Orientation of C_{60} clusters in solids

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The (hopping) interaction energy between C_{60} clusters as a function of their relative orientation is studied with a tight-binding model derived from an *ab initio* calculation. Different structures are compared, and factors determining the cluster orientation and the lattice are discussed both without and with doping. Comparison with experiment suggests that chemical bonding (hopping) is important for the cluster orientation and the cohesive energy.

C_{60} has attracted much interest after the discovery that these clusters form solids [1], and that K and Rb doped C_{60} solids are superconductors with relatively high transition temperatures [2]. Undoped C_{60} forms an fcc lattice, probably with orientational disorder, above 249K and an sc lattice with 4 clusters per unit cell below 249K [3]. In the latter case the 4 clusters are believed to be located on an fcc lattice, but to have different orientations [3]. The mechanisms determining the orientations are not known. It is also not known whether the inter cluster binding is due to chemical bonding or van der Waals interaction, and what factors determine the lattice structure. These issues are addressed in this paper. Since the C_{60} clusters are almost spherical, we assume that the van der Waals interaction has a weak directional dependence and that the orientations and the lattice structures are mainly determined by chemical bonding. We provide support for this view.

The atoms in the C_{60} cluster span 12 pentagons and 20 hexagons, and are connected via two kinds of edges: one is shared by two hexagons (hexagon edges) and the other is shared by a hexagon and a pentagon (pentagon edges). For *two* C_{60} clusters, we may compare geometries where, e.g., two faces (pentagon or hexagon), two edges (pentagon or hexagon), or two corners are pointing towards each other. We first consider factors influencing the energies for these orientations. As the C_{60} clusters are on a lattice, there are additional geometrical constraints on the possible orientations. Below we use a tight-binding model for studying the orientational dependence of the hopping energy for undoped and doped C_{60}. Repulsive forces are not explicitly included.

Before we present the full calculations, we discuss some general aspects. Since, the separation ($\sim$ 3 Å) between two atoms on different clusters is large compared with a C-C bond ($\sim$ 1.4 Å), the interaction between the clusters can be treated in perturbation theory. Thus we first calculate the states of an isolated cluster. Far below and far above the Fermi level there are bonding (σ) and antibonding (σ^*) states, respectively, formed from sp^2-like hybrids lying in the sphere surface. The $2p_z$-like states pointing out of the surface are located closer to the Fermi energy due to their weaker π type of interaction [5]. The latter states give the main contribution to the inter cluster interaction, both due to their direction and their relative closeness to the Fermi energy. We therefore only consider the $2p_z$ orbitals. The interaction between two clusters is then calculated in perturbation theory, and expressed in terms of the hopping matrix elements V_{ij} between the 30 (33) occupied states (energy E_i) on one cluster and the 30 (27) unoccupied states (energy E_j) on the other cluster in the undoped (heavily doped) case.

$$E = 2\sum_{i}^{occ}\sum_{j}^{unocc}\frac{|V_{ij}|^2+|V_{ji}|^2}{E_i-E_j}, \qquad (1)$$

where the two terms in the numerator describes hopping from the left to the right cluster and vice versa. A factor 2 comes from spin. If the clusters interact via *corner* atoms only, say atom 1 on the left cluster and atom 2 on the right cluster, we have $V_{ij} = V_{pp\sigma}c_1^i c_2^j$, where $V_{pp\sigma}$ is the hopping matrix element between two $2p_z$ orbitals pointing towards each other, and c_μ^i is the coefficient of the ith wave function on the μth atom. For the interaction between two *edges* (1-2 and 3-4), the hopping matrix element is

$$V_{ij} = V_\alpha(c_1^i c_3^j + c_2^i c_4^j) + V_\beta(c_1^i c_4^j + c_2^i c_3^j), \qquad (2)$$

where V_α and V_β are the hopping matrix elements between the two orbitals on the two edges "directly" and "diagonally", respectively, across from each other. In the case of two *faces* with N atoms directed towards each other, there may be N^2 important terms in the matrix element V_{ij}, and N^4 terms in $|V_{ij}|^2$. This will tend to favor a large value of N. However, the phase factors of these terms are expected to lead to large cancellations. For instance, if for an edge an occupied bonding state ($c_1^i = c_2^i$) is coupled to an unoccupied antibonding state ($c_3^j = -c_4^j$), the matrix element is exactly zero. More generally, the unoccupied states must have additional nodes to be orthogonal to the occupied ones. If the inter cluster interaction between the occupied and unoccupied states goes via many atoms, there is a greater chance to have a large cancellation due to the extra nodes. It is therefore not immediately clear if it is favorable to couple the clusters via many or few atoms.

To discuss this in more detail we consider coupling via two equivalent edges. We first perform the sums in Eq. (1) over the g_k (g_l) degenerate states with energy $E_i = E_k$ ($E_j = E_l$), where k and l denote irreducible representations of the icosahedral group. Since all atoms

are equivalent, $\sum_{i\in k}|c_\mu^i|^2 = g_k/60$, independently of μ. We then introduce phases ϕ,

$$\cos\phi_k = \sum_{i\in k} c_1^i c_2^i / \sum_{i\in k}|c_1^i|^2, \tag{3}$$

where all coefficients have been chosen real. The interaction is then

$$\sum_{i\in k}^{occ}\sum_{j\in l}^{unocc}|V_{ij}|^2 = 2\frac{g_k}{60}\frac{g_l}{60}[(V_\alpha^2+V_\beta^2)(1+\cos\phi_k\cos\phi_l)$$

$$+2V_\alpha V_\beta(\cos\phi_k+\cos\phi_l)]. \tag{4}$$

If $\phi_k = \phi_l = 0$ and $V_\alpha = V_\beta = V$, Eq. (4) gives a contribution $16 g_k g_l V^2/60^2$, i.e., $\sim$ as N^4 with $N = 2$, as expected. However, the phase factors will obviously strongly reduce this contribution.

To illustrate this we have performed tight-binding calculations for C_{60} clusters, with the nearest neighbor distances 1.46 Å and 1.40 Å in the single and double bonds, respectively. The tight-binding hopping parameters $V_{pp\sigma}$ and $V_{pp\pi}$ are fitted to the 5 highest occupied and the 3 lowest unoccupied bands in a linear-muffin-tin-orbital band structure calculations in the atomic sphere approximation. Following Harrison [4] we use $V_{pp\pi}/V_{pp\sigma} = -1/4$. Using the experience of tight-binding calculations, we include only nearest neighbor intra cluster interactions. For the inter cluster interaction such a prescription is ill-defined, since very similar distances may occur as the clusters are rotated. We therefore use an exponentially decaying intercluster interaction. From the fit we obtain $V_{pp\sigma} = v_\sigma R\exp[-\lambda(R-1.43)]$, where $v_\sigma = 6.7$ eV/Å and $\lambda = 1.98$ Å^{-1}. The intra cluster hopping parameters are then -2.59 eV and -2.78 eV and the inter cluster hopping is -0.84 eV for the fcc structure (lattice parameter 14.04 Å) deduced below. The band width obtained from these parameters is consistent with electron energy loss spectroscopy (EELS) [6] and photoemission (PES) [7] data.

Table I shows results for the states of an isolated cluster. To understand the results for the phase factors ϕ (see Eq.(3)), we follow Ref. 6 and first consider the (complex) states for an *isolated* pentagon

$$\frac{1}{\sqrt{5}}\sum_{\mu=1}^{5}\exp(\frac{2}{5}im\mu\pi)\chi_\mu \tag{5}$$

where $m = 0, \pm1, \pm2$, and χ_μ are the orbitals at the 5 pentagon corners. When the pentagons are coupled to each other via hexagon edges, degeneracies are lifted but the states belonging to different $|m|$ do not mix very strongly. Consider the phase ϕ^{p1} for two neighboring atoms connected by a pentagon edge. If there were no mixing, the lowest 12 states (4 energies in Table I) would have $\phi^{p1} = 0°$ ($m = 0$) the next 24 states (6 energies), $\phi^{p1} = 72°$ ($m = \pm1$) and the highest 24 states (6 energies) $\phi^{p1} = 144°$ ($m = \pm2$). For the second nearest neighbors the angles (ϕ^{p2}) would be twice as large. This is indeed fairly close to the calculation. With respect to the hexagon edges and without doping, the occupied states tend to have [5] primarily bonding ($\phi^{h1} = 0°$) and the unoccupied states antibonding ($\phi^{h1} = 180°$) character.

Combining Table I and Eq. (4), we can see that coupling clusters via two pentagon edges is rather favorable. The Fermi energy cuts through the 72° degree states, and there are interactions $i-j$ = 0°-72°, 72°-72°, 0°-144° and 72°-144°. Among these pairs, the cosine terms lead to a negative contribution only for the 0°-144° and 72°-144° pairs, and we expect the coupling via pentagon edges to be larger than the coupling via corners. Coupling via hexagon edges is much less favorable for the undoped case, because of the tendency to have $\phi \sim 0°$ for the occupied states and $\phi \sim 180°$ for the unoccupied states. With doping, however, an antibonding state is occupied, and this interacts efficiently with the unoccupied antibonding states.

We next consider numerical results for the interaction (hopping) energy between two clusters. We have considered the case when the centers of the clusters are kept at a fixed distance. If two corner atoms point towards each other, the separation between the closest atoms is smaller than if edges or faces point towards each other. In the latter case one may expect that the cluster centers move closer, but due to the repulsive forces (not explicitly considered in the calculation) acting between a larger number of atoms, the separation of the closest atoms is expected to be larger than for the case of two corner atoms facing each other. We have therefore also performed calculations where the shortest distance between two atoms on the two clusters is kept fixed (which would be appropriate for a hard core interaction), expecting reality to be between these extremes. In each case the second cluster is obtained from the first via a rigid translation.

Table II shows results both for the undoped case and for the heavily doped case, with 6 additional electrons per cluster. We assume that doping only changes the number of electrons. This neglects, e.g., the indirect hopping between the clusters via the dopants, as well as the question if there is room for 6 dopants in a given structure. As expected, for the undoped case coupling via pentagon edges is more efficient than via hexagon edges, while for the heavily doped case the interaction energies are comparable. For a fixed distance between the closest neighbors, coupling between pentagon faces gives the largest interaction energy. The hexagon face interaction is weaker, due to less favorable phases, and despite the larger number N of atoms involved. For fcc, bcc and hcp lattices, with one atom per cell, the pentagon faces can, however, not point towards each other for all nearest neighbor pairs.

In the fcc lattice pentagon edges, and in the bcc lattice hexagon faces, can be rather well oriented towards each other. Since there are 8 and 12 neighbors in the bcc and fcc lattices, respectively, we may expect the bcc lattice to be favored if the hexagon-face interaction is more than 1.5 times the pentagon-edge interaction. Whether or not this is the case depends on how close the atoms can get in the bcc phase.

We have also performed calculations for different lattice structures both with and without doping, varying the orientation(s) of the cluster(s) in the cell to find the energy minimum. Table III shows the lowest hopping energies we have found in our $T = 0$ calculations. The exchange-correlation (e.g., van der Waals) and repulsive energies are not included in our tight-binding model and should be added to the energies in Table III. For the fcc lattice and without doping, the energy is minimized when the four 3-fold axes going through hexagon face centers point along the [±1,±1,±1] cubic directions (see, e.g., Fig. 1 in Ref. 8). In this orientation a hexagon edge, parallel to the xy-plane, has the largest z coordinate, and we call this the "top hexagon edge". The same orientation was obtained both when the distance between the centers of the clusters or the separation of the closest atoms on two neighboring clusters were kept fixed. In this orientation the clusters interact via pentagon edges.

We next consider the low-temperature sc structure, where the *centers* of the clusters seem [3] to be located on an fcc lattice, but the *orientations* of the 4 clusters in the unit cell are believed to differ. The pentagon edge matching obtained in the fcc lattice can now be further improved. If the "top hexagon edge" mentioned above, is parallel to the x-axis, the pentagon edge of the central cluster lies 3.5° "above" the $[0,1,1]$ line, while on the (0,1,1) cluster it lies 3.5° "below" this line. In the sc lattice, this mismatch can be reduced by rotating two of the four clusters in the unit cell, e.g., the two clusters in the $x-y$ plane, 90° around the z-axis. The edge in the $[0,1,1]$ direction on the central cluster then also lies 3.5° "below" the $[0,1,1]$ line, while in the $[1,0,1]$ direction both the edge on the central and the neighboring cluster lie 3.5° "above" the $[1,0,1]$ line. In this way the directions of the edges are matched for 8 of the 12 neighbors of each cluster. This bi-directional structure forms a tetragonal lattice with two clusters per unit cell. The nearest neighbor hopping matrix element is $\cos^2\alpha V_{pp\sigma} + \sin^2\alpha V_{pp\pi}$, where α is the angle of the p_z orbital to the line connecting the two atoms. For the sc case (for 8 of the 12 neighbors) $\alpha = 3.5°$ and for the fcc (uni-directional) case 11.7°. Since $V_{pp\sigma}$ and $V_{pp\pi}$ have opposite signs, the interaction is stronger in the bi-directional case. When the more long-range interaction is included, this difference is reduced in the undoped case but increased for the new interactions in the doped case.

The binding energy is of the right order of magnitude to explain the experimental heat of sublimation (1.7 eV) [10]. Since the hopping parameters are consistent with the experimentally observed level broadening of the isolated cluster levels [6,7], we believe this shows that inter cluster hopping is important both for the cluster orientation and the cohesive energy. Our structure does, however, not reproduce all the intensities in an X-ray scattering experiment [3] very well, suggesting that the structure proposed above is not the optimum one. The reason may be that we have not found the absolute minimum in the 12 dimensional space of all possible rotations. It could also be that relaxing the constraint that all cluster centers are on an fcc lattice or introducing additional interactions, would make one of the many other low-lying minima, with possibly a quite different X-ray diffraction pattern, the absolute minimum. We believe, however, that the presented arguments provide an important guide in the search for the correct structure. For instance, the structure proposed by Heiney et al [3] gives an unfavorable interaction energy (-0.88 eV per cluster with the closest atom separation 2.99 Å) in the same tight-binding model as above, suggesting that this is not the correct structure either.

Table III further shows that the fcc structure is always favored over the hcp structure, in agreement with experiment. Whether or not the fcc or bcc structure wins, depends on the form of the repulsive forces (not included in our calculation), since the interaction goes via more atoms in the bcc lattice (6 atoms) than in the fcc lattice (2 atoms). We therefore expect a larger separation between the closest atoms in the bcc structure, somewhere between the two extremes in Table III. Table III does not show any increased preference for the bcc structure when the system is doped. The experimentally seen bcc structure for C_{60} doped with 6 K or Cs atoms [9] is therefore presumably entirely due to the lack of room for 6 large dopants in the fcc structure.

We have discussed the interaction between C_{60} clusters, using a tight-binding model with *ab initio* parameters. These parameters lead to a level broadening due to inter cluster hopping which is consistent with experiment [6,7]. Although the number of terms contributing to the interaction energy increases with the number, N, of atoms in contact, interference terms (orthogonality effects) may, nevertheless, make a large value of N unfavorable. We find that in the undoped case the interactions via two pentagon faces ($N = 5$) and two pentagon edges ($N = 2$) are relatively favorable. In the fcc structure (and at $T = 0$) we find that the interaction takes place via pentagon edges, since geometrical constraints prevent interaction via pentagon faces. In the sc structure with 4 clusters per unit cell, the rotation of two clusters relative to the fcc structure, allows for a more efficient pentagon edge interaction, at least in the doped case, but it is probably not the correct structure in the undoped case. The results obtained above should provide guidance in the search for the correct structure. The calculations

give a binding energy of the right order of magnitude, suggesting that the inter cluster hopping plays an important role. In future calculations it would be interesting to include van der Waals interactions and repulsive forces, as well as the interactions with the dopants. One may also consider more complicated couplings between, e.g., edges and faces.

After this work was completed, experimental work on K_3C_{60} at room temperatureappeared [11], where the structure was found to be the same as our bi-directional structure above, except that there was a disorder in the orientations (along the x- or y-axis) of the "top hexagon edge". For the undoped case, the correct structure has been found to involve the interaction of hexagon edges with pentagon faces [12]. The dominating interaction is described by Eq. (4) with $V_\beta << V_\alpha$ and the columns ϕ^{p2} and ϕ^{h1} in Table I, and leads to slightly more favorable phases than the pentagon edge coupling. Compared with the fcc structure at the same closest atom separation, the energy is slightly higher (-1.013 eV), but it is somewhat lower (-1.139 eV) if the average of the nearest and second nearest neighbor distances (differing by only 3 % [13]) is taken equal to the closest atom separation in the fcc case.

ones due to our use of only two intra cluster distances.

TABLE I. The one-electron energies E_k, the irreducible representations k, the degeneracies g_k, the l-values of the representations and the phases ϕ_k (see Eq. (3)) of an isolated icosahedral C_{60} cluster. We use the notations ϕ_k^{pn} and ϕ_k^{hn} for the pentagons and hexagons, respectively, where $n = 1$ stands for nearest neighbor, $n = 2$ for second nearest neighbor and so on. For the hexagon $n = 1$ refers to a hexagon edge. All phase are given modulus 180°. The highest occupied state lies at -1.69 and at 0.52 in the undoped and doped cases, respectively. All energies are relative to the $2p$-orbital energies and measured in eV.

E_k	k	g_k	l	ϕ_k^{p1}	ϕ_k^{p2}	ϕ_k^{h1}	ϕ_k^{h2}	ϕ_k^{h3}
-7.97	a_g	1	0	0	0	0	0	0
-7.32	t_{1u}	3	1	23	37	24	41	48
-6.11	h_g	5	2	38	61	43	71	82
-4.75	t_{2u}	3	3	34	21	81	113	140
-4.23	g_u	4	3	73	143	14	75	80
-2.72	g_g	4	4	81	131	46	100	131
-2.66	h_g	5	4	71	107	90	111	113
-1.69	h_u	5	5	87	124	60	112	144
0.52	t_{1u}	3	5	67	127	156	116	50
1.17	t_{1g}	3	6	72	144	180	108	72
3.39	h_g	5	6	127	72	95	118	42
3.76	t_{2u}	3	5	130	68	99	115	17
4.28	h_u	5	7	124	87	120	97	72
5.31	g_g	4	6	131	81	133	80	81
6.82	g_u	4	7	143	73	166	42	133
6.97	t_{2g}	3	8	144	72	180	36	144

TABLE II. The interaction energy between two clusters, oriented so that corner atoms, equivalent edges or equivalent faces point towards each other. The cases when the cluster centers are separated by 9.93 Å and when the distance between the closest atoms is 2.99 Å, as well as the undoped and heavily doped cases are considered. All energies are in eV.

	Fixed center sep.		Fixed closest atom sep.	
	undoped	doped	undoped	doped
Corner	-0.188	-0.168	-0.098	-0.087
Pentagon edge	-0.199	-0.168	-0.173	-0.145
Hexagon edge	-0.145	-0.174	-0.121	-0.143
Pentagon face	-0.153	-0.130	-0.482	-0.422
Hexagon face	-0.066	-0.059	-0.261	-0.246

TABLE III. The interaction energy per C_{60} cluster for different structures. The same cases as in Table II are considered. The number of atoms per cell are shown in parenthesis. All energies are in eV.

structure	Fixed center sep.		Fixed closest atom sep.	
	undoped	doped	undoped	doped
fcc (1)	-1.029	-0.903	-1.029	-0.882
bcc (1)	-0.667	-0.610	-1.197	-1.054
hcp (1)	-0.939	-0.891	-0.923	-0.756
bi-dir (2)	-1.133	-1.018	-1.028	-0.924

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