Non-adiabatic vibrations in doped graphene

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The Born-Oppenheimer approximation (BO) is the standard ansatz to describe the interaction between electrons and nuclei. BO assumes that the lighter electrons adjust adiabatically to the motion of the heavier nuclei, remaining at any time in their instantaneous ground-state. BO is well justified when the energy gap between ground and excited electronic states is larger than the energy scale of the nuclear motion. In metals, the gap is zero and phenomena beyond BO (such as phonon-mediated superconductivity or phonon-induced renormalization of the electronic properties) occur. The use of BO to describe lattice motion in metals is, therefore, questionable. In spite of this, BO has proven effective for the accurate determination of chemical reactions, molecular dynamics and phonon frequencies in a wide range of metallic systems. Graphene, recently discovered in the free state, is a zero band-gap semiconductor, which becomes a metal if the Fermi energy is tuned applying a gate-voltage Vg. Graphene electrons near the Fermi energy have two-dimensional massless dispersions, described by Dirac cones. I will show that a change in Vg induces a stiffening of the Raman G peak (i.e. the zone-center E2g optical phonon), which cannot be described within BO [1,2]. Indeed, the E2g vibrations cause rigid oscillations of the Dirac-cones in the reciprocal space. If the electrons followed adiabatically the Dirac-cone oscillations, no change in the phonon frequency would be observed. Instead, since the electron-momentum relaxation near the Fermi level is much slower than the phonon motion, the electrons do not follow the Dirac-cone displacements. This invalidates BO and results in the observed phonon stiffening. This spectacular failure of BO is quite significant since BO has been the fundamental paradigm to determine crystal vibrations from the early days of quantum mechanics.

[1] M. Lazzeri, F. Mauri, Phys. Rev. Lett. (to be published), cond-mat/0611708

[2] S. Pisana, M. Lazzeri, C. Casiraghi, K.S. Novoselov, A.K.Geim, A.C. Ferrari, F. Mauri, cond-mat/0611714