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Abstract. We calculate the binding of two added electrons or holes for several clusters described by the extended Hubbard model. Pairing is found only away from half filling and for the geometries which give particle–hole symmetric spectra. In these situations the intersite repulsion is essential and pairing depends on it very strongly. We conclude that small-cluster results are adequate to answer the question of whether the binding is possible only if the one-particle spectra are qualitatively similar to those of the considered lattice. Altogether, the results suggest that a purely electronic mechanism of superconductivity is not likely in alkali metal doped fullerides.

1. Introduction

Since the discovery of high-temperature superconductivity, there has been tremendous effort to understand whether purely electronic interactions in strongly correlated systems could be responsible for the microscopic mechanism of pairing. The simplest and generic model to describe strong correlations is the non-degenerate Hubbard model. Indeed, the superexchange interaction, which stabilizes antiferromagnetic long-range order in the half-filled Hubbard model, leads to a superconducting ground state away from half filling when this model is solved in the mean field approximation [1–3]. It is still disputable, however, whether such a mean field approximation reproduces the realistic properties of the system, as the pairs are small and hardly overlap with each other at low doping. Moreover, it is not obvious that two holes (or electrons) added to an antiferromagnetic insulator will experience an effective attraction, if all the interactions in the system are repulsive. In principle, this question can be answered in a satisfactory way only by exact diagonalization of finite clusters which became popular recently.

In finite-cluster diagonalization one calculates usually the binding energy for a cluster of size N as follows,

$$E_b(n) = E_{min}(N + n + 1) + E_{min}(N + n - 1) - 2E_{min}(N + n). \qquad (1)$$

Here for convenience we have labelled the binding energy by the actual electronic doping level n with respect to half filling, i.e., $n = 0$ corresponds to the Mott–Hubbard insulator, if the Coulomb interaction U is large. In equation (1) $E_{min}(N_e)$ denotes the minimum value from the set $E_0(N_e, S_z = 0)$, $E_0(N_e, S_z = 1)$, $E_0(N_e, S_z = 2)$, ..., and $E_0(N_e, S_z)$ is the lowest energy for the system filled by N_e electrons in the subspace of fixed z component of total spin S_z.

It is interesting to investigate systematic trends in $E_b(n)$ as a function of the doping. Although negative binding energy by itself does not guarantee superconductivity, it is

suggestive. As the CuO_2 subsystem in high-temperature superconductors is two dimensional (2D), most of the numerical studies have been performed in two dimensions. Different groups obtained negative binding energy in the 2D Hubbard model, suggesting this mechanism of pairing in high-temperature superconductors [4–9]. However, the binding in 2D systems depends strongly on the geometry of the cluster, as pointed out by Callaway *et al* [7]. Somewhat surprisingly, binding has also been observed in large one-dimensional (1D) Hubbard rings [10]. It has been proposed as well that binding may occur in fullerene-like clusters and this binding might be responsible for the observed superconductivity in alkali metal doped fullerites [11, 12]. Chakravarty and Kivelson showed that pair binding can occur in small molecular clusters described by the Hubbard Hamiltonian [11, 12]. In the present contribution we report the results of similar calculations, extending the previous results by a more systematic treatment of the size dependence and the role of intersite Coulomb interactions in molecules described by the Hubbard model. In particular, the intersite Coulomb interactions are important in C_{60}, and it is thus unrealistic to describe the fullerene molecule by the Hubbard model. We use therefore the extended Hubbard Hamiltonian as introduced for 1D systems [13–16], with the model parameters appropriate for the bonds between carbon atoms in C_{60}. Thereby we use the same topology of the clusters of even number of atoms, $N = 6, ..., 12$, as that in a fullerene molecule.

The paper is organized as follows. In section 2 we introduce the model and justify three different parameter sets used in most of our calculations. The numerical results obtained for five different clusters introduced to simulate the C_{60} molecule are presented and analysed in section 3. Our conclusions are given in section 4.

2. Model

The more strongly correlated π electrons in a fullerene molecule are in a good approximation independent from the remaining weakly correlated σ electrons. Therefore, we shall use the extended Hubbard Hamiltonian [6, 11–14] which describes only π electrons in a clusters of carbon atoms,

$$H = \sum_{\langle ij \rangle \sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{\langle ij \rangle} V_{ij} n_i n_j \qquad (2)$$

where i labels C sites (all π orbitals in the cluster), $\langle ij \rangle$ run over all nearest-neighbour sites (note that the sum includes both terms: $i = 1$, $j = 2$, and $i = 2$, $j = 1$). Furthermore, $c_{i\sigma}^{\dagger}$ is the creation operator of a π electron with spin σ on site i, $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ is the respective electron number operator, and $n_i = n_{i\uparrow} + n_{i\downarrow}$. t_{ij} are hopping integrals, and the Coulomb interactions are described by the on site parameter U, and the intersite parameters V_{ij}. We do not consider the chemical potential as its contributions cancel in equation (1) for electron pair binding energy E_b.

Unfortunately, the values of the parameters entering the model Hamiltonian (2) are not precisely known for C_{60}. However, some good estimates do exist and several parameter sets have received considerable publicity in the literature. In the following we will use three different sets. The first, corresponding to the Hubbard model, $t_{i,j} = -2.35$ eV; $U = 5.5$ eV; $V_{i,j} = 0$, was introduced to describe C_{60} aggregates [17]. It has been claimed that it gives good estimates of the experimental ionization energies and other chemical characteristics of C_{60} [17]. The two other sets were used for polyacetylene and seem to be appropriate for C_{60} as well. The second set is derived from that of König and Stollhoff [18, 19]: $t_{ij} = t_s = -2.29$ eV for 'single' bonds (two adjacent carbons on a pentagon in C_{60}); $t_{ij} = t_d = -2.71$ eV for 'double' bonds (the bonds connecting different pentagons in C_{60});

$U = 11.5$ eV, and $V_{ij} = 2.4$ eV. We note that for these parameters $U = 4.24|t|$ which is very close to the value of $U = 4.5|t|$ estimated by Salkola from the excitation spectra of neutral C_{60} using second-order perturbation theory in $U/|t|$ [20]. Such an estimation is rather insensitive to the value of intersite Coulomb repulsion V, as long as this interaction is small. However, the large value of U entering this latter set of parameters is not universally accepted as the correct one for polyacetylene. Both experimental and theoretical arguments were given that a lower value is more realistic [21–25]. Therefore we consider as well the third set of model parameters being [21–25] $t_{ij} = t_s = -2.29$ eV; $t_{ij} = t_d = -2.71$ eV; $U = 6.25$ eV; and $V_{ij} = V_s = 4.15$ eV for single bonds; $V_{ij} = V_d = 4.25$ eV for double bonds. Instead of using the value of $U/2$ for V_{ij} in double bonds [21–25], the values of V_{ij} were somewhat modified. They were estimated using the Ohno formula [26] with the distance dependence and the parameters given in [27, 28]. The hopping parameters t_s and t_d were taken from polyacetylene [18, 19, 21]. However, when one accepts the 'average' value of t to be -2.5 eV [21–25, 28], and takes into account the difference between single and double bond lengths, t splits into t_s and t_d, and, according to formulas given in [28], the resulting values are practically the same as those accepted for polyacetylene [21]. Therefore, we expect the resulting parameter values of set No 3, which agree nicely with general estimates given in [22–25], to provide the most realistic description of a fullerene molecule.

For a small number of cluster sites the Lanczos algorithm [29–33] can provide the exact values of the lowest-lying eigenvalue E_{min} of the Hamiltonian. We examined five different clusters with the number of sites varying from $N = 6$ to $N = 12$, labelled A–E:

(A) six atoms, triangular base parallelepiped;
(B) eight atoms, square base parallelepiped;
(C) ten atoms, pentagonal base parallelepiped;
(D) twelve atoms, hexagonal base parallelepiped;
(E) twelve atoms, truncated tetrahedron.

The last figure has perhaps the closest similarity to the topology of C_{60} molecule. It is obtained from a tetrahedron with its corners cut away by planes parallel to the tetrahedron bases. The resulting figure E has thus four triangular and four hexagonal faces. The important common feature of all the considered clusters is that each corner has three nearest neighbours and the clusters edges belong to two different symmetry classes. The local environment of any atom in A–E is thus identical to that in the true fullerene, i.e., at each carbon site two identical 'single' bonds and one 'double' bond meet. The expectation that such clusters mimic the electronic states in true fullerene follows quite naturally.

We performed calculations of the lowest energies (using the Lanczos algorithm) for the above clusters, for different parameter sets and for different numbers of up and down spin electrons (i.e. for fixed value of the z component of total spin S_z). The total spins S of the determined energy levels were inferred from their degeneracy, as the eigenenergies are degenerate for different values of S_z and fixed S for the Hamiltonian given in equation (2). By comparing the lowest energies in the subspaces of fixed S_z this allowed us to determine the total spin S of the ground state. For instance, $E_0(N_e, S_z = 0) \neq E_0(N_e, S_z = 1)$ implies a singlet ground state $S = 0$, whereas $E_0(N_e, S_z = 0) = E_0(N_e, S_z = 1) \neq E_0(N_e, S_z = 2)$ implies a triplet ground state. In most cases, the ground state for an even number of electrons N_e is found to be a singlet.

We note that the electronic states of *non-interacting* clusters A–E fall into two classes. The spectra of two clusters, B and D, exhibit particle–hole symmetry, while the other spectra do not possess this symmetry. This follows from a general observation that the

irreducible representations of the symmetry group of the considered physical system have to appear pairwise, if the spectrum is particle–hole symmetric. In other words, if for each representation k with the corresponding energy $E(k)$, there exists the representation k' with the opposite energy, $E(k') = -E(k)$, the spectrum is particle–hole symmetric (here we assume that the first moment of the spectrum vanishes). It appears that this property of the electronic spectrum has important implications for the pairing, as we discuss below.

The pair binding energy E_b of two extra electrons added to the system with N_e electrons (close to half filling) is defined by equation (1). In particular, $n = -1$ in $E_b(n)$ corresponds to the binding in a cluster which is positively ionized in its ground state. Similarly, $n = 1$ corresponds to such a cluster being negatively ionized (like those in the crystal lattice of superconducting alkali metal doped fullerides), whereas $n = 0$ corresponds to neutral clusters. If $E_b(n) < 0$, a pair of two non-interacting clusters with $N_e = N + n + 1$ and with $N_e = N + n - 1$ electrons, respectively, has lower total energy than the energy of two clusters with $N_e = N + n$ electrons, which implies that pairing is favoured. As a result, there is a tendency for the system of fullerene molecules to undergo a transition into the system with unequal electron numbers on different individual molecules. The eventual transfer of electrons in such a system involves transfer of pairs rather than of single electrons.

3. Numerical results

The results of numerical calculations are summarized in table 1. First of all, no binding was found at $n = 0$, i.e. for the clusters which correspond to the Mott insulators at large U. This result corroborates with the experimental finding that in the solid form of fullerene, as well as in the parent compounds of high-temperature superconductors, no superconductivity exists without doping. Thus the small-cluster results fully support the experimental situation.

In contrast, for either $n = -1$ or $n = 1$ binding is possible for certain geometries and parameters, while for some other situations it does not occur. In particular, no binding (for any set of the investigated parameters) was found for the clusters A (six sites) and C (10 sites). For the cluster B (eight sites) the binding occurs for the parameter sets No 1 and No 3, while it is absent for the parameters from set No 2. This agrees with the exact diagonalizations of Callaway *et al* [7] who reported that the binding may be realized only if the on site Coulomb interaction is not too strong. Therefore, we conclude that the large value of $U = 11.5$ eV in set No 2 suppresses the binding. In contrast, the strongest binding occurs for set No 3, believed to be the most realistic one for the description of polyacetylene [21]. Quite similar results were obtained for cluster D (12 sites) as well. On the contrary, only weak binding has been found in cluster E (12 sites—truncated tetrahedron) for the electronic doping ($n = 1$) and the parameter set No 1. These results obtained for two clusters (D and E) having the same number of sites ($N = 12$), the same local topology of bonding, but different global pattern of bonds clearly demonstrate that the presence or absence of binding strongly depends on the geometry of the physical system, as also found for 2D clusters by Callaway *et al* [7]. Furthermore, the results presented in table 1 suggest that the binding is favoured in the systems with the one-particle (tight-binding) energy spectra exhibiting electron–hole symmetry. Although we do not have a formal proof that this property holds for larger clusters and in the thermodynamic limit, we argue that electron–hole symmetry of the electronic structure is an important factor which promotes pairing. We note that for small systems and simple geometries this property is fulfilled by the clusters with all the faces having an *even* number of sides. Some of those clusters, such as those considered here (B and D), have the number of sites being a multiplicity of four. It is well known that such clusters have somewhat different properties from other systems of similar geometry

Table 1. Binding energy $E_b(n)$ for extra electron pair on the following clusters of N atoms: A—parallelepiped with triangular base; B—parallelepiped with square base; C—parallelepiped with pentagonal base; D—parallelepiped with hexagonal base; E—truncated tetrahedron. Parameter sets (in eV): No 1: $t_s = -2.35$, $t_d = -2.35$, $U = 5.5$, $V_s = V_d = 0$; No 2: $t_s = -2.29$, $t_d = -2.71$, $U = 11.5$, $V_s = V_d = 2.4$; No 3: $t_s = -2.29$, $t_d = -2.71$, $U = 6.25$, $V_s = 4.15$, $V_d = 4.25$.

Cluster	Parameter set	N	$E_b(n)$ (eV)		
			$n = -1$	$n = 0$	$n = 1$
A	No 1	6	0.605	1.359	0.257
	No 2	6	2.491	4.606	1.806
	No 3	6	2.689	3.439	2.677
B	No 1	8	−0.038	5.006	−0.038
	No 2	8	1.356	6.596	1.356
	No 3	8	−0.135	15.686	−0.135
C	No 1	10	0.212	0.805	0.527
	No 2	10	0.278	5.178	0.657
	No 3	10	1.592	3.810	2.078
D	No 1	12	−0.070	2.387	−0.069
	No 2	12	0.436	6.049	0.436
	No 3	12	−0.470	15.590	−0.470
E	No 1	12	0.136	2.584	−0.045
	No 2	12	0.786	5.179	0.679
	No 3	12	0.951	5.402	1.399

due to their closed shell character [16, 21, 31].

It has been claimed [33, 34] that the parameters of the Hamiltonian (2) appropriate for the description of fullerene fall into a special crossover regime, in which the low-spin (singlet) ground state of the cluster changes into the high-spin ground state suggested by Hund's rule. Therefore we investigated the total spin of the ground state in the considered clusters. In most cases the ground state is a singlet, but in several cases a triplet ground state was found instead, as shown in tables 2 and 3. The latter situations are characterized by the degeneracy of the partially occupied highest energy level of the tight-binding Hamiltonian (at $U = 0$). This results in *strong spin correlations* and in this respect our results confirm the results of earlier studies [33, 34]. However, the calculations did not provide clear evidence that strong spin correlations enhance the tendency of the considered clusters towards superconductivity. In fact, pairing was found both for cluster D with the triplet ground state at $N_e = 10$ and 14, and for cluster B which has a singlet ground state for the parameter sets considered.

The results presented in table 1 demonstrate that the intersite repulsion V plays an essential role in the possible electronic mechanism of pairing. For example, for the clusters B and D weak pairing was found for the Hubbard model (parameter set No 1); no pairing exists for large U and small V (set No 2); while strong pairing was obtained with smaller U and $V > U/2$ (set No 3). We investigated therefore the effect of the intersite repulsion V on the electronic paring in a systematic way, starting from the Hubbard model with $t_s = t_d = -2.35$ eV and $U = 5.5$ eV (set No 1). Here we assume $t_s = t_d$ as the presence of non-equivalent bonds does not have a crucial effect on the pairing. The results are shown in figures 1–3 for the clusters B, D, and C, respectively. The pairing in clusters B and D (figures 1 and 2) is found for two separate regions of V: (i) very small V, and (ii) above a certain critical value of V. This result agrees with the conclusions of White *et al* who found that increasing V stabilizes the binding for the cube and for the truncated

Table 2. Cluster geometries A–E and parameter sets No 1–No 3 (see table 1) for which a triplet ground state was found for the filling by N_e electrons.

Cluster	Parameter set	N	N_e
A	No 1	6	6
	No 3	6	6
C	No 1	10	10
	No 2	10	12
D	No 2	12	10
	No 3	12	10
	No 2	12	14
	No 3	12	14
E	No 1	12	10
	No 2	12	10
	No 3	12	10

Table 3. Cluster geometries A–E and parameter sets No 1–No 3 (see table 1) for which the lowest singlet and triplet energies are almost degenerate for the filling by N_e electrons.

Cluster	Parameter set	N	N_e
A	No 2	6	6
B	No 1	8	6
D	No 1	12	10
	No 1	12	12
	No 2	12	12
	No 2	12	14
E	No 1	12	14
	No 2	12	14
	No 3	12	14

tetrahedron [12]. By analysing the density–density correlation functions $\langle n_i n_j \rangle$ we observed that the nature of binding is quite different depending on the value of V. While for small V the doped holes (electrons) occupy mostly different atoms, at large V ($V > U/2$) the probability of doubly occupied configurations (by holes or electrons) increases with respect to the independent electron picture. Thus, in agreement with intuition, the hole binding originates from different physical processes in these two regimes: at small U the gain of the kinetic energy in a correlated system is the driving force, while the tendency towards phase separation dominates at large V. As shown by Hirsch *et al* [4, 5], the superconductivity may occur in this latter regime, if V does not exceed the critical condition for phase separation. The above physical picture of two distinct regimes of parameters, depending on the value of the intersite Coulomb repulsion V, is supported by the binding energy in pentagon based parallelepiped C (figure 3), where also two different parameter regimes could be identified in the absence of binding.

4. Conclusions

Our results support the conclusion of Chakravarty and Kivelson [11] that the electronic binding is feasible in purely repulsive systems. However, the binding is a result of a delicate balance of the parameters and depends strongly on the cluster geometry. If the cluster topology results in the electron–hole symmetric one-particle spectrum, binding is
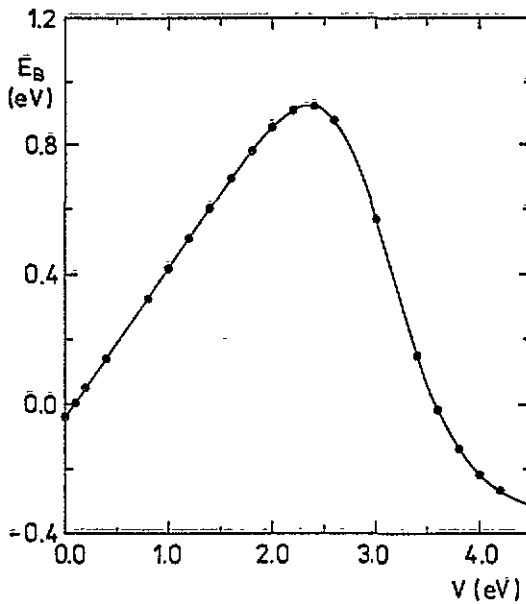
Figure 1. Binding energy $\bar{E}_b(n)$ for square based parallelepiped (cluster B) for hole doping ($n = -1$), as a function of intersite repulsion $\bar{V}$, for $U = 5.5$ eV, and $t_s = t_d = -2.35$ eV. The results of numerical calculations are shown by points, while the line is a guide to the eye.
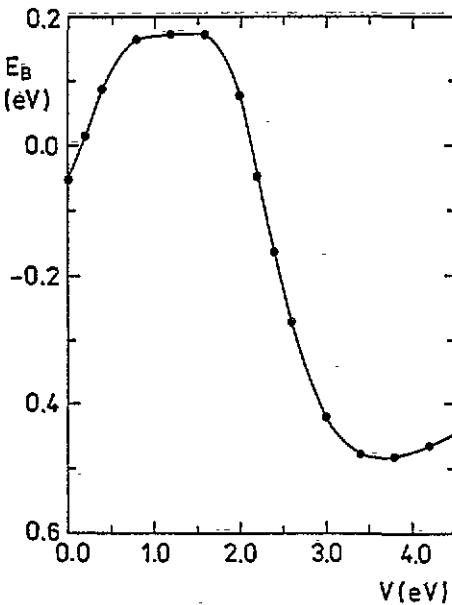

Figure 2. Binding energy $\bar{E}_b(n)$ for hexagon based parallelepiped (cluster D) for hole doping ($n = -1$), as a function of intersite repulsion V, for $U = 5.5$ eV, and $t_s = t_d = -2.35$ eV. Points and line as in figure 1.

possible. Whether it occurs or not depends to a large extent on the value of the intersite Coulomb repulsion which was found to stabilize the binding in those situations where the electron–hole symmetry allows it.
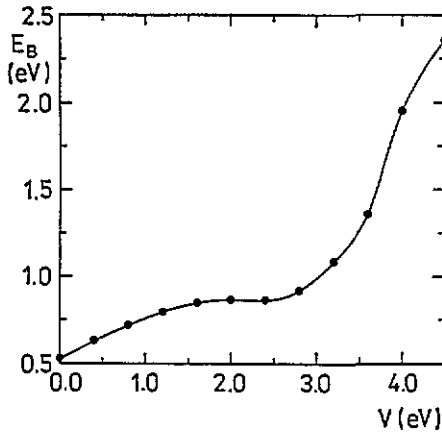
Figure 3. Binding energy $E_b(n)$ for pentagon based parallelepiped (cluster C) for hole doping ($n = -1$), as a function of intersite repulsion V, for $U = 5.5$ eV, and $t_s = t_d = -2.35$ eV. Points and line as in figure 1.

As already mentioned, there is no evidence that intersite Coulomb interaction V is large in the C_{60} molecule, as the optical excitation spectra of neutral C_{60} could be explained quantitatively by the Hubbard model [20]. Therefore, our set No 2 is the closest one to the parameters extracted recently from the experimental data by Salkola [20]. For these parameters we found no pairing in any of the considered geometries. Furthermore, the electronic states of the C_{60} molecule do not exhibit particle–hole symmetry. Therefore, the present calculations suggest that the binding of electron pairs in doped C_{60} is not likely to follow from a purely electronic mechanism. However, we would like to point out that although the results obtained for finite clusters are suggestive, one has to realize that the strong dependence of the binding energy $E_b(n)$ on the cluster geometry does not allow for more than qualitative conclusions from the present study of small clusters. Moreover, only in cluster E has the first excited state a threefold degeneracy, and the particle–hole symmetry is broken, as in C_{60}. Thus, one could answer the question about the possibility of a purely electronic pairing mechanism in doped C_{60} in principle only after performing the complete analysis of π electrons interacting by realistic on site and intersite Coulomb interactions in the full C_{60} molecule.

The third observation concerns the ground state of small carbon atom clusters with various electron numbers. The Hamiltonian parameters used to describe π electrons in the clusters are in the regime which corresponds to crossover from low-spin ground state to high-spin ground state (suggested by Hund's rule). This finding corroborates the results of several earlier investigations [12, 33, 34].

Acknowledgment

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