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Resonating Valence Bonds in Chemistry and Solid State

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4.1

Introduction

This chapter is conceived as a combination of two complementary parts. In the first part, we discuss (largely qualitatively) the relations between the resonance valence bond (RVB) and tight-binding/linear combination of atomic orbitals (LCAO) pictures of the electronic structure using the archetypal example: the π -system of benzene well known to chemists – the principal readers of this volume. The substance of the differences between the two is rarely clearly recognized, although the divergence between them in “molecular” quantum chemistry is well appreciated even as potentially reaching the degree of a “never-ending rivalry” [1]. The second more formal, more physical, and more solid-state part is devoted to extensions of the RVB ideas to solids. This requires a modification of the single determinant form of the electronic wave function based on the tight-binding/LCAO scheme characteristic for solids to enable it to model RVB states. We exemplify these issues by several simple models ranging from the one-dimensional polyene chain: an infinite extension of benzene (*hexatriene*) molecule – through graphene and finish by probably the most spectacular example of the enigmatic quantum RVB state of copper(II) carbodiimide (CuNCN) – a new material, where an assumption of the RVB character of its electronic phases was crucial for explaining its room- and low-temperature physics. The possibility of the RVB phase/state of high- T_c cuprate superconductors is also briefly discussed.

4.2

Historical Overview

The concept of resonating bonds is very dear to the hearts of chemists and this is well deserved. Yet at the dawn of theoretical *organic* chemistry, almost right after the concept of an integer valence characteristic for each atom had been introduced [2], the chemists faced the problem of benzene molecule: one composed of six carbon and six hydrogen atoms (C_6H_6) [3–6]. Counting the number of isomers of disubstituted benzenes (C_6H_4XY) led to the idea of the hexagonal-cyclic structure of this molecule and of the sixfold symmetry of the original benzene molecule itself. Such an assumption is incompatible with the formal valence theory ascribing precisely four valences to the carbon atoms: One cannot uniquely distribute three bonds (the fourth is always assigned to one with a hydrogen atom) in a hexagon preserving its sixfold symmetry as shown, for example, in either of bracketed structures of Figure 4.1.

It was August Kekulé who first suggested the real molecule to “oscillate” between two possible distributions of “double” bonds, each possessing a three-fold symmetry so that the sixfold symmetry of the molecule itself is preserved. The nature of this oscillation was pretty much enigmatic and was an occasion for rather caustic jokes like one reproduced in Figure 4.2.¹⁾

The situation reached its tentative resolution after works by Lewis, Pauling, and Rumer who could convince chemists that it goes not about jumps of monkeys rather about resonance of electronic pairs that, nevertheless, could not be properly (not breaking the sixfold symmetry) distributed among six carbon atoms. The solution based on the early theory of spin valence [8–11] was to represent the delocalized bonds as a superposition of the individual states (the term “resonance” of structures aimed to replace Kekulé’s “oscillation” had been coined by Pauling [12,13]), each being a product of electronic pair functions distributed in the molecule, as shown in Figure 4.3.

Switching to a more formal representation necessary for our further discussion, two Kekulé structures denoted as K_1 and K_2 in Figure 4.3 can be written

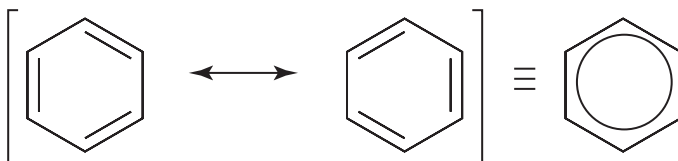


Figure 4.1 Archetypal example of resonating valence bonds: benzene. Six hydrogen atoms each consuming one valency each carbon atom are not shown for simplicity.

1) Remarkably, Ladenburg [7] proposed a three-dimensional trigonal prismatic arrangement of six CH units conformant with the number of doubly XY-substituted isomers of benzene, but not with that of XX ones. Such a molecule indeed exists and is known as “prismane.”

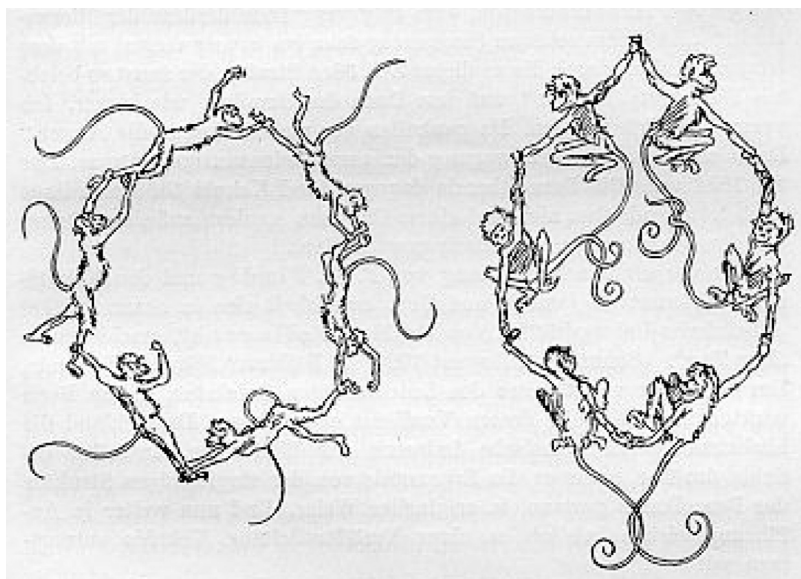


Figure 4.2 The picture is most probably due to German chemist H. Kolbe. (Berichte der deutschen Chemischen Gesellschaft Unerhörter Jahrgang, Nr. 20 zum 20.9.1886 Sitzung vom 20. September 1886. Vorsitzender: Hr. August Kuleké, Präsident.) The message is pretty clear:

first you invent something which you call "bond" and "valence" and then you say that they "oscillate" since the ends do not come together any way. Why not to assume, that there are some invisible monkeys?

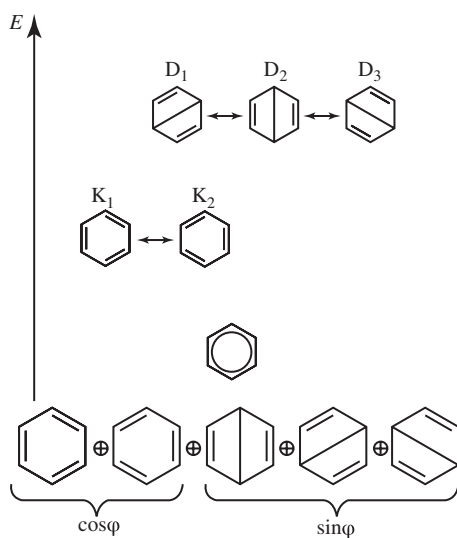


Figure 4.3 Oscillation, mesomerie, resonance: three names for the same thing now called quantum mechanical superposition of independent valence states, not necessarily observed as

individual compounds. Hexagons themselves are only eyeguides, the additional dashes represent individual electronic pairs that or other way distributed in the molecule [14].

as many-electronic wave functions:

$$\begin{aligned} |K_1| &= \frac{1}{\sqrt{8}} [(c_{1\uparrow}^\dagger c_{2\downarrow}^\dagger - c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger)(c_{3\uparrow}^\dagger c_{4\downarrow}^\dagger - c_{3\downarrow}^\dagger c_{4\uparrow}^\dagger)(c_{5\uparrow}^\dagger c_{6\downarrow}^\dagger - c_{5\downarrow}^\dagger c_{6\uparrow}^\dagger)]|0|, \\ |K_2| &= \frac{1}{\sqrt{8}} [(c_{1\uparrow}^\dagger c_{6\downarrow}^\dagger - c_{1\downarrow}^\dagger c_{6\uparrow}^\dagger)(c_{2\uparrow}^\dagger c_{3\downarrow}^\dagger - c_{2\downarrow}^\dagger c_{3\uparrow}^\dagger)(c_{4\uparrow}^\dagger c_{5\downarrow}^\dagger - c_{4\downarrow}^\dagger c_{5\uparrow}^\dagger)]|0|, \end{aligned} \quad (4.1)$$

and analogous expressions for three “Dewar benzenes” $|D_1\rangle \div |D_3\rangle$ built following the same pattern – as products of the singlet electronic pairs residing in the respective pairs of the site orbitals (here we use the second quantization notation described in all details, for example, in Refs [15,16]). In the expressions above, $|0\rangle$ stands for the state containing no electrons at all (*vacuum* state) and the symbols $c_{n\sigma}^\dagger$ (creation operators) refer to adding to the n th atomic state of the system an electron with the spin projection $\sigma = \uparrow, \downarrow$. The symbols $c_{n\sigma}^\dagger$ are subject to the *anticommutation* relations:

$$\{c_{n\sigma}^\dagger, c_{m\tau}^\dagger\} = c_{n\sigma}^\dagger c_{m\tau}^\dagger + c_{m\tau}^\dagger c_{n\sigma}^\dagger = 0 \quad (4.2)$$

of which the most transparent consequence is the *nilpotence* of the creation operators, that is, $c_{n\sigma}^\dagger c_{n\sigma}^\dagger = (c_{n\sigma}^\dagger)^2 = 0$, which formalizes the known Pauli principle preventing two electrons with equal spin projection to occur in the same state. The rows of the form $c_{s\sigma}^\dagger c_{t\tau}^\dagger \dots c_{r\rho}^\dagger c_{m\mu}^\dagger |0\rangle$ thus represent Slater determinants uniquely (up to an overall sign) defined by the lists of the occupied one-electron states. Anticommutation of $c^\dagger$'s takes care of (or formalizes) the known property of a determinant to change its sign when two rows (columns) of the latter are exchanged. (The nilpotence is of course the same as the evanescence of the determinant with two coinciding rows or columns).

The above construct was baptized as the resonance valence bond (RVB) state of benzene. It represented a great advantage in describing the electronic structure of benzene and other π -conjugated hydrocarbons and is actually if not the simplest, but for sure best-known example of an RVB state in chemistry. Nowadays one can frequently read that “since in the π -system of benzene the bonds are nonlocalizable and a resonance takes place, it is advisable/convenient/reasonable to introduce delocalized description of electrons in this system.” It is thus tacitly assumed that it is not important what is delocalized: bonds or electrons. The delocalization of electrons is formalized by the electronic wave function taken as a single Slater determinant of the occupied MOs, as proposed by Hückel [17–26]. This construction is very well known (see Figure 4.4).

For its more formal representation, first, the linear combinations of the above creation operators $c_{n\sigma}^\dagger$ are formed:

$$\begin{aligned} \Psi_{6\sigma}^\dagger &= \frac{1}{\sqrt{6}} \sum_n^6 e^{i\pi n} c_{n\sigma}^\dagger \\ \Psi_{4\sigma}^\dagger &= \frac{1}{\sqrt{3}} \sum_n^6 \cos\left(\frac{4\pi}{6}n\right) c_{n\sigma}^\dagger ; \quad \Psi_{5\sigma}^\dagger = \frac{1}{\sqrt{3}} \sum_n^6 \sin\left(\frac{4\pi}{6}n\right) c_{n\sigma}^\dagger \\ \Psi_{2\sigma}^\dagger &= \frac{1}{\sqrt{3}} \sum_n^6 \cos\left(\frac{2\pi}{6}n\right) c_{n\sigma}^\dagger ; \quad \Psi_{3\sigma}^\dagger = \frac{1}{\sqrt{3}} \sum_n^6 \sin\left(\frac{2\pi}{6}n\right) c_{n\sigma}^\dagger \\ \Psi_{1\sigma}^\dagger &= \frac{1}{\sqrt{6}} \sum_n^6 c_{n\sigma}^\dagger \end{aligned}$$

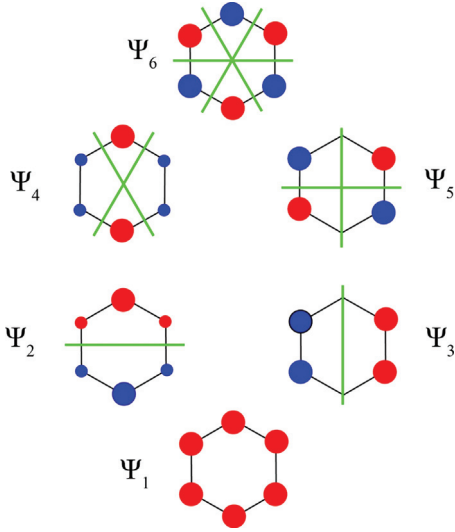


Figure 4.4 The pictorial representation of MO LCAOs of benzene.

Similar to the $c_{n\sigma}^\dagger$ ones, these expressions are operators creating electrons with spin projections σ in the *molecular orbitals*, which are the respective linear combinations of the atomic (site) orbitals (MO LCAO).

This wave function of six electrons is the single Slater determinant formed of the orbitals with the smallest available number of nodes (see Figure 4.4), that is, $\Psi_{1\sigma}^\dagger \div \Psi_{3\sigma}^\dagger$ for both spin projections:

$$\Psi_{1\downarrow}^\dagger \Psi_{1\uparrow}^\dagger \Psi_{2\downarrow}^\dagger \Psi_{2\uparrow}^\dagger \Psi_{3\downarrow}^\dagger \Psi_{3\uparrow}^\dagger |0| \quad (4.3)$$

It is thus of interest to know what is the relation between the functions Eq. (4.1) (Pauling) and Eq. (4.3) (Hückel). Since, in general, the wave functions themselves are not observable, the only way of comparing the functions is to compare the averages of some observable physical quantities. The simplest one is the electron density – the average over the wave function of the operators $\hat{n}_{i\sigma}$ – those of the number of electrons with the spin projection σ in the i th site (orbital). Operators $\hat{n}_{i\sigma}$ are projection operators, since acting on a Slater determinant with the state $i\sigma$ occupied it produces a factor of unity, whereas for the similar determinant with the empty $i\sigma$ state it yields the factor zero. Anything else is not possible due to the Pauli principle. Opening brackets in (4.1) immediately shows that each of the two Kekulé states contains only singly occupied site (atomic) orbitals. As one can easily check, the number of particles operator $\hat{n}_{1\sigma}$ stumbles only upon one of the terms in only one of the two-electron products (singlets) entering the basis configurations $|K_1\rangle$, $|K_2\rangle$, and $|D_1\rangle \div |D_3\rangle$ used for representing the RVB state (Eq. 4.5). The calculation yields the sought average to be $1/2$. The same is true for all other i 's. “Similarly” one sees that in the Hückel solution (Eq. 4.3), the one-center averages of all $\hat{n}_{i\sigma}$ equal to the same $1/2$. It does not seem to be counterintuitive and it is indeed true that the number of electrons per atom (site) – sum of $\langle \hat{n}_{i\sigma} \rangle$ over σ – in both approximations

(LCAO and RVB) equals to unity, Thus, this quantity is absolutely insufficient to distinguish two states of benzene.

In the style characteristic for the solid-state applications, let us consider another average, one related to correlation functions – the observables characterizing different many-electronic states or, respectively, electronic or magnetic phases of solids. The simplest and best of all suitable for our purposes is the average $\langle \hat{n}_{1\downarrow} \hat{n}_{1\uparrow} \rangle$ – a two-electron correlation function – which can also be interpreted as the density of an electronic pair on the single site. Even more general operator products of number of particle operators, $\hat{n}_{i\sigma} \hat{n}_{j\tau}$, are as well projection operators counting electron pairs. The shown operator produces a factor of unity in case when in a Slater determinant both spin orbitals $i\sigma$ and $j\tau$ are occupied and zero otherwise. Operator $\hat{n}_{1\downarrow} \hat{n}_{1\uparrow}$ is a specific case of the previously mentioned projection operator. It produces a factor of unity acting on a Slater determinant with a doubly occupied i th orbital and zero otherwise. One can easily conclude that for the RVB function (Eq. (4.5)), this (and all other similar one-center pair densities) is vanishing. This is very easy to understand since either of the basis configurations $|K_1\rangle$, $|K_2\rangle$, and $|D_1\rangle \div |D_3\rangle$ used for representing the RVB state (Eq. (4.5)) contains in its expansion no more than one creation operator $c_{1\sigma}^\dagger$. Thus, the term on which, say, $\hat{n}_{1\downarrow}$ “stumbles” and produces a factor of unity for sure does not contain $c_{1\uparrow}^\dagger$ and thus will be killed by the $\hat{n}_{1\uparrow}$ multiplier. Thus, we have $\langle \hat{n}_{1\downarrow} \hat{n}_{1\uparrow} \rangle_{\text{RVB}} = 0$ and the same holds for all i 's. The calculation of the average of the same operator over the Hückel wave function cannot be done that easily, but the result is known and reads $\langle \hat{n}_1 \hat{n}_1 \rangle_{\text{Hückel}} = 1/4$ and we see that the RVB and LCAO (respectively, Pauling and Hückel) functions are by far nonequivalent. One may be even surprised by the extent of this nonequivalence. If one performs what in our days is called “wave function VB reading” [27], that is, calculates the projection of the Hückel wave function to the subspace spanned by the homeopolar configurations $|K_1\rangle$, $|K_2\rangle$, and $|D_1\rangle \div |D_3\rangle$ and other (singly, doubly, and triply ionic) configurations (Figure 4.5), one finds that all the homeopolar states together contribute to the Hückel function only 12.5% ($1/8$ – for more details, see below and Ref. [28]). The rest is supplied by the singly, doubly, and even triply ionic configurations depicted in Figure 4.5 with the weights given next to respective configuration classes.

The result looks pretty counterintuitively at a first glance: In the system where the atomic *charges* are all vanishing, the by far predominant contribution to the wave function is produced by the ionic configurations, which must be (and actually are) well balanced. Based on this analysis, one is forced to conclude that Pauling and Hückel had suggested two pretty much different wave functions for the benzene π -system so that the “common sense explanation” quoted above makes in fact no sense and “a rivalry between the MO and VB pictures” that is believed to be finally conciliated by the prominent authors [1] is in fact more than real. Turning to the solid-state context that is our main occupation in this chapter, we notice that there is a *theorem* [30] expressing the weight (sum of the squared overlaps) of the k -ionic configurations in the Hückel solution of a cyclic polyene (linear chain of carbon atoms supplied by one π -orbital each or a similar

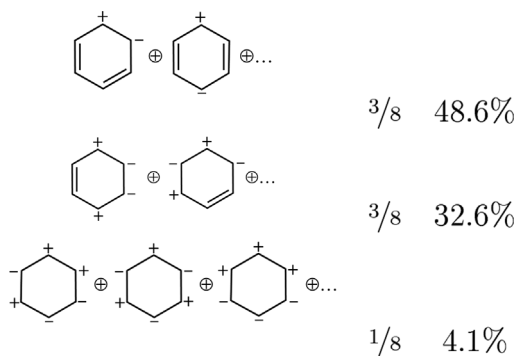


Figure 4.5 Exemplary singly, doubly, and triply ionic configurations of the π -system of benzene molecule with their weights in the expansion of the Hückel wave function and a correlated wave function [29] with a moderate interaction strength U . The weight of the homeopolar (RVB) configurations in the correlated wave function amounts the remaining 14.7%.

chain of the hydrogen atoms with 1s-AO each with periodic boundary conditions) (Figure 4.4) with $2n$ nodes (n -ene; benzene is a *triene*) as follows:

$$w_k \rightarrow \binom{n}{k} 2^{-n}; \quad w_k = w_{n-k} \quad (4.4)$$

The estimate for the weight of the RVB state from above is apparently w_0 , which flows to zero when it comes to infinite number of nodes as characteristic for the solid state. This creates somewhat inconvenient situation: Although, one may expect that at least under certain conditions, the states of the type proposed by Pauling for benzene might exist in solids, there is no chance to reproduce them by any of available numerical methods of solid-state quantum chemistry since these latter by brute force impose the Hückel view of the electronic structure of solids (tight-binding approximation!) by using the Bloch theorem/sums. Thus, some special moves going beyond the standard tight-binding LCAO scheme are necessary to access these states.²⁾

- 2) Currently, the plane waves are widely used for calculating electronic structure of crystals. At a first glance, they represent completely different approach to constructing basis states for such problems and the mentioned concerns seem not to apply to them. Nevertheless, in practice, pure plane waves are used rarely, and the so-called augmentation – that is adding atom-like states inside the so-called Wigner–Seitz spheres around each atom to cheaper mimic their nodal structure close to nuclei, is made. This produces a strange hybrid in which the original *plane waves* of which there was that much buzz in the beginning in fact appear only in the empty space between the spheres where they honestly serve ensuring required flexibility of the electronic states in the interatomic space – the feature very costly in the methods with fixed atomic basis states. Nevertheless, the major part of electronic density resides in the atom-like augmentation parts. It is particularly true when it comes to highly correlated d- or f-shells. The augmentation parts enter in the play effectively exactly as the Bloch sums so that the RVB states have no chance to emerge in the (augmented) plane wave setting either.

One more aspect needs to be mentioned. This is the nature of interactions producing the delocalized structures. The Hückel and Pauling models rely upon completely different types of the coupling. The Hückel model employs hopping of single electrons between the neighbor sites. Such an interaction when applied to either *K*- or *D*-benzene structures immediately produces ionic configurations not entering in the original basis of the homeopolar configurations shown in Figure 4.3. By contrast, the states $\Psi_{n\sigma}^{\dagger}|0\rangle$ are the eigenstates of the hopping operator of single electrons that are not changed under the action of the hopping operator. On the other hand, the exchange interaction couples the effective electronic spins residing in each of the sites in the six-membered cycle in each individual Kekulé and Dewar structures. However, as one can check (see, for example, Ref. [31]), the matrix element of the exchange between the Kekulé states $|K_1\rangle$ and $|K_2\rangle$ is vanishing. This means that in fact no resonance (in our days it is usually called a quantum mechanical superposition) of these states is possible – the double arrow connecting these two structures in Figure 4.3 is a fake. One needs additional states, namely, the Dewar structures (states), to ensure the coupling between them to arrive to the RVB state (Eq. (4.5)) to mediate the exchange interaction and thus to lower the energy due to quantum mechanical superposition of all five basis configurations:

$$\frac{\cos \varphi}{\sqrt{2}}(|K_1\rangle + |K_2\rangle) + \frac{\sin \varphi}{\sqrt{3}}(|D_1\rangle + |D_2\rangle + |D_3\rangle) \quad (4.5)$$

and by this generate the observed bond delocalization. It is thus necessary to realize that the Pauling and Hückel models of benzene not only employ very different wave functions but also recognize that this difference is stipulated by the difference of the underlying model of electron dynamics formalized by the Hamiltonian used in either setting: ultimately the antiferromagnetic Heisenberg one for the Pauling model and the one-electronic hopping in the case of Hückel. For that reason, either the very concept of resonance or the value of the resonance (stabilization) energy has absolutely different meaning and value within these two models. Populating six electrons into lowest three states of the one-electron hopping operator (Eq. (4.9)) – see below – we have

$$E = -8t, \quad (4.6)$$

which must be compared with the energy of a hypothetical configuration where the hopping is allowed only within three fixed bonds. In the spirit of the hopping operator (Eq. (4.6)), such a setting is equivalent to three copies of a two-site system with an extremely simple Hamiltonian:

$$H_2 = -t \sum_{\sigma} (c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma}),$$

(actually ethylene or H_2 molecule) having the ground-state energy of $-2t$ so that three copies of it have the energy of $-6t$, which is by $2t$ higher than the Hückel ground state energy (Eq. (4.6)). This gives a specific value of the “resonance” characteristic for the Hückel setting. In the Pauling picture, benzene is described

by the Heisenberg Hamiltonian. Its ground state is the RVB type with the energy of $-(\sqrt{13}-1)J$ to be compared with $-9J/4$ for three isolated (nonresonating) singlets in either of the two Kekulé structures. We see that the relative stabilizing effect of delocalization (resonance) of the bonds in the Heisenberg picture is much weaker than in the Hückel one.

If one considers either the Hückel Hamiltonian and Hückel wave function or the Heisenberg exchange Hamiltonian and the Pauling wave function, respectively, together, either is the *exact* solution of the corresponding ground-state problem. From the first glance, only one of the models can be correct, but we cannot decide which one is better. A problem is that the exchange interaction between electrons in all involved site orbitals of the usual Heisenberg form is an effective one: There is no fundamentally antiferromagnetic coupling between electrons/spins occupying otherwise orthogonal site AOs, which would enable them to form *singlet* rather than triplet pairs. A step toward resolving this complication is to imbed both settings into a more general model for the energy. Both Hamiltonians mentioned so far miss a very important ingredient – the electron–electron repulsion. The simplest medication against this flaw is provided by the Hubbard–Anderson model, which is the hopping (Hückel) one supplied by additional terms increasing the energy of ionic configurations. Formally, it is expressed by adding the terms of the form:

$$U\hat{n}_{i\downarrow}\hat{n}_{i\uparrow}$$

for each site. Here U is the energy ascribed to a pair of electrons occupying the same site with opposite spin projections (note that the operator multiplier in the above additive is nothing, but the projection operator counting the number of such pairs). Apparently, with such a term added to the diagonal energy, matrix elements of the k -ionic configurations acquire the contribution of kU . It had been shown yet quite long ago [29] that the weights of the ionic configurations in a correlated wave function are consistently suppressed and the symmetry relation for the weights of the dual ionicity (Eq. (4.4)) does not hold anymore (see rightmost column in Figure 4.5). This observation indicates the trend: The larger the electron–electron repulsion, the higher the weight of the homeopolar configurations eventually yielding the (RVB) state. On the other hand, it had been shown [32] that in the limit of very large U , the Hubbard–Anderson Hamiltonian reduces to the Heisenberg one with $J = 4t^2/U$. This latter can be considered as acting in the subspace of the homeopolar electronic functions: The strong Coulomb repulsion restricts the possibilities of electrons to move around the benzene π -system so that in this limit instead of a “free” hopping of electrons – one restricted solely by the antisymmetry of the many-electronic wave function – only a correlated motion is possible: that is, simultaneous (ex)change of the positions of the two electrons with oppositely oriented spins.

These considerations show that in fact one cannot and should not try to separate the issues of the Hamiltonian used and the method of its treatment since they are pretty much interpenetrating. The problem thus is that for the standard solid-state quantum chemical Hamiltonian containing the one-electron hopping

of different magnitudes between different atomic orbitals within and between the unit cells together with the electron–electron repulsion terms, the true electronic wave function may have very little to do with the Hückel (tight-binding) one as characterized by the high contribution of the ionic configurations. Indeed, the parameters of the Hubbard–Anderson Hamiltonian scale at the first approximation as

$$U \propto \frac{Z}{n}; \quad t \propto \exp\left(-\frac{Zr}{n}\right), \quad (4.7)$$

where Z is the atomic number, n is the principal quantum number of an AO, and r is the interatomic separation. In the solid-state quantum chemical setting, each unit cell may contain several atoms, each containing several orbitals. The transition metal or rare-earth atoms contain those with different n values. Thus, different pairs of orbitals may have very different ratios U/t such that some of them fall in the parameters' range where the electronic structure is better described by the Hückel model, whereas for other pairs of orbitals the ratio U/t may get so that the contribution of the homeopolar configurations become dominating.

The problem is thus to implement in a tractable way the reduction/suppression of the ionic configurations or, in other words, to steer the solution into physically substantiated subspace of the wave functions in case it is necessary. The problematic itself is known under the disguise of “taking into account electronic correlation,” to which several other chapters of this volume are devoted [33,34]. Technically, this problem can be differently distributed between manipulation with the trial wave function or with the Hamiltonian, which in this case turns into effective one. Transition from the bare Hamiltonian containing the hopping (kinetic energy) and Coulomb repulsion terms to the Heisenberg is one of the examples of reloading the information about the subspace accommodating the ground state upon an effective Hamiltonian, although it seems to be too direct and rigid.

The dominance of the homeopolar configurations in the description of the electronic structure of a solid does not automatically mean that the RVB state represents its best solution. By contrast, in a predominant number of cases, the Heisenberg Hamiltonian results in magnetically ordered structures (e.g., antiferromagnetic or more sophisticated ones). Such behavior is widespread and has well-known experimental manifestations: in magnetic neutron scattering, characteristic magnon contributions to the heat capacity, and, finally, a transition to magnetically unordered high-temperature paramagnetic phases. The magnetically ordered states (phases) form easily only for a restricted class of lattices – so-called bipartite ones when the nodes can be colored in white and black in an alternate manner. In this case, an antiferromagnetic interaction of the spins accordingly arrange them on the nearest-neighbor sites (those occupying the sites of different colors) and produce the so-called Néel state of an antiferromagnet.

For archetypic example of benzene, the Néel state although being unlikely for the real physical conditions can be easily built by setting spin-up electrons on

the even sites and spin-down ones on the odd ones:

$$|N_1\rangle = c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger c_{3\downarrow}^\dagger c_{4\uparrow}^\dagger c_{5\downarrow}^\dagger c_{6\uparrow}^\dagger |0\rangle$$

or vice versa ($|N_2\rangle$). Like either of the Kekulé structures, either of the Néel ones breaks the sixfold symmetry, which like in the Kekulé case at least formally reinstalls by taking the wave function of “antiferromagnetic” benzene as a linear combination of the two:

$$|N_1\rangle + |N_2\rangle.$$

Like in case of the Kekulé structures, two equivalent Néel structures are not mixed directly by the Hamiltonian. This means that the energy of the above-symmetrized state can be obtained by performing the calculation of the mean value of the Hamiltonian with either of the components with broken symmetry.

For lattices other than bipartite ones and among them first of all for the lattices featuring odd-membered rings of spins, for example, triangular ones – the spins cannot arrange antiferromagnetically, which leads to frustration, so the competition between the magnetically ordered (with the superstructure wave vector proportional to $4\pi/3$ in the specific case of the triangular lattice) and RVB (spin-liquid) states may lead to the preference of the latter. The Néel state, however, is not the ground state of the Heisenberg Hamiltonian, although it gives a plausible approximation to its energy [35]. It is subject to quantum fluctuations, more important for smaller values of effective spins. These fluctuations may steer the ground state to the RVB segment. This type of state had been assumed on the experimental grounds for a series of halocuprate compounds [36,37]. Corresponding *phases* are assumed to exist at extremely low temperatures. The most spectacular early example as well as fairly established experimentally had been provided by the NiGa_2S_4 compound featuring a two-dimensional triangular arrangement of $S = 1$ effective electronic spins residing in the d-shells of the Ni ions [38].

4.3

Formal Constructs

The very successful idea to describe benzene in terms of RVB [13] had been later [12] applied to the description of metals. The result was a very counter-intuitive model of a metal that was in apparent contradiction with common sense, experiments, and the band theory. This idea was shortly forgotten and only decades later, Anderson proposed to apply it in a study of the Heisenberg model on triangular lattice [39], where the dominance of singlets was justified by the frustration. Soon after the discovery of high-temperature superconductivity (high- T_c), Anderson has reformulated the RVB ideas proposing a wave function *Ansatz* [40,41]. This wave function became an object of intense studies both numerical and analytical, using a number of approximations. Below we describe three approaches to tackle this wave function. These are (i) a numerically exact

variational Monte Carlo study of the RVB wave function; (ii) the formalism allowing for calculation of approximate energy of an RVB (spin-liquid) state, namely, the auxiliary-boson theory; and (iii) its limiting case at the half-filling important for insulating systems with frustrating exchange interactions.

4.3.1

Hückel, Néel, and RVB States of Polyene

The simplest model illustrating the idea of the (resonating) valence bonds in infinite systems (aka “solids”) is the model of an N -site long planar hydrocarbon molecule – polyene (Figure 4.6). The (Hückel) Hamiltonian for it in general case reads:

$$H = -t \sum_{n,\sigma} (c_{n\sigma}^\dagger c_{n+1\sigma} + c_{n+1\sigma}^\dagger c_{n\sigma}). \quad (4.8)$$

It is habitually expressed in terms of the creation operators $c_{n\sigma}^\dagger$ introduced above and their Hermitian conjugates $c_{n\sigma}$. As the creation operators increase the number of electrons in the system by 1, their Hermitean conjugates respectively reduce the number of electrons in the system by 1, thus being destruction (annihilation) operators. The annihilation operator applied to the vacuum state $|0\rangle$ with no electrons yields zero. This is the basis of all calculations that can be performed in the so far informally described second quantization technique. The electronic structure problem for polyene with the Hamiltonian (Eq. (4.8)) can be easily solved by transforming the fermionic operators from coordinate representation to the (quasi)momentum (or wavenumber) one:

$$a_{k\sigma} = \frac{1}{\sqrt{N}} \sum_n \exp(-ikn) c_{n\sigma},$$

$$k = \frac{2\pi}{N} j, \quad j \in \left[-\frac{N}{2} + 1, \frac{N}{2}\right],$$

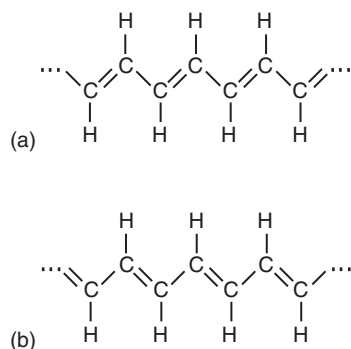


Figure 4.6 Two resonance structures of infinite polyene. (Reprinted with permission from Ref. [42].)

for each spin component σ . Such a transformation leads to the quasi-particle spectrum as follows:

$$\varepsilon_{k\sigma} = -2t \cos k, \quad (4.9)$$

so that the hopping Hamiltonian acquires the diagonal form:

$$H_p = \sum_{k,\sigma} \varepsilon_{k\sigma} a_{k\sigma}^\dagger a_{k\sigma} = \sum_{k,\sigma} \varepsilon_{k\sigma} \hat{n}_{k\sigma}, \quad (4.10)$$

($\hat{n}_{k\sigma}$ is the number of particles operator referring to those occupying the state with quasi-momentum – wavenumber – k and spin projection σ .)

The polyene contains N sites that is $2N$ spin-orbital states of which only N with the lowest energies have to be filled by N electrons in the ground state. These are the orbitals with $|k| < k_F = \pi/2$. Thus, the ground state of the N -site polyene is a Slater determinant (the product sign is an abbreviation of the above-mentioned string of the creation operators):

$$\Psi = \prod_{|k| < k_F, \sigma} a_{k\sigma}^\dagger |0\rangle. \quad (4.11)$$

The wave numbers k are distributed in the interval $[-\pi, \pi]$ of length 2π that play the role of the Brillouin zone in this case. In the case of an infinite (or at least very long) chain, the summation in (4.10) becomes an integral and the ground state energy is $-(4/\pi)\beta$ (per electron) to be compared with $-\beta$ – the similar quantity for a system of isolated bonds like those depicted in Figure 4.6a. We see that the energy of the resonance stabilization counted per electron is somewhat smaller in polyene: $-((4/\pi) - 1)t$, than in benzene: $-(t/3)$.

Turning to the description of the polyene with use of the Heisenberg Hamiltonian, we notice that the Néel state acquires the energy of $-J/4$ per spin, whereas the ground state of two coupled $1/2$ spins is $-3J/4$, which produces an amount of $-3J/8$ per spin³⁾: a considerable energy gain with respect to the Néel state even without any true resonance (the singlets in either of the Kekulé-like structures in Figure 4.6 remain isolated; the second structure restoring the symmetry does not in fact resonate with the first one, like K_1 and K_2). This reasoning shows that even the components of the RVB state have lower energy than the magnetically ordered state in one dimension. However, this conclusion reverts when applied to a simple square lattice with antiferromagnetic interactions between nearest neighbors. In it the Néel state is preferable ($-J/2$ per spin, whereas the isolated singlets produce as previously $-3J/8$ per spin). This allows one to think that in the lattices of intermediate effective coordination (e.g., featuring frustration), the magnetically ordered and RVB states can compete. Indeed, in graphene represented in Figure 4.7, each atom bears as average $3/2$ bonds that produce the energy of $-3J/8$ per spin in its hypothetical Néel state – equal to that of the RVB component states produced by either of the bond distributions (Figure 4.7). Thus, it is not surprising that an RVB state of graphene had

3) The same amounts are valid for the benzene molecule.

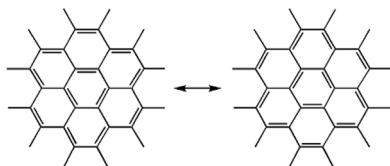


Figure 4.7 Two equivalent (resonating) configurations of valence bonds in the π -system of graphite monolayer (graphene).

been detected numerically [43] (see below). The example of triangular lattice is even more spectacular. In the latter, each site has six nearest neighbors that produce three bonds per site. However, the frustration prevents the usual antiferromagnetic ordering of the $1/2$ -spins when the mean value of their scalar product equals to $-1/4$. Instead of that a spiral ordered state is formed where the spins are placed in the plane and the neighbor ones form angles of 120° and 240° producing the mean value of the scalar product of the spin operators of $-1/8$. This as well results in an estimate of the energy of such magnetically ordered state of $-3J/8$ per spin degenerate with one of the valence bond ones.

4.3.2

Trial Variational RVB Wave Function

As proposed originally by Anderson, the RVB wave function is essentially a many-body state. It is in general difficult to evaluate analytically the expectation value of energy in such a state. Without employing any approximation, it could only be evaluated numerically. The most widespread technique applied for such studies is variational Monte Carlo (VMC) minimizing the variational energy with stochastic bias.

Before discussing the RVB wave function, it is worth to discuss once again the wave function – Hamiltonian dualism typical for the variational methods. A wave function with a fixed structure and depending on a number of parameters is assumed to approximate the true ground state of a quantum system. The expectation value of the Hamiltonian over this wave function, called (fixed form) variational or trial wave function, is minimized as a function of its parameters, which are called variational parameters (VPs). Subsequently, at minimum, the properties of the least energy variational wave function can be analyzed, thanks to its known structure. Two variational wave functions can be easily compared based on their expectation values. It is clear that a variational wave function can only exhibit features prescribed by its structure. On the other hand, the impossibility to gain energy by introducing a new VP in the trial wave function (e.g., superconductivity) can be used as an indication to rule out the possibility of the corresponding *order parameter* (in variance with VPs, OPs are observable physical quantities and do not necessarily coincide with the VPs) in a given system. In this sense, the RVB wave function was proposed to explain several properties of high- T_c superconductors, while the very properties of the wave function

are a subject of active studies nowadays. The Hamiltonian under consideration can vary from Hubbard, t - J , t - U - J , and so on, which fixes the optimal values of VPs. In this setting, the wave function becomes more important than the exact form of the Hamiltonian. The variational approach was shown to correctly reproduce both the weak [44,45] and the strong [46] coupling limits of the Hubbard model.

A typical VMC problem eventually leading to an RVB state consists in searching by, for example, the stochastic minimization methods for the best wave function of the form:

$$|\Psi\rangle = A\hat{P}_N\hat{P}_J\hat{P}_G|\Psi_{\text{BCS}}\rangle, \quad (4.12)$$

where A is a normalization factor, $|\Psi_{\text{BCS}}\rangle$ is a Bardeen–Cooper–Schieffer (BCS) wave function written either as

$$|\Psi_{\text{BCS}}\rangle = \prod_k \left(u_k + v_k a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger \right) |0\rangle \quad (4.13)$$

or equivalently:

$$|\Psi_{\text{BCS}}\rangle = \prod_{k,\sigma} \left(u_k a_{k\sigma} - 2\sigma v_k a_{-k-\sigma}^\dagger \right) |0\rangle \quad (4.14)$$

using $\hat{P}_G$:

$$\hat{P}_G = \prod_i \left(1 - \alpha_0 \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \right), \quad (4.15)$$

the “partial” Gutzwiller projector since it removes the double occupancy not completely, but only to the extent stipulated by the variation parameter α_0 , and the Jastrow factor $\hat{P}_J$:

$$\hat{P}_J = e^{-\alpha_1 \sum_{\langle ij \rangle} \hat{n}_i \hat{n}_j - \alpha_2 \sum_{\langle\langle ij \rangle\rangle} \hat{n}_i \hat{n}_j - \dots}, \quad (4.16)$$

where “...” stands for the summation over next, next-next, and so on nearest neighbor sites (i.e., all those possible on a finite-size sample) applied to suppress the charge density fluctuations at longer distances. In the second form of the BCS wave function, one easily recognizes a single Slater determinant built of (quasi)particles representing superposition of electrons and holes, so that the resulting BCS function does not have definite number of electrons. This is restored by the projection operator $\hat{P}_N$ onto a fixed number of particles. The Slater determinant form of the BCS function considerably simplifies the calculations. On the other hand, it can be easily shown that applying the $\hat{P}_N$ projection operator to the BCS function breaking the particle conservation symmetry produces precisely an RVB-like state. We show here an exemplary derivation to give the reader a flavor of calculations used in our days [47,48]. We start from the BCS function and first factorize the constant terms for each k :

$$\prod_k \left(u_k + v_k a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger \right) |0\rangle = \left(\prod_k u_k \right) \prod_k \left(1 + \frac{v_k}{u_k} a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger \right) |0\rangle, \quad (4.17)$$

where the numerical coefficients u_k, v_k are subject to the normalization condition and can be determined in the single-determinant approximation. Nilpotence of the fermion operators allows transforming this expression beyond recognition. Indeed, the functions of operators are defined as Taylor series of analytic functions where the “numeric” argument x is replaced by an operator. Due to nilpotence of the fermion creation operators (its square and in the row all higher powers are vanishing), the following is true:

$$\left(1 + \frac{v_k}{u_k} a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger\right) = \exp\left(\frac{v_k}{u_k} a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger\right) \quad (4.18)$$

Moreover, the operator products $a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger$ for different values of k commute with each other so that we can use the fact that the product of exponents is the exponent of the sum of their powers:

$$\prod_k \left(1 + \frac{v_k}{u_k} a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger\right) = \prod_k \exp\left(\frac{v_k}{u_k} a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger\right) = \exp\left(\sum_k \left[\frac{v_k}{u_k} a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger\right]\right) \quad (4.19)$$

To ensure the singlet character of the original BCS state, the coefficients u_k, v_k must be even functions of k . Then returning from the wavenumber (k) to the site representation, we get

$$\sum_k \left[\frac{v_k}{u_k} a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger\right] = \frac{1}{2} \sum_{n,m} w_{nm} (c_{n\uparrow}^\dagger c_{m\downarrow}^\dagger - c_{n\downarrow}^\dagger c_{m\uparrow}^\dagger), \quad (4.20)$$

where

$$w_{nm} = \frac{1}{N} \sum_k \frac{v_k}{u_k} \exp(ik(n-m)).$$

We see precisely the singlet pair states like those entering as multipliers in the Rumer basis states for the benzene RVB wave function Eq. (4.1). Inserting the sum of the singlet pair states back in the exponent, we get

$$|\Psi_{\text{BCS}}\rangle = \left(\prod_k u_k\right) \exp\left[\frac{1}{2} \sum_{n,m} w_{nm} (c_{n\uparrow}^\dagger c_{m\downarrow}^\dagger - c_{n\downarrow}^\dagger c_{m\uparrow}^\dagger)\right]. \quad (4.21)$$

Taylor expansion of the exponent contains all powers, that is, it is the superposition of the states with all numbers of particles. The projection of such a state on a specified number of particles is obtained by simply taking the term of the corresponding power from that expansion:

$$\hat{P}_N |\Psi_{\text{BCS}}\rangle = \frac{1}{(N/2)!} \left(\prod_k u_k\right) \left(\frac{1}{2} \sum_{n,m} w_{nm} (c_{n\uparrow}^\dagger c_{m\downarrow}^\dagger - c_{n\downarrow}^\dagger c_{m\uparrow}^\dagger)\right)^{N/2} |0\rangle$$

The Gutzwiller projection operator then takes care about removing the double site occupancies.

This way of doing things is a specific example of a very general trick: first building a Slater determinant with orbitals of broken symmetry (in this case, the

BCS formed of the states being not the particle states, but partially particle, partially hole) and then projecting such broken-symmetry many-electron state on the correct symmetry. This trick is particularly useful since it frequently happens that different components having themselves broken symmetry are not coupled with each other and thus only one of them, namely, a broken symmetry Slater determinant itself, suffices for the energy determination.

Now we exemplify the application of the complete numeric VMC method by considering an extended t - U - J model in two dimensions:

$$\begin{aligned} \hat{H} = & -t \sum_{\langle ij \rangle} \sum_{\sigma} \left(c_{i\sigma}^{\dagger} c_{j\sigma}^{\dagger} + H.c. \right) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \\ & + J \sum_{\langle ij \rangle} \left(S_i \cdot S_j - \frac{1}{4} \hat{n}_i \hat{n}_j \right) + V \sum_{\langle ij \rangle} \hat{n}_i \hat{n}_j, \end{aligned} \quad (4.22)$$

where, in addition to the on-site repulsion U , we add a nearest-neighbor spin-exchange and a charge-repulsion term, with strengths J and V , respectively. The latter nearest-neighbor interactions compete, J favoring a singlet pairing away from half-filling while V opposes it. For $V = 0$ and U strictly equal to ∞ , (4.22) reduces to the standard t - J model, which also corresponds to the large U limit of the pure Hubbard model, in which case $J \rightarrow 4t^2/U$. However, contrary to the latter, model (4.22) for $J > V$ is undoubtedly a superconductor at weak coupling (U , V , and J all much smaller than t) also in the Hartree-Fock approximation. For this reason, model (4.22) is more suitable to address electron-electron correlation effects on d-wave superconductivity. Moreover, since V scales charge-density while J spin-density operators, the presence of both gives the opportunity to test the effect of U on charge and spin.

Numerical optimization of the mean value of Eq. (4.22) over the wave function $|\Psi\rangle$ of the form Eq. (4.12) reveals the enhancement of the superconducting correlations (originating from $|\Psi_{\text{BCS}}\rangle$) through the attraction in the Cooper channel coming from the Heisenberg term) at large on-site repulsion U due to suppression of the local charge fluctuations (thanks to Gutzwiller projection) and long-range charge ones (thanks to Jastrow factors). These superconducting correlations, however, do not necessarily lead to superconductivity itself, since the mobility of charge carriers is heavily damped by U . Moreover, at half-filling, and sufficiently large U , the system undergoes a transition to the Mott insulating state, although retaining sizable superconducting fluctuations. The combination of features occurring in this state is the ideal implementation of the Anderson's RVB ideas.

At small doping δ , the system becomes a narrow (proportional to δ) band metal featuring superconducting fluctuations. A further increase of δ enhances the superconductivity with an optimal $\delta_{\text{opt}} \approx 0.16$ comparable to the optimal doping in cuprates. It can be seen that spin and charge interactions (J and V , respectively) differently influence the superconducting correlations at large U (see Figure 4.8). In the weak coupling limit, it can be shown that both V and J contribute at the same order of magnitude to the attraction in the superconducting channel (formation of Cooper pairs). That is why, if $J > 0$ and $V < 0$ that is

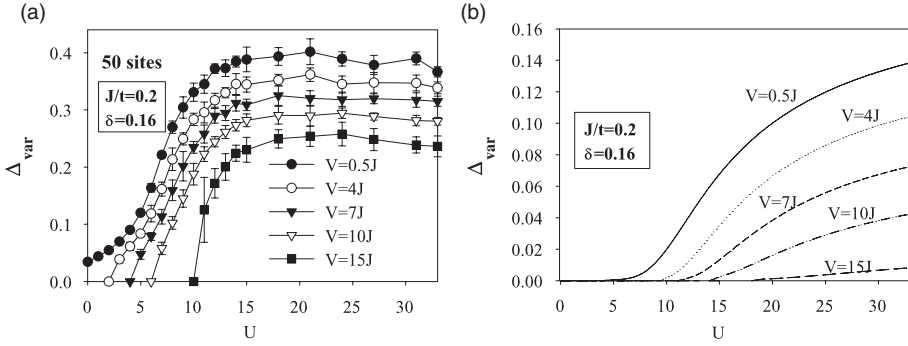


Figure 4.8 Variational gap as function of U for different values of V within variational Monte Carlo (a) and Gutzwiller approximation (b). (Reproduced with permission from Ref. [49]. Copyright 2003, American Physical Society.)

compete, then at $V \sim J$ the superconductivity vanishes. This is not the case in the strong coupling limit (large U and V) when even an order of magnitude larger V is unable to destroy the superconducting correlations (Δ_{var} in Figure 4.8). It happens since at large U the interactions J , V and the kinetic energy acquire different renormalizations: J remains almost unchanged, V scales down by a factor of δ^2 , while $t \rightarrow t\delta$. Since the interactions enter the BCS gap equations multiplied by the density of states at Fermi level $\rho^* \sim 1/(t\delta)$, we indeed obtain that $\rho^* V \rightarrow \delta V/t$, while $\rho^* J \rightarrow J/(t\delta)$. It follows that large on-site repulsion U enhances spin-exchange-generated superconductivity by a factor of $1/\delta$, while suppressing density-attraction-generated one by a factor of δ .

Figure 4.8 also suggests that a qualitative analysis of a doped RVB state can be made by using a so-called Gutzwiller approximation. In this approach, the effect of large U is taken into account by ascribing to each term of (4.22) a renormalization factor depending on δ from very beginning (for more details, see Ref. [47]). Such a renormalization factor is determined on the basis of simple combinatorial considerations [49,50].

As shown in Ref. [49], the VP Δ_{var} is not to be confused with the true superconducting order parameter in RVB states (Δ_{LRO}) defined through the long-range four-fermion correlation function f :

$$\Delta_{\text{LRO}} = \frac{1}{2} \sqrt{f - f_{\text{norm}}},$$

and

$$f = \lim_{\Delta \rightarrow \infty} \sum_{\sigma, \sigma'} \left(c_{r, \sigma}^\dagger c_{r \pm 1, -\sigma}^\dagger c_{r + \Delta \pm 1, -\sigma'} c_{r + \Delta, \sigma'} \right).$$

The OP Δ_{LRO} goes to zero as $\delta \rightarrow 0$ and $U \rightarrow \infty$, due to evanescence of electron mobility in that case (f_{norm} stands for the same correlation function as f , but calculated in the normal state at $\Delta_{\text{var}} = 0$). It follows that an insulating RVB state is not identical to a superconductor, although has sizable short-range

superconducting correlations without the phase coherency, ensuring its unique properties. It is worth mentioning that a similar approach, involving an RVB-derived antisymmetrized geminal power with the Jastrow factor variational wave function, was also applied at the *ab initio* level to a number of carbon-based molecules (C_2 and C_6H_6) with the conclusions extending to graphene [51], which confirm the possibility of the RVB states in these systems.

4.3.3

Auxiliary-Boson Theory

Numerical results obtained for models with finite numbers of sites and electrons are useful, but do not allow to derive general statements. These latter require analytical treatment that can be performed only under additional assumptions. When speaking about RVB states, one cannot avoid mentioning (and using) the auxiliary-boson theory (ABT), also called slave-boson theory. Here, we briefly sketch its formulation for the case of the single-band t - J model. We refer the readers, interested in learning more details of ABT and its generalizations, to the multiorbital case to the dedicated reviews and book chapters [48,52,53].

Within the ABT, one usually needs to reduce the contribution of the ionic (doubly occupied) configurations in the ground state steering the solution into homeopolar subspace. This is done by moving the restrictions on the functional (sub)space from the wave function to the (effective) Hamiltonian. In the most general (VMC) setting, the reduction of the ionic configurations is in a direct way done by the above $\hat{P}_G$, projection operator factor. Comparable effect is achieved by the replacement

$$\begin{aligned} c_{i\sigma}^\dagger &\rightarrow \tilde{c}_{i\sigma}^\dagger = c_{i\sigma}^\dagger (1 - \hat{n}_{i-\sigma}) \\ c_{i\sigma} &\rightarrow \tilde{c}_{i\sigma} = c_{i\sigma} (1 - \hat{n}_{i-\sigma}) \end{aligned}$$

performed on the level of the electronic variables. This replacement ensures that the double occupancy is not accessible through the action of the Hamiltonian itself. The problem is that the “tilded” operators do not satisfy the Fermi anti-commutation relations. Nevertheless, the above replacement represents a correct idea: that of renormalizing the original Fermi operators through a multiplier. The ABT method develops these observations by introducing the spin and charge degrees of freedom of each electron explicitly as separate variables. The electron destruction operator $c_{i\sigma}$ is expressed as

$$c_{i\sigma} = b_i^\dagger f_{i\sigma}, \quad (4.23)$$

where $f_{i\sigma}$ is assigned Fermi and $b_i^\dagger$ Bose statistics, respectively, are dubbed a spinon $f_{i\sigma}$ and a holon b_i operators. So redefined operators $c_{i\sigma}$ do not automatically obey the fermionic commutation relation: $c_{i\sigma}^\dagger c_{i\sigma} + c_{i\sigma} c_{i\sigma}^\dagger = 1$, which is recovered by imposing the local constraints:

$$\sum_{\sigma} f_{i\sigma}^\dagger f_{i\sigma} + b_i^\dagger b_i = 1, \quad (4.24)$$

at each site i . It can be easily shown that once (4.24) is fulfilled, the mapping from $c_{i\sigma}$ to $f_{i\sigma}$ and b_i is exact [54–58]. In these new variables, the Hamiltonian of the t – J model rewrites:

$$H_{ab} = - \sum_{\langle ij \rangle, \sigma} \left(t_{ij} f_{i\sigma}^\dagger f_{j\sigma} b_j^\dagger b_i + \text{h.c.} \right) + H_{\text{ex}} - \mu \sum_{i, \sigma} f_{i\sigma}^\dagger f_{i\sigma} \\ - \sum_i \lambda_i \left(\sum_{\sigma} f_{i\sigma}^\dagger f_{i\sigma} + b_i^\dagger b_i - 1 \right),$$

where we included local constraints (4.24) with Lagrange multipliers λ_i and the chemical potential term, while H_{ex} is given by

$$H_{\text{ex}} = J \sum_{\langle ij \rangle} \left[\frac{1}{2} \left(f_{i\uparrow}^\dagger f_{i\downarrow} f_{j\downarrow}^\dagger f_{j\uparrow} + f_{i\downarrow}^\dagger f_{i\uparrow} f_{j\uparrow}^\dagger f_{j\downarrow} \right) \right. \\ \left. + \frac{1}{4} \left(f_{i\uparrow}^\dagger f_{i\uparrow} - f_{i\downarrow}^\dagger f_{i\downarrow} \right) \left(f_{j\uparrow}^\dagger f_{j\uparrow} - f_{j\downarrow}^\dagger f_{j\downarrow} \right) \right. \\ \left. + \frac{\alpha}{4} \left(f_{i\uparrow}^\dagger f_{i\uparrow} + f_{i\downarrow}^\dagger f_{i\downarrow} \right) \left(f_{j\uparrow}^\dagger f_{j\uparrow} + f_{j\downarrow}^\dagger f_{j\downarrow} \right) \right].$$

In the above formula, the contributions from bosonic variables of the type $(1 + b_i^\dagger b_i) \times (1 + b_j^\dagger b_j)$ were neglected since $(1 + b_i^\dagger b_i)(1 + b_j^\dagger b_j) \approx 1$. If $\alpha = -1$, H_{ex} can be rewritten in a more compact way stressing the singlet correlations:

$$H_{\text{ex}} = -\frac{J}{2} \sum_{\langle ij \rangle} \left(f_{j\uparrow}^\dagger f_{i\uparrow} + f_{j\downarrow}^\dagger f_{i\downarrow} \right) \left(f_{i\uparrow}^\dagger f_{j\uparrow} + f_{i\downarrow}^\dagger f_{j\downarrow} \right).$$

The mean-field ABA derives from the above by introducing the following averages serving as VPs of the method:

$$\chi_\tau = \langle f_{i\sigma}^\dagger f_{i+\tau\sigma} \rangle, \\ \eta_\tau = \langle b_i^\dagger b_{i+\tau} \rangle, \\ \Delta_\tau^* = \langle f_{i\uparrow}^\dagger f_{i+\tau\downarrow} \rangle. \quad (4.25)$$

Here, the first two VPs are usually called fermion and boson bond order parameters, respectively, while the third one – the RVB order parameter. A usual simplification made in the ABA is to replace the local constraints (Eq. (4.24) by the global ones by setting equal all Lagrange multipliers: $\lambda_i = \lambda$, so that λ starts playing the role of chemical potential for (auxiliary) bosons. After that the auxiliary boson approximate (ABA) mean-field Hamiltonian becomes

$$H_{\text{ABMF}} = \sum_{k, \sigma} \epsilon_k f_{k\sigma}^\dagger f_{k\sigma} + \sum_k \omega_k b_k^\dagger b_k - \sum_k \left(F_k f_{k\uparrow}^\dagger f_{-k\downarrow}^\dagger + \text{h.c.} \right) + H_0, \quad (4.26)$$

where H_0 is a c -number:

$$H_0 = \frac{J}{2}(3 + \alpha)(\chi_x^2 + \chi_y^2) + \frac{J}{2}(3 - \alpha)(|\Delta_x|^2 + |\Delta_y|^2) \\ + 4 \sum_{\tau} t_{\tau} \eta_{\tau} \chi_{\tau} - (\mu_f + \lambda) \delta - \frac{J\alpha}{2}(1 - \delta)^2.$$

and the following notations are introduced:

$$\begin{aligned} \varepsilon_k &= -2 \sum_{\tau} t_{\tau} \eta_{\tau} \cos k_{\tau} - \frac{J}{2}(3 + \alpha)(\chi_x \cos k_x + \chi_y \cos k_y) - \mu_f, \\ \mu_f &= \mu + \lambda - \alpha(1 - \delta)J, \\ \omega_k &= -4 \sum_{\tau} t_{\tau} \chi_{\tau} \cos k_{\tau} - \lambda, \\ F_k &= \frac{J}{2}(3 - \alpha)(\Delta_x \cos k_x + \Delta_y \cos k_y). \end{aligned}$$

The self-consistency conditions within ABA read as follows:

$$\begin{aligned} \Delta_{\tau} &= \frac{1}{N} \sum_k \frac{F_k}{2E_k} \cos k_{\tau} \tanh \frac{E_k}{2T}, \\ \chi_{\tau} &= -\frac{1}{N} \sum_k \frac{\varepsilon_k}{2E_k} \cos k_{\tau} \tanh \frac{E_k}{2T}, \\ \eta_{\tau} &= \frac{1}{N} \sum_k \frac{\cos k_{\tau}}{e^{\omega_k/T} - 1}, \\ 1 - \delta &= \frac{1}{N} \sum_k \left[1 - \frac{\varepsilon_k}{E_k} \tanh \frac{E_k}{2T} \right], \\ \delta &= \frac{1}{N} \sum_k \frac{1}{e^{\omega_k/T} - 1}. \end{aligned} \tag{4.27}$$

Once the self-consistency is reached, the free energy F per site can be represented:

$$\frac{F}{N} = -2 \frac{T}{N} \sum_k \ln \left(2 \cosh \frac{E_k}{2T} \right) + \frac{T}{N} \sum_k \ln \left(1 - \exp \left(-\frac{\omega_k}{T} \right) \right) + H_0$$

as a sum of entropy contributions of spinons (fermions) and holons (auxiliary bosons) and of the internal energy. Apart from the chemical potentials μ (μ_f), there are three types of VPs: η_{τ} , χ_{τ} , and Δ_{τ} equal for each pair of sites separated by τ . If only $\eta_{\tau}, \chi_{\tau} \neq 0$, while $\Delta_{\tau} = 0$, the system is said to be in the uniform RVB phase (uRVB). If, in addition to η_{τ} and χ_{τ} , also $\Delta_{\tau} \neq 0$, the phase is called a singlet RVB (sRVB) one. Several symmetry choices of the possible solutions should be commented. Since the range of the interaction in the employed Hamiltonian is limited to the next-nearest-neighbor distance, the range of τ in (4.25) does so as well. On a 2D square lattice, τ can be classified according to the lattice symmetries as shown in Table 4.1.

Among other applications, ABT was used in Ref. [43] to describe the graphite individual sheets and graphitic compounds in order to explore the possibility of superconductivity upon doping. The doping was assumed to come from several sources: impurities, intercalation, interlayer coupling, and so on. It was shown

Table 4.1 Classification of nearest-neighbor superconducting order parameter $(\Delta(k_x, k_y))$ and the corresponding phases on a 2D square lattice.

Type	Δ	χ	ϑ
$d_{x^2-y^2}$	$\Delta_y = -\Delta_x$	$\chi_y = \chi_x$	$\vartheta = \pi$
s	$\Delta_y = \Delta_x$	$\chi_y = \chi_x$	$\vartheta = 0$
$s + id_{x^2-y^2}$	$\Delta_y = i\Delta_x$	$\chi_y = \chi_x = 0$	$\vartheta = \frac{\pi}{2}$ ^{a)}
1D	$\Delta_y = 0, \quad \Delta_x \neq 0$	$\chi_y = 0, \quad \chi_x \neq 0$	—
Flux	$\Delta_x = \Delta_y = 0$	$\chi_\tau = \chi_0 e^{i\vartheta_\tau}$	— ^{b)}

Here the angle ϑ is defined as $\Delta_y = e^{i\vartheta} \Delta_x$.

a) In case of $s + id_{x^2-y^2}$ phase, an alternative (and more general) definition of the order parameter reads as $\Delta(k_x, k_y) = s(\cos k_x + \cos k_y) + d(\cos k_x - \cos k_y)$ with two arbitrary complex numbers s and d (see Ref. [59]).

b) More details on flux phase are reported in Refs [48,60].

that the d-wave order parameter is favored over the s-wave one. Moreover, it was shown that the d-wave superconducting solution may also break the time-reversal symmetry, thus opening the possibility to the coexistence with ferroelectricity (charge density waves [61]). However, it is not clear to which extent the results of a mean-field-like theory can be trustfully applied to a quasi-2D material with nonnegligible interaction.

4.4

Mean Field RVB as Applied to the Heisenberg Model

Exactly at half-filling and large U , the Hubbard model reduces to the Heisenberg one. Considering the equations of ABT (4.27), one can easily see significant simplifications in this limit. Indeed, the condition $\delta = 0$ satisfies by the values of energies of auxiliary bosons: $\omega_k \rightarrow \infty$, which induces the self-consistent values for the VPs $\eta_k = 0$. If the exchange interactions resulting from this limit transition are frustrated, then the sought ground state has chances to be an RVB state. The half-filling case, in principle, can be treated within the general formalism, described in the previous chapter. However, we will show here an alternative approach, which starts directly from the Heisenberg model and gives the same results (Figure 4.9).

Starting from the Heisenberg Hamiltonian with the interactions J_τ acting between the sites connected by lattice vectors τ , the Hamiltonian can be written:

$$H = \sum_{i,\tau} J_\tau \mathbf{S}_i \mathbf{S}_{i+\tau}. \quad (4.28)$$

We express each of the spin operators in (4.28) through the effective fermionic (above spinon) operators:

$$\mathbf{S}_i^\gamma = \frac{1}{2} \sum_{\alpha,\beta} \sigma_{\alpha\beta}^\gamma f_{i\alpha}^\dagger f_{i\beta},$$

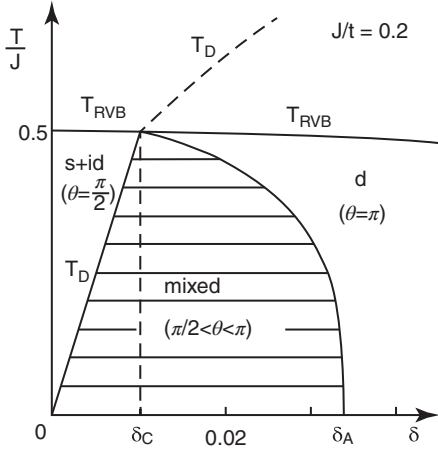


Figure 4.9 The phase diagram of the 2D t - J model on the δ - T plane. Here T_{RVB} and T_D are the onset temperatures of RVB and coherent motion of both spinons and holons, respectively. RVB order parameter is $s + id$, mixed or d type depending on δ and T . (Reprinted with permission from Ref. [62].) Reprinted with permission from [53], Japanese Chemical Society.

where $\sigma_{\alpha\beta}^{\gamma}$ are the Pauli matrices. This ensures that the wave function of the system is squeezed to the subspace of homeopolar configurations from very beginning. Substituting these operators into (4.28), we end up with the four-fermion interaction terms. This Hamiltonian is then solved in the mean-field approximation, assuming the decoupling of the four-fermion products with use of the following normal and anomalous averages:

$$\begin{aligned}\langle f_{i,\alpha}^{\dagger} f_{i+\tau,\beta} \rangle &= \delta_{\alpha,\beta} \xi_{\tau} \\ \langle f_{i,\alpha}^{\dagger} f_{i+\tau,\beta}^{\dagger} \rangle &= 2\alpha \delta_{\alpha,-\beta} \Delta_{\tau}^*.\end{aligned}$$

With these notations, the average of (4.28) becomes

$$\langle H \rangle = 3N \sum_{\tau} J_{\tau} (\xi_{\tau}^2 + |\Delta_{\tau}|^2).$$

The corresponding mean-field Hamiltonian transformed to the k -space reads as follows:

$$\begin{aligned}H_{\text{MF}} &= 3N \sum_{k,\tau} J_{\tau} \cos k\tau \left[\xi_{\tau} (f_{k,\uparrow}^{\dagger} f_{k\uparrow} - f_{-k,\uparrow}^{\dagger} f_{-k\uparrow}^{\dagger}) + \Delta_{\tau}^* f_{-k,\downarrow}^{\dagger} f_{k\uparrow} + \Delta_{\tau} f_{k,\uparrow}^{\dagger} f_{-k,\downarrow}^{\dagger} \right] \\ &+ 3N \sum_{k,\tau} J_{\tau} \xi_{\tau} \cos k\tau - \langle H \rangle.\end{aligned}\quad (4.29)$$

It can be rewritten in a more compact way by introducing the Nambu spinors:

$$\Psi_k = \begin{pmatrix} f_{k,\uparrow} \\ f_{-k,\downarrow}^{\dagger} \end{pmatrix}; \quad \Psi_k^{\dagger} = \begin{pmatrix} f_{k,\uparrow}^{\dagger} & f_{-k,\downarrow} \end{pmatrix}.$$

Then in the Nambu notations, the first row of H_{MF} becomes

$$= \sum_k \Psi_k^\dagger H_k \Psi_k,$$

where H_k are 2×2 matrices defined as

$$H_k = \begin{pmatrix} \xi_k & \Delta_k \\ \Delta_k^* & -\xi_k \end{pmatrix},$$

with

$$\begin{aligned} \xi_k &= 3 \sum_\tau J_\tau \xi_\tau \cos k\tau, \\ \Delta_k &= 3 \sum_\tau J_\tau \Delta_\tau \cos k\tau. \end{aligned}$$

H_k 's are easily diagonalized, immediately giving the eigenvalues' spectrum: $\mp E_k$, with $E_k = \sqrt{\xi_k^2 + |\Delta_k|^2}$ and the eigenvectors' matrices:

$$S_k = \begin{pmatrix} u_k & v_k \\ -v_k^* & u_k \end{pmatrix},$$

where

$$\begin{aligned} u_k &= \sqrt{\frac{E_k - \xi_k}{2E_k}}, \\ v_k &= \frac{\Delta_k}{\sqrt{2E_k(E_k - \xi_k)}}. \end{aligned}$$

In terms of the eigenvectors of H_k (we denote them Φ_k : $\Phi_k = S_k \Psi_k$, $\Phi_k^\dagger = (\alpha_k^\dagger, \beta_k^\dagger)$), the first row of H_{MF} assumes the canonical form:

$$H_{\text{MF}} = \sum_k \Phi_k^\dagger \begin{pmatrix} -E_k & 0 \\ 0 & E_k \end{pmatrix} \Phi_k = \sum_k E_k (\beta_k^\dagger \beta_k - \alpha_k^\dagger \alpha_k).$$

The population of the eigenstates $|\alpha_k\rangle$ and $|\beta_k\rangle$ obey the Fermi–Dirac statistics at temperature T and energies $\mp E_k$ respectively. To close the self-consistency conditions, we note that

$$\begin{aligned} \xi_\tau &= \langle f_{i,\alpha}^\dagger f_{i+\tau,\alpha} \rangle = -\frac{1}{N} \sum_k (u_k^2 - v_k^2) \left\{ f\left(-\frac{E_k}{T}\right) - f\left(\frac{E_k}{T}\right) \right\} \\ 2\alpha\delta_{\alpha,-\beta}\Delta_\tau^* &= \langle f_{i,\alpha}^\dagger f_{i+\tau,\beta}^\dagger \rangle = \frac{1}{N} \sum_k u_k v_k \left\{ f\left(-\frac{E_k}{T}\right) - f\left(\frac{E_k}{T}\right) \right\}. \end{aligned}$$

(f stands for the Fermi–Dirac distribution function). After further simplifications, the self-consistency equations becomes

$$\xi_\tau = \frac{1}{2N} \sum_k e^{ik\tau} \frac{\xi_k}{E_k} \tanh \frac{E_k}{2T}, \quad (4.30)$$

$$\Delta_\tau = \frac{1}{2N} \sum_k e^{ik\tau} \frac{\Delta_k}{E_k} \tanh \frac{E_k}{2T}. \quad (4.31)$$

At this point, a number of observations have to be made. First of all, it is surprising to see how a system of fermions having kinetic part and superconducting correlations emerges out from a purely insulating spin exchange model. The answer to this riddle is that the fermions meant by this theory are not the original physical charged electrons, rather the fictitious spinons bearing no charge and thus carrying no current. Second, if the number M of different couplings J_τ is less than or equal to 3, it is convenient to introduce the SU_2 invariant solution. Namely, such a solution that

$$\xi_\tau \xi_{\tau'} + \Delta_\tau \Delta_{\tau'}^* = 0, \quad \forall \tau \neq \tau'.$$

In this way, E_k becomes

$$E_k = 3 \sqrt{\sum_{\tau} J_{\tau} (\xi_{\tau}^2 + |\Delta_{\tau}|^2) \cos^2 k\tau}.$$

Third, if we have several Heisenberg couplings along different directions τ_i , $i = 1, \dots, M$, how many independent parameters ξ_i, Δ_i can we have? Taking into account that ξ_i 's are real, while Δ_i 's may, in general, be complex, one would naively assume a total of $3M$ independent parameters. However, it can be easily demonstrated that at each τ_i , instead of three independent parameters there is only one independent parameter $\zeta_i = \sqrt{\xi_i^2 + |\Delta_i|^2}$. Indeed, if we set $\xi_i = \zeta_i \cos \theta_i$ and $\Delta_i = \zeta_i e^{i\phi_i} \sin \theta_i$, we immediately see that two equations (4.30) and (4.31) reduce to a single one for ζ_τ not depending on ϕ_i, θ_i :

$$\zeta_\tau = \frac{3J_\tau}{2N} \sum_k \frac{\cos^2 k\tau}{E_k} \tanh \frac{E_k}{2T}. \quad (4.32)$$

Here, we used the orthogonality of $\cos k\tau$ and $\sin k\tau$ functions over the Brillouin zone and the positiveness and periodicity of $(1/E_k) \tanh(E_k/2T)$ with a period of at least 2π in units of inverse lattice spacing. Summarizing, we have demonstrated that the number of independent parameters is actually M instead of $3M$.

Different ζ_τ 's are coupled through E_k so that Eq. (4.32) represents a system of nonlinear equations that admit the solutions with several nonvanishing ζ_τ 's. Such an interoperability between ξ_τ and Δ_τ is due to the fact that the pure isotropic Heisenberg model produces identical contributions to the effective kinetic and superconducting coupling. If the true kinetic energy term (proportional to t) is retained in the Hamiltonian ξ_τ and Δ_τ also remain independent and a usual BCS-type solution recovers for (antiferromagnetic) $J_\tau > 0$ in the t - J model.

As already mentioned, Eq. (4.32) allows for the coexistence of resonating valence bonds in different directions. As was found in Ref. [63] and shown in Figures 4.10 and 4.11, a number of phases can be identified in a 2D Heisenberg model on rectangular lattice with couplings along the nearest neighbors (J_a and J_c) and along the diagonal, corresponding to the next-nearest ones (J_{ac}) – the c - a - ca -model. This model has been recently proposed to describe an important case of copper carbodiimide (CuNCN) – very probably the first material

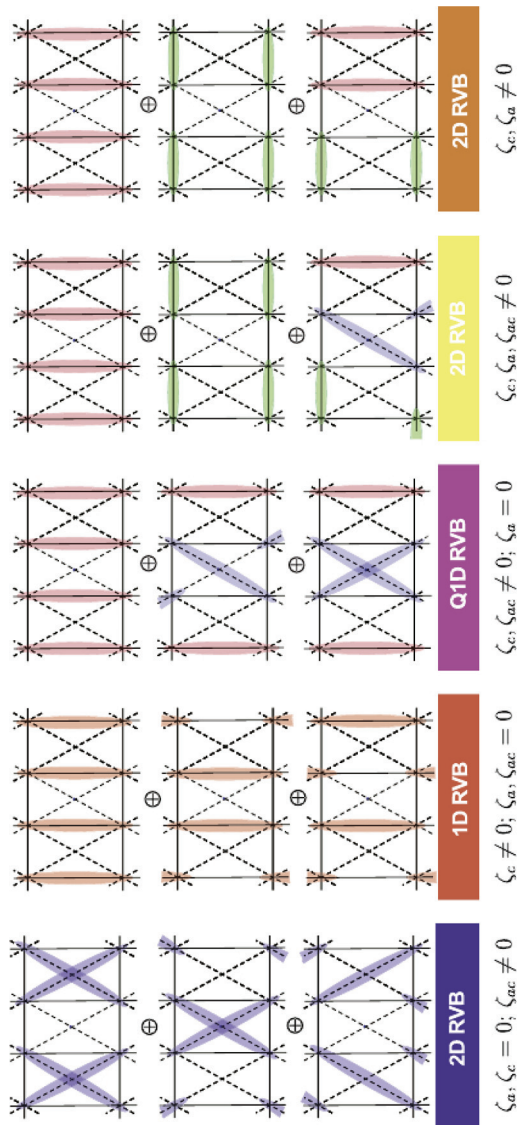


Figure 4.10 Characteristic spin-pairing (valence bond) states of the c - a - ca -model of CuNCN. (Reprinted with permission from Ref. [63].)

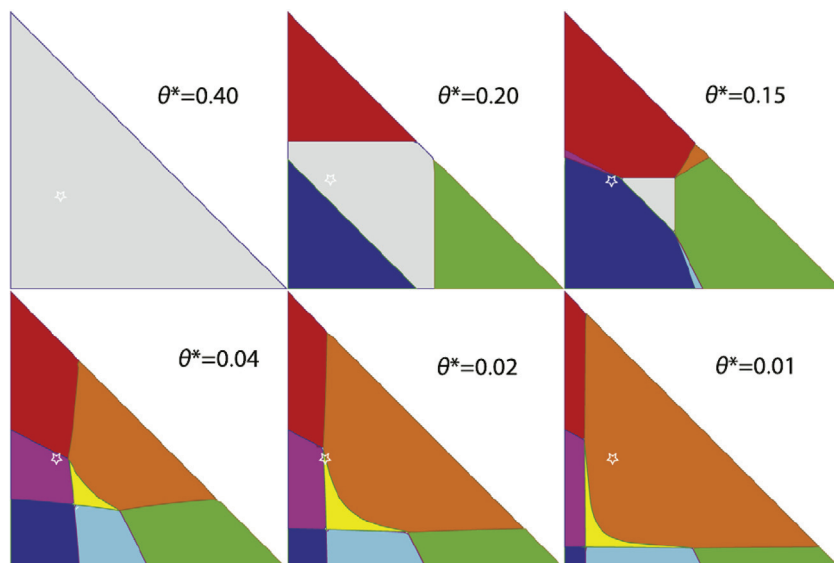


Figure 4.11 Parameter phase diagrams for the c - a - ca -RVB model in the high-temperature approximation. The abscissa and ordinate represent the reduced parameters J_a^* and J_c^* ; these parameters, respectively, are equal to unity in the lower right and upper left corners; the entire set of reduced parameters is subject to the condition $J_a^* + J_c^* + J_{ac}^* = 1$. The reduced temperatures θ^* are fractions of $J_a^* + J_c^* + J_{ac}^*$. The color coding for phases is as follows: Curie paramagnetic, with all VPs zero = gray, only one nonvanishing VP = red or green (1D RVB, Pauli paramagnet), = blue for $\zeta_c, \zeta_a, \zeta_{ac} \neq 0$,

respectively; one VP vanishing = magenta, cyan (Q1D-RVB, Pauli paramagnet), = orange for ζ_a , or ζ_c , or $\zeta_{ac} = 0$, respectively—observe the order of the list; yellow codes the phase with three nonvanishing VPs. Orange and yellow phases (2D RVB) feature a combination of the gapped Arrhenius-like temperature dependence of magnetic susceptibility and its linear dependence well below the pseudogap. The small star shows the tentative position of CuNCN on the parameter phase diagram. (Reprinted with permission from Ref. [63]).

featuring the RVB phases already at the room temperature and manifesting rich variety of RVB phases [64,65]. As shown in Figure 4.11, as the temperature lowers, a fixed point on the parameter's phase diagram undergoes a series of phase transitions. This is the case for parameters expected to be realistic for CuNCN (depicted in Figure 4.11 by a star symbol), which successfully describes the unusual physics of CuNCN.

4.5

Discussion and Conclusions

In this chapter, we review the applications of the theory of RVB in chemistry and condensed matter. The idea of constructing the ground-state wave function as a product of singlet states, distributed among the pairs of sites, revealed to be very

fruitful [66–68]. However, a unique distribution of bonds (two-electron singlets) is not always possible, benzene molecule being the best-known example. In such cases the electronic ground state is assumed to be a superposition of numerous individual states with different (equivalent) distributions of the bonding singlets – the resonating valence bond (RV) state. The RVB *Ansatz* first appeared in *organic* chemistry and then spread to the field of frustrated magnets, high- T_c , and lightly doped Mott insulators. This versatility due to its general and intrinsically many-body nature being an advantage is at the same time one of the reasons why this wave function type cannot be treated analytically exactly. There is a fundamental difference between the approximations used in many-body and *ab initio* methods. Namely, the former uses an approximate (effective and simplified) Hamiltonian applied to a (strongly) correlated wave function, while the latter uses an, in principle, exact Hamiltonian (hence the name *ab initio*) at the expense of applying it to a much simpler and “uncorrelated” wave function of the Hartree–Fock (single determinant) type. Quantum chemical setting is somewhat misleading in this respect. The Hamiltonians used there tend to disguise as “exact” and only possible ones being predetermined by the composition and/or structure of the material. It is only partially true: Different *ab initio* basis sets and DFT functionals in reality define different Hamiltonians for the same composition and structure. More important, however, is the diversity of the solutions’ types characteristic for different relations between Hamiltonian’s matrix elements like Eq. (4.7) steering the exact solutions to the areas of the functional space inaccessible for the standard solid-state quantum chemistry codes because of the restricted forms of the trial wave functions implemented in these latter. Some more specific forms of effective model Hamiltonians like Hubbard, t – J , or similar ones looking out fairly arbitrary from the purist quantum chemical point of view, can nevertheless trace the key information about the type of the wave function relevant for the target class of compounds predetermined by the interrelations between matrix elements of the “exact” quantum chemical Hamiltonian. Among these general lines, two types of approaches have been developed in the RVB context and reviewed here: (i) approximate analytical (mean-field auxiliary- (slave)-boson, Gutzwiller approximation) and (ii) numerically exact Variational Monte Carlo one. The models studied are normally the effective t – J , single-band Hubbard, t – J – U , or three-band Hubbard Hamiltonians at different electron counts (fillings). Recently, a tendency to combine both approaches stepped forward, thanks to the variational principle renewing the interest to the RVB ideas in general. This was the possibility to estimate the energy of the RVB states and the relevant order parameters with use of the so-called mean-field RVB, actually a broken symmetry Slater determinants mimicking the structure of the RVB state through its variational parameters at least at half-filling.

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