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Interactions, Pair Binding and Ferromagnetism on Spherical Molecules.

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Abstract. – The energy of a system of electrons on a sphere with purely repulsive interactions is computed by perturbation theory. Second-order results yield an effective attraction between added electrons, in the $L = 0$ singlet state or in the $L = 1$ triplet state, which depends on the magnitude and range of the interaction. An estimate of third-order corrections bounds the regime where these predictions are expected to hold. We discuss the relevance of this model to superconductivity and ferromagnetism in doped fullerenes.

For many years, theorists have been intrigued by the possibility of pair binding and superconductivity in electronic systems with purely *repulsive* interactions. Superconductivity in strongly correlated metals (*e.g.* heavy electron compounds and high-T_c cuprates) suggests that large repulsive interactions can sometimes be transformed into an effective attraction between quasi-particles.

Following the recent discovery of superconductivity in alkali-buckminsterfullerene [1] (X_3C_{60}, X = K, Rb) Baskaran and Tosatti [2] and Chakravarty and Kivelson (CK) [3] have proposed that here too, electron interactions might contribute substantially to the pairing mechanism. Each isolated C_{60} in a system of 60 interacting π-electrons. The effective interaction («pair binding energy») between two extra electrons added to an N-electron system is defined as [1]

$$\Delta \equiv E_{N+2} - 2E_{N+1} + E_N \,. \tag{1}$$

Here E are the ground-state energies. *Pair binding* ($\Delta < 0$) occurs when two added electrons on one molecule have lower energy than when they occupy two separate molecules. Pair binding in conjunction with intermolecule hopping processes was proposed by CK as an explanation of the relatively high-temperature superconductivity in the fullerenes. CK have considered the Hubbard model on the tight-binding truncated icosahedron (soccer ball) lattice, with hopping energy t and on-site repulsion U. Since X_3C_{60} has an average of 63 electrons per C_{60} molecule, the relevant Δ is that of $N = 62$. Δ was computed up to

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[1] Here the pair binding energy Δ is opposite in sign to the definition of ref. [3].

second-order perturbation theory in U/t. For $U \geq 3t$, Δ truncated at second order becomes negative in the singlet channel.

The existence of pair binding due to repulsive interactions is supported by exact numerical solutions of the Hubbard and the t-J models on finite clusters [4].

In this paper we briefly address three questions which are motivated by the afore-mentioned work: i) Is the underlying lattice potential essential for pair binding? ii) What are the effects of long-range Coulomb interactions? iii) In what cases can one trust the extrapolated results of second-order perturbation theory? Detailed results will be presented elsewhere [5].

We consider a system of *free* electrons of mass m^* moving *continuously* on a sphere of radius R. The noninteracting Hamiltonian is

$$H_0 = e_0 \sum_{l=0}^{l_{cut}} \sum_{m=-l}^{l} \sum_{s=\uparrow\downarrow} l(l+1)\, c^\dagger_{lms} c_{lms} , \tag{2}$$

l, m denote the spherical-harmonics states $Y_{lm}(\hat{\Omega})$, where $\hat{\Omega}$ is a unit vector, s is the spin, and $e_0 = \hbar^2/(2m^* R^2)$. The soccer ball lattice effects of the real C_{60} molecule are absent in eq. (2). In particular, the structure of the states near the Fermi level is different. The lattice splits the degenerate $l = 5$ multiplet, and the Fermi level of 60 electrons lies in the semiconducting gap between the 5-fold and 3-fold degenerate orbitals [3]. Here we are interested primarily in the effects of Coulomb interactions which are larger than the lattice-induced gaps. Our zeroth-order ground state has the full spherical degeneracy which is lifted only by the Coulomb interactions. The cut-off angular momentum l_{cut} limits the number of single-particle states (including spin degeneracy) to $2(l_{cut}+1)^2$. Fluctuations at scales smaller than $r_{min} = 2(l_{cut}+1)$ are not included. Physically, the discarded states with energy higher than $e_0 l_{cut}(l_{cut}+1)$ are unbound (ionized) sates which contribute negligibly to the effects of the interactions.

The interactions are parametrized by two dimensionless variables g, α.

$$\begin{cases} \hat{V}^\alpha = \dfrac{1}{2} \int d\hat{\Omega}_1\, d\hat{\Omega}_2\, V^\alpha(\hat{\Omega}_1 - \Omega_2) : \rho(\hat{\Omega}_1)\, \rho(\hat{\Omega}_2) : \\ V^\alpha = g 2\pi r_{min} \sum_{LMss'} \left(\dfrac{2}{r_{min}(2L+1)} \right)^\alpha Y^*_{LM}(\hat{\Omega}_1)\, Y_{LM}(\hat{\Omega}_2) , \end{cases} \tag{3}$$

$\rho = \sum_s \psi^\dagger_s \psi_s$ is the density operator, where $\psi^\dagger_s = \sum_{lm} Y_{lm}(\hat{\Omega})\, c^\dagger_{lms}$. $g = e^2/(\varepsilon R e_0)$ is the *strength* of the interaction. The power law tail of $V(r)$ depends on α such that as α decreases, the potential has shorter range. $0 \leq \alpha \leq 1$ interpolates smoothly between a δ-function and an unscreened $1/r$ Coulomb potential:

$$V^{\alpha=0} = g 2\pi r_{min}\, \delta(\hat{\Omega}_1 - \hat{\Omega}_2); \qquad V^{\alpha=1} = \frac{g}{|\hat{\Omega}_1 - \hat{\Omega}_2|} . \tag{4}$$

When α changes from 0 to 1, the averaged interaction over an area of radius r_{min} (analogous to Hubbard's U) is held fixed. The interaction in the basis of H_0 is

$$\begin{cases} \hat{V}^\alpha = g\pi r_{min} \sum_L \left(\dfrac{2}{r_{min}(2L+1)} \right)^\alpha (-1)^{m'+\mu} C^{Ll l'}_{Mm-m'} C^{L\lambda\lambda'}_{M\mu-\mu'} c^\dagger_{l'm's} c^\dagger_{\lambda'\mu'\sigma} c_{\lambda\mu\sigma} c_{lms} , \\ C^{Ll l'}_{Mm-m'} \equiv \sqrt{(2L+1)(2l+1)(2l'+1)} \begin{pmatrix} L & l & l' \\ M & m & -m' \end{pmatrix} \begin{pmatrix} L & l & l' \\ 0 & 0 & 0 \end{pmatrix} , \end{cases} \tag{5}$$

where summation of repeated indices is assumed and $M = m' - m$. $\hat{V}$ is depicted in diagram 1*a*). The brackets denote standard $3j$ symbols [6].

In the following we consider the cases of $N = 2l_c^2$ electrons in the closed shells $l = 0, \ldots, l_c - 1$ plus $n = 0, 1, 2$ electrons in the open «conduction» shell l_c. The energies E_{N+n} are computed perturbatively in g. The noninteracting ground states are

$$\Phi_0 = |N\rangle, \quad \Phi_1 = c^\dagger_{l_c 0\uparrow}|N\rangle, \quad \Phi_2 = \sum_m (L0|l_c - m, l_c m)\, c^\dagger_{l_c -m\uparrow} c^\dagger_{l_c m\downarrow}|N\rangle, \tag{6}$$

where $|N\rangle$ is the closed-shell state, and $(L0|l_c - m, l_c m)$ is a Clebsch-Gordan coefficient [6]. The quantum numbers $(LL^z SS^z)$ of Φ_2 are $(L0S0)$, where $S = 0, 1$ and $L + S$ must be even by antisymmetry.

The perturbation expansion of the energy is given by

$$\begin{cases} E_{N+n}(L;g) = \sum_{k=1}^{\infty} g^k E^{(k)}_{N+n}, \\ E^{(0)} = \langle \Phi_n(L)|H_0|\Phi_n(L)\rangle, \quad gE^{(1)} = \langle \Phi_n(L)|\hat{V}|\Phi_n(L)\rangle, \\ g^2 E^{(2)} = \langle \Phi_n(L)|\hat{V}\dfrac{1-\mathscr{P}_0}{E^{(0)} - H_0}\hat{V}|\Phi_n(L)\rangle, \end{cases} \tag{7}$$

where $E^{(0)}$ is the energy of (2), and $\mathscr{P}_0$ projects onto the degenerate ground-state manifold.

To eliminate errors in the numerical program, we have computed the pair binding energy by two separate methods. The first is a brute-force computation of $E^{(k)}_{N+n}$ for $n = 0, 1, 2$, and $k = 0, 1, 2$ using (7). Here, all the core excitations and the blocking of excited states by the conduction electrons have to be included. The second method reduces the coefficients of the pair binding energy to a set of diagrams depicted in fig. 1*b*). (The diagrams are derived by successively commuting the conduction electrons with the potential.) Similar diagrams were previously used by Iwata and Freed [7] and by Brandow [8] to calculate effective Hamiltonians for π-electrons in organic molecules. Each diagram separately conserves total angular momentum, and does not include core excitations or blocking effects.

In fig. 2, $\Delta(L)$ for $\alpha = 0.2$, $l_c = 5$ and $l_{cut} = 6$ is plotted as a function of g. This system has 50 closed-shell electrons and 98 available states in the Hilbert space. The ratio of occupied to

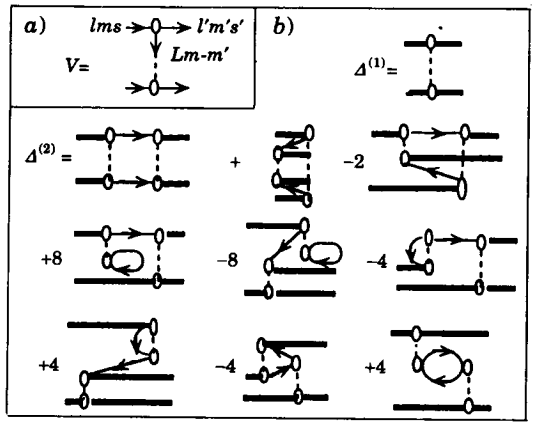

Fig. 1. – *a*) A diagrammatic representation of the interaction of eq. (5). Each vertex represents a factor of C. *b*) First- and second-order diagrams for the pair binding energy with their combinatorial factors. Right (left and vertically) pointing arrows denote unoccupied (occupied) states of the $n = 0$ system. Thick lines denote conduction electron states.

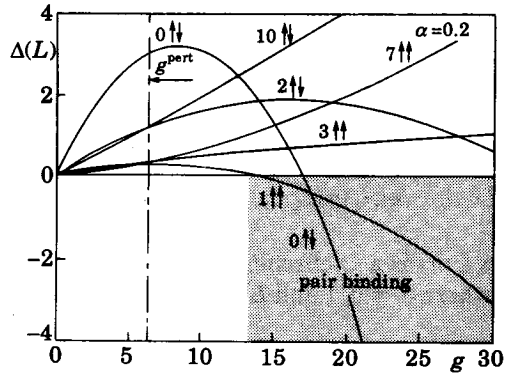

Fig. 2.

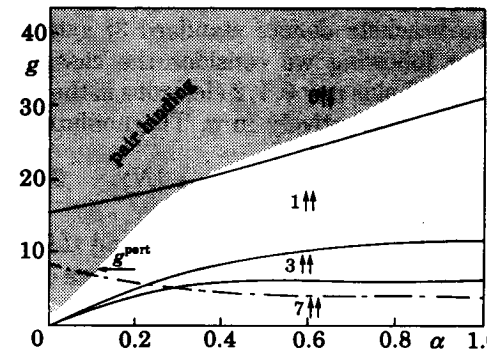

Fig. 3.

Fig. 2. – Second-order approximation for the pair binding energies (in units of e_0) of several angular-momentum channels. ↑ ↓ and ↑ ↑ denote spin singlet and triplet, respectively. Pair binding region is shaded. Left of g^{pert} (dash-dotted line), higher-order corrections are expected to be small. Here $l_c = 5$, $l_{\text{cut}} = 6$ and $\alpha = 0.2$ (see text for definitions).

Fig. 3. – Second-order prediction for the ground-state phase diagram of the $l_c = 5$, $l_{\text{cut}} = 6$ system. g and α describe the strength and range of the interaction, respectively. Smaller α corresponds to shorter-range interactions. Shaded region represents pair binding. Below g^{pert} (dash-dotted line) higher-order corrections are expected to be small.

unoccupied states resembles the corresponding ratio in the Hubbard model of C_{60}. The $n = 2$ system has 11 multiplets in its ground-state manifold with $0 \leqslant L \leqslant 10$. The first-order coefficients $\Delta^{(1)}$ are always nonnegative. The singlet ($L = 0, S = 0$) state is initially the highest state in the multiplet, and the ($L = 7, S = 1$) is the lowest. This is a weak violation of Hund's rule which would predict ($L = 9, S = 1$) to be the lowest state. Due to Pauli's principle, for the δ-function potential ($\alpha = 0$), the odd L coefficients vanish $\Delta^{(1)}(L) = 0$, $L = 1, 3, 5, 7, 9$.

The results for the second-order coefficients $\Delta^{(2)}(L)$ are less predictable. The polarization of the closed-shell electrons enters at this order. Negative-pair binding implies that the two electrons prefer to share that polarization. For all $l_c \leqslant 6$, $l_{\text{cut}} \leqslant 7$ and α we have found that $\Delta^{(2)}(0)$ is always negative and largest in magnitude. Second-order perturbation theory implies that there would be level crossings, and at some g the $L = 0$ singlet would become the ground state, as seen in fig. 2. At $g = g^{\text{pair}} = -\Delta^{(1)}(0)/\Delta^{(2)}(0)$ the singlet pair binding energy becomes negative.

We also find that $\Delta^{(2)}(L = 1) < 0$ for the range of filling parameters $4 \leqslant l_c \leqslant l_{\text{cut}} \leqslant 8$. For the δ-function potential, since $\Delta^{(1)}(1) = 0$ this negativity implies that *triplet pairing is possible in the $L = 1$ channel for arbitrary small g!* This effect clearly survives the higher-order corrections. In fig. 3 the ground-state phase diagram in the (g, α)-space is shown.

In order to bound the regime where the second-order results are trustworthy, we estimate the magnitude of the third-order coefficient as follows. From eq. (7) it is apparent that $E^{(1)}$ is qualitatively different from the higher-order corrections $E^{(k)}$, $k \geqslant 2$. The latter involve summations over excited states and energy denominators. Thus the magnitude of $g^{\text{pair}} = E^{(1)}/E^{(2)}$ could be quite different than the value at which third- and higher-order corrections become important $g^{\text{pert}} = |E^{(3)}/E^{(2)}|$ [2]. To estimate g^{pert}, we first evaluate the

[2] We are indebted to S. Kivelson for bringing this fact to our attention.

wieghted average of the matrix elements

$$M = \overline{|\langle lms, \lambda\mu\sigma|\hat{V} - \langle V(n,L)\rangle|l'm's', \lambda'\mu'\sigma\rangle|(2L_{\min}+1)^{\alpha}}, \tag{8}$$

where $\overline{\{\cdot\}}$ denotes an average over initial and final states, and $\langle V(n,L)\rangle$ is the first-order ground-state energy of the system with n added electrons with total angular momentum L. This is just an additive constant to the energy and will not affect energy denominators. $L_{\min}$ is the minimum allowed momentum connecting two states at different shells. Our main assumption is that the matrix elements do not depend strongly on the quantum numbers of the initial and final states, except through the factor $(2L_{\min}+1)^{-\alpha}$. Under this assumption, we factorize M out of the second-order sum, and use the known values of $E^{(2)}$ to evaluate its magnitude. Subsequently, using the same M for the third-order terms yields an estimate for $E^{(3)}$. This is probably an overestimate, since it ignores all relative sign cancellations. We have verified that for various l_c, l_{cut}, M is indeed weakly dependent on α, which justifies the choice of weighted averaging in (8).

The values of g^{pert} are plotted in fig. 2 and 3 by dash-dotted lines. For $g \ll g^{\text{pert}}$ the results of second-order perturbation theory are expected to hold. We note that the exact solution of the 2-4 electron system with $l_c = l_{cut} = 1$ has no pair binding [9]. For that system $g^{\text{pair}} = 16\pi$ is considerably larger than $g^{\text{pert}} \approx 15$.

In general we have found that $g^{\text{pair}}(L=0)$ and g^{pert} decrease as the cut-off momentum l_{cut} increases, although g^{pert} decreases faster. On the other hand, $g^{\text{pair}}(L=1)$ increases with l_{cut}. We hve not yet included the lattice potential or different electron fillings. By comparing our results to CK's Hubbard model, we learn that the singlet pair binding is robust, while the triplet pair binding does not survive the lattice potential in the tight-binding limit. Their results also suggest that the pair binding energy is insensitive to the precise filling of the $L = 5$ multiplet.

To emulate the C_{60} molecule with our model, we use $R = 3.5$ Å, the bare electron mass, and a dielectric constant of unity to obtain $e_0 = 0.242$ eV, and a bare interaction parameter $g_0 \approx \approx 8.4$. It is heartening to realize that g_0 is situated in a physically interesting regime of fig. 3, for sufficiently screened interactions (small α). The effective g depends on the effective mass and the short-distance dielectric constant. The precise value of α is difficult to estimate for X_3C_{60}. It depends on the detailed polarization of the σ and core electrons, as we as the full crystal environment.

If singlet pair binding occurs, the negative-U Hubbard model on the f.c.c. lattice might be appropriate. This model exhibit superconductivity for strong [5] couplings. If triplet pair binding occurs, *a novel ferromagnetic superconductor may be obtained*! The recent discovery of weak ferromagnetism in TDAE-C_{60} [10] indicates that the physical parameters of that system might not be forbiddingly far from achieving triplet pair binding.

In summary, we can now answer the three questions posed earlier: i) The lattice is not essential for pair binding. ii) Longer-range interactions (larger α) push g^{pair} to higher values, where the second-order results are less reliable. iii) One can trust the second-order results for the pair binding energies in the regime $g \ll g^{\text{pert}}$.

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