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Double-valence-fluctuating molecules and superconductivity

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We discuss the possibility of "double-valence-fluctuating" molecules, having two ground-state configurations differing by two electrons. We propose a possible realization of such a molecule, and experimental ways to look for it. We argue that a weakly coupled array of such molecules should give rise to a strong-coupling Shafroth-Blatt-Butler superconductor, with a high transition temperature.

The first theory of superconductivity where electron pairs played an essential role was proposed by Shafroth, Blatt, and Butler.[1] In their picture, electron pairs tightly coupled in real space undergo a Bose condensation to the superconducting state. As is well known, the subsequent BCS theory,[2] with the essentially opposite point of view in which weakly coupled highly overlapping electron pairs form at T_c has been enormously successful in explaining the properties of most known superconductors. Nevertheless, the possibility of very strongly coupled superconductors where the Shafroth-Blatt-Butler picture applies is appealing and has not been ruled out theoretically. In fact, quantum Monte Carlo calculations on one-dimensional models[3–5] clearly show that tightly coupled electron pairs can develop power-law correlations typical of the type of superconducting pairing correlations expected in one-dimensional systems.

In this paper we discuss a possible mechanism to obtain such tightly bound pairs at the molecular level which, when weakly coupled through an intermolecular matrix element would give rise to a strong-coupling superconductor of the type discussed above. The idea is to obtain "negative-U centers" through an electronic excitation mechanism. Such centers have been proposed by Anderson[6] to exist in amorphous semiconductors. In Anderson's and subsequent models, however, the source of the electron-electron attraction is a local electron-phonon interaction. In that case, the pair-hopping matrix element is exponentially suppressed by a Frank-Condon overlap matrix element, and a superconducting state is therefore unlikely. In our model, the effective intermolecular hopping is reduced by an algebraic instead of an exponential factor.

Our model consists of weakly coupled "double valence fluctuating" molecules. Similarly to the case in rare-earth atoms where one can have two electronic valence configurations differing by one electron being degenerate or very close in energy,[7] we envisage a situation where the two degenerate states differ by *two* electrons. We discuss below one possible realization of this idea. It should be pointed out, however, that there well could be other different mechanisms by which this is achieved; in fact, double-valence-fluctuating molecules may already have been observed in organic charge-transfer salts.[8]

Consider a transition-metal atom surrounded by ligands, as shown in Fig. 1. A Hamiltonian that describes the valence electrons of this basic unit in a tight-binding scheme is

$$\begin{aligned} H = {} & \epsilon_{xz} n_{xz} + \epsilon_{yz} n_{yz} + \epsilon_{p_1} n_{p_1} + \epsilon_{p_2} n_{p_2} - \bar{t}(d_{xz}^{\dagger} p_1 + p_1^{\dagger} d_{xz}) \\ & - \bar{t}(d_{yz}^{\dagger} p_2 + p_2^{\dagger} d_{yz}) + \tilde{U} n_{xz} n_{yz} + \bar{U}(n_{xz} n_{zz} + n_{yz} n_{zz}) \\ & + U n_{zz\uparrow} n_{zz\downarrow} , \end{aligned} \tag{1}$$

where d_{xz}, d_{yz}, d_{zz} are d orbitals of the transition-metal atom, and p_1 and p_2 are p orbitals of the neighboring ligands,[9] which hybridize with the transition-metal orbitals d_{xz} and d_{yz}, respectively, through a matrix element $\bar{t}$. For simplicity we will treat the case in which

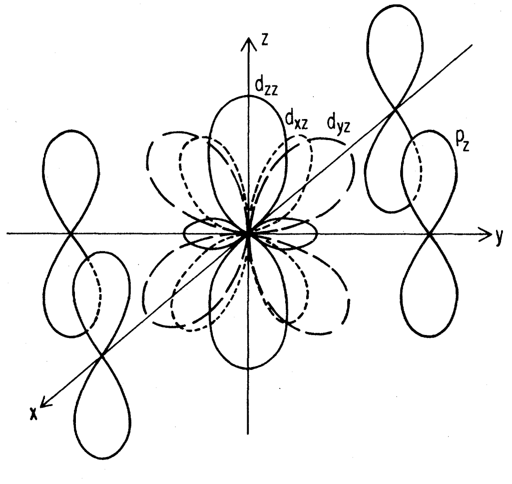

FIG. 1. Schematic view of a transition-metal atom and surrounding ligands. The transition metal d_{xz} orbital (short-dashed line) and d_{yz} (long-dashed line) hybridize with the antisymmetric linear combination of p_z orbitals on neighboring ligands in the x and y directions, respectively, through a matrix element $\bar{t}$.

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$\epsilon p_1 = \epsilon p_2 = \epsilon p$, $\epsilon_{xz} = \epsilon_{yz}$, and only one electron is in each of the d_{xz}-ligand and d_{yz}-ligand orbitals. Including additional electrons does not alter our conclusions. Finally, we assume the d_{zz} orbital overlaps with similar orbitals on neighboring units and carries the conduction electrons. Denoting by $E(n)$ the ground-state energy of one such unit with $n = (n_{zz\uparrow} + n_{zz\downarrow})$ d_{zz} electrons, the "effective Hamiltonian" for the d_{zz} electrons in this unit is

$$\begin{aligned} h_{\rm eff} &= U_{\rm eff} n_{zz\uparrow} + n_{zz\downarrow} - \mu(n_{zz\uparrow} + n_{zz\downarrow}) + c \ , \\ U_{\rm eff} &= E(2) + E(0) - E(1) \ . \end{aligned} \tag{2}$$

It is straightforward to solve for $U_{\rm eff}$ and study its dependence on the parameters of the Hamiltonian Eq. (1). As we will see, in the atomic limit U is larger than $\bar{U}$ and $\tilde{U}$. However, $(U - \bar{U})/U \ll 1$ so that in studying the dependence of $U_{\rm eff}$ on $\bar{t}$, ϵ_p, and ϵ_{xz} it is useful to set $U = \bar{U} = \tilde{U}$. Figure 2 shows the dependence on $\bar{t}$ and $\epsilon = \epsilon_{p_1} - \epsilon_{xz} = \epsilon_{p_2} - \epsilon_{yz}$ for $U = \bar{U} = \tilde{U}$. It can be seen that the Coulomb repulsion is completely screened out for $\bar{t} \to 0$, $\epsilon = \bar{U}$, and would become negative if $\bar{U}$ could exceed U. The basic idea is simply that the first d_{zz} electron pushes the d_{xz} and d_{yz} electrons onto the neighboring p-orbitals, so that the next d_{zz} electron does not feel the U repulsion from the d_{xz} and d_{yz} electrons. It is this highly nonlinear mechanism that opens up the possibility of overcoming the direct Coulomb repulsion U between d_{zz} electrons.

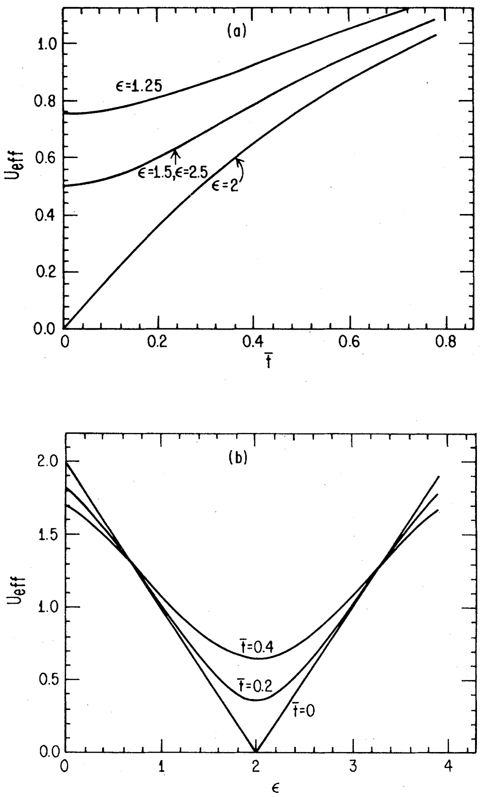

FIG. 2. Effective interaction $U_{\rm eff}$ for the d_{zz} electrons of the unit shown in Fig. 1 with $U = \bar{U} = 2$. (a) Dependence on $\bar{t}$. (b) Dependence on $\epsilon = \epsilon_p - \epsilon_{xz}$. Note that $U_{\rm eff} \geq 0$ the most favorable situation ($U_{\rm eff} = 0$) occurs when $\epsilon = \bar{U}$, $\bar{t} = 0$.

Having seen that $\bar{t} \to 0$ and $\epsilon = \bar{U}$ provide the most favorable conditions, we consider the effective interaction in this limit for $\bar{U} > \tilde{U}$. It has the form

$$U_{\rm eff} = U + \tilde{U} - 2\bar{U} \ . \tag{3}$$

We can obtain the transition-metal d-orbital Coulomb interactions from the appropriate integrals over atomic orbitals:[10]

$$\begin{aligned} U &= (d_{zz} d_{zz} \,|\, e^2/r_{12} \,|\, d_{zz} d_{zz}) = F_0 + 4F_2 + 36F_4 \ , \\ \bar{U} &= (d_{zz} d_{xz} \,|\, e^2/r_{12} \,|\, d_{zz} d_{xz}) = F_0 + 2F_2 - 24F_4 \ , \\ \tilde{U} &= (d_{xz} d_{yz} \,|\, e^2/r_{12} \,|\, d_{xz} d_{yz}) = F_0 - 2F_2 - 4F_4 \ . \end{aligned} \tag{4}$$

The effective interaction, Eq. (3), is then

$$U_{\rm eff} = 2F_2 + 80F_4 \ ,$$

and from calculations based on Slater orbitals for transition metals,[11] one finds $F_4/F_2 \sim 0.7$, so that

$$U_{\rm eff} = 3.6F_2 \ .$$

For Ni, we obtain[12] $U_{\rm eff} \sim 0.69$ eV. This is certainly much smaller than the bare interaction $U \sim 24$ eV, but it is still positive. Thus, the "excitonic mechanism" in our molecule certainly succeeds in screening the Coulomb interaction by a large amount, however, it does not overscreen it. Now Eq. (3) can be written in the form:[13]

$$U_{\rm eff} = \int d^3x \int d^3x' \, [\rho_1(x) - \rho_2(x)] \frac{e^2}{|x - x'|} \times [\rho_1(x') - \rho_3(x')] \ , \tag{5}$$

with $\rho_1 = \rho_{zz}$, $\rho_2 = \rho_{xz}$, and $\rho_3 = \rho_{yz}$. As noted above, this is positive for atomic d orbitals, but it can in principle become negative.[13] Here, however, we will explore a dynamic mechanism for achieving a net attractive interaction.

To incorporate dynamics, we consider two units similar to the one described by Eq. (1) which are coupled by a hopping t_1 between the d_{zz} orbitals. For simplicity, we now neglect the d_{yz} orbital and consider just a d_{xz} orbital hybridized with one ligand in each unit. We again consider the case $U = \bar{U}$, which for a single transition metal atom unit gives a $U_{\rm eff}$ which cannot become negative just as for the case discussed above. However, it turns out that the dynamics of the d_{zz} electrons in the two-unit model can produce a net attractive interaction for realistic parameters. Figure 3 shows the effective interaction for various values of the parameters. The reason that the net interaction can now be attractive is essentially that the excitonic mechanism can still be arranged to be as effective as for the single-site case for appropriate parameters, while the repulsive interaction U is reduced by the dynamical motion of the d_{zz} electrons. The fact that U is greater than $\bar{U}$ does not alter this conclusion. It only slightly reduces the attraction. Note that a crucial parameter is the energy difference $\epsilon_p - \epsilon_{xz}$ between ligand orbital and the transition metal atom xz orbit. This must be in a

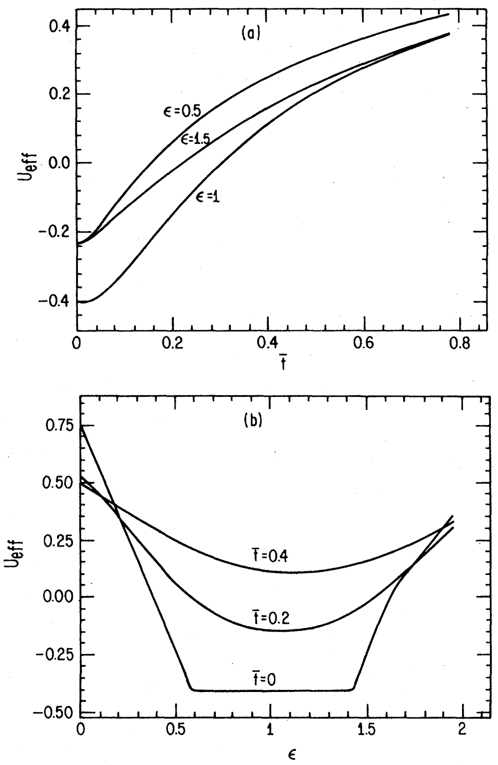

FIG. 3. Effective interaction for a two transition-atom unit surrounded by ligands. $t_1=1$, $U=\bar{U}=2$. (a) Dependence on $\bar{t}$. (b) Dependence on ϵ. Note that U_{eff} can now become negative. The most favorable situation is $\epsilon=\bar{U}/2$, $\bar{t}=0$. Larger t_1 gives a wider range of parameters with $U_{eff}<0$ (always centered around $\epsilon=\bar{U}/2$).

well-defined range to give an effective attractive interaction. Furthermore, the hybridization $\bar{t}$ cannot be overly large. For complexes with more units, for example of three atoms, we find that the range of parameters where attractive interactions occur is further enlarged. We believe that it should be possible to synthesize materials whose parameters lie within the required range to make U_{eff} attractive.

From an experimental point of view, there are various approaches for identifying these "pairing molecules." The energy to remove one electron from such a molecule should be larger than the one needed to remove a second electron. This should easily be seen with various spectroscopic techniques such as photoemission or optical absorption. Very recently, Vardeny and Tauc[14] have discussed an optical modulation technique for the determination of U_{eff} for defects. Furthermore, when two such molecules are brought together a disproportionation reaction should occur.

Assume now that we arrange these units to form an extended structure. The simplest geometry is one-dimensional, with the d_{zz} orbitals overlapping and forming a conducting spine. We require the overlap between d_{zz} orbitals of different units t to be much smaller than the intramolecular overlap t_1, so that the above discussion remains valid. One could also imagine pairing molecules which could be arranged in higher-dimensional structures. In the limit where the overlap between units t is much smaller than the hybridization energy $\bar{t}$, the Hamiltonian describing the motion of the d_{zz} electrons is the attractive Hubbard model. The parameter $\bar{t}$ plays a similar role to the phonon frequency in the electron-phonon case and if it becomes comparable to or smaller than t, retardation effects start to play a role.[5,15] In that case the attractive Hubbard model is no longer applicable, and in particular, in one dimension superconducting correlations are strongly suppressed by retardation. Thus, we assume $t \ll \bar{t}$ in what follows.

Even though one cannot solve the attractive Hubbard model exactly, a great deal is known about it. In the half-filled-band case, an exact symmetry exists which interchanges charge-density-wave (CDW) and singlet pairing correlations. In one dimension, it is known[16] that both decay algebraically with the same power independent of the size of U_{eff}. In two dimensions, the ground state has long-range order in these correlations for arbitrary U_{eff}, which corresponds to the antiferromagnetic order of the repulsive Hubbard case, if the Fermi surface is nested.[17] For non-nested Fermi surface, this is still likely to occur for sufficiently large U_{eff}. In three dimensions, one expects a transition at a finite temperature to a state exhibiting coexisting CDW and superconducting long-range order. If the band is not half full, it is known in one dimension that superconducting correlations will dominate over CDW correlations.[16] In higher dimensions, since there will not be nesting of the Fermi surface in general, superconductivity will certainly dominate in the non-half-filled band case. This has been recently verified by Monte Carlo simulations.[18]

In the limit $t \ll U_{eff}$ we can perform a strong-coupling expansion which leads to an effective Hamiltonian having the form of an antiferromagnetic Heisenberg model:

$$H_{eff}=J_{eff}\sum_{\langle i,j\rangle}\sigma_i\cdot\sigma_j+h\sum_i\sigma_i^z ,$$

with J_{eff} determined by the overlap matrix elements of various states of the molecules. Details of this calculation for a one-dimensional array are given in Ref. 5. Figure 4 shows J_{eff} versus $\bar{t}$ for one case. The main feature of J_{eff}

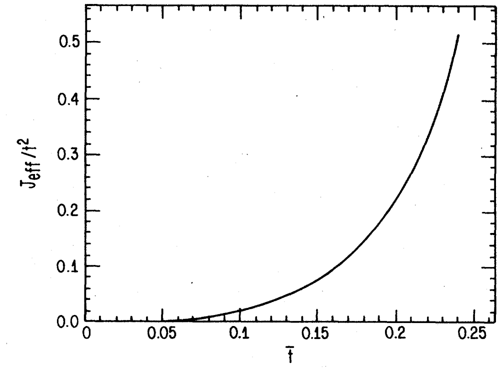

FIG. 4. Effective Heisenberg coupling J_{eff}/t^2 between two-atom units versus $\bar{t}$ for $U=\bar{U}=2$, $\epsilon=1$, $t_1=1$.

is that it vanished as $t \rightarrow 0$ but only algebraically instead of exponentially as in the electron-phonon case, and we can have a parameter regime where both $J_{\rm eff}$ and $U_{\rm eff}$ are appreciable. In the Heisenberg model, pairing correlations correspond to in-plane (x-y) correlations, and CDW correlations correspond to z-z correlations. If retardation effects are not negligible, the effective Hamiltonian becomes an *anistropic* Heisenberg model, with larger coupling in the z directions, favoring a CDW state.[5] The $\frac{1}{2}$-filled-band sector corresponds to the zero magnetization (or magnetic field) sector.

We can obtain estimates for the transition temperature in the strong-coupling regime from studies of the antiferromagnetic Heisenberg model in three dimensions. High-temperature series results for the $s=\frac{1}{2}$ Heisenberg antiferromagnet estimate $T_c = 1.93J/k_B$ in the zero-field sector.[19] We are not aware of calculations for the nonzero field case. For the classical Heisenberg model, Monte Carlo calculations have been performed both without and with a magnetic field.[20] For $h=0$, $T_c = 2.89J/k_B$ and this is slowly reduced as the magnetic field increases. Thus, it is clear that T_c is of the order of $J_{\rm eff}/k_B$, which can be up to tenths of an eV for typical molecular parameters. In two dimensions,[21] we expect a Kosterlitz-Thouless-like transition in the absence of interplane coupling, while in 1D there is no transition at finite temperatures. However, in those cases we would still have large superconducting fluctuations at temperatures of order of $J_{\rm eff}$, and a small three-dimensional coupling would stabilize the superconducting state at a lower temperature.

The superconducting properties of a system such as the one considered here have been discussed by Alexandrov and Ranninger (AR).[22] They find properties similar to a superfluid of Bose particles, somewhat differing from the BCS case. In their case of "bi-polarons," the critical temperature decreases rapidly with the electron-phonon coupling constant because of a band-narrowing effect. In our model, that effect does not occur. To illustrate this, Fig. 5 shows the dependence of $U_{\rm eff}$ and $J_{\rm eff}$ on $U=\bar{U}$ for fixed ϵ, $\bar{t}$, and t_1. In addition, the effect of retardation in the bi-polaron case (neglected in the AR treatment) will give a highly anisotropic Heisenberg Hamiltonian,[15] which is likely to give CDW rather than superconductivity. The reason is that the model requires $\lambda^2/2K \gg t$ ($\lambda =$ electron-phonon coupling constant, $K =$ phonon elastic constant) for the strong-coupling expansion to be valid, and unless $\omega \gg \lambda^2/2K$ ($\omega =$ phonon frequency) retardation will be dominant. It appears unlikely that one would obtain a superconductor with appreciable transition temperature under those constraints. In our model, since all energies are electronic in origin, it appears to be much easier to obtain the desired regime.

An omission of our model is the neglect of longer-range Coulomb interactions. If these are large, they would presumably stabilize a CDW state even in the non-half-filled band cases. It may be necessary to have other electrons in the system to provide sufficient screening to stabilize the superconducting state discussed here.

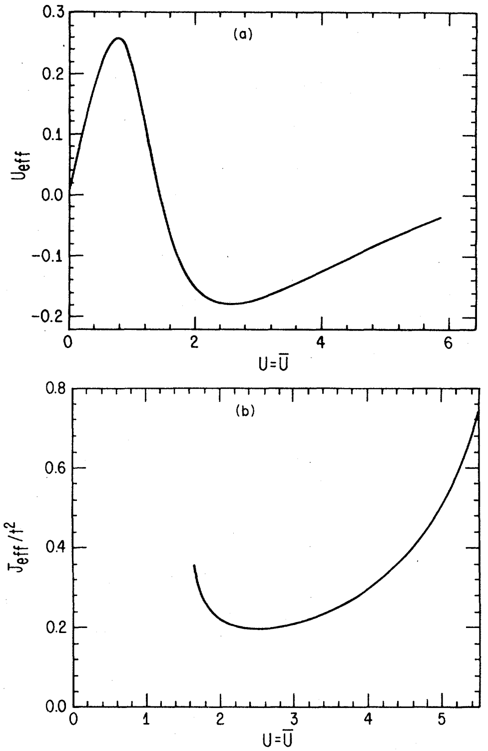

FIG 5. Dependence of (a) $U_{\rm eff}$ and (b) $J_{\rm eff}$ on $U=\bar{U}$ for $\bar{t}_1=1$, $\bar{t}=0.2$, $\epsilon=1$.

In summary, theoretical calculations on a variety of many-body models[3–5,21,22] show that a strong coupling Shafroth-Blatt-Butler superconducting state can indeed occur if there exist molecular units having two ground-state configurations which differ by a single electron pair. As discussed, the concentration, transfer overlap and screening of the pairs must also be within certain parameter regimes. In the model described here, the local pairing is produced by a dynamic electronic excitation mechanism which not only sets the energy scale to be eV but also produces only an algebraic decrease in the intermolecular hopping. Physically, our model describes one realization of a "double-valence-fluctuating" molecule. We believe that the possibility of achieving this new type of superconducting state is such that an experimental effort to produce and identify double-valence-fluctuating molecules is warranted.

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