarantees a lower total energy because, by the variational principle, to a larger variational freedom corresponds a lower total energy. However a larger \( n \) may improve too much the atomic description-depending on high energy details-at the price to deteriorate the low-energy chemical properties (see next section).

\[ e_L(x) = \frac{\langle x | H | \Psi_{\text{newRVB}} \rangle}{\langle x | \Psi_{\text{newRVB}} \rangle} \tag{19} \]
All the other random variables can be obtained by replacing in the above expression the hamiltonian $H$ with the corresponding physical operator $O$.

IV. EXAMPLES ON BERYLLIUM DIMER AND WATER MOLECULE

In this section we present one of the most successful examples, among many of them, of the simultaneous optimization of the Jastrow and the determinantal part of the wave function. The Beryllium dimer is one of the most difficult molecules to describe by ab-initio methods. The simplest Hartree-Fock does not predict a stable molecule and, despite the fact the correct binding energy is very small ($\simeq 0.1eV$), the hybridization of 2s and 2p atomic orbitals together with a weak van der Waals (vdW) interaction yield a rather short bond length.

Several attempts have been made, using DFT methods with sophisticated RPA treatments of the long-range interaction [13], but so far a reasonable description of the bonding has been obtained only by using an expansion in several (billion) determinants [9, 15]. Fortunately, recently there was a very accurate experimental paper [10], that has proven to be very useful to benchmark the various calculations.

In Fig. (4) we report two different variational Monte Carlo calculations: the most accurate (nRVB) is obtained by applying a Jastrow factor $u$ and a pairing function $f$ with $n = n^* = 4$ molecular orbitals (the basis set is $4s4p2d$ and $5s2p1d$ respectively for $u$ and $f$), fully optimized within an accuracy of 0.01$mH$; whereas the less accurate one (JDFT) is obtained by using DFT (with standard LDA approximation) with a large VTZ basis (11s11p2d1s) for determining the molecular orbitals, and only $u$ is fully optimized in the same basis used for the nRVB. We remark here that the small basis used in the nRVB case is already enough to reach an accuracy on the total energy within 0.1$mH$. This is because the full optimization of the wave function in presence of a large Jastrow factor, allows a rapid convergence, and requires therefore a minimal basis for $f$. Indeed, despite the small basis, the nRVB total energy is about 3$mH$ below the JDFT one in all the interatomic distances under consideration.

As it is shown in this picture, the simultaneous optimization of the Jastrow and the determinantal part of the wave function is fundamental for obtaining a good agreement with the experimental results. The most important ingredient to describe this bond is clearly given by our accurate Jastrow factor, which is capable to correctly describe the long-range vdW interaction. Without the optimization of the determinantal part, however, the agreement with

![Figure 4: Dispersion energy for Be$_2$ molecule. The nRVB calculation refers to the full optimization of a simple Slater determinant in presence of the Jastrow term. In the JDFT calculation only the Jastrow factor is optimized. The experimental curve is derived by direct evaluation of vibrational frequencies [10]. In the inset the atomic force is displayed.](image-url)
Within this approach, it is easy to obtain converged results for the total energy and in all the interesting physical properties of the molecule, such as the atomization energy, the dipole and the quadrupole tensor, the equilibrium structure and the vibrational frequencies. We see in Table I that the JDFT calculation is rather accurate and it describes all these properties in a quantitative way. In the water molecule, the physics of the RVB is certainly not as crucial as for Be₂. However, also here the larger variational freedom allows us to improve significantly the agreement of the estimated quantities with the experiments or the estimated exact results. The improvement is observed in particular in the charge distribution (see the dipole in Table I) and in the potential energy surface (see equilibrium structure and frequencies). It is important to emphasize that this improvement in the description of the water molecule is achieved at convergence, because the cost to optimize the simple Slater determinant in presence of the Jastrow factor is essentially the same as for the full nRVB wave function with no constraint on molecular orbitals.

V. CONCLUSIONS

In this chapter we have described in a simple, yet complete, way the main reasons why the new RVB variational ansatz opens a new frontier for electronic simulations. Until now we have lived in the DFT era, where the detailed and often subtle (e.g., the long range interactions such as the van Der Waals one) correlations are assumed to be implicitly described by a function of one electron coordinate, the local density n(r) (see in particular chapters of Giringhelli, von Lilienfeld and Watermann et al.). In this approach instead the explicit many-body correlation is determined.
often quite accurately, by two functions $f$ and $u$ of two electronic coordinates, the pairing function and the Jastrow correlation term, respectively.

It is important to emphasize at this point the crucial role played by the mutual interplay of the Jastrow factor $u$ and the pairing function $f$. In a clean uncorrelated system ($u = 0$), the pairing function represents a metal if it is enough long range $|f(r, r')| \sim \frac{1}{rr'}$ since it behaves as the density matrix of a free electron gas for $|r - r'| \gg 1$. When it decays exponentially or in general faster than $1/|r - r'|^2$ it may represent either a band insulator or a superconductor. In the latter case, the correlation factor can play a crucial role because it can suppress phase coherence and give raise to a RVB insulator, that may be considered a “correlation frustrated” superconductor. This simple example shows that the nRVB paradigm, described in this chapter, is not only useful to improve on a “naive correlation”, but allows us to change the qualitative properties of an uncorrelated picture, opening the path to the description of new phases of matter.

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