Research Articles

Electronic Correlation Effects and Superconductivity in Doped Fullerenes

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A theory of the electronic properties of doped fullerenes is proposed in which electronic correlation effects within single fullerene molecules play a central role, and qualitative predictions are made which, if verified, would support this hypothesis. Depending on the effective intrafullerene electron-electron repulsion and the interfullerene hopping amplitudes (which should depend on the dopant species, among other things), the calculations indicate the possibilities of singlet superconductivity and ferromagnetism.

BUCKMINSTERFULLERENE, C_{60}, IS A MOLECULE OF REMARKable symmetry and intrinsic beauty; it would attract serious study for this reason alone (*1*). The recent discovery that in the solid state it can be readily doped and that it exhibits unexpected and fascinating electronic properties has greatly intensified the interest in this and related materials. In particular, when doped with alkali metals, fullerene crystals exhibit metallic conduction and superconductivity at unprecedentedly high temperatures for a molecular solid (*2, 3*). Most recently, it has been found that when doped with an organic counterion, the crystals become weak, presumably itinerant, ferromagnets (*4*).

Undoubtedly, the full elucidation of the properties of these materials will require a wide variety of ideas and methods. Nonetheless, we argue that it is ultimately the special electronic states on the scale of a single molecule that produce the novel physics of C_{60} (*5*). The many-electron states comprising the 60 π electrons of C_{60} provide a scale intermediate between the microscopic energetics at the level of a single carbon atom and the macroscopic scale of the molecular solid. We believe that these π electrons should not be treated within an effective single particle picture; electronic correlation effects are crucial. An interesting consequence of strong electronic correlation effects is the occurrence of an effective attraction between two added electrons (pair-binding), even though the microscopic Coulomb interactions are repulsive. We show that the phenomenon of pair-binding can give rise to superconductivity in doped C_{60}.

We first study the electronic spectrum of a single C_{60} molecule and then use the resulting low lying many-body states as the basis for an effective Hamiltonian that describes the physics at length scales larger than the size of the molecule. We begin with the simplest possible model of the one-electron spectrum and the simplest possible electron-electron interactions, known as the Hubbard model, but defined on the truncated icosahedral C_{60} lattice. The electron-electron interaction is represented in the Hubbard model as a short-ranged on-site interaction. This approach is reasonable as long as electronic screening is adequate as should be the case for doped C_{60} since it is metallic in the normal phase.

The Hubbard model. Let us consider the Hubbard model on a single C_{60} molecule. The Hamiltonian is

$$H = -t \sum_{\langle i,j\rangle\sigma}{}' (c^{\dagger}_{i\sigma}c_{j\sigma} + \text{h.c.}) - t' \sum_{\langle i,j\rangle\sigma}{}'' (c^{\dagger}_{i\sigma}c_{j\sigma} + \text{h.c.}) + \frac{U}{2}\sum_{i\sigma} n_{i\sigma}n_{i-\sigma} \tag{1}$$

where the primed sum runs over all distinct nearest-neighbor bonds on the pentagons and the double-primed sum runs over all distinct bonds that connect these pentagons (h.c. stands for hermitian conjugate). The fermion operator $c^{\dagger}_{i\sigma}$ creates an electron with spin σ on site i, and $n_{i\sigma} = c^{\dagger}_{i\sigma}c_{i\sigma}$ is the density of electrons of spin σ on site i. We shall assume, merely as a guide, that the nearest-neighbor hopping amplitude $t \sim 2$ to 3 eV and the on-site Coulomb interaction $U \sim 5$ to 10 eV, similar to the values known for polyacetylene (*6*). It is believed (*7*) that $1.0 < t'/t < 1.3$.

In the noninteracting limit, that is, $U = 0$, we simply recover Hückel theory and the electronic structure of the molecule is well known (*8*). The states can be labeled according to the irreducible representations of the icosahedral group. We shall not emphasize the labeling of the states according to icosahedral symmetry, although our calculations are fully consistent with it. Because of the nearly spherical shape of the molecule, it is simpler to label the states according to their approximate transformations under the operations of the full rotation group, that is, by their angular momentum.

The threefold degeneracy of the lowest lying unoccupied orbitals is an important property of the molecule. It can be thought of as though the lowest lying unoccupied orbital has "angular momentum" $L = 1$. In the noninteracting limit, the symmetry of the various states with one or more additional electrons in this orbital can be determined with the rules for addition of angular momentum (which in this case reproduce the composition laws of the representations of the icosahedral group). Because of the existence of a gap in the spectrum, the symmetry assignments must persist in the presence of interactions, at least for a finite range of U. Thus, we shall omit the quotation marks when we refer to the angular momentum L.

The pair-binding energy: the RVB picture. In this section we define the central concept of pair-binding and give an intuitive picture of its origin. This intuitive picture is firmly rooted in the resonating valence bond (RVB) picture of Pauling (*9*) and Anderson (*10*) and follows from the phenomenon of spin-charge separation. Spin-charge separation in a strongly correlated system implies that an electron is a composite object made up of two quasiparticles, a spinon which carries spin 1/2 and no charge and an eon which carries charge e but no spin (*5, 10, 11*).

Let us define Φ_0 to be the ground-state energy of the neutral

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molecule, and $\Phi_n \equiv \Phi_0 + E_n$ to be the ground-state energy of the charged molecule with n added electrons. Then the pair-binding energy, E_{pair}, is given by $E_{\text{pair}} \equiv 2E_1 - E_2 = 2\Phi_1 - \Phi_2 - \Phi_0$. Note that in our notation a positive E_{pair} implies that a pair is favored and not the converse.

From spin-charge separation, the energy to add one electron to a molecule is $E_1 = \Phi_1 - \Phi_0 = E_s + E_e + V_{es}$, where E_e (>0) is the eon creation energy, E_s (>0) is the spinon creation energy, and V_{es} is the spinon-eon interaction energy, which can be of either sign. If the eon-spinon interaction is repulsive, the system would minimize its energy by keeping them as far apart as possible; as a consequence, $V_{es} \approx 0$. If, on the other hand, the eon-spinon interaction is attractive, the eon and spinon would form a bound state with the same quantum numbers as an electron, although the state would have substantial internal structure (*6*). In this case, $V_{es} < 0$ and E_1 is the creation energy of a renormalized electron.

The energy to add two electrons in a spin singlet state is the energy to create two eons. For simplicity, we ignore the eon-eon and spinon-spinon interactions, because we imagine that C_{60} is large enough that the quasiparticles are weakly interacting. Then $E_2 = 2E_e$, so the pair-binding energy is $E_{\text{pair}} = 2(E_s + V_{es})$. The energy to add two electrons in the triplet state is the energy to add two eons and two spinons, plus the interactions between them, so the splitting between the singlet and the triplet state is also $\Delta_{\text{FM}} \equiv 2(E_s + V_{es})$. If $E_s + V_{es} < 0$, the pair-binding energy is negative and the triplet state of the doubly charged molecule is favored over the singlet, consistent with Hund's rule. However, when $E_s + V_{es} > 0$, pair-binding occurs and the singlet state has lower energy than the triplet state. Within this simple picture, there should be a single critical value of U/t at which both Δ_{FM} and E_{pair} change sign. Which of these two particular cases is realized depends on the values of E_e, E_s, and V_{es} which in turn depend on the microscopic parameters, such as U/t. A similar RVB picture has also been put forward by Baskaran and Tossatti (*12*), although there are quite significant differences between their theory and ours.

It is easy to extend this analysis to the case of more than two added electrons. We define generalized pair-binding energies (i = 1, 3, and 5) to be $E^{(i)}_{\text{pair}} = 2\Phi_i - \Phi_{i-1} - \Phi_{i+1}$, so that $E^{(1)}_{\text{pair}} \equiv E_{\text{pair}}$. We also define generalized splittings between the minimum and maximum spin states, for a given charge (n = 2, 3, and 4), to be $\Delta^{(n)}_{\text{FM}} = E_n(S_{\max}) - E_n(S_{\min})$, so that $\Delta^{(2)}_{\text{FM}} \equiv \Delta_{\text{FM}}$. (The low-energy states for n = 0, 1, 5, and 6 have unique values of the total spin.) A consequence of the simple quasiparticle picture presented above is that $\Delta^{(n)}_{\text{FM}} \approx E^{(i)}_{\text{pair}} \approx 2(E_s + V_{es})$, independent of i and n.

Perturbation theory. The Hubbard model defined on the truncated icosahedral lattice of C_{60} is a many-electron problem of considerable complexity; consequently, a direct numerical assault on this problem is likely to be unsuccessful. Faced with this dilemma we adopt the textbook approach of second-order perturbation theory in the Hubbard-U (*13*).

We first discuss the simple case of E_{pair}. In Fig. 1 we show the calculated E_{pair} for the singlet ($L = 0$, $S = 0$) and the triplet ($L = 1$, $S = 1$) states as a function of U/t. The ($L = 2$, $S = 0$) state is always an excited state for this problem. For $U > U_{\text{pair}} \approx 3t$, $E_{\text{pair}} > 0$ in the singlet state, which implies that it is energetically favorable to have a single molecule with two added electrons rather than two molecules with one electron each. The splitting between the singlet and the triplet states vanish at $U_{\text{FM}} \approx U_{\text{pair}}$. There is, however, a narrow region between U_{FM} and U_{pair} in which $E_{\text{pair}} < 0$, but still the singlet state is energetically preferred.

Because the concentration of donors in the superconducting fullerenes is three per molecule, we have calculated the energies Φ_n, hence generalized pair-binding energies for up to six added electrons. As mentioned earlier, we can classify the states according to the total angular momentun and spin. For six electrons, the unique state corresponds to ($L = 0$, $S = 0$); for five electrons, there are a total of 6 states corresponding to ($L = 1$, $S = 1/2$); for four electrons, there are a total of 15 states corresponding to the multiplets ($L = 2$, $S = 0$) (5 states), ($L = 1$, $S = 1$) (9 states), and ($L = 0$, $S = 0$) (1 state); for three electrons, there are 20 states corresponding to the multiplets ($L = 2$, $S = 1/2$) (10 states), ($L = 1$, $S = 1/2$) (6 states), and ($L = 0$, $S = 3/2$) (4 states); for two electrons there are 15 states which were enumerated above; for one electron there are 6 states corresponding to ($L = 1$, $S = 1/2$); the state of the neutral molecule is unique and corresponds to ($L = 0$, $S = 0$). Note that there is an approximate symmetry about three added electrons (where the shell is half-filled); thus, zero is analogous to six, one to five, and two to four. In Fig. 2 we have plotted the energy, E_n, versus the number of electrons, n, added to the neutral molecule for $U = 4t$ and $t'/t = 1.2$ (*14*). For zero, one, five, and six added electrons, the unperturbed ground-state is nondegenerate except for the degeneracy dictated by the total angular momentum and the total spin. For two, three, and four electrons there are level crossings at $U^{(2)}_{\text{FM}}$, $U^{(3)}_{\text{FM}}$, and $U^{(4)}_{\text{FM}}$, respectively, where the ground state changes from being in the maximal spin sector to the minimal spin sector upon increasing U.

The nature of pairing can be seen in the nonconvexity of E_n versus n in Fig. 2 and only takes place in the form $1 + 1 \rightarrow 0 + 2$ (meaning that it is more favorable to have two molecules with zero and two electrons each rather than two molecules with one electron each), $3 + 3 \rightarrow 2 + 4$, $5 + 5 \rightarrow 4 + 6$, with respective critical values $U^{(1)}_{\text{pair}}$, $U^{(3)}_{\text{pair}}$, $U^{(5)}_{\text{pair}}$. That there is no tendency for the electrons to bind in other ways, such as $3 + 3 \rightarrow 0 + 6$ or $1 + 1 + 1 + 1 \rightarrow 0 + 4$, can be seen from the convexity of the piecewise linear curve obtained by joining the points n = 0, 2, 4, and 6. It is perhaps not obvious in Fig. 2 that $E^{(1)}_{\text{pair}} \approx E^{(3)}_{\text{pair}} \approx E^{(5)}_{\text{pair}}$, so in Fig. 3 we plot all of the $E^{(i)}_{\text{pair}}$ versus U for $t'/t = 1.2$. One sees that $E^{(1)}_{\text{pair}}$ and $E^{(5)}_{\text{pair}}$ are quite close at all U, as expected from the approximate particle-hole symmetry within the triplet of lowest lying unoccupied orbitals of C_{60}. The behavior of $E^{(3)}_{\text{pair}}$ is rather remarkable: after decreasing more strongly

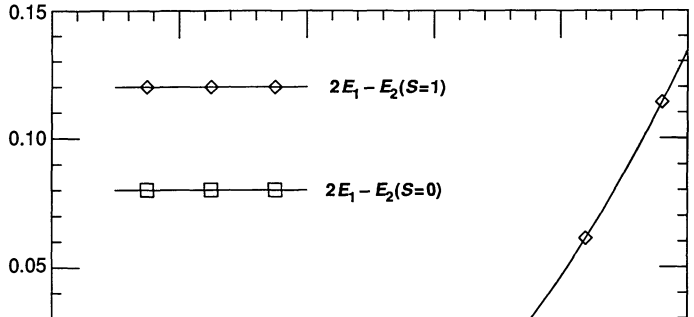

Fig. 1. The C_{60} singlet and triplet E_{pair} (in units of t) as functions of U/t for $t' = t$.

at small U than the other $E_{\mathrm{pair}}^{(i)}$, it rejoins them at $U = U_{\mathrm{FM}}^{(3)}$. We see that all of the $U_{\mathrm{FM}}^{(n)}$ are clustered together and do not lie far from the values of U where the $E_{\mathrm{pair}}^{(i)}$ cross zero. In addition, the typical magnitudes of the $\Delta_{\mathrm{FM}}^{(n)}$ are similar to those of the $E_{\mathrm{pair}}^{(i)}$, hence our RVB arguments above are justified nearly in full. Moreover, the symmetry of Fig. 2 implies that all else being unchanged, the physics should be similar for electron concentrations between two and four electrons per fullerene as it is between zero and two electrons per fullerene.

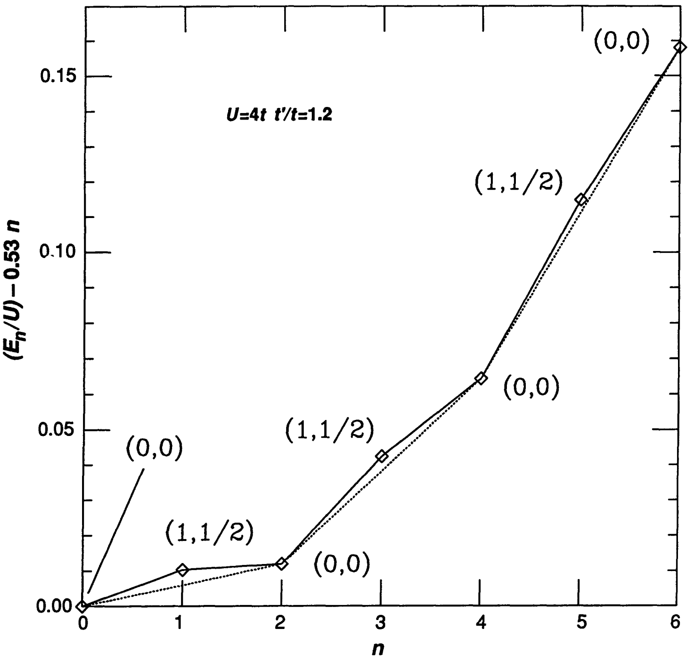

Fig. 2. The energy E_n (in units of t) versus n, for C_{60} at $U = 4t$, $t'/t = 1.2$. Note that a linear piece has been subtracted for clarity. The values of L and S for the lowest energy states at each n are indicated in the form of (L, S).

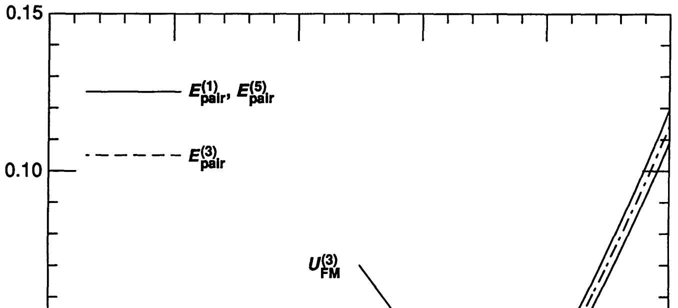

Fig. 3. Values for C_{60} of all of the $E_{\mathrm{pair}}^{(i)}$ (in units of t) versus U/t at $t'/t = 1.2$. $E_{\mathrm{pair}}^{(5)}$ is the lower of the two solid curves. Also indicated are the values of U/t for which the lowest energy states of the two-, three-, and four-charged molecule switch from the maximal to the minimal spin state as U increases.

Positive pair-binding energies, and hence the effective attractive interaction between electrons, are necessarily a core polarization effect. If all of the 60 valence electrons were treated as an inert Fermi sea, the net interaction between two electrons added to a given molecule would necessarily be repulsive; there is no bound-state solution to the Cooper problem with purely repulsive interactions. It is the dynamic interactions with the valence electrons that are crucial in producing overscreening of the purely bare repulsive interaction. Although the first-order term does not involve any virtual excitations, the second-order theory includes important core-polarization effects.

Finally,·we note that the reliability of the second-order perturbation theory has been examined in considerable detail elsewhere (*15*). From exact numerical studies of small Hubbard clusters up to 12 sites we have concluded that indeed the pair-binding can be positive at an intermediate scale, that perturbation theory never produces a misleading sign for the pair-binding energy for relevant values of U smaller than the bandwidth, and that it produces a reasonable magnitude for the pair-binding energy up to values of U of order half the bandwidth. We are therefore quite confident that the perturbative results described above are at least qualitatively correct.

Long-ranged Coulomb interactions and metallic screening. It may appear that the attraction between two electrons that we have obtained is spurious, as we have neglected the effect of the long-range Coulomb repulsion between electrons. If a single molecule is considered in isolation in a dielectric medium, there would be a larger contribution to the energy than those included. In fact, adding electrons to a neutral molecule can be viewed as charging a capacitor. Although, strictly speaking such a macroscopic picture is not correct, it is a reasonable guide for understanding the large electrostatic Hartree contribution. The charging energy is given by $e^2n^2/2C$, where the capacitance, C, is proportional to the diameter, l, of the molecule. If this contribution is added to the energies calculated above, the pair-binding phenomenon can disappear if the charging energy is sufficiently large.

It is important to note that even in the context of the Hubbard model, this charging energy is already present in a crude form; it is simply the first-order energy in powers of U, that is, the Hartree-Fock contribution to the pair-binding, which in the singlet sector of interest is always strongly repulsive.

The long-range Coulomb contribution to the interaction between electrons must be compared to the repulsion already present in our model, not to the much smaller pair-binding energy which is the difference between a large first-order repulsion and a large second-order attraction between electrons. In other words, we might try obtaining a better estimate of the Hartree charging energy within a model-that includes long-range Coulomb interactions, but we must not add this energy to the energies we have already computed from the Hubbard model; rather we should replace the first-order energies with the more realistic estimates.

For instance, for the Hubbard model, the first-order contribution to E_{pair} is $-(1/20)U$ (*5*), which is ~ -0.5 eV for $U = 4t \sim 10$ eV. Thus, the question to be considered is whether this is a physically reasonable magnitude for the Hartree-Fock contribution to the pair-binding energy. If we compare this estimate with that obtained from the capacitive charging energy, where $C = (\epsilon_\infty l)/2$, $l \approx 8$ Å, and ϵ_∞ is the background dielectric constant (which we estimate to be 2 to 3), then the capacitive estimate of the pair-binding energy is $-(2e^2)/(\epsilon_\infty l)$, which is between -1.2 and -1.8 eV, depending on the value assumed for ϵ_∞. This capacitive estimate is larger than the first-order repulsion present in the Hubbard model calculation for reasonable values of U, but not enormously so.

However, this estimate ignores an important effect, namely, the screening of the repulsion between two electrons on a given molecule due to the rearrangement of the charges on neighboring molecules, that is, metallic screening. This would result in a large decrease in the Hartree-Fock energy.

In order to estimate the effect of metallic screening on the electrons on the same molecule, we imagine embedding a molecule in a spherical metallic cavity. The metallic cavity mimics the effect of the metallic electrons on the other molecules in an effective medium approximation. A simple calculation now leads to the following expression for the charging energy, E_C:

$$E_C = \frac{e^2 n^2}{\epsilon_\infty l}\left(\frac{2d}{l + 2d}\right) \qquad (2)$$

where $(l + 2d)$ is the diameter of the cavity. This is reduced from its value in the absence of screening by a factor $[2d/(l + 2d)]$. Here, d should be of the order of the separation between fullerene molecules, that is, $d \approx 3$ Å, so for $\epsilon_\infty = 3$, $(E_C/n^2) \approx 0.27$ eV $\sim (1/10)t$. The corresponding pair-binding energy (approximately -0.5 eV) is roughly the same as the first-order contribution to the pair-binding energy we obtained from the Hubbard model for $U = 4t$. Moreover, if anything, we have overestimated this energy due to the use of a Hartree approximation. Thus, in the presence of metallic screening, the long-range Coulomb interactions are unlikely to destroy the effective attraction between electrons we have derived, at least at low frequencies, where metallic screening is effective.

Superconductivity. The existence of a positive pair-binding energy induced by electron-electron interaction is suggestive of superconductivity. Two different limits of the problem can be addressed, with an expected smooth crossover between them: (i) If the intermolecular hopping matrix element, t_i, is small compared to E_{pair}, we have the "preformed-pair" limit, consisting of a lattice gas of charge $2e$ bosons. In effect, the system would behave as a granular superconductor with each C_{60} molecule playing the role of a superconducting grain coupled through the Josephson mechanism. In this regime we also expect T_c to be an increasing function of t_i and so to increase with pressure. (ii) If t_i is large compared to E_{pair}, then the added electrons should form an extended band of width $W_i \sim 2Zt_i$, where $Z \sim 12$ is the effective coordination number of the fullerene crystal. In this limit E_{pair} would simply play the role of a short-range, weak, instantaneous attraction between electrons. This limit can be treated within the framework of a "BCS-like" mean-field theory, and the gap equation can be solved. Recall, once again, that $E^{(n)}_{\text{pair}}$ is approximately independent of n. In this mean-field limit, we expect the superconducting transition to be sharp. Qualitatively, because the superconducting transition temperature $T_c \propto \exp(-W_i/E_{\text{pair}})$, T_c should decrease strongly with increasing W_i, hence with pressure. In a conventional electron-phonon superconductor the pressure dependence is usually weak, because the decrease in the density of states is usually compensated by the increased stiffening of the phonons. In contrast, in the present problem the application of pressure would predominantly decrease the density of states at the fermi surface; because E_{pair} is primarily a property of a single molecule, it would not be greatly affected by pressure. Finally, because the effective attractive interaction between the electrons in this limit is mostly nonretarded and spread over the entire bandwidth, we expect that some of the superconducting properties would not be quite "BCS-like." Hence, the phrase "BCS-like" is simply a reminder that mean-field theory of pairing holds, with a pair size large compared to both the separation between electrons and the size of a C_{60} molecule.

Further consequences. *Magnetism.* Because our crude estimate of U places it in the neighborhood of the critical value at which the $E^{(i)}_{\text{pair}}$ curves cross 0, it is easy to imagine that if C_{60} is doped with different types of dopants, a regime of parameters can be accessed in which the triplet states have lower energy. Although two electrons in this regime do not tend to attract on a molecule, if they happen to lie on a single molecule they will be in a triplet state, hence we see the possibility of the existence of itinerant ferromagnetism. The possibility of the formation of a ferromagnet is a unique signature of electron-electron interaction and clearly distinguishes the electronic mechanism for superconductivity from a mechanism based on electron-phonon interaction. In fact, as mentioned earlier, such a ferromagnet has recently been found (*4*).

Charge density wave. It might be argued that at exact commensurability, for example, when the number of added electrons is three per molecule, the negative U_{eff} ($\propto -E_{\text{pair}}$) system would form a charge density wave. However, this is unlikely for two reasons. First, it is easy to see that even a very small departure from commensurability would destroy the charge density wave phase. Secondly, and more importantly, note that the face-centered cubic (fcc) structure (*16*) of K_3C_{60} is likely to frustrate the formation of the charge density wave in favor of superconductivity. In the small U_{eff} limit this can readily be seen by a simple Hartree-Fock calculation. In the limit $U_{\text{eff}} \rightarrow -\infty$ this is evident from a second-order degenerate perturbation theory (*17*).

Doped C_{70}. From an analogous calculation described in the text we found that doped C_{70} should not superconduct unless the relevant value of the intramolecular Hubbard-U is considerably larger. However, because the perturbation theory for large values of U should be suspect, it is an open question whether the pair-binding in C_{70} can ever be positive.

Measurement of E_{pair}. We make some cautionary remarks regarding measurements of pair-binding energy through photoemission. In view of our discussion of the charging energy, it is important that these measurements be carried out in the metallic phase. If the screening is not adequate, the large capacitive charging energy of the doubly charged molecule over the singly charged molecule can swamp the small pair-binding energy.

Novel effects for partially filled shells. Elementary arguments (*18*) are sufficient to demonstrate that, in the noninteracting limit, E_n versus n should exhibit kinks as the added electrons complete closed shells: this forms the basis for an elementary discussion of the stability of aromatic molecules. What Fig. 2 shows is that similar kinks are found even when a shell (namely the lowest unoccupied level) is only partially filled. This is entirely an electronic correlation effect and signifies a novel mechanism for the stability of certain partially filled shells.

Electron-phonon interactions. Out of 174 intramolecular phonon modes only 2 are symmetry preserving, and these make a positive contribution to E_{pair} (*5*). The symmetry-breaking Jahn-Teller phonons make a negative, pair-breaking contribution to E_{pair}. The reason is as follows: due to its orbital degeneracy, the singly charged molecule can lower its energy considerably by a Jahn-Teller distortion, whereas for $U > U_{\text{pair}}$, the doubly charged molecule is an orbital singlet and so cannot Jahn-Teller distort. The details are discussed elsewhere (*19*).

Franck-Condon effect. One might ask why have we focused on a subtle electronic correlation effect as the source of the attraction between electrons when there is an obvious source of pair-binding in the form of the Jahn-Teller effect. In the noninteracting limit ($U = 0$), the doubly charged molecule (like the singly charged molecule) is subject to a substantial Jahn-Teller distortion. However, although this is a possible source of attraction between electrons, it is not a possible mechanism for superconductivity. An exponential suppression of the bipolaron bandwidth owing to the Franck-Condon effect results in a nearly infinite bipolaron mass and, consequently, no superconductivity. Rather, a Jahn-Teller distortion would produce self-localized "negative-U" centers (*20*). An important feature of the present theory is that the correlation effect suppresses the Jahn-Teller distortion and eliminates, to a large degree, the Franck-Condon reduction of the bandwidth.

Experimental consequences. (i) Because pair-binding does not occur for two and four added electrons, we expect that materials such as K_2C_{60} or K_4C_{60} would not superconduct (*21*). (ii) The superconducting transition temperature, T_c, should peak when there are approximately an odd number of electrons per molecule. Of course, some of the long-distance physics not included in this calculation may favor a particular concentration of dopants in the solid (*22*). (iii) With the help of different dopants it is possible to drive the system ferromagnetic. In fact, there is also a narrow range of U, between U_{FM} and U_{pair}, in which the singlet state is favored over the triplet state, and hence in principle it is possible to drive the system antiferromagnetic as well. (iv) The pressure dependences of T_c discussed above should be noted. For the case in which $W_i > E_{pair}$ we predict an approximately linear dependence of $\ln T_c$ on the intermolecular bandwidth (*23*). (v) Because for large enough U, the doubly charged C_{60} should be in an orbital singlet state, the infrared absorption should be quite different from what one would expect from the single particle theory (*19*).

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24. It is a great pleasure to thank P. W. Anderson for his comments and K. Holczer for numerous exciting discussions of the rapidly developing experimental scene. In particular, we would like to thank P. W. Anderson for drawing our attention to the fact that the symmetry-preserving intramolecular phonons are pair enhancing whereas the symmetry breaking phonons are pair breaking. We thank S. R. White and M. Salkola for collaborations to be reported elsewhere (*15, 19*). Thanks are also due to E. Abrahams, A. Auerbach, V. Emery, I. Pimentel, D. Rokhsar, and P. Scharf for particularly helpful discussions. Supported by the National Science Foundation grants no. DMR-89-07664 (S.C.) and no. DMR-90-11803 (S.K.).

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Protein Hydration in Aqueous Solution

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High-resolution proton nuclear magnetic resonance studies of protein hydration in aqueous solution show that there are two qualitatively different types of hydration sites. A well-defined, small number of water molecules in the interior of the protein are in identical locations in the crystal structure and in solution, and their residence times are in the range from about 10^{-2} to 10^{-8} second. Hydration of the protein surface in solution is by water molecules with residence times in the subnanosecond range, even when they are located in hydration sites that contain well-ordered water in the x-ray structures of protein single crystals.

PROTEIN FOLDING, THAT IS, THE RELATIONS BETWEEN AMINO acid sequence, folding pathways, and kinetics, and the functional spatial arrangement of a polypeptide chain, is presently the least well understood step in a "central dogma" relating storage of genetic information with its expression by protein functions (*1*). New insights can be anticipated from structural characterization of both the unfolded and the functional folded polypeptide chain under the conditions of the folding milieu. Because water is excluded almost entirely from the interior of globular proteins (*1, 2*), different solvation of the polypeptide chain in the unfolded and folded forms must be an important factor. This article reports on investigations of the hydration of two polypeptides in aqueous solution. The hormone oxytocin has been chosen as a model for the

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