Electron–phonon coupling in charged buckminsterfullerene

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Abstract

A simple, yet accurate solution of the electron–phonon coupling problem in \( C_{60} \) is presented. The basic idea behind it is to be found in the parametrization of the ground state electronic density of the system calculated making use of ab initio methods, in term of \( sp^2 q_x \) hybridized orbitals. This parametrization allows for an economic determination of the deformation potential associated with the fullerene’s normal modes. The resulting electron–phonon coupling constants are used to calculate Jahn–Teller effects in \( C_{60}^- \) and multiple satellite peaks in the corresponding photoemission spectrum. Theory provides an accurate account of the experimental findings. © 1998 Published by Elsevier Science B.V.

The discovery of fullerenes [1], and the subsequent “mass synthesis” [2] of these hollow molecules, have prompted the search for a new class of materials such as fullerides (salts like \( K_xC_{60} \)), fullerites (\( C_{60} \) molecular crystals), etc., in which fullerenes play the role of the building blocks. The understanding of the response of these building blocks to external fields is essential in the characterization of the associated new materials. A central issue in this quest is how the electronic properties of fullerenes are modified by the coupling of electrons to phonons. This question can be answered in terms of ab initio methods (e.g., Refs. [3,4] and references therein; cf. also Ref. [5]). These methods are, however, computationally demanding and not particularly transparent, and much of the physical insight is lost in the complexity of mathematics.

In the present Letter we present a simple, yet accurate solution of the electron–phonon coupling problem particularly suited for fullerenes, and apply it to \( C_{60}^- \). The central idea behind this solution is based on a parametrization of the ground state electronic density of the system calculated making use of ab initio methods in terms of hybridized atomic orbitals. In particular, in the case of \( C_{60}^- \), fullerenes, of \( sp^2 q_x \) orbitals. Such parametrization allows for an economic determination of the deformation potential associated with the different normal modes. The resulting electron–phonon coupling constants are used to calculate Jahn–Teller effects in \( C_{60}^- \) and multiple satellite peaks in the corresponding photoemission spectrum. The resulting cross section agrees well with the experimental data, better than any of the cross sections obtained making use of the elec-
tron–phonon coupling constants available in the literature [3,4,6–8]. Furthermore, the extension of the hybrid orbital model to describe the electron–phonon coupling phenomenon in fullerenes other than C\textsubscript{60} as well as in nanotubes is simple to carry out.

The electron–phonon coupling is determined by the matrix element of the deformation potential

$$ V_{\text{def}}(r) = \sum_\beta \sum_{k=1}^3 \left( Q_\beta \cdot \nabla \right)_k V_\epsilon(\{r\},\{R\}) \bigg|_{\{R\}=\{r\}^s}, $$

where \{R\} represents the set of ionic coordinates with equilibrium values \{R\}^s. \{(Q_\beta)\}_k\ the displacement field associated with the normal modes of the \beta-ion in the \(k = (x,y,z)\) directions, while \(V_\epsilon\) is the total potential acting on the electrons. This potential can be expressed, in the local density approximation (LDA), as

$$ V_\epsilon(\{r\},\{R\}) = V_{\text{pseudo}}^t(\{r\},\{R\}) + V_{\text{Hartree}}(\rho(\{r\},\{R\})) $$

$$ + V_{\text{xc}}(\rho(\{r\},\{R\})) + V_{\text{pseudo}}^s(\{r\},\{R\}). $$

The first three terms are local and arise from: a) the pseudopotential associated with the ions; b) the Coulomb interaction acting among the electrons (Hartree field); and c) exchange (Fock field) and correlation effects. The last term in Eq. (2) reflects the non-local part of the ionic pseudopotential.

Because the first and the last terms of Eq. (2) display simply an explicit dependence on the ion positions, the calculation of their gradient (cf. Eq. (1)) presents no difficulties. This is not the case for the second and third terms of Eq. (2), which depend on \{R\} implicitly via the electronic density, a fact which can be used to write

$$ \sum_\beta Q_\beta \cdot \nabla \rho V_\epsilon(\{r\},\{R\}) \bigg|_{\{R\}=\{r\}^s} $$

$$ = \sum_\beta \frac{\partial V_\epsilon}{\partial \rho} Q_\beta \cdot \nabla \rho(\{r\},\{R\}). $$

where \(i = \text{Hartree,xc}\). Because in the LDA there is an explicit relation between \(V_\epsilon\) and \(\rho\), the derivative \(\partial V_\epsilon/\partial \rho\) can be calculated analytically. Consequently, the basic difficulty associated with the calculation of the deformation potential defined in Eq. (1), and thus of the electron–phonon coupling constants, lies in the calculation of the gradient of the electronic density along the normal displacements. To overcome this difficulty, we shall parametrize the LDA results in term of \(SP^\pm\) hybrid orbitals, in such a way that three of the four orbitals are directed along the carbon bonds of fullerene C\textsubscript{60}, while the fourth takes care of the \(\pi\) bonding present in the hexagons and is directed essentially perpendicularly to the fullerene surface.

In keeping with the fact that in C\textsubscript{60} each atom has three nearest neighbours, the hybrid orbitals we are interested in can be written as

$$ |\phi_1\rangle = a_1|s\rangle + b_1|p_x\rangle + c_1|p_y\rangle + d_1|p_z\rangle, $$

$$ |\phi_2\rangle = a_2|s\rangle + \delta_2(m_2|p_x\rangle + n_2|p_y\rangle + t_2|p_z\rangle), $$

$$ |\phi_3\rangle = a_3|s\rangle + \delta_3(m_3|p_x\rangle + n_3|p_y\rangle + t_3|p_z\rangle), $$

$$ |\phi_4\rangle = a_4|s\rangle + \delta_4(m_4|p_x\rangle + n_4|p_y\rangle + t_4|p_z\rangle). $$

Here \(m_j = \cos \alpha_j\), \(n_j = \cos \beta_j\), \(t_j = \cos \gamma_j\), and \(\alpha_j, \beta_j, \gamma_j\) \((j = 2,3,4)\) are the angles which define the direction of the bond between a Carbon atom and each of its three nearest neighbours, in a system of reference centered on the atom. After having fixed the direction of these orbitals, there still remain ten free parameters in Eq. (4), parameters which are completely determined by the orthonormalization condition.

To describe the radial dependence of the \(|s\rangle\) and \(|p\rangle\) orbitals, we have used the functions

$$ R_i = \frac{2}{\sqrt{\sigma_i}} e^{(-r/\sigma_i)} \quad \text{and} \quad R_p = \frac{2}{\sqrt{3 \sigma_2}} e^{(-r/\sigma_2)}, $$

usually employed in the description of the Carbon atom. We have however adjusted the parameters \(\sigma_1\) and \(\sigma_2\) in order to obtain the best fit to the LDA C\textsubscript{60}-density (see, for instance, Ref. [9]). One can then write the contribution to the total density arising from a single atom and, with the help of standard techniques, carry out a multipole expansion of this contribution around the center of the molecule. Adding the contributions of the 240 electrons one obtains the total density.

In Fig. 1 we display the two lowest multipoles of the C\textsubscript{60} ground state density, calculated in the LDA.
Fig. 1. Comparison between the results of LDA (full lines) and hybrid orbital model (dashed lines) for the two main multipole contributions to the ground state density of C\(_{60}\). (a) and (b) refer to the \((L,M) = (0,0)\) and \((6,0)\) contributions respectively.

including exchange-correlation effects according to the parametrization of Perdew and Zunger [10]. The role of the carbon atoms were taken into account in terms of norm-conserving pseudopotentials [11]. In the same figure we show the results of the hybrid orbital model, for \(\sigma_1 = 0.78\ \text{\AA}\) and \(\sigma_2 = 0.31\ \text{\AA}\).

The next step consists in the calculation of the gradient of the density and, through Eqs. (3) and (4), the deformation potential. Within the hybrid orbital model, moving around the ions change the direction of the orbitals but not their shape. This means that the weights \(\delta_j\) in Eq. (4) are fixed, and the only quantities which change are the angles \(\alpha_j\), \(\beta_j\), and \(\gamma_j\). The calculation of \(\nabla \rho(r,\{R\})\) becomes then quite simple.

\[\text{These values can be compared to the atomic values, } \sigma_1 = 0.65 \ \text{\AA}\text{ and } \sigma_2 = 0.17 \ \text{\AA}, \text{ and testify to the effect that nearest neighbour atoms have on the extension of the wavefunction of each C-atom in C}_{60}.\]

In Fig. 2 we display the two lowest, and most important, multipole contributions of the local part of the deformation potential of C\(_{60}\) for the lowest \(A_g\) phonon, corresponding essentially to a breathing mode of the system, as calculated in the LDA. The wavenumber of this mode is equal to 491 cm\(^{-1}\) and 496 cm\(^{-1}\) for C\(_{60}\) in solution and in the solid phase, respectively [12,13]. The wavenumber and zero point motion of the isolated molecule, calculated in the bond-charge model, are 493 cm\(^{-1}\) and 53.4 \(10^{-3}\) \(\text{\AA}\) respectively [14]. As seen from Fig. 2, the hybrid orbital model provides an overall account of the ab initio results. The discrepancies observed for small values of \(r\) for the multipole \((L,M) = (0,0)\) have little influence on the corresponding matrix elements, because the electronic wavefunctions are quite small around the origin of the molecule.

Making use of these results, one can calculate the...
electron–phonon coupling matrix elements in C\textsubscript{60}. These are the matrix elements needed, for example, in the evaluation of the lineshape of allowed as well as of forbidden electronic transitions in C\textsubscript{60}. To carry out similar calculations in C\textsubscript{60} one should employ a deformation potential which is evaluated by making use of the electronic density of the negative ion, at the ground state geometry. Because the density of the 240 valence electrons of C\textsubscript{60} is not appreciably altered by adding one more electron, one expects the deformation potentials associated with C\textsubscript{60} and C\textsubscript{60} to be quite similar. In fact, we have carried out fully relaxed, ab-initio calculations of the matrix elements in C\textsubscript{60} and found that they agree with those of C\textsubscript{60} within less than 10\%. In keeping with these results, the electron–phonon matrix elements calculated starting from the C\textsubscript{60} electronic density and ground state ionic configuration are used in the following. In C\textsubscript{60} the state t\textsubscript{1u} is occupied with a single electron. This level is separated by an energy of the order of the eV from neighbouring levels, while the electron–phonon coupling matrix elements to be found below are of the order of the meV. Consequently, it seems justified to consider, within the present context, that the electronic motion is confined to the t\textsubscript{1u} level. Under such circumstances, and because of symmetry reasons, the only possible couplings are to phonons with A\textsubscript{g} and H\textsubscript{g} symmetries (e.g., Ref. [7]).

The matrix elements \( \langle t_{1u}| v | \text{def} | t_{1u} \rangle \), where \( v \) stands for the quantum numbers of the phonon, are related to the partial electron–phonon coupling constant \( \lambda_{v}/N(0) \) by

\[
\lambda_{v}/N(0) = \alpha \frac{g_{v}^{2}}{\omega_{v}} \frac{N(0)}{\omega_{v}},
\]

according to

\[
\langle t_{1u}| v | \text{def} | t_{1u} \rangle = \left( \frac{g_{v}^{2}}{2} \right) W_{v}^{u} \text{ (e.g., Ref. [15] and references therein).}
\]

In the above expression \( N(0) \) is the density of states at the Fermi energy. \( \alpha \) is equal to 1/3 for A\textsubscript{g} phonons and 5/3 for H\textsubscript{g} phonons, while \( \omega_{v} \) is the energy of the phonon. The quantities \( W_{v}^{u} \text{ (e.g., Ref. [15])} \) are geometric coefficients, the index \( u \) distinguishing between the different degenerate states of each phonon (H\textsubscript{g} is five-fold degenerate while A\textsubscript{g} is single-fold degenerate).

In Table 1 we display the multipole contributions to the matrix element \( \langle t_{1u}| A_{g} \text{def} | t_{1u} \rangle \), associated with the lowest energy A\textsubscript{g} mode calculated making use of the LDA and of the hybrid orbital model. The different contributions of the model display the same sign and similar order of magnitude as those calculated in LDA, while the summed contribution agree within 20\%.

Following the same steps as those leading to the results displayed in Table 1, the different matrix elements \( \langle t_{1a}| v | \text{def} | t_{1a} \rangle \text{ (} v = \Lambda_{s} \text{, } \text{H}_{g} \text{)} \) have been calculated. Our results have been compared with those from other theoretical calculation available in the literature [3,4,7,8], as well as with the empirical values obtained from Gunnarsson’s systematic analysis of the photoemission spectra of C\textsubscript{60}[6]. While this analysis indicates that the coupling of the t\textsubscript{1a} electron to the H\textsubscript{g}(2) leads to the largest value of \( \Lambda_{s}/N(0) \), the results reported in Refs. [3,4,7,8] indicate the coupling to the H\textsubscript{g}(7)–phonon to be the most important. In the hybrid orbital model discussed above, the largest coupling of the t\textsubscript{1a} level is to the H\textsubscript{g}(2)–phonon, in agreement with the analysis by Gunnarsson and co-workers [7].

Making use of the matrix elements \( \langle t_{1u}| v | \text{def} | t_{1u} \rangle \text{ (} v = \Lambda_{s} \text{, } \text{H}_{g} \text{)} \) calculated in the hybrid orbital model, and of the results of the bond charge model [14] to describe the properties of the phonons, we have solved the total electron–phonon Hamiltonian containing an electronic term, a phonon term, and a

<table>
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<tr>
<th>Matrix element [meV]</th>
<th>L</th>
<th>LDA</th>
<th>hybrid orbital model</th>
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<tr>
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<td>15.473</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2.139</td>
<td>1.777</td>
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</tr>
<tr>
<td>total</td>
<td>9.399</td>
<td>-11.309</td>
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</tr>
</tbody>
</table>

The electron–phonon coupling constant \( \lambda_{v}/N(0) \) obtained by Gunnarsson from the analysis of the photoemission experimental data are, in meV: 0.023 (H\textsubscript{g}(6)), 0.017 (H\textsubscript{g}(7)), 0.005 (H\textsubscript{g}(6)), 0.012 (H\textsubscript{g}(5)), 0.018 (H\textsubscript{g}(4)), 0.013 (H\textsubscript{g}(3)), 0.040 (H\textsubscript{g}(2)), 0.019 (H\textsubscript{g}(1)), 0.011 (A\textsubscript{g}(2)), 0.000 (A\textsubscript{g}(1)). The corresponding result of the hybrid orbital model are, in the same units: 0.008, 0.016, 0.003, 0.006, 0.005, 0.011, 0.026, 0.010, 0.006, 0.001 respectively.
linear coupling term (e.g., Ref. [6]) in a basis of one $t_{1u}$ electron and up to three phonon states. The lowest eigenvalue $|t_{1u}\rangle = C^{(0)}|t_{1u}\rangle + \sum_{n} C^{(1)}|t_{1u} \otimes \nu^n\rangle + \ldots$ was calculated using the Lanczos method. The first term in $|t_{1u}\rangle$ describes a state with no phonons, the second term a state with one phonon, etc. Making use of these results, we have calculated the photoemission cross section assuming the sudden approximation, where the emitted electron does not interact with the system left behind [6].

In Fig. 3 we show the results of the hybrid orbital model, in comparison with the results of the analysis of the photoemission data carried out by Gunnarsson and co-workers [6]. Although the hybrid orbital model leads to a somewhat weaker electron–phonon coupling than required by the experimental finding, and consequently to a somewhat too large value of $C^{(0)}$, it provides a much better account of the empirical spectrum than the other theoretical models, whose partial electron–phonon coupling constant have been reported in Refs. [3,4,7,8] (cf. also Table 1 of Ref. [6]).

We conclude that the hybrid orbital model of the electron–phonon coupling displays a number of attractive features: i) it leads to matrix elements of the deformation potential which reproduce quite accurately the results of ab initio calculations; ii) it provides an excellent account of the photoemission spectra of $C_{60}$; iii) it is quite economic to use, and can be extended at profit to fullerenes other than $C_{60}$ as well as to nanotubes.

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### References