Many-Body Effects on the Zero-Point Renormalization of the Band Structure

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We compute the zero-point renormalization (ZPR) of the optical band gap of diamond from many-body perturbation theory using the perturbative G_0W_0 approximation as well as quasiparticle self-consistent GW. The electron-phonon coupling energies are found to be more than 40% higher than standard density functional theory when many-body effects are included with the frozen-phonon calculations. A similar increase is observed for the zero-point renormalization in GaAs when G_0W_0 corrections are applied. We show that these many-body corrections are necessary to accurately predict the temperature dependence of the band gap. The frozen-phonon method also allows us to validate the rigid-ion approximation which is always present in density functional perturbation theory.

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The coupling of electrons to a bosonic field generally causes a renormalization of the energy levels. Whereas in vacuum, the electromagnetic fluctuations lead to the Lamb shift observed in the hydrogen atom levels, in condensed matter, the phonon field renormalizes the band structure, even at zero temperature. Being as large as several hundreds of meV [1], this renormalization is critical to the predictive power of *ab initio* calculations when it comes to absorption spectra [2], photovoltaic materials [3], or topological insulators [4].

Following the early work of Fan and others in the 1950 s [5–7], the problem was addressed by Allen, Heine, and Cardona (AHC) [8,9], whose theory provides perturbative expressions in terms of the electron-phonon coupling; they find, at the lowest order, that two diagrams contribute to the renormalization, the Fan diagram coming from two first-order electron-phonon coupling vertices, and the Debye-Waller diagram coming from one second-order vertex. Using semiempirical methods, and later on, density functional theory (DFT), the temperature dependence of the band gap could be obtained for several semiconductors [10–18]. Among those, diamond has been a case study [19], both for the strong band gap renormalization it exhibits [20–25] and its phonon-driven superconductivity enabled by boron doping [26–29].

The reliability of DFT for the electron-phonon coupling has however been questioned in recent years. Since the scattering of an electron by a phonon probes the excited states of a system, a theory describing this process should rely on an accurate unrenormalized band structure, unlike the one of DFT. This has motivated the use of nonlocal DFT functionals [30–33]. These studies have shown that, as well as correcting the band gap, exact exchange functionals are also necessary to accurately describe the electron-phonon coupling. A truly *ab initio* scheme, however, would rely on many-body perturbation theory. As such, it was reported that G_0W_0 corrections led to a significant increase of the electron-phonon coupling in C_{60} fullerene and in graphene [31,32]. In this work, we show that the G_0W_0 [34] and GW [35] treatments of the electron-electron interaction enhance the zero-point renormalization (ZPR) in diamond by more than 40% with respect to DFT in the local-density approximation (LDA), and that these corrections allow us to obtain the correct temperature dependence of the band gap.

We combine the frozen-phonon method and density functional perturbation theory (DFPT) [36,37] to compute the direct band gap renormalization. This allows us to revise an important approximation of the AHC theory, namely, the rigid-ion approximation. In all perturbative calculations, the Debye-Waller interaction term is simplified to allow its computation from linear response. The approximation breaks down in the case of diatomic molecules [38], but its reliability in solids has not been verified to our knowledge. Here we assert the validity of the rigid-ion approximation in diamond, and in general for three-dimensional systems.

Method.—The temperature dependence of the electronic eigenvalues originates from the phonon population and the thermal expansion of the lattice [1,13], the latter effect being relatively small. Neglecting dynamical effects (i.e., the phonon energy is assumed to be small with respect to electronic excitations), the phonon contribution gives

$$\varepsilon_\alpha(T) = \varepsilon_\alpha^0 + \frac{1}{N}\sum_j \frac{\partial \varepsilon_\alpha}{\partial n_j}\left[n_j(T) + \frac{1}{2}\right], \qquad (1)$$

where ε_α^0 are the eigenvalues at equilibrium, and the sum over the N phonon modes involves the electron-phonon coupling energies (EPCEs) $\partial\varepsilon_\alpha/\partial n_j$, and the Bose-Einstein occupation numbers n_j. With the frozen-phonon method,

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and in the harmonic approximation, the EPCEs are obtained from the second-order derivatives of the eigenvalues at equilibrium:

$$\frac{\partial \varepsilon_\alpha}{\partial n_j} = \frac{\hbar}{2M\omega_j}\frac{\partial^2}{\partial z^2}\varepsilon_\alpha\left[z\mathbf{u}_\tau^j\right]\Big|_{z=0}, \tag{2}$$

where M is the reduced atomic mass, ω_j is the phonon frequency, and $\varepsilon_\alpha[z\mathbf{u}_\tau^j]$ is an eigenvalue computed with the atoms displaced along the normalized polarization vector $\mathbf{u}_\tau^j$, with τ labeling the atoms of the unit cell. Each EPCE requires a supercell calculation to account for the wavelength of the phonon. Although this makes the technique more computationally demanding than DFPT, it offers several theoretical advantages. It makes no approximation for the Debye-Waller term, and it gives complete liberty on the method to compute the electronic structure.

We compute the ZPR of the top of the valence band of diamond (Γ'_{25v}) and the first optically accessible state (Γ_{15c}) using a $4\times4\times4$ Γ-centered q-point grid. The lattice parameter (3.55 Å) was obtained by relaxation of the structure with a Trouiller-Martins LDA pseudopotential [39]. All calculations were done with the ABINIT code [40].

Rigid-ion approximation.—In the AHC theory, the EPCEs are expressed as

$$\frac{\partial \varepsilon_\alpha}{\partial n_j} = \frac{\hbar}{2M\omega_j}\sum_{\tau,\tau'}\Phi^\alpha_{\tau,\tau'}:\left[\mathbf{u}_\tau^{j\dagger}\mathbf{u}_{\tau'}^j - \frac{1}{2}\left(\mathbf{u}_\tau^{j\dagger}\mathbf{u}_\tau^j + \mathbf{u}_{\tau'}^{j\dagger}\mathbf{u}_{\tau'}^j\right)\right], \tag{3}$$

where Φ is the Hessian matrix of an eigenvalue derived with respect to all atomic positions, given by

$$\Phi^\alpha_{\tau,\tau'} = \left(\langle\psi_\alpha|\nabla_\tau H|\nabla_{\tau'}\psi_\alpha\rangle + \text{c.c.}\right) + \langle\psi_\alpha|\nabla_\tau\nabla_{\tau'}H|\psi_\alpha\rangle. \tag{4}$$

The first term in Eq. (3) splits into the Fan and the Debye-Waller terms, when combined with the first and second terms of Φ, respectively. The former describes the scattering of electronic states by a phonon, and the latter corresponds to a second-order electron-phonon interaction, which is difficult to compute in DFPT. By virtue of the acoustic sum rule [8], the two other "rigid-ion" terms in Eq. (3) give a null contribution to the EPCE, but they allow for the desired approximation. Assuming the Debye-Waller term to be diagonal in atom sites ($\tau = \tau'$), the second-order derivative can be completely dropped, since Eq. (3) is explicitly off diagonal. The rigid-ion terms now assume the Debye-Waller contribution using only the first-order derivatives of the Hamiltonian and the wave functions, which are obtained self-consistently in DFPT. This simplification of the perturbation theory expressions is a major achievement of the AHC theory, albeit depending critically on the validity of the rigid-ion approximation.

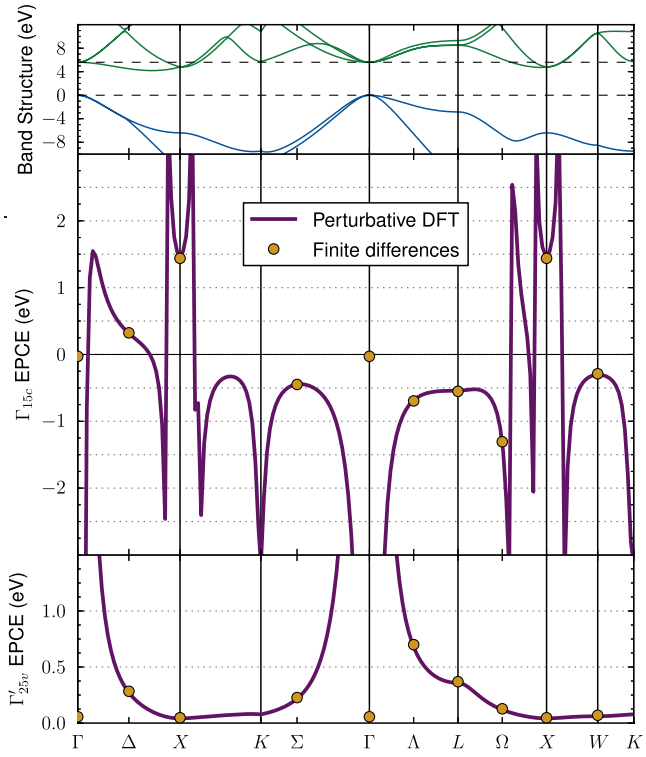

FIG. 1 (color online). Electron-phonon coupling energies for the top of the valence band (lower panel) and the bottom of the conduction band at Γ (middle panel), calculated in DFPT (solid line) and with the frozen-phonon method (circles). The top panel shows the band structure with dashed lines indicating the $\Gamma_{25v}{}'$ and Γ_{15c} energies.

The DFPT scheme allows for a fine sampling of the Brillouin zone (BZ), as shown on Fig. 1. Diamond being an indirect gap insulator, a divergence occurs in the Γ_{15c} EPCEs when a phonon wave vector connects this state to another one with close energy. This is handled by adding a small imaginary part to the energy differences (0.1 eV) [41]. Although most of the divergences cancel out after integration, the broad peak at Γ gives an important contribution to the renormalization of electronic energies. The central region covering one eighth of the BZ, accounts for 45% of the Γ'_{25v} ZPR and 20% of the Γ_{15c} ZPR.

The rigid-ion approximation is not present in the frozen-phonon approach. Remarkably, using minute displacements (~0.01% of the bond length), the coupling energies computed from Eq. (2) fall closely on the DFPT curve. The total ZPR obtained with the frozen-phonon method differs by less than 3% from the DFPT value (see Table I), a discrepancy we attribute to the rigid-ion approximation. Since the neglected nondiagonal Debye-Waller term is a short-ranged interaction between neighboring atomic sites, it does not become any stronger near Γ than it is at the BZ boundary. Therefore, this term should be of negligible importance in any three-dimensional crystal, where the BZ center area accounts for a significant portion of the ZPR.

TABLE I. Zero-point renormalization (meV) computed on a $4 \times 4 \times 4$ q-point grid in frozen-phonon (finite differences) and in DFPT (perturbative DFT).

	Γ'_{25v}	Γ_{15c}	Gap
Rigid-ion approximation			
Perturbative DFT	113	−314	−427
Finite differences harmonic [a]	117	−320	−437
Many-body effects			
Finite differences DFT [b]	119	−318	−437
Finite differences G_0W_0 [b]	145	−477	−622

[a]Phonon displacement: ∼0.01% of the bond length.
[b]Phonon displacement: ∼0.1% of the bond length.

Many-body corrections.—Displacing the atoms by 0.1% of the bond length causes the electrons to move from the contracting bonds to the stretching bonds, in favor of lower kinetic energy. This charge transfer pushes the Γ'_{25v} energy upward, causing a renormalization of 119 meV in the LDA. With the G_0W_0 corrections [41], the EPCE is uniformly increased all over the Brillouin zone by about 50 meV per q point, as shown on Fig. 2. Although the Γ_{15c} state shows a negative renormalization of −318 meV in LDA, the EPCE elements are positive in the Γ-X direction, where the lowest conduction band reaches its minimum. The G_0W_0 corrections increase the amplitude of the negative EPCE elements while reducing the positive elements, bringing the Γ_{15c} ZPR to −477 meV, and increasing the band gap renormalization by more than 40%, as reported in Table I. We observed the same trend in gallium arsenide, which is a direct band gap semiconductor. Whereas the LDA predicts a band gap renormalization of −23 meV in this material, the ZPR is increased by −10 meV when G_0W_0 corrections are applied.

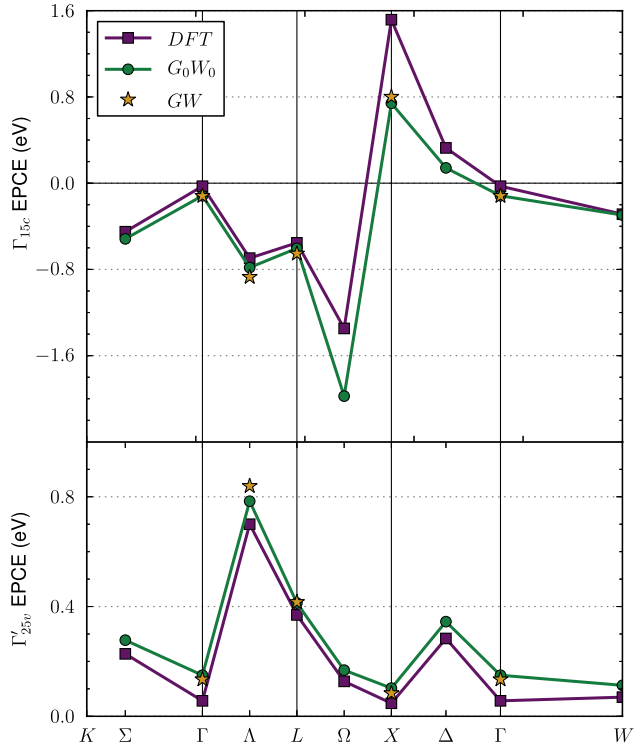

FIG. 2 (color online). Electron-phonon coupling energies for the top of the valence band (lower panel) and the bottom of the conduction band at Γ (top panel), in DFT (squares), in G_0W_0 (circles) and in GW (stars).

The self-energy is thus more sensitive to the perturbation than the LDA exchange-correlation potential. This reflects the fact that the LDA is based on the jellium model. The electron-electron interaction is overly screened in the bonding region, where the charge density packs up. In contrast, retaining only the bare exchange corresponds to a Hartree-Fock calculation with the DFT wave functions. Such a calculation overestimates the renormalization of the Γ'_{25v} (207 meV), which is located in the bonds, while the Γ_{15c} ZPR (−473 meV) does not suffer from the lack of correlation. This illustrates the importance of proper screening in the high density region. The same feature was reported in graphene to a higher extent, due to the shorter sp^2 bonds[32].

Quasiparticle GW calculations of the EPCE were performed on a subset of our q-point grid (Γ, Λ, L, X). The self-consistency increases slightly the EPCE of the Γ'_{25v} (∼8 meV, on average) and the Γ_{15c} (∼ − 22 meV). Such a small change results from two cancelling effects. While the self-energy allows for a greater interstitial charge density, it also reduces the electron mobility by opening the band gap much more than G_0W_0 does [41]. Overall, the LDA + G_0W_0 calculation seems to agree well with the electron-phonon coupling obtained from self-consistent GW.

Temperature dependence of the band gap.—Our coarse sampling of the Brillouin zone might not capture the relative importance of the strongly coupling modes. Hence, we interpolate the many-body corrections on a dense q-point grid using a cubic polynomial fit for the G_0W_0 corrections to the EPCE [41]. We obtain the band gap renormalization and its temperature dependence from a DFPT calculation on a $32 \times 32 \times 32$ q-point grid, as reported in Table II. This fine sampling reveals a bigger G_0W_0 correction to the Γ_{15c} ZPR due to the strong positive contributions near X being reduced and those near Γ being enhanced. As a result, the band gap ZPR is increased from −404 meV to −628 meV when many-body corrections are applied.

TABLE II. Zero-point renormalization (meV) computed on a $32 \times 32 \times 32$ q-point grid. The G_0W_0 and GW corrections are interpolated with the models discussed in the text.

	Γ'_{25v}	Γ_{15c}	Gap
DFPT	141	−263	−404
Δ G_0W_0	+26	−183	−209
Δ GW-G_0W_0	+4	−11	−15
Total	171	−457	−628

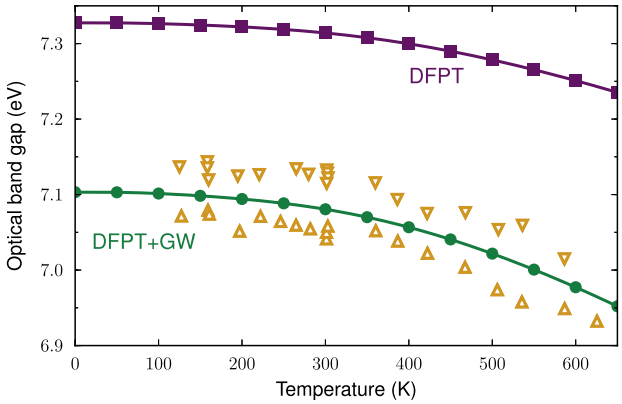

FIG. 3 (color online). Temperature dependence of the direct band gap computed in DFPT (squares) and with GW corrections (discs). The band gap (7.732 eV) is computed in G_0W_0, and the two experimental data sets (upper and lower triangles) are from Ref. [42].

Figure 3 shows the temperature dependence of the direct band gap of diamond computed in DFPT and with many-body corrections. In this figure, the bare band gap (7.732 eV) was obtained from a full-frequency G_0W_0 calculation starting from an LDA band structure with a scissor shift of 1.5 eV which reproduces the *renormalized* gap [41]. Clearly, the DFPT method underestimates the ZPR, and the many-body corrections are critical to restore the agreement with experiments. The high-temperature slope is also increased from $-0.42\,\mathrm{meV/K}$ to $-0.67\,\mathrm{meV/K}$ with many-body corrections, in good agreement with experimental data (-0.60 and -0.69 meV/K [42]).

The correspondence between theoretical and experimental results is remarkable, given that several approximations were made. On the one hand, our calculations were performed in the adiabatic approximation, whereas the full treatment should include dynamical effects as well. We checked, using the dynamical AHC theory, that those effects have a small impact, changing the band gap ZPR by +5 meV. However, it was reported that the dynamical electron-phonon self-energy causes a spreading of the main quasiparticle peak in the Γ_{15c} spectral function, reducing further the optical gap by about 50 meV [23]. On the other hand, the harmonic approximation was used throughout the study, whereas anharmonic effects are believed to reduce the renormalization of the band gap (in absolute value) [24]. Hence, it would seem that those effects we neglected tend to cancel each other, leading to the agreement of the static harmonic DFPT + GW scheme to within 50 meV of the experimental data.

In conclusion, the frozen-phonon method allowed us to go beyond the DFPT framework for the zero-point renormalization of the optical band gap of diamond and gallium arsenide. We validated the rigid-ion approximation for crystals, proving the DFPT scheme to be a reliable DFT calculation of the EPCE. The electron self-energy as obtained from G_0W_0 corrections revealed to be much more sensitive to ionic displacements than the LDA exchange-correlation potential. Bringing GW calculations to self-consistency further increased the coupling, but the G_0W_0 approximation captures most of the many-body corrections. Those corrections increase the zero-point renormalization of the band gap as well as its high-temperature slope by more than 40%. Overall, we find that the DFPT + GW scheme reproduces accurately the temperature dependence of the direct band gap of diamond. While DFPT remains the most efficient method to treat the electron-phonon interaction, our results call for a more accurate scheme. Ideally, an improvement of the linear response would include nonlocal exchange and dynamical screening in the ways of the many-body perturbation theory. We hope this work motivates such development.

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