Ab initio studies of electron-phonon coupling in single-walled nanotubes

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Abstract.
We present *ab initio* calculations of electron-phonon coupling in single-walled nanotubes and graphene. The perturbation of the electronic energies due to the atomic distortion caused by totally symmetric phonons was calculated, yielding the matrix elements of the electron-phonon interaction. For the radial breathing mode (RBM) we obtained a decrease of the electron-phonon interaction with increasing diameter. This is in good agreement with the fact that the equivalent mode for graphene is an out-of-plane translation which cannot affect the electronic system. The matrix elements for the RBM and the optical A_{1g} mode show different behaviours for armchair and zig-zag nanotubes.

Raman spectroscopy is a powerful technique, which yields not only information about the vibrational properties of physical systems, but also about the electronic properties and the interaction between electrons and lattice vibrations. For a single resonant Raman process, the Raman scattering cross section is given by [1]:

$$P \propto \left| \sum_{a,b} \frac{< f|H_{e-r}|b><b|H_{e-ph}|a><a|H_{e-r}|i>}{(E_{laser} - E_{ai} - i\gamma)(E_{laser} - \hbar\omega_{ph} - E_{bi} - i\gamma)} \right|^2 . \quad (1)$$

In this work, we are interested in the electron-phonon coupling matrix element $< b|H_{e-ph}|a>$, which scales the intensity of the Raman peaks. We will concentrate on the totally symmetric vibrational modes which give origin to two of the main features of the Raman spectrum of carbon nanotubes [2]. A totally symmetric phonon can only cause transitions between electronic states of the same symmetry, thus, we will concentrate on diagonal matrix elements. Khan *et al.* [3] showed that such a matrix element can be related to the shift of the electronic bands under the atomic displacement pattern of the phonon as follows:

$$< \mathbf{k}, n|H^i_{e-ph}|\mathbf{k}, n> = \sum_a \sqrt{\frac{\hbar}{2MN\omega^i}} \varepsilon^i_a \frac{\partial E_n(\mathbf{k})}{\partial \mathbf{u}_a}, \quad (2)$$

where the sum runs over all atoms in the unit cell. $\mathbf{k}$ and n denote, respectively, the wave vector and band index of the electronic state, i indexes the phonon, M is the atomic mass, N the number of atomic cells taken into account, ε^i is the polarization vector of the phonon, $E_n(\mathbf{k})$ the electronic energy and $\mathbf{u}_a$ the atomic displacement.
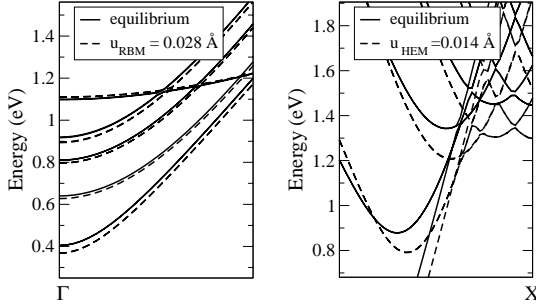
FIGURE 1. **Left:** Solid lines: equilibrium band structure of a (10,0) nanotube. Dotted lines: band structure of a (10,0) nanotube distorted after the pattern of the RBM, with an atomic displacement of 0.028 Å. The first quarter of the Brillouin zone is represented. **Right:** Solid lines: equilibrium band structure of an (8,8) nanotube. Dotted lines: Band structure of an (8,8) nanotube distorted after the pattern of the A_{1g} optical mode, with an atomic displacement of 0.014 Å. The last fourty percent of the Brillouin zone is shown. In both panels the Fermi energy lies at 0 eV.

Following this idea, we studied the electron-phonon coupling for totally symmetric phonons based on *ab initio* band structure calculations for achiral single-walled nanotubes with diameters between 4 and 15 Å. All calculations were performed with the SIESTA code [4, 5] within the local density approximation, as parameterized by Perdew and Zunger.[6] The core electrons were replaced by non-local norm-conserving pseudopotentials.[7] A double-ζ, singly polarized basis set of localized atomic orbitals was used for the valence electrons, with cutoff radii of 5.12 a.u. for the *s* and 6.25 a.u. for the *p* and *d* orbitals as determined from an energy shift of 50 meV by localization. [8, 9]

First, the structures were relaxed minimizing the atomic forces down to 0.04 eV/Å and the phonon spectrum at the Γ-point was calculated by the finite differences method. Then, the electronic band structure was calculated for the relaxed geometry and for different values of the atomic displacement. The shift of the bands showed a linear dependence on the atomic displacement, as expected for small displacements.

As can be seen in Fig. 1 both displacement patterns yield band shifts, but no splitting, as expected for an A_{1g} phonon. The band shift shows a strong dependence on the specific electronic state under study. In this work, we are interested on the effect of the electron-phonon interaction on Raman spectra, thus we focus in the regions of the Brillouin zone in which the absorption of photons takes place, that is the Γ-point for zig-zag nanotubes and the region close to the K-point for armchair nanotubes.

In Table 1 the calculated electron-phonon matrix elements for the RBM at the conduction and valence bands yielding the optical transition of lowest energy are listed. The highest matrix elements correspond to the smallest nanotubes, they become lower for bigger radii. The same RBM yields a smaller change on the bond lengths for bigger diameters, so the effect on the electronic states is weaker. This is in agreement with the fact that the RBM mode corresponds to an acoustic out-of-plane mode in graphene, which

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TABLE 1. Calculated diameters, frequencies and electron-phonon coupling matrix elements (in eV) for the RBM at the absorbing region of the Brillouin zone for the lowest conduction band (c) and the highest valence band (v).

	(5,0)	(3,3)	(6,0)	(10,0)	(6,6)	(8,8)	(15,0)	(11,11)	(19,0)
d(Å)	4.1	4.2	4.8	7.9	8.2	10.9	11.8	15.0	15.0
ω (cm^{-1})	520	542	446	287	278	209	188	151	149
c	**0.30**	0	**0.07**	**0.23**	0.04	0.05	**0.17**	0.03	**0.16**
v	**0.86**	1.56	**0.03**	**0.22**	0.11	0.09	**0.26**	0.05	**0.16**

TABLE 2. Same as Table 1 for the A_{1g} optical mode.

	(5,0)	(3,3)	(6,0)	(10,0)	(6,6)	(8,8)	(15,0)	(11,11)	(19,0)
ω (cm^{-1})	1598	1531	1587	1661	1626	1623	1567	1611	1635
c	**0**	0.52	**0.36**	**1.00**	0.58	0.38	**1.07**	-	**1.03**
v	**1.5**	0.61	**0.62**	**1.00**	0.43	0.32	**1.06**	-	**1.01**

cannot affect the electronic system. Thus, the electron-phonon coupling must tend to zero in the limit of infinite diameter. This trend becomes clearer when separating zig-zag and armchair nanotubes. The matrix elements of zig-zag nanotubes are a factor of 5 higher than those of armchair nanotubes with similar radii, except for the smallest nanotubes which do not share the general features of the bigger nanotubes due to the high curvature.

In Table 2 the analogous matrix elements are shown for the A_{1g} optical mode. Again, we see different behaviors for armchair and zig-zag nanotubes. For zig-zag nanotubes bigger than 5 Å, the electron-phonon coupling matrix elements are practically constant, while for armchair nanotubes they tend to diminish for increasing radius. This trend is characteristic of the bands closest to the Fermi energy, and is related to the vanishing coupling at the K-point. With increasing radius, the absorbing zone of the band shifts towards the K-point and the matrix element tends to vanish.

Comparing the two modes, is clear that the matrix elements of the A_{1g} optical mode are, in general, significantly higher than those of corresponding to the RBM.

In Fig. 2 the band structure of graphene close to the K-point is shown for equilibrium geometry, and for displaced atoms after the E_{2g} in-plane optical phonon which corresponds to the optical A_{1g} mode in achiral nanotubes. Within the zone folding scheme (only applicable to nanotubes with big diameters), the Γ-point of the lowest absorbing bands of big zig-zag nanotubes correspond to the shown graphene bands close to the K-point. As can be seen, close to the K-point, the band shift is almost constant, which explains the constant matrix elements obtained for zig-zag tubes. However, changes may be expected for bands with higher energies.

Summarizing, we studied the electron-phonon interaction in achiral carbon single-walled nanotubes. We were able to show different behaviors for zigzag and armchair nanotubes, for both the RBM and the A_{1g} optical mode. For the RBM matrix element, a decreasing trend with increasing radius was found, as well as a factor 5 difference
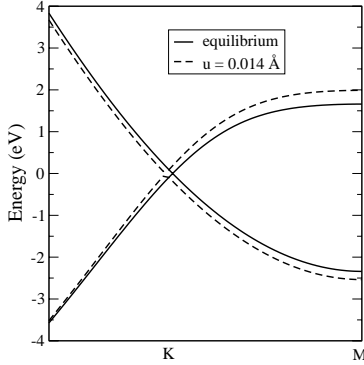
FIGURE 2. Electronic band structure of graphene. Solid line: equilibrium geometry. Dotted line: atoms displaced after the E_{2g} in-plane optical mode analogous to the optical A_{1g} mode in achiral nanotubes.

between both chiralities; the zig-zag nanotubes have the highest matrix elements. The A_{1g} optical mode was shown to have larger matrix elements than the RBM, which are practically constant for the zig-zag nanotubes, and decreasing for increasing radius for the armchair nanotubes, at least for the bands close to the Fermi energy.

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REFERENCES

1. Martin, R. M., and Falicov, L. M., "Resonant Raman Scattering," in *Light Scattering in Solids I: Introductory Concepts*, edited by M. Cardona, Springer-Verlag, Berlin, Heidelberg, New York, 1983, vol. 8 of *Topics of Applied Physics*, p. 79.
2. Maultzsch, J., Reich, S., and Thomsen, C., *Phys. Rev. B*, **65**, 233402 (2002).
3. Khan, F., and Allen, P., *Phys. Rev. B*, **29**, 3341 (1984).
4. Sanchez-Portal, D., Ordejón, P., Artacho, E., and Soler, J. M., *Int. J. Quantum Chem.*, **65**, 453 (1997).
5. Soler, J. M., Artacho, E., Gale, J. D., García, A., Junquera, J., Ordejón, P., and Sánchez-Portal, D., *J. Phys. Condens. Mat.*, **14**, 2745 (2002).
6. Perdew, J. P., and Zunger, A., *Phys. Rev. B*, **23**, 5048 (1981).
7. Troullier, N., and Martins, J., *Phys. Rev. B*, **43**, 1993 (1991).
8. Junquera, J., Paz, O., Sánchez-Portal, D., and Artacho, E., *Phys. Rev. B*, **64**, 235111 (2001).
9. Artacho, E., Sánchez-Portal, D., Ordejón, P., García, A., and Soler, J., *phys. stat. sol. (b)*, **215**, 809 (1999).