

Pair binding in small Hubbard-model molecules

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(Received 5 August 1991)

We calculate exact ground-state energies for small Hubbard-model clusters (molecules) and show that two electrons added to a molecule can experience an effective attraction despite their bare repulsive interaction (pair binding). This phenomenon takes place *only* for intermediate strength of the repulsive interactions, and on intermediate length scales. All the results are in qualitative agreement with those obtained using second-order perturbation theory up to surprisingly large values of the interactions and provide support for a purely electronic mechanism of superconductivity in doped C_{60} .

INTRODUCTION

Can two electrons added to a many-electron system experience an effective attraction even when their bare interactions are repulsive? If so, can this phenomenon have important physical consequences? In the present paper we address these questions. It was recently proposed by two of us¹ that superconductivity² in doped C_{60} , arises primarily from an effective attraction between two electrons on the same molecule despite their repulsive microscopic interactions. Of course, there have been many occasions in the past, especially in the context of high-temperature superconductivity, when these questions were raised and a variety of answers have been given. However, we shall focus on a specific problem. We shall consider small clusters (molecules) of atoms, which we model by a repulsive Hubbard Hamiltonian for which *exact* numerical solutions can be obtained. We believe that these "Hubbard-model molecules" are representative of the actual molecules in which short-range electronic correlations are crucially important. At present we know of at least one important molecule, C_{60} , which is arguably well described by this model defined on a truncated icosahedral lattice.^{1,3} Unfortunately, C_{60} is too big; state-of-the-art numerical methods do not permit diagonalization of Hubbard molecules bigger than 18 atoms.⁴ It is precisely for this reason that we analyze a variety of small "molecules" and try to draw inferences that are sufficiently general to hold for C_{60} . Of course, there is also the intriguing possibility that some of these smaller molecules can be synthesized as well.

The interaction between electrons in the Hubbard model is short ranged; in fact, it is an on-site interaction. Is this realistic? If we consider these molecules in isolation, the answer is likely to be "no" due to purely electrostatic charging considerations. Thus, we imagine that these molecules are embedded in a solid which exhibits *metallic screening*, yet the macroscopic energy scales of

the solid are sufficiently distinct from the energy scales of a single molecule that we can first deal with the degrees of freedom of the isolated molecule. Since we have discussed the problem of electronic screening at some length elsewhere,³ we shall not discuss it further here. We shall also study the effect of somewhat longer-ranged interactions by including a nearest-neighbor repulsion.

We define the pair-binding energy, E_{pair} , to be

$$E_{\text{pair}} = 2\Phi_1 - (\Phi_0 + \Phi_2), \quad (1)$$

where Φ_n is the many-electron ground-state energy of the neutral molecule plus n added electrons; a positive pair-binding energy is equivalent to an effective attraction between electrons on the scale of the single molecule⁵ and, as argued elsewhere, can serve as a mechanism for superconductivity.^{1,3} We can also define generalized pair-binding energies: $E_{\text{pair}}^{(i)} = 2\Phi_i - \Phi_{i-1} - \Phi_{i+1}$, $i = 1, 3, 5$, etc., where $E_{\text{pair}}^{(1)} \equiv E_{\text{pair}}$. We want to emphasize at the very outset that the pair-binding energy is generally a small difference of large numbers, and hence the individual energies must be calculated with great precision.

We discuss the following: (1) The effective attraction between the electrons is a subtle correlation effect at the single molecule level, which causes an overscreening of the purely repulsive microscopic interactions between electrons. (2) It is essential that the phenomenon occurs on intermediate scales of size and interaction strength; under most circumstances the pair-binding energy vanishes as the size of the molecule goes to infinity⁶ or as the strength of the interaction either vanishes (which is obvious) or becomes very strong as we show below. (3) Pair binding is a generic phenomenon for a large class of Hubbard molecules. (4) Second-order perturbation theory in the Hubbard interaction captures qualitatively all the aspects of the phenomenon of pair binding for what appears to be surprisingly large values of the Hubbard interaction; hence perturbation theory is an effective tool

to study large molecules such as C_{60} or C_{70} .

The above statements will now be elucidated by considering one-dimensional (1D) finite chains (for which an exact Bethe-ansatz solution is known⁷), the 16-site torus, the 8-site cube, and most importantly the 12-site truncated tetrahedron. As discussed below, the truncated tetrahedron mimics in many respects the molecule C_{60} .

THE MODEL

We consider the extended Hubbard model, where t_{ij} is the hopping matrix element between nearest-neighbor sites i and j , U is the Hubbard interaction, and V is the repulsion between electrons on nearest-neighbor sites:

$$H = - \sum_{\langle i,j \rangle, \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + \frac{U}{2} \sum_{i,\sigma} n_{i\sigma} n_{i-\sigma} + V \sum_{\langle i,j \rangle, \sigma, \sigma'} n_{i\sigma} n_{j\sigma'}, \quad (2)$$

where $c_{i\sigma}^\dagger$ creates an electron with spin σ on site i , and $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ is the density of electrons of spin σ on site i . For the truncated tetrahedron, there are two classes of inequivalent nearest-neighbor bonds: the bonds on the edges of the triangular faces, for which $t_{ij} = t$, and those connecting the triangles, for which $t_{ij} = t'$. For the rest of the molecules we consider, all nearest-neighbor bonds are equivalent, so $t_{ij} = t$. The molecule is said to be neutral when there is one electron per site.

In general, we shall find that E_{pair} first becomes positive on a given molecule only for U larger than a critical value, which we call U_{pair} , and that the ground state of the doubly charged molecule changes from the maximal spin state for $U < U_{\text{FM}}$ to the minimal spin state for $U > U_{\text{FM}}$. Note that U_{pair} and U_{FM} can be zero (pair binding occurs immediately) or infinite (pair binding never occurs).

THE HUBBARD MODEL ON A ONE-DIMENSIONAL RING

The pair-binding energy for this model was recently obtained by Fye, Martins, and Scalettar⁸ for even membered rings for up to $N = 64$ sites. For $N = 4n+2$, where the noninteracting ground state of the neutral molecule is nondegenerate, they find that the pair-binding energy is negative for all positive U , and it approaches 0 as $N \rightarrow \infty$. (U_{pair} and $U_{\text{FM}} = \infty$.) By contrast, for $N = 4n$, where the noninteracting ground state of the neutral molecule is sixfold degenerate due to a pair of half-filled orbitals at the Fermi energy, they find that the sign of E_{pair} for fixed N depends on the value of U/t : E_{pair} is, of course, 0 for $U/t = 0$; E_{pair} is positive up to $U = U_{\text{max}}$, which depends on N and is negative thereafter. ($U_{\text{pair}} = U_{\text{FM}} = 0$.)

We find that perturbation theory agrees qualitatively with the exact results on all rings for $U < U_{\text{max}}$, and for $N \geq 4$ (i.e., it gives the correct sign of the pair-binding energy), it is quantitatively reasonable for $U/t < 4$, i.e., for U equal to the full noninteracting bandwidth. For

example, in perturbation theory and for $N = 64$, E_{pair} is 0.009, 0.036, 0.080, 0.143, for $U/t = 1, 2, 3, 4$, respectively. The corresponding numbers from the exact Bethe-ansatz calculation⁸ are 0.010, 0.035, 0.046, 0.045. By contrast, $(4n+2)$ rings do not exhibit pair binding in perturbation theory for $U/t < 4$ in agreement with the exact results. To compare, for $N = 6$, the pair-binding energy in perturbation theory is $-0.037, -0.148, -0.333$, for $U/t = 1, 2, 3$, respectively. The corresponding exact results are $-0.036, -0.129, -0.244$. We find these results remarkable because one would have expected perturbation theory to fail badly for such a correlated 1D system.

THE HUBBARD MODEL ON A 4×4 TORUS

The 4×4 torus has been studied by exact diagonalization by Fano, Ortolani, and Parola⁶ and by Lin⁴, and in second-order perturbation theory by Friedman.⁹ The pair-binding energy of this molecule is positive for all positive U/t ($U_{\text{pair}} = 0$) up to the largest values considered ($U/t = 40$) so far. This result is in qualitative agreement with the results of second-order perturbation theory, although for $U/t \sim 4$, i.e., half the bandwidth, perturbation theory overestimates E_{pair} by about a factor of 3. We have also calculated the generalized pair-binding energies in perturbation theory and find similar qualitative agreement with the exact numerical results.⁴ ($E_{\text{pair}}^{(3)}$ is underestimated; $E_{\text{pair}}^{(5)}$ is overestimated.)

However, the noninteracting ground state of the neutral molecule is 524-fold degenerate. For this reason, this molecule is of limited interest in the present context (cf. below). We do not pursue this model further here. For the same reason we have not studied here the icosahedron or the dodecahedron for which the noninteracting ground states are 210-fold and 28-fold degenerate, respectively.

THE CUBE

We performed the exact diagonalizations for the cube (and for the truncated tetrahedron described below) on

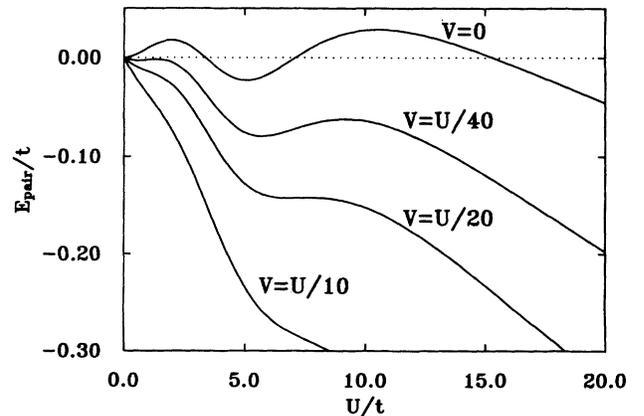


FIG. 1. The pair-binding energy E_{pair} for the cube for $V = 0, U/40, U/20$, and $U/10$. Note, especially, the second region in which the pair-binding energy becomes positive again.

a real-space basis using Davidson's algorithm¹⁰ which we found to converge much more quickly than the commonly used Lanczos method in systems with nearly degenerate ground states. We find that pair binding occurs on the cube at small to moderate U/t . (See Fig. 1.) Thus, there is no reason to believe that frustration is important for pair binding to occur. Unexpectedly, for $V = 0$ and $U/t \sim 10$, E_{pair} becomes positive again for a second range of U/t . We do not have the slightest idea what causes this remarkable oscillatory behavior shown in Fig. 1. Again, perturbation theory is qualitatively correct up to $U \sim 4t$. We see also that longer-range interactions ($V > 0$) strongly suppress pair binding.

THE TRUNCATED TETRAHEDRON

The truncated tetrahedron is perhaps the most interesting molecule among the group we have considered as it is analogous to the truncated icosahedron, which is the structure of C_{60} . The geometry of both molecules is such that all sites are equivalent and threefold coordinated, and that there are two inequivalent classes of faces, one with an odd number of edges, and the other with an even number of edges; correspondingly, both structures have two inequivalent classes of nearest-neighbor bonds. Moreover, the one-electron spectrum is similar in both cases, with a nondegenerate ground state for the neutral molecule and a threefold degenerate lowest-lying unoccupied orbital.

In Fig. 2 we show the pair-binding energies for $V = 0$ and $t'/t = 1.3$. At quite large U/t , E_{pair} again becomes negative, and approaches approximately -0.4 as $U/t \rightarrow \infty$. We shall discuss this limit below. Hund's rule is obeyed at small values of U/t and, in general, $U_{\text{FM}} \propto U_{\text{pair}} > 0$; for larger values of U , a level crossing takes place, and the ground state changes from the maximal to the minimal spin state. Note also that $U_{\text{FM}}(t'/t = 1) = U_{\text{pair}}(t'/t = 1) = 0$, and that $U_{\text{FM}}(t'/t)$ and $U_{\text{pair}}(t'/t)$ are of order $(t'/t - 1)^2$ for t' close to t . In general, we

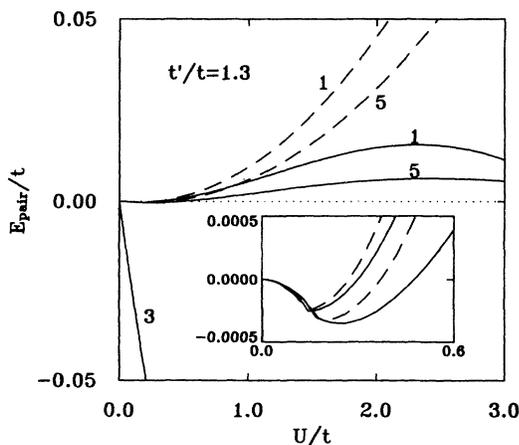


FIG. 2. Pair-binding energies for the truncated tetrahedron for $V = 0$. The dashed lines are from perturbation theory, while the solid lines represent the exact results. The labels i on the figure refer to $E_{\text{pair}}^{(i)}$. The inset is an expansion of the region for small U/t .

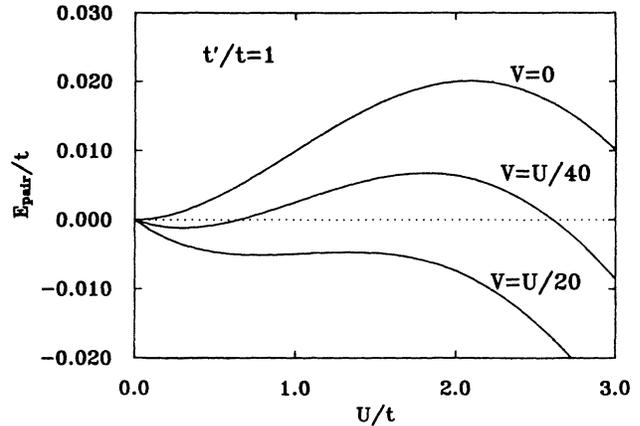


FIG. 3. The pair-binding energy E_{pair} for the truncated tetrahedron for $V = 0, U/40$, and $U/20$.

find that pair binding is suppressed for larger values of V/U . The results for $V = 0, U/40$, and $U/20$ are shown in Fig. 3. Note that the effect of V on E_{pair} is smaller in the truncated tetrahedron than in the cube. Pair binding always occurs in a state for which the total $S = 0$.

THE LIMIT $U/T \rightarrow \infty$

In this limit it is possible to prove a theorem concerning the absence of pair binding. The proof works, however, for added electrons to the neutral molecule ($n > 0$) and *not* for added holes. We sketch the proof here, without details.¹¹ (1) It is easy to prove that for $n \geq 0$ and $U/t \rightarrow \infty$, $\Phi_n - nU \geq -n \sum_j |t_{ij}|$. (2) For any value of U and n , one can construct a family of exact many-body eigenstates by examining the sector of maximum S , the ferromagnetic or Nagaoka¹² states. These states have energy $\Phi_n^{(\text{ferro})} = nU + \epsilon_n$, where ϵ_n is the sum of n one-particle energies χ_j . Thus, $\Phi_n \leq \Phi_n^{(\text{ferro})}$. (3) By Nagaoka's theorem¹² it follows that for $U/t \rightarrow \infty$, $\Phi_1 = \Phi_1^{(\text{ferro})} = \sum_j t_{ij}$, where in the final equality we have assumed $t_{ij} \geq 0$. It is obvious that for $U/t \rightarrow \infty$, $\Phi_0 = 0 + O(t^2/U)$. It therefore follows at once that $E_{\text{pair}} \leq 0$. We can, moreover, obtain an estimate of E_{pair} in this limit, which should be a lower bound to E_{pair} , by adopting the ferromagnetic estimate of Φ_2 : $E_{\text{pair}} \geq \chi_1 - \chi_2$. Thus, for the truncated tetrahedron $E_{\text{pair}} \geq -1$, while for the cube $E_{\text{pair}} \geq -2$. The numerical results are, of course, in accord with this theorem.

SYMMETRY BREAKING

In both the truncated tetrahedron and the cube, the first unoccupied orbital had a threefold orbital degeneracy dictated by symmetry, as in C_{60} . Is this fact important for pair binding? For instance, for C_{70} the noninteracting ground state of the neutral molecule is unique and is separated by a large gap from the first excited unoccupied orbital, which is nondegenerate, although it is separated by a rather small gap from a pair of degenerate unoccupied orbitals.³ Using nearly degenerate perturbation theory, we have found³ that the pair-binding energy

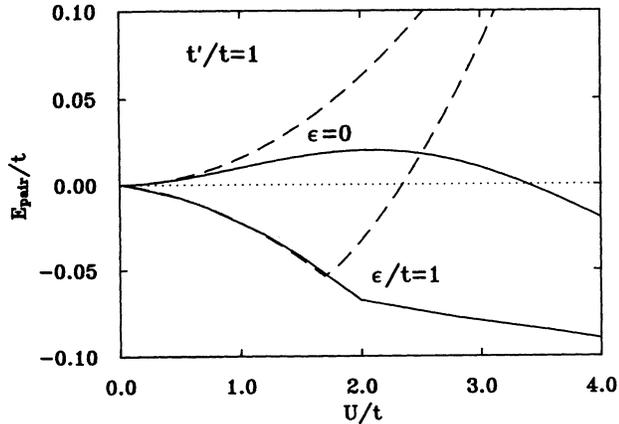


FIG. 4. The pair-binding energy E_{pair} for the truncated tetrahedron for $V = 0$, in the presence of a single-site symmetry breaking field $\epsilon = t$; for comparison, we also show the results for $\epsilon = 0$. The dashed lines are from second-order perturbation theory and the solid lines are from the exact diagonalization.

for this molecule is negative for all values of U for which it is reasonable to expect perturbation theory to be valid. Thus, we tentatively conclude that the orbital degeneracy of the unoccupied level is important for pair binding. To verify this conclusion, we have repeated our exact diagonalization studies of the truncated tetrahedron by breaking the symmetry of the cluster by introducing a "impurity" potential on a site, $j = 1$, of magnitude ϵ

(i.e., $\epsilon \sum_{\sigma} n_{1\sigma}$). We find that for $\epsilon = t$, the pair-binding energy is dramatically suppressed as shown in Fig. 4.

TO SUMMARIZE

We find that pair binding is a common phenomenon in Hubbard molecules for intermediate sizes and coupling strengths. This is a form of attraction between electrons that arises from an overscreening of the purely repulsive microscopic interactions. We feel that there is every reason to expect this phenomenon to occur in real molecules so long as it is embedded in a medium that can screen sufficiently the long-range part of the Coulomb interaction. The effect is well captured by perturbation theory, so perturbation theory can be used with reasonable confidence on larger molecules for which other methods cannot be used.

ACKNOWLEDGMENTS

We thank L. Chayes and D. Rokhsar for interesting discussions and R. Singh for drawing our attention to Ref. 9. We also thank R. Fye and R. T. Scalettar for informing us about their work on 1D Hubbard chains. This work was supported by the National Science Foundation, Grant Nos. DMR-89-07664 (S.C.) and DMR-90-11803 (S.K.), and by the Office of the Naval Research, Grant No. N00014-91-J-1143 (S.R.W.). This work was also supported in part by the University of California through an allocation of computer time on the UC Irvine Convex.

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⁵It is important to note that a positive pair-binding energy does not imply that in the solid state, electron pairs hop from molecule to molecule. Rather, E_{pair} should be viewed as an effective short-range attraction (on the scale of one

molecule) between electrons.

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