

Effect of the Quantum Zero-Point Atomic Motion on the Optical and Electronic Properties of Diamond and Trans-Polyacetylene

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The quantum zero-point motion of the carbon atoms is shown to induce strong effects on the optical and electronic properties of diamond and *trans*-polyacetylene, a conjugated polymer. By using an *ab initio* approach, we interpret the subgap states experimentally observed in diamond in terms of entangled electron-phonon states. These states also appear in *trans*-polyacetylene causing the formation of strong structures in the band structure that even call into question the accuracy of the band theory. This imposes a critical revision of the results obtained for carbon-based nanostructures by assuming the atoms frozen in their equilibrium positions.

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Carbon-based nanostructures represent the natural candidates to replace silicon-based materials in the devise of efficient opto-electronic devices. Conjugated polymers, in particular, have been shown to have peculiar properties related to the very fast relaxation of charge carriers due to the electron-phonon coupling [1]. Nevertheless, despite the rapid development of technological applications, the role of atomic vibrations in carbon-based nanostructures has been only treated in a semiempirical manner, boosted by the essential question of the mobility of charged carriers in organic devices [2]. However, these approaches are based on Hamiltonians that rely on parameters which are difficult to extract from experiments and clear-cut conclusions are still elusive. In contrast, the most accurate, parameter-free and up-to-date description of the electronic properties of bulk and nanosized materials, is based on *ab initio* methods. These techniques benefit of the predictivity and accuracy of density functional theory (DFT) [3] merged with many-body perturbation theory (MBPT) [4]. The goal of the *ab initio* methods is to describe and predict in a quantitative manner, the optical and electronic properties of any electronic system, starting from its atomic configuration. The result is a wealth of techniques like the *GW* method [3] that has been successfully applied to a large number of different systems, among which carbon-based nanostructures.

In the *GW* approach, as well as in other applications of the *ab initio* methods, a standard approximation is to assume the atoms frozen in their equilibrium positions. Many years ago [5], however, the pioneering works of Heine, Allen, and Cardona (HAC) pointed to the fact that, even when the temperature vanishes, the quantum zero-point motion of the atoms (the zero-point motion effect) can induce large corrections to the electronic levels, making

purely electronic theories (like the *GW* method) inadequate. Nevertheless, the enormous numerical difficulties connected with the calculation of the electron-phonon interaction has *defacto* prevented the systematic application of the HAC theory. Nowadays, the advent of more refined numerical techniques, has made possible to ground the HAC approach in a fully *ab initio* framework [6]. More recently, on this journal, Giustino *et al.* [7,8] found a large zero-point renormalization (615 meV) of the band-gap of bulk diamond. The HAC approach is, however, based on a static theory of the electron-phonon coupling that, as pointed out by Giustino *et al.* [7], is not fully justified. The static HAC approach leads, indeed, to an agreement between theory and experiment that can be somewhat fortuitous as dynamical effects are completely neglected.

In this work we show, indeed, that when the temperature vanishes, the quantum zero-point motion of the atoms induces strong *dynamical* effects on the optical and electronic properties of diamond and *trans*-polyacetylene, a paradigmatic conjugated polymer. The subgap peaks appearing in the experimental absorption spectrum of diamond are interpreted in terms of polaronic states, composed of entangled electron-phonon pairs, that cannot be described by the HAC theory. When the reduced dimensionality of the system enhances the amplitude of the atomic vibrations, the zero-point motion effect even fragments the electrons in a continuum of polaronic states. This is the case of *trans*-polyacetylene, where the single-particle band-structure is replaced by a jellylike electronic distribution and the wave functions of electrons and atoms are stretched along the polymer axis. This is the breakdown of the band theory. By disclosing the physical motivations of the zero-point motion effect, we discuss how the present results lead to potentially ground-breaking consequences

on our understanding of the optical and electronic properties of carbon-based nanostructures.

The zero-point motion effect can be understood by using simple arguments. At finite temperature the atoms oscillate around their equilibrium positions. These oscillations can be mapped in a system of noninteracting harmonic oscillators. As a consequence of the quantum nature of the atoms, when the temperature goes to zero the atoms collapse in a ground state with a finite energy. This is the zero-point energy that induces quantum fluctuations of the atoms. The effect of this purely quantum motion on the electronic levels can be described using MBPT applied to the electron-phonon problem [4]. It can be shown that, at zero temperature, the electron-phonon self-energy, taken to the lowest non vanishing order of perturbation theory, is composed of two contributions. The first term is the Fan self-energy

$$\Sigma_I^{\text{Fan}}(\omega) = \sum_{J\lambda} \sum_{\xi=\pm} \frac{N_{\xi}^J |\langle I | H_{\text{el-ph}} | J \rangle \otimes |\lambda\rangle|^2}{N_q(\omega - \varepsilon_J + \xi\omega_{\lambda} - i0^+)}, \quad (1)$$

with $|J\rangle$ and $|\lambda\rangle$ the generic electronic and phononic state. $N_{+}^J = f_J$ and $N_{-}^J = 1 - f_J$, with f_J the electronic occupations. N_q is the total number of transferred momenta used to integrate the self-energy. The key quantities in Eq. (1) are the electron-phonon matrix elements $g_{IJ}^{\lambda} \equiv \langle I | H_{\text{el-ph}} | J \rangle \otimes |\lambda\rangle$, with $H_{\text{el-ph}}$ the electron-phonon Hamiltonian [4] which, written in the second quantization, reads $H_{\text{el-ph}} = \sum_{IJ} g_{IJ}^{\lambda} c_I^{\dagger} c_J (b_{\lambda}^{\dagger} + b_{\lambda})$. The g_{IJ}^{λ} are calculated *ab initio* using density functional perturbation theory (DFPT) [9]. A frequency independent Debye-Waller term, Σ_I^{DW} is added to Σ_I^{Fan} in order to preserve the translational invariance of the theory. More details about the Debye-Waller term can be found, for example, in Ref. [8]. The DFPT scheme allows us to introduce, fully *ab initio*, the nonlocality (in momentum space) of the coupling constants g_{IJ}^{λ} , whose importance in the case of conjugated polymers has been highlighted by using model Hamiltonians [10].

The full frequency-dependent Green's function $G_I(\omega)$ is readily defined to be $G_I(\omega) = (\omega - \varepsilon_I - \Sigma_I^{\text{Fan}}(\omega) - \Sigma_I^{\text{DW}})^{-1}$. The true single-particle excitations of the system are obtained as poles of G_I . The HAC theory and the more general quasiparticle approximation (QPA) can be obtained making approximations on the frequency dependence of $\Sigma_I^{\text{Fan}}(\omega)$. However, we would like to follow a different path.

Physically Eq. (1) describes the scattering of the bare electronic state $|I\rangle$ with the continuum of phonons that surrounds the state $|J\rangle$. These scatterings are weighted by the coupling terms g_{IJ}^{λ} . This scenario can be described using the well-known Fano theory [11] which describes, in general, the coupling of a discrete state ($|I\rangle$) with a set of final states surrounded by a continuum of excitations ($|J\rangle \otimes |\lambda\rangle$). The scattering with many possible final states induces interference effects. When these effects are small

the term with $J = I$ dominates the sum in Eq. (1), and the Fano theory predicts the spectral function (SF) $A_I(\omega) \equiv \frac{1}{\pi} |\Im[G_I(\omega)]|$ to be a Lorentzian. This is the QPA, and the center of the Lorentzian is the quasiparticle (QP) energy, defined to be $\varepsilon_I + Z_I \Sigma_I^{\text{Fan}}(\varepsilon_I) + \Sigma_I^{\text{DW}}$, with $Z_I = (1 - \frac{\partial \Re \Sigma_I^{\text{Fan}}(\omega)}{\partial \omega} |_{\omega=\varepsilon_I})^{-1}$ the renormalization factor [4]. If in addition $|g_{IJ}^{\lambda}|^2 \ll \omega_D$, with ω_D the Debye frequency, the Lorentzian width goes to zero, $Z = 1$ and we have the HAC approach. This corresponds to a frequency independent Σ_I^{Fan} . When the coupling factors g_{IJ}^{λ} are large the interference effects force the system to create coherent packets of electron-phonon pairs,

$$|P\rangle = \Lambda_I^P |I\rangle + \sum_{J\lambda} \Xi_{J\lambda}^P |J\rangle \otimes |\lambda\rangle. \quad (2)$$

We define $|P\rangle$ a polaronic state with energy E_P . Indeed, it can be demonstrated [12] that, by choosing the coefficients Λ_I^P and $\Xi_{J\lambda}^P$ as eigenvectors of an effective Hamiltonian, the Green's function corresponding to Eq. (1), can be rewritten as $G_I(\omega) = \sum_P |\Lambda_I^P|^2 (\omega - E_P + i0^+)^{-1}$. It also follows that $\langle P | P \rangle = 1$. Physically, Eq. (2) describes a system where the electrons are replaced by a continuum of polarons whose purely electronic part is weighted by $|\Lambda_I^P|^2$. The QPA is recovered when the $|\Lambda_I^P|^2$ factors have a Lorentzian distribution around the QP energy. However, in general, if the $|\Lambda_I^P|^2$ are small the second term in the right-hand side of Eq. (2) is large making the $A_I(\omega)$ to deviate from the simple Lorentzian lineshape. In this case the electron is fragmented in several polaronic states and the QPA is expected to fail. The entangled nature of the polaronic state $|P\rangle$ is known [13] to be related to its spatial localization. In Eq. (2) the change in the polaronic spatial

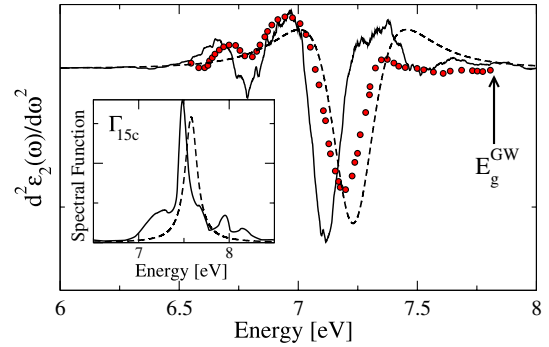


FIG. 1 (color online). The experimental [19] $d^2 \varepsilon_2(\omega)/d\omega^2$ of bulk diamond near the absorption edge (red spheres) is compared with the QPA (dashed line) and with the full-dynamical theory (full line). The optical gap is defined by transitions between the Γ'_{25v} (occupied) and Γ_{15c} (empty) states. The Γ'_{25v} state is a genuine QP state. The Γ_{15c} SF, instead (shown in the inset), is characterized by strong side peaks that well reproduce the subgap peaks appearing in the experimental spectrum below 7.1 eV. E_g^{GW} represents the QP direct gap obtained by neglecting the zero-point motion effect.

localization is caused by the $\Xi_{J\lambda}^P$ factors that drive the modifications of the polaronic Green's function and of the polaronic wave function, as discussed below.

In the inset of Fig. 1 the SF $A_I(\omega)$ of bulk Diamond, obtained by using the dynamical dependence of the self-energy, is compared with the QPA for the Γ_{15c} state, the bottom of the conduction bands [14]. The SF, instead of being a simple Lorentzian, shows peaks at 7.25 and 7.9 eV. These peaks are due to polaronic states $|P\rangle$ each carrying a fraction (given by $|\Lambda_I^P|^2$) of the total electronic charge. They allow us to explain the subgap states observed experimentally. Indeed the Γ_{15c} state contributes to the onset of the absorption via transitions with the top of the valence bands, represented by the Γ'_{25v} state. The corresponding contribution to the absorption edge will be given by the convolution of the Γ'_{25v} and Γ_{15c} SFs [15]. This convolution is used, in Fig. 1, to calculate the second derivative of the dielectric function and to compare it with the experimental spectrum [19]. The experimental absorption clearly shows the absorption gap at 7.19 eV together with some subgap structures at 6.71 and 6.94 eV. Such structures are completely absent in the QPA or using the HAC approach. The dynamical theory, instead, leads to an excellent agreement with the experimental result.

This result, while supporting the correctness of a dynamical theory of the zero-point motion effect, questions the validity of the QPA and of the static HAC approach. The strength of the dynamical zero-point motion effect in diamond is unexpected, and opens the path to potentially stronger effects in carbon-based nanostructures. Indeed, the strength of the electron-phonon self-energy is linked to the amplitude of the atomic vibrations that in a nanostructure is enhanced. This can be easily verified by considering a *conjugated* polymer, as *trans*-polyacetylene. This is a 1D chain made up of repeated structural units linked by alternated single and double bonds between the carbon atoms [20]. The unit cell contains 2 carbon and 2 hydrogen atoms, which lay on the same plane, as shown in the upper frames of Fig. 2. We can associate an average quantum size to the atoms by using the standard deviation $\bar{\sigma}_i$ of the atom i with mass M_i , in its ground-state wave function [5]. This is $\bar{\sigma}_i \approx \sqrt{\sum_{\lambda} (M_i \omega_{\lambda})^{-1} |\tilde{\xi}_i(\lambda)|^2}$, with $\tilde{\xi}_i(\lambda)$ the polarization vector of the phonon mode λ . In diamond $\sigma_C \approx 0.1$ a.u., independently on the direction. In *trans*-polyacetylene the smaller distance between carbon atoms, slightly reduces the standard deviation along the \hat{x} direction where $\sigma_C \approx 0.08$ a.u. while in the \hat{y} direction $\sigma_C \approx 0.16$ a.u.. Hydrogen is much lighter than carbon and, as $\bar{\sigma}_i \sim (\sqrt{M_i})^{-1}$, its standard deviation in the polymer plane is such that $\sigma_H \approx 0.2$ a.u..

To clearly visualize the dramatic effect of the zero-point motion effect on the electronic structure of *trans*-polyacetylene we define a global SF $A(k, \omega) \equiv \sum_n \frac{1}{\pi} |\Im[G_{nk}(\omega)]|$, where we have explicitly expressed the index I in terms of the band (n) and k -point (k) indexes. k is taken in the $\Gamma - X$

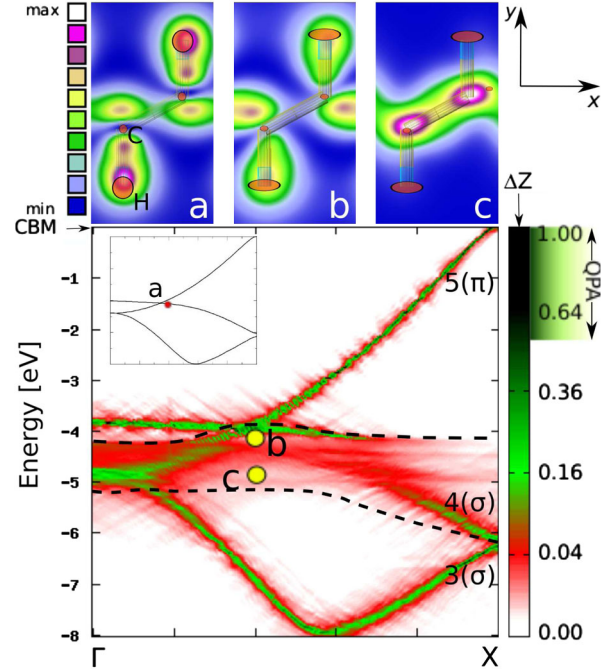


FIG. 2 (color online). Two-dimensional plot of the SF $A(k, \omega)$ in the energy region of the last three occupied bands. CBM represents the conduction band maximum and the bands have been explicitly numbered indicating the corresponding hybridization (σ or π). The range of values of A (lower panel) are given in terms of the dimensionless quantity ΔZ (see text) that measures the elemental charge carried by the SF. Except the π states, perpendicular to the polymer plane, the electronic levels acquire a large energy indetermination that is particularly dramatic in the region enclosed by the two dashed line. This destructive effect is, instead, a cooperative interaction between atoms and electrons that is reflected in the stretching of the polaronic states in the direction of the polymer axis. This is evident from the comparison of the wave functions of a reference bare state (left frame, point a) with two polaronic states (central and right frame, points b and c). The standard deviation of the atoms in their unperturbed state and in the polaronic states is represented by the size of the spheres in the three upper frames.

direction [14]. Physically $\Delta Z \equiv A(k, \omega)\Delta\omega$ gives the fraction of electronic charge carried by the state with k -point k in the small energy range $\Delta\omega$. From the definition of $A(k, \omega)$ it follows that $\Delta Z \propto |\Lambda_I^P|^2$. The A function is a very peaked function of k and ω both in the HAC approach and in the QPA with the charge confined in very sharp single-particle states. The plot of the A function, shown in Fig. 2 in the energy range of the last three occupied bands, gives instead a completely different picture. The lower panel color scale of Fig. 2 refers to the dimensionless quantity ΔZ calculated with $\Delta\omega = 50$ meV. As a reference we show the range of values of ΔZ corresponding to the QPA. Note that the static HAC theory corresponds to $\Delta Z = 1$.

With the exception of the 5th band, the charge carried by the SF is lower than 0.4, well below the range of values

where the QPA or the HAC theory is accurate. More importantly, very small values of ΔZ mean small $|\Lambda_I^P|^2$ and, consequently, large contributions of the electron-phonon pairs in the polaronic state [second term in the right-hand side of Eq. (2)]. This effect is even more dramatic in the central energy region, where the bands *disappear* being replaced by an almost uniform, jellylike charge distribution that, in Fig. 2, is represented by the region enclosed by the two dashed lines. Physically the system is forced to split the electronic levels in several polaronic states. Single-particle states are not allowed anymore. This is an unambiguous signature of the breakdown of the band theory.

With respect to the 3rd and the 4th, the 5th band, near the X point, has a π character, corresponding to states distributed perpendicular to the polymer axis. As a consequence they feel less the effect of the on-plane vibrations and almost all electronic charge is confined in sharp quasi-particle-like peaks.

A more careful analysis reveals that the destructive effect of the zero-point motion effect on the electronic band-structure is, instead, a signature of a cooperative electron-atom dynamics. Indeed, Eq. (2) allows us to calculate, *ab initio*, several properties of the polaronic states. By projecting $|P\rangle$ on the real-space we can define the polaronic wave function, $\langle \mathbf{r}|P\rangle$, and also calculate the standard deviation $\tilde{\sigma}_i^P$ of the atom i that participates in the polaronic state. This can be used to explain the physical properties of the wide region enclosed by the two dashed lines in Fig. 2. In the upper frame (a) of Fig. 2 we consider a bare electronic state that is localized on the $C-H$ bond. The zero-point motion effect splits the charge of this state in several polaronic states. Two of the most intense are the states (b) and (c) whose wave-functions are shown in the upper frames of Fig. 2. By moving towards the center of the region the electronic charge is gradually moved from the $C-H$ bond towards the polymer axis. In the state (c) this charge transfer is more pronounced and the wave function is completely delocalized along the polymer axis. Even more stunning is the effect of the zero-point motion on the atomic standard deviation. In both states (b) and (c) $\tilde{\sigma}_i^P$ is decreased by 50% in the \hat{y} direction and increased by 150% in the direction of the axis. The present results show that the zero-point motion effect works to enhance the delocalization of the charge carriers by stretching both electrons *and* atoms along the polymer axis. This cooperative effect agrees with the general interpretation of the high electronic mobility in polymers as dictated by the efficient hopping of the charge carriers [21,22].

In conclusion, we have shown that, when the temperature vanishes, the quantum zero-point motion of the atoms induces large corrections to the optical and electronic properties of diamond and *trans*-polyacetylene. The electronic bands are replaced by a continuum of polaronic states composed by entangled electron-phonon pairs.

This successfully explains the subgap states observed experimentally in the absorption spectrum of diamond, and the rich structures that appear in the spectral functions of *trans*-polyacetylene. The cooperative dynamics between electrons and atoms that leads to the formation of the polaronic states rules out any description in terms of bare atoms, bare electronic states or quasiparticles. This inevitably leads to the failure of the band-theory. The present results highlight the limitations of an approach to carbon-based nanostructures and organic materials that neglects the effect of the electron-phonon coupling. The deep change of the electronic and atomic wave functions induced by the formation of the polaronic states can have important implications on related properties. This inevitably, imposes a critical revision of the results obtained using purely electronic theories with atoms frozen in their equilibrium positions.

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