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Shake-up effects and intermolecular tunneling in C_{60} ions

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The multiplet structure induced by the Coulomb interactions in C_{60}^{n-} ($n=1-12$) is analyzed. The lowest partially occupied molecular orbital gives rise to a set of levels that fill a relatively wide band ($\approx 2-3$ eV). A large (~ 1 eV) intramolecular effective repulsion is found. The anions are also shown to be highly polarizable. The optical-absorption and photoemission spectra are calculated. The probability of exciting the molecule upon the addition or removal of one electron is shown to be significant, and this effect may give rise to the insulating behavior of K_4C_{60} . The role of intermolecular interactions in suppressing the net repulsion within the C_{60} molecules is discussed.

The small size of the C_{60} molecule implies that charging effects are significant. Estimates for the repulsion between two additional electrons in a free molecule are in the range of 3–4 eV.¹⁻³ In a crystal, screening is expected to reduce this value, to about 1 eV.¹

The most straightforward consequence of a significant Coulomb repulsion is the existence of different multiplets, when the outer shells are partially filled.⁴⁻⁶ In C_{60} , the lowest unoccupied molecular orbitals (LUMO's) are two triply degenerate levels (t_u and t_g), which lie close in energy (≈ 0.5 eV). Given the magnitude of the Coulomb interactions, both these levels should be considered when discussing the low energy multiplet structure.

The excitations within these multiplets are the likely cause of a feature identified as a "LUMO plasmon" in HREED experiments.⁷ They should also show up in optical absorption measurements. There is a finite probability that the injection or emission of one electron will leave the molecule in an excited state. These shake-up processes give an intrinsic width to the LUMO peaks, as measured in photoemission experiments.

In a crystal, the intermolecular hybridization is an additional source of broadening. Intramolecular shake-up and intermolecular tunneling are almost incompatible processes. Strong shake-up effects reduce intermolecular hopping, while a large hybridization implies the irrelevance of intramolecular interactions. Experimentally, a significant width has been observed.⁸⁻¹³ Shake-up effects have also been dis-

cussed in connection with electron emission from a single C_{60} molecule.¹⁴

The competition between shake-up and tunneling also has consequences for other electronic properties, like the conductivity. A large energy gap between successive multiplets and a reduced hopping rate favors insulating behavior, while the opposite happens if tunneling dominates.¹⁵

In the present work, we analyze the multiplet structure of C_{60}^{n-} . We diagonalize the Coulomb interaction in the space of the two LUMO's. We use a continuum approximation, which correctly describes these lowest lying orbitals.¹⁶

Within a continuum description, it can be shown that the two lowest triplets correspond to the zero modes of an effective Dirac equation.¹⁶ In this scheme, the angular momentum is a good quantum number. These states correspond to $l=1$. The wave functions in these two triplets are³

$$\begin{aligned}\Psi_{1,a}^\alpha &= \sqrt{\frac{3}{8\pi}} \sin^2\left(\frac{\theta}{2}\right) e^{i\phi}, & \Psi_{1,a}^\beta &= 0 \\ \Psi_{0,a}^\alpha &= \sqrt{\frac{3}{4\pi}} \sin\left(\frac{\theta}{2}\right) \cos\left(\frac{\theta}{2}\right), & \Psi_{0,a}^\beta &= 0, \\ \Psi_{-1,a}^\alpha &= \sqrt{\frac{3}{8\pi}} \cos^2\left(\frac{\theta}{2}\right) e^{-i\phi}, & \Psi_{-1,a}^\beta &= 0, \\ \Psi_{1,b}^\alpha &= 0, & \Psi_{1,b}^\beta &= \sqrt{\frac{3}{8\pi}} \cos^2\left(\frac{\theta}{2}\right) e^{i\phi},\end{aligned}\quad (1)$$

TABLE I. Lowest lying multiplets for charged states of C_{60} . The parameters used are $E_C = 1$ eV, $\Delta = 0.3$ eV. States are classified in terms of their spin, angular momentum, and parity. Energies are in eV. The ground state polarizability (in \AA^3) is also listed.

C_{60}^{-}		C_{60}^{2-}		C_{60}^{3-}		C_{60}^{4-}		C_{60}^{5-}		C_{60}^{6-}	
Total width 0.600		Total width 1.581		Total width 2.585		Total width 4.009		Total width 4.542		Total width 5.137	
Polarizability 73.9		Polarizability 67.6		Polarizability 39.6		Polarizability 48.8		Polarizability 67.5		Polarizability 61.1	
state	energy	state	energy	state	energy	state	energy	state	energy	state	energy
$^2P_+$	-0.300	$^3P_+$	0.300	$^4S_-$	1.743	$^3P_+$	4.383	$^2P_-$	7.941	$^1S_+$	12.419
$^2P_-$	0.300	$^1S_+$	0.319	$^2D_-$	1.912	$^1D_+$	4.476	$^2P_+$	8.254	$^1S_-$	12.671
		$^1D_+$	0.360	$^2P_-$	1.931	$^1S_+$	4.486	$^4D_+$	8.323	$^3D_-$	12.902
		$^1S_-$	0.600	$^4S_+$	1.946	$^3P_-$	4.664	$^4P_+$	8.357	$^3S_-$	12.950
		$^3P_-$	0.700	$^4D_+$	2.140	$^5P_-$	4.700	$^4S_+$	8.369	$^3P_-$	12.960
		$^3D_-$	0.760	$^2P_+$	2.252	$^1S_-$	4.719	$^2F_+$	8.454	$^1S_+$	12.981

$$\Psi_{0,b}^\alpha = 0, \quad \Psi_{0,b}^\beta = -\sqrt{\frac{3}{4\pi}} \sin\left(\frac{\theta}{2}\right) \cos\left(\frac{\theta}{2}\right),$$

$$\Psi_{-1,b}^\alpha = 0, \quad \Psi_{-1,b}^\beta = \sqrt{\frac{3}{8\pi}} \sin^2\left(\frac{\theta}{2}\right) e^{-i\phi}.$$

Each wave function is a spinor [components labeled as (α, β)], reflecting the fact that they are defined on a lattice with two sites per unit cell. The subscripts a, b refer to the two possible ‘‘flavors’’ of the states. This additional degeneracy (discussed in detail in Refs. 2 and 3) is related to the well-known ‘‘fermion doubling problem.’’ These levels, which are degenerate and lie at zero energy in the continuum approximation, are shifted and split by the icosahedral symmetry of the molecule. The effect can be included, in a phenomenological way, by introducing a one body Hamiltonian which mixes the two different flavors. Within this scheme, the system is described by means of two parameters only: the splitting already mentioned, $=2\Delta$, and the magnitude of the Coulomb repulsion, $E_C = e^2/(\epsilon R)$.

Within the continuum description, the total angular momentum L is a good quantum number, as is the total spin S and the parity. The existence of the flavor degeneracy allows us to define an isospin operator S' .

The interaction between two electrons was discussed in Ref. 3. The electron-electron term of the Hamiltonian, when projected onto the basis spanned by the two lowest triplets [Eq. (1)] can be written as

$$\begin{aligned} \mathcal{H}_{e-e} = E_0 & \left(k_1 \sum_{i,j} \hat{n}_i \hat{n}_j + k_2 \sum_{i,j} \hat{l}_i \cdot \hat{l}_j + k_3 \sum_{i,j} \hat{s}_i \cdot \hat{s}_j \right. \\ & \left. + k_3 \sum_{i,j} \hat{s}'_i \cdot \hat{s}'_j + k_4 \sum_{i \in a, j \in b} \hat{l}_i \cdot \hat{l}_j \right), \end{aligned} \quad (2)$$

where \hat{l} is the angular momentum operator, \hat{s} the spin, and \hat{s}' the isospin. The energy scale E_0 and the dimensionless constants k_1 , k_2 , k_3 , and k_4 depend on the nature of the interaction. For a simple Coulomb repulsion, we have $E_0 = E_C$, $k_1 = 49/50$, $k_2 = 11/50$, $k_3 = -3/25$, and $k_4 = -1/2$. Other interactions, such as a contact coupling, modify the overall scale, but leave the relative values of the k 's almost unchanged. Equation (2) makes explicit how exchange effects favor a high spin or isospin.

The local field splitting can be added to (2), as

$$\mathcal{H}_{\text{split}} = \Delta \sum_{m,s} c_{a,m,s}^\dagger c_{b,m,s} + \text{H.c.} \quad (3)$$

Indices a, b stand for the isospin, $s = \pm$ is the real spin, and $m = 0, \pm 1$ is the angular momentum.

In Table I we give the lowest lying multiplets, and the total width of the spectrum for $\Delta/E_C = 0.3$ and $E_C = 1$ eV. These parameters have been adjusted so as to reproduce the ordering of the lowest levels, and the overall scale of the multiplet structure of the discrete C_{60}^{n-} anions, for $n = 1 - 5$,¹⁷ when the electrostatic interaction is modeled to fit well the optical absorption of neutral C_{60} .¹⁸ The electron-electron repulsion in Ref. 18 is of the form $V(r) = 1/\sqrt{1/U^2 + r^2/(r_0 V)^2}$, where r_0 is the average interatomic distance, $U = 7.2$ eV and $V = 3.6$ eV.¹⁹

Some of the salient features of these results are as follows.

There is always a net repulsion between electrons, defined as $U_{\text{eff}} = E_{N-1} + E_{N+1} - 2E_N$. Its is of order E_C . It is somewhat reduced by screening induced by rearrangements within the LUMO's. U_{eff} shows local maxima for $N = 3, 6$, and 9 . If no other effects are present, a crystal built up of C_{60}^{3-} anions should be an insulator.^{8,15} Electrochemical measurements²⁰ also suggest the existence of this intramolecular repulsion.

While Hund's rule is not strictly followed, some of the lowest lying states have high spins. These results may help to explain the anomalously large signal found in electron spin resonance experiments.²¹ The higher lying states tend to have lower spins, which is also consistent with the observed decrease in the spin relaxation rate with increasing temperature.

Multiplets tend to appear in pairs with the same quantum numbers but opposite parity. This is related to the approximate isospin symmetry described earlier.

The electrical polarizability associated with transitions within these multiplets is also listed in Table I. These values should be added to the polarizability arising from the remaining π levels. Within the same model,²² this value is 90 \AA^3 .

We have also analyzed the leading dipole allowed transitions out of the C_{60}^{2-} , C_{60}^{3-} and C_{60}^{4-} lowest states, which are given in Table II. In the convention that we use to

TABLE II. Leading dipole allowed transitions from low lying multiplets for different charge states of C_{60} . The parameters are the same as in Table I.

Charge state	transition	energy (eV)	dipolar strength
C_{60}^{2-}	${}^3P_+ \rightarrow {}^3D_-$	0.460	0.410
	${}^3P_+ \rightarrow {}^3S_-$	1.300	0.821
	${}^1S_+ \rightarrow {}^1P_-$	1.121	0.480
	${}^1D_+ \rightarrow {}^1P_-$	1.080	0.923
	${}^3D_- \rightarrow {}^3P_+$	0.840	0.923
C_{60}^{3-}	${}^4S_- \rightarrow {}^4P_+$	0.957	0.854
	${}^2D_- \rightarrow {}^2F_+$	0.568	0.262
	${}^2D_- \rightarrow {}^2P_+$	0.604	0.127
	${}^2D_- \rightarrow {}^2P_+$	1.390	1.061
	${}^2P_- \rightarrow {}^2D_+$	0.483	0.280
C_{60}^{4-}	${}^3P_+ \rightarrow {}^3D_-$	0.840	0.526
	${}^3P_+ \rightarrow {}^3S_-$	1.137	0.526
	${}^1D_+ \rightarrow {}^1F_-$	0.803	0.431
	${}^1D_+ \rightarrow {}^1P_-$	1.602	1.382
	${}^1S_+ \rightarrow {}^1P_-$	1.002	0.922

define the dipolar strengths, they obey the sum rule $\sum_j |(i|\hat{P}|j)|^2 \leq N$.

The spectral strengths show a peak for energies $\sim 0.6-0.8E_C$, in all three cases. Identification of this peak with the lowest feature observed in Ref. 7 implies that $E_C \sim 1$ eV in K_3C_{60} , showing the adequacy of the parameters employed.

The previous analysis shows the existence of a large intramolecular Coulomb repulsion, ~ 1 eV, a result consistent with most theoretical analyses. Its scale is beyond the range which can be reasonably compensated by intramolecular phonon effects. Our results, however, also indicate the existence of a large intermolecular polarizability. The bulk dielectric constant is $\epsilon = 1 + 4\pi\rho P$, where ρ is the density of C_{60} molecules, and P is the polarizability. We find $\epsilon = 3.75$. The reduction in energy due to the polarization of a neutral molecule in the presence of a unit charge at distance D is $\Delta E = e^2/D(P/D^3)$. Setting $D = 3R$, where $R = 3.5$ Å is the radius of the C_{60} molecule, we find $\Delta E = 0.18$ eV. If we consider a charged molecule and its twelve nearest neighbors, including all electrostatic interactions between them, we find a polarization energy $\Delta E \approx 1.6$ eV. Thus, the intermolecular polarization can well compensate the intramolecular repulsion. Other couplings can also contribute to give a net intramolecular attraction, but, unless a very precise cancellation takes place, the intermolecular electrostatic interaction is the only one with the right order of magnitude. Note that no intermolecular interaction can influence the multiplet splitting within a given charge state.

We have calculated the probability of exciting the molecule upon the addition, or removal of a single electron. The probability for transitions between different ground states is 0.87 for the $C_{60}^{2-} \leftrightarrow C_{60}^{3-}$ transition, 0.37 for the $C_{60}^{3-} \leftrightarrow C_{60}^{4-}$ transition, and 0 for the $C_{60}^{4-} \leftrightarrow C_{60}^{5-}$ one. These numbers reduce intermolecular hopping. In the last case, the lowest lying allowed transition is from the ground state of C_{60}^{4-} (${}^3P_+$) to the second excited state of C_{60}^{5-} (${}^4D_+$), which lies 0.38 eV above the ground state

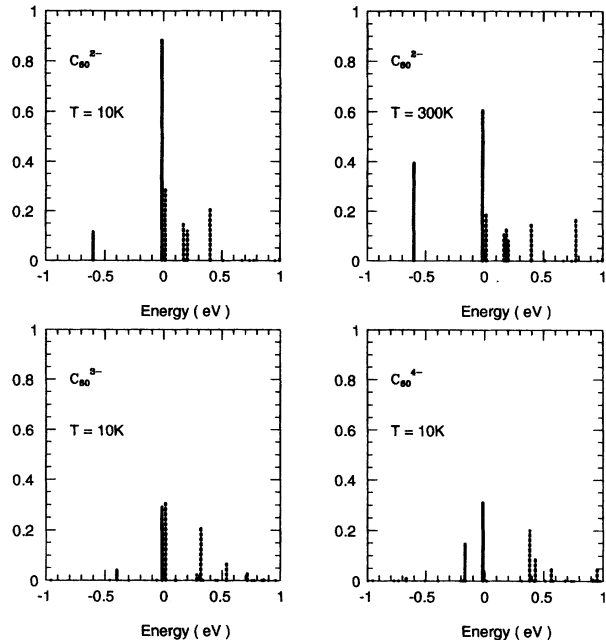


FIG. 1. Direct (full lines) and inverse (dashed lines) photoemission spectra of different C_{60}^{n-} anions. The temperature dependence in the spectra of C_{60}^{3-} and C_{60}^{4-} is negligible.

(see Table I). This mismatch may help to explain the insulating behavior of K_4C_{60} . Metallic behavior in this compound implies that the C_{60} molecules fluctuate, at least, between the 3^- , 4^- , and 5^- charge states. If the $C_{60}^{3-} \leftrightarrow C_{60}^{4-}$ transition is inhibited (by a factor 0.37), and the $C_{60}^{4-} \leftrightarrow C_{60}^{5-}$ one is completely suppressed, the system should be insulating.

The coherence length in superconducting M_3C_{60} , which gives the size of the Cooper pairs, is comparable to the C_{60} radius. Thus, the creation of a Cooper pair can be roughly described as a transition from C_{60}^{2-} to C_{60}^{4-} . The operator which relates these two ground states is of the 1S type, which should give the symmetry of the order parameter.

In Fig. 1 we show the photoemission spectra of C_{60}^{2-} , C_{60}^{3-} , and C_{60}^{4-} . They have a non-negligible width, although the highest lying multiplets do not contribute. The existence of two closely spaced levels with different symmetries in C_{60}^{2-} gives a strong temperature dependence to the spectra, in agreement with experimental results.¹⁰ These results suggest that the width observed in photoemission is intrinsic to the charged C_{60} anion. It would be interesting if similar features are observed in C_{60} with metal atoms in an endohedral position.²³

It is worth noting that the ground state of most anions considered shows orbital degeneracy ($L = 1$). It will give rise to a Berry phase when quantizing the intramolecular vibrations.^{16,24} In addition, the adiabatic transport of a charge also generates a Berry phase. For instance, the motion of a charged “vacancy” (C_{60}^{2-}) in a background of “neutral” C_{60}^{3-} leads to a nontrivial phase. It will manifest itself as a “spin-orbit” coupling, where the “spin” refers to the angular momentum of the C_{60}^{2-} anion, and the “orbit” is given by

its motion throughout the lattice. The effects of these phases will be studied elsewhere.

The electrostatic interactions considered here do not rule out the relevance of couplings mediated by phonons.²⁴ The intramolecular charging energy depends on the radius of the C₆₀ molecule, which is modified by breathing modes. More importantly, changes in the intermolecular distances alter the polarization energy, which we are assuming to give the leading contribution to a net attraction. The main physical effects should be approximately described by an attractive Hubbard model at half filling, described in terms of the intermolecular hopping, $t \sim 0.02 - 0.04$ eV,²⁵ and the intramolecular attraction, $|U| \sim 0.1 - 0.3$ eV. This model is a superconductor, with $T_c \sim |U|e^{-W/|U|}$, where $W = 16t$ is the bandwidth. Thus, we expect a dependence of T_c on the lattice parameter, and the existence of an isotope effect. The dependence of U on the mass of the carbon atoms is not the conventional one,

$\sim M^{-1/2}$, and the isotope effect need not show standard behavior.

The previous study shows that electrostatic interactions dominate over other electron-electron couplings. Intramolecular charging effects should give rise to insulating behavior, but intermolecular electrostatic interactions can compensate this tendency. We have analyzed the influence of the electrostatic interactions on properties which lie beyond the scope of usual band structure calculations, like the satellite structure in photoemission and the renormalization of intermolecular hopping. The global picture obtained here is consistent with the observed linewidth in photoemission spectra and their temperature dependence. It also shows a "LUMO plasmon" in good correspondence with HREED experiments. The shake-up processes upon intermolecular charge transfer give a reasonable explanation for the insulating behavior in K₄C₆₀.

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- ¹V. P. Antropov, O. Gunnarson, and O. Jepsen, *Phys. Rev. B* **46**, 13 647 (1992).
- ²R. Friedberg, T. D. Lee, and H. C. Ren, *Phys. Rev. B* **46**, 14 150 (1992).
- ³F. Guinea, J. González, and M. A. H. Vozmediano, *Phys. Rev. B* **47**, 16 576 (1993).
- ⁴R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **46**, 9906 (1992).
- ⁵R. L. Martin and J. T. Ritchie, *Phys. Rev. B* **48**, 4845 (1993).
- ⁶L. Bergomi and Th. Jolicœur (unpublished).
- ⁷S. Modesti, S. Cerasari, and P. Rudolf, *Phys. Rev. Lett.* **71**, 2469 (1993).
- ⁸T. Takahashi *et al.*, *Phys. Rev. Lett.* **68**, 1232 (1992).
- ⁹S. L. Molodtsov, A. Gutiérrez, M. Domke, and G. Kaindl, *Europhys. Lett.* **19**, 369 (1992); A. Gutiérrez, Thesis, Universidad Autónoma de Madrid, Madrid.
- ¹⁰P. J. Bennis, F. Stepniak, and J. H. Weaver, *Phys. Rev. B* **48**, 9086 (1993). See also P. J. Benning *et al.*, *ibid* **47**, 13 843 (1993).
- ¹¹M. Knupfer *et al.*, *Phys. Rev. B* **47**, 13 944 (1993).
- ¹²M. D. Seta and F. Evangelisti, *Phys. Rev. Lett.* **71**, 2477 (1993).
- ¹³L. Q. Jiang and B. E. Koel, *Phys. Rev. Lett.* **72**, 141 (1994).
- ¹⁴M. E. Lin, R. P. Andres, R. Reifenberger, and D. R. Huffman, *Phys. Rev. B* **47**, 7546 (1993).
- ¹⁵R. W. Lof, M. A. van Veenendaal, B. Koopmans, H. T. Jonkman, and G. A. Sawatzky, *Phys. Rev. Lett.* **68**, 3924 (1992).
- ¹⁶J. González, F. Guinea, and M. A. H. Vozmediano, *Phys. Rev. Lett.* **69**, 172 (1992).
- ¹⁷J. González, F. Guinea, and M. A. H. Vozmediano (unpublished).
- ¹⁸K. Harigaya and S. Abe, *Phys. Rev. B* **49**, 16 746 (1994).
- ¹⁹With other choice of parameters ($\Delta/E_c = 0.12, E_c \approx 3.5$ eV), we approximate the SCF+CI calculation reported by F. Negri, G. Orlandi, and F. Zerbetto, *J. Am. Chem. Soc.* **114**, 2909 (1992). We think that our choice takes into account better, albeit still in a phenomenological way, the average screening from the rest of the crystal.
- ²⁰R. E. Haufler *et al.*, *J. Phys. Chem.* **94**, 8634 (1990); D. Dubois *et al.*, *J. Am. Chem. Soc.* **113**, 4364 (1991).
- ²¹A. Jánossy, O. Chauvet, S. Pekker, J. R. Cooper, and L. Forró, *Phys. Rev. Lett.* **71**, 1091 (1993). See also P. Bhyrappa *et al.*, *J. Am. Chem. Soc.* **115**, 11 005 (1993). The last authors find $S = 1$ for C₆₀²⁻, but $S = 1/2$ for C₆₀³⁻. For any sensible choice of parameters, we obtain $S = 3/2$ for C₆₀³⁻.
- ²²J. González, F. Guinea, and M. A. H. Vozmediano, *Mod. Phys. Lett. B* **7**, 1593 (1993).
- ²³In S. Hino *et al.*, *Phys. Rev. Lett.* **71**, 4261 (1993), La@C₈₄ was analyzed. The LUMO peaks indeed show a significant broadening.
- ²⁴A. Auerbach, N. Manini, and E. Tosatti, *Phys. Rev. B* **49**, 12 988 (1994).
- ²⁵S. C. Erwin and E. J. Mele (unpublished).