Nonadiabatic effects lead to the breakdown of the semiclassical phonon picture

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Phonon properties of realistic materials are routinely calculated within the density functional perturbation theory (DFPT). This is a semiclassical approach where the atoms are assumed to oscillate along classical trajectories immersed in the electronic Kohn–Sham system. In this paper, we demonstrate that, in metals, nonadiabatic effects induce a deviation of the DFTP phonon frequencies from the quantistic solution of the Dyson equation—a deviation that increases with the phonon energy width, reflecting the breakdown of the semiclassical DFPT description. The final message is that nonadiabatic phonon effects can be described only by using a fully quantistic approach.

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I. INTRODUCTION

The research on the physics induced or mediated by lattice vibrations is crucial in many and disparate fields of modern solid-state physics: infrared spectroscopy, Raman, neutron-diffraction spectra, and thermal transport are just a few of them [1]. Density functional theory (DFT) [2] and density functional perturbation theory (DFPT) [1,3,4] have emerged as successful and widely used approaches to calculate the structural, electronic properties and also atomic dynamics in a fully *ab initio* framework. DFT and DFPT are, nowadays, available in many public scientific codes [5,6] and routinely used to calculate phonon frequencies and related properties.

Within DFT and DFPT, the atoms are treated classically and the atoms are assumed to move around the minimum of the Born-Oppenheimer surface [7], with the electrons tightly bound to the atoms during their oscillations. In metallic materials, the electronic excitations resonant with the phonon frequency cause a retardation between the electronic and atomic oscillations. This retardation is a nonadiabatic effect that induces, for example, the broadening of the phonon energy.

Indeed, from the experimental point of view it is well-known that the phonon peaks observed in inelastic x-ray scattering [8] or in Raman spectra [9] have an intrinsic energy width. This energy width is a natural concept within the many-body perturbation theory (MBPT) [10–16], while the actual possibility to describe it in a semiclassical theory like DFPT is still debated. Some works [17–19] have used perturbation theory to propose a frequency-dependent extension of DFPT (FD-DFPT). This theory leads to the introduction of a frequency dependent and non-Hermitian dynamical matrix whose eigenvalues, the phonons frequencies, are complex. FD-DFPT thus provides a picture conceptually equivalent to MBPT where nonadiabatic effects induce a renormalization and broadening of the phonon energies. Moreover, the enormous simplicity of FD-DFPT compared to more involved MBPT approaches and its availability in many *ab initio* codes has favored the application of the semiclassical DFPT phonon concept beyond the adiabatic regime. FD-DFPT has been applied to calculate, for example, phonon widths [8,19,20], dynamical Kohn anomalies [17,21], Raman spectra [9,18,22,23], and nonadiabatic Born effective charges [24,25].

These works have cemented the idea that a description based on a semiclassical representation of the atomic degrees of freedom is formally equivalent to the more involved many-body approach, with the difference that FD-DFPT relies on a change of the electronic density while MBPT requires solving complicated equations written in terms of nonlocal phonon and electron Green's functions.

This paper mathematically demonstrates that, within nonadiabatic DFPT, phonon widths are strictly zero. This implies that semiclassical atomic oscillations never decay in time, even when they are resonant with quantistic electron–hole pairs. We show that an infinite phonon lifetime is necessary to ensure that the dynamics conserves the total energy. The FD–DFPT approach will be demonstrated to correspond to the energy-violating, and thus nonphysical, solution of the time-dependent (TD)-DFPT equation. We conclude the paper by comparing the TD-DFPT and MBPT phonon frequencies. We show that the two solutions diverge as the MBPT phonon width increases, thus demonstrating that nonadiabatic effects can be described only by using a fully quantistic approach.

II. SEMI–CLASSICAL TRAJECTORIES AND QUANTUM FLUCTUATIONS

To describe nonadiabatic effects, we rewrite DFPT in the time domain. We start from the perturbed DFT Hamiltonian written in second quantization:

$$\hat{H} = \sum_i \epsilon_i \hat{\rho}_{ii} + \sum_\lambda \left[\frac{\omega_\lambda}{2} \hat{p}^\dagger_\lambda \hat{p}_\lambda + \frac{\left(\omega_\lambda - C^{e-n}_\lambda\right)}{2} \hat{u}^\dagger_\lambda \hat{u}_\lambda + \sum_{ij} g^\lambda_{ji} \Delta\hat{\rho}_{ij} \hat{u}_\lambda \right] + \sum_{ij} \Delta V^{\mathrm{Hxc}}_{ji} \hat{\rho}_{ij}. \quad (1)$$

This Hamiltonian has been introduced by several authors [11–16] to discuss the connection between DFTP and MBPT. The procedure to derive Eq. (1) from the full DFT Hamiltonian is outlined in the Appendix A.

Equation (1) is written in terms of the single–particle DFT electronic and DFPT phononic energies, ϵ_i and ω_λ. $\hat{\rho}_{ij}$ is the density matrix and $\hat{u}_\lambda$ and $\hat{p}_\lambda$ are the atomic displacement and momentum. g^λ_{ji} is the bare electron–phonon potential that appears together with the variation of the the Hartree plus exchange-correlation potential (Hxc), $\Delta V^{\rm Hxc}_{ji}$. $\hat{\rho}_{ij}$ is written in terms of the electronic creation and annihilation operators: $\hat{c}^\dagger_i/\hat{c}_j$ and $\Delta\hat{\rho}_{ij} = \hat{c}^\dagger_i\hat{c}_j - \langle\hat{c}^\dagger_i\hat{c}_j\rangle$.

In Eq. (1), C^{e-n}_λ is the electron-nuclei (e-n) component of the reference DFPT phonon dynamical matrix. As explained in Refs. [11,14,15] this term is already included in the ω_λ definition and needs to be removed to avoid double-counting effects.

The Hamiltonian $\hat{H}$ induces a time-dependent dynamics of all operators, electronic and atomic. These equations are derived in detail in the Appendix B.

In the case of the atomic displacement operator, we have

$$\hat{\mathcal{D}}_\lambda(t)\hat{u}_\lambda(t) = i\sum_{ij} g^\lambda_{ji}\int_0^t e^{i\Delta\epsilon_{ij}(t-\tau)} \times [\underline{\hat{\rho}}(\tau), \underline{g}^\lambda\hat{u}_\lambda(\tau) + \underline{\Delta V}^{\rm Hxc}[\rho]]_{ij}, \quad (2)$$

with $\hat{\mathcal{D}}_\lambda(t) = \frac{1}{\omega_\lambda}(\frac{d^2}{dt^2} - \omega_\lambda(C^{e-n}_\lambda - \omega_\lambda))$. $t = 0$ is the initial time, underlined quantities are matrices in the single-particle basis, and $\Delta\epsilon_{ij} = \epsilon_i - \epsilon_j$.

The role of the $\underline{\Delta V}^{\rm Hxc}$ potential is to dress the e-p interaction, as demonstrated in the Appendix C. In practice, this means that we can remove $\underline{\Delta V}^{\rm Hxc}$ from Eq. (2) and replace, in the commutator, $\underline{g}^\lambda$ with the *screened* and frequency-dependent electron–phonon interaction, $\underline{\tilde{g}}^\lambda(\omega) = \underline{\underline{\epsilon}}^{-1}(\omega)\underline{g}^\lambda$, with $\underline{\underline{\epsilon}}^{-1}$ the dielectric tensor. For simplicity, here we ignore the time dependence of $\underline{\underline{\epsilon}}^{-1}$ and assume $\underline{\tilde{g}}^\lambda(\omega) \approx \underline{\tilde{g}}^\lambda(\omega = 0)$ [26].

If we now take the average of both sides of Eq. (2), we note that the term $\langle\underline{\hat{\rho}}(t)\hat{u}_\lambda(t)\rangle$ appears on the right-hand side (RHS). This term prevents Eq. (2) from being written in terms of the electronic density matrix $\underline{\rho}(t) = \langle\underline{\hat{\rho}}(t)\rangle$ and atomic trajectory $u_\lambda(t) = \langle\hat{u}_\lambda(t)\rangle$ because

$$\langle\underline{\hat{\rho}}(t)\hat{u}_\lambda(t)\rangle = \underline{\rho}(t)u_\lambda(t) + \langle\underline{\Delta\hat{\rho}}(t)\Delta\hat{u}_\lambda(t)\rangle. \quad (3)$$

In Eq. (3), $\Delta\hat{u}(t) = \hat{u}(t) - u(t)$. The first term in Eq. (3) corresponds to the classical mean-field approximation and the second term represents the quantum corrections. From a physical point of view, Eq. (3) makes clear that the mean-field term describes the trajectory ($\langle\hat{u}_\lambda(t)\rangle$) while the second term describes the fluctuations ($\langle\Delta\hat{\rho}(t)\Delta\hat{u}_\lambda(t)\rangle$) around the classical trajectories. The term $\langle\Delta\underline{\hat{\rho}}(t)\Delta\hat{u}_\lambda(t)\rangle$ can be written in terms of the phonon propagator and self–energy [11–16].

The semiclassical picture corresponds to assume $\langle\underline{\hat{\rho}}(t)\hat{u}_\lambda(t)\rangle \approx \underline{\rho}(t)u_\lambda(t)$. It is *semi*classical because the atomic dynamics is described by a trajectory $[u_\lambda(t)]$ while the electronic subsystem is treated fully quantistic.

As we are in the harmonic approximation, we can further assume that the atomic displacements are tiny enough to approximate $\rho_{ij}(t) \sim f_i\delta_{ij}$, with f_i the electronic occupations. It follows that

$$\hat{\mathcal{D}}_\lambda(t)u_\lambda(t) = -\int_0^t C_\lambda(t-\tau)u_\lambda(\tau)d\tau, \quad (4a)$$

$$C_\lambda(t) = -i\sum_{ij}\Delta f_{ij}g^\lambda_{ji}\tilde{g}^\lambda_{ij}e^{i\Delta\epsilon_{ij}t}, \quad (4b)$$

with $\Delta f_{ij} = f_i - f_j$. Equations (4) are the time-dependent DFPT equations of motion whose solution is defined in terms of the the boundary conditions at $t = 0$. Here we define $u_\lambda(0) = u^0_\lambda$ and $\frac{d}{dt}u_\lambda(0) = v^0_\lambda$.

III. ADIABATIC AND TIME–DEPENDENT DENSITY–FUNCTIONAL PERTURBATION THEORY

The adiabatic DFPT can now be obtained from Eqs. (4) by assuming $\Delta\epsilon_{ij} \gg \omega_\lambda$. This implies that during the rapid electronic oscillations the atoms do not move and, on the RHS of Eqs. (4), $u_\lambda(\tau) \approx u_\lambda(t)$. In this way, the RHS of Eqs. (4) can be calculated analytically to give

$$\hat{\mathcal{D}}_\lambda(t)u_\lambda(t) = \left[-C^{\rm st}_\lambda + \sum_{ij}\frac{\Delta f_{ij}g^\lambda_{ji}\tilde{g}^\lambda_{ij}}{\Delta\epsilon_{ij}}e^{i\Delta\epsilon_{ij}t}\right]u_\lambda(t), \quad (5)$$

with $C^{\rm st}_\lambda = \sum_{ij}\frac{\Delta f_{ij}g^\lambda_{ji}\tilde{g}^\lambda_{ij}}{\Delta\epsilon_{ij}}$. As $\Delta\epsilon_{ij} \gg \omega_\lambda$, Eq. (5) can be time integrated over an electronic period much shorter than the phonon period, where the integral of the last term on the RHS of Eq. (5) vanishes. This means that, within the adiabatic approximation, ω_λ represents the frequency of the slow oscillation of the solution of Eq. (5) when $C^{e-n}_\lambda = C^{\rm st}_\lambda$, confirming that DFPT corresponds to taking the static (adiabatic) limit of the TD-DFPT kernel.

In metals, the adiabatic ansatz breaks down as the metallic electronic transition and atomic oscillation energies are similar, $\Delta\epsilon_{ij} \sim \omega_\lambda$. Therefore, nonadiabatic effects appear and, in Eq. (4), it is not possible to assume $u_\lambda(\tau) \sim u_\lambda(t)$.

The TD-DFPT phonon frequencies correspond, therefore, to the solution of Eqs. (4). This is a second–order Volterra linear integrodifferential equation [27] with a separable kernel ($e^{i\Delta\epsilon_{ij}(t-\tau)}$). The Volterra equations are the subject of intense mathematical research activity as they appear in many physical contexts, such as the dynamics of viscoelastic materials [28] or applications of physical engineering [29].

A crucial property of Eqs. (4) is that, being based on the mean-field approximation, it leads to an energy-conserving dynamics. This means that if $E = \langle\hat{H}\rangle$, the solution of Eqs. (4) must lead to a time-independent and constant E.

To solve Eqs. (4), we use the Laplace transformation, which is commonly used to solve the free quantum harmonic oscillator equation [27,30]:

$$f(z) = \mathcal{L}[f](z) = \int_0^\infty e^{-zt}f(t)dt. \quad (6)$$

When $z = -i\omega$, Eq. (6) reduces to the Fourier transformation. We consider here both transformations because, as will demonstrated shortly, the use of the Fourier will lead to the FD-DFPT theory proposed in Refs. [17–19], and widely used in the literature, which predicts the nonadiabatic effects to induce a finite phonon energy indetermination, corresponding to complex phonon frequencies.

We now proceed to apply Eq. (6) to Eqs. (4) and we note that, when $z = -i\omega$ (Fourier), $\mathcal{L}[\hat{\mathcal{D}}_\lambda u_\lambda](-i\omega)$ is well-defined if and only if $u_\lambda(t=\infty)=0$. The mathematical reason is that, to transform the time differential operator, we need to use the integration by parts method which requires the integrand of Eq. (6) to vanish at $t=\infty$ (Appendix D). This means, in practice, that the Fourier case can be used only by applying a tiny exponential prefactor, $e^{-\eta t}$, and send η to zero at the end of the derivation. We thus consider $f(z)$ and $f(-i\omega+\eta)$, with $\eta \to 0$.

By using Eq. (6), it follows that

$$u_\lambda(z) = \frac{z u_\lambda^0 + v_\lambda^0}{z^2 + \omega_\lambda^2 + \omega_\lambda \Delta C_\lambda(z)}, \tag{7a}$$

with $\Delta C_\lambda(z) = C_\lambda(z) - C_\lambda^{e-n}$ and

$$C_\lambda(z) = -i \sum_{ij} g_{ji}^\lambda \tilde{g}_{ij}^\lambda \frac{\Delta f_{ij}}{z - i\Delta\epsilon_{ij}}. \tag{7b}$$

$u_\lambda(t)$ can be analytically obtained from $u_\lambda(z)$ by using the Bromwhich integral [30] method that involves a complex plane integral of $u_\lambda(z)$. From Eqs. (7), it follows that the solution of Eqs. (4) is equivalent to finding the poles of $u_\lambda(z)$. In the Laplace case, this corresponds to finding the zeros of

$$z^2 + \omega_\lambda^2 + \omega_\lambda \Delta C_\lambda(z) = 0, \tag{8a}$$

while in the Fourier case we have

$$-\omega^2 + \omega_\lambda^2 + \omega_\lambda \lim_{\eta\to 0} \Delta C_\lambda(-i\omega+\eta) = 0. \tag{8b}$$

We now remind that $\lim_{\eta\to 0} \frac{1}{\omega+\Delta\epsilon_{ij}+i\eta} = \mathcal{P}[\frac{1}{\omega+\Delta\epsilon_{ij}}] - i\pi\delta(\omega+\Delta\epsilon_{ij})$, with $\mathcal{P}$ the Cauchy principal and real value. Therefore, it follows that

$$\lim_{\eta\to 0} \Delta C_\lambda(-i\omega+\eta) = \mathcal{P}[\Delta C_\lambda(-i\omega)] + i\Gamma_\lambda(\omega), \tag{9}$$

with

$$\Gamma_\lambda(\omega) = -\pi \sum_{ij} g_{ji}^\lambda \tilde{g}_{ij}^\lambda \Delta f_{ij} \delta(\omega + \Delta\epsilon_{ij}). \tag{10}$$

Equation (9) implies that the poles defined by Eq. (8b) are complex. In the Laplace case, instead, as demonstrated in Appendix E, $C_\lambda^{e-n} \in \mathbb{R}$ and $\Delta C_\lambda(z) = \mathcal{P}[C_\lambda(z)]$. It follows that the Laplace solution leads to imaginary poles [in Eq. (8a), $z^2 < 0$], corresponding to real frequencies.

If we call the zeros of Eq. (8a) $i\Omega_\lambda^{\mathrm{CM}}$, we thus finally get

$$u_\lambda(t) = \sum_{s=\pm} \begin{cases} e^{is\Omega_\lambda^{\mathrm{CM}} t} u_{\lambda s} & \text{Laplace} \\ e^{is\mathrm{Re}[\Omega_\lambda^{\mathrm{CM}}]t} e^{-\mathrm{Im}[\Omega_\lambda^{\mathrm{CM}}]t} u_{\lambda s} & \text{Fourier} \end{cases} \tag{11}$$

In Eq. (11), the $u_{\lambda s}$ constants are defined in terms of the initial position and velocity, u_λ^0 and v_λ^0. Equation (11) demonstrates that $u_\lambda(t\to\infty)=0$ only when the TD-DFPT master equation is solved by using the Fourier transformation. In this case, we recover the FD-DFPT [17–19]. Equation (11) is schematically represented in Fig. 1.

FD-DFPT is obtained, therefore, when $u_\lambda(t)$ and the kernel $C_\lambda(t)$ are dumped (via $e^{-\eta t}$) from the beginning. Physically, this damping would describe an electronic broadening that is zero in DFT and in DFPT. This means that the physical solution is obtained when $\eta \to 0$. However, in this limit the FD-DFPT produces a damped solution which corresponds to an unphysical and energy-violating decay of the oscillations.

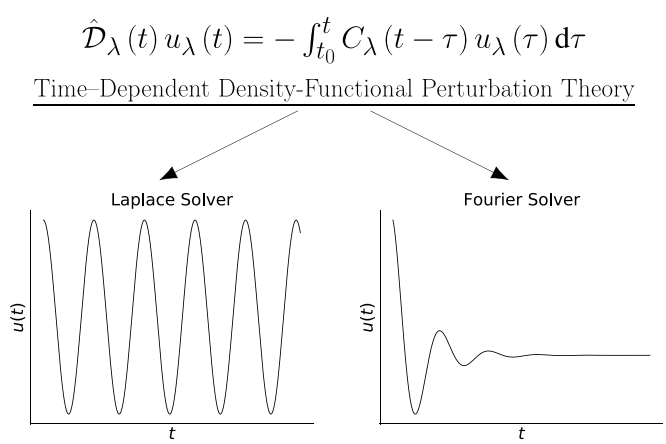

FIG. 1. The two solvers (Laplace and Fourier) of the TD-DFPT equation, Eqs. (4), are schematically compared. $u(t)$ is the atomic displacement function. While the Laplace approach leads to persistent oscillations, the Fourier solution produces an unphysical damping that violates the energy conservation. The Fourier solution corresponds to the frequency-dependent DFPT proposed by Refs. [17–19].

This decay is nonphysical as it makes $\langle H \rangle$ time dependent while the Hamiltonian, Eq. (1) is not time dependent. More importantly, as we are in the linear regime and f_i is time independent, decaying atomic oscillations lead to a decaying total energy. This is in contrast with the fact that within the mean-field approximation, the energy is conserved. The Laplace solution instead corresponds to persistent oscillating solutions which represent a set of undamped independent harmonic oscillators whose total energy is constant and conserved.

IV. THE BREAKDOWN OF THE SEMI–CLASSICAL PHONON PICTURE

Now the natural question is what the impact is on the phonon energies of the absence, in the semiclassical TD-DFPT case, of any energy indetermination. Are the TD-DFPT phonon energies still reliable?

To answer this question, we need to estimate the impact of the phonon linewidth on its energy. To do this, we use the MBPT approach where the phonon frequencies are defined as the solution of the Dyson equation for the phonon Green's function, $D_\lambda(t,t') = -i\langle \mathcal{T}\{\Delta\hat{u}_\lambda(t)\Delta\hat{u}(t')\}\rangle$ [10]. The poles of the Fourier transformed $D_\lambda(-i\omega)$ [using the convention defined by Eq. (6)] with respect to $(t-t')$ are the MBPT phonon energies, $\Omega_\lambda^{\mathrm{QM}} + i\gamma_\lambda^{\mathrm{QM}}$. Here I use the quantum mechanics (QM) label for MBPT quantities. Those poles are the solution of the fixed point equation

$$\omega^2 - \omega_\lambda^2 + \omega_\lambda C_\lambda^{e-n} - \omega_\lambda \Pi_\lambda(-i\omega) = 0. \tag{12}$$

The usual interpretation is that while $\Omega_\lambda^{\mathrm{QM}}$ is the renormalized phonon energy, $\gamma_\lambda^{\mathrm{QM}}$ defines its energy indetermination.

In Eq. (12), $\Pi_\lambda(-i\omega)$ is the Fourier transformed of the phonon self-energy [31]:

$$\Pi_\lambda(-i\omega) = \sum_{ij} g_{ji}^\lambda \tilde{g}_{ij}^\lambda \frac{\Delta f_{ij}}{\omega + \Delta\epsilon_{ij} + i\xi}. \tag{13}$$

In Eq. (13), ξ is a tiny positive number that appears because of the adiabatic switching-on of the interaction. Thanks to the Gell-Mann and Low theorem [32], it is possible to send $\xi \to 0$. Thanks to this basic theorem of MBPT, $\Pi_\lambda(-i\omega)$ acquires a finite imaginary part and, consequently, provides the phonon with a finite energy indetermination.

The formally analogy of Eqs. (13) and (8b) has instilled the idea that nonadiabatic effects can be described by DFPT with the same accuracy of MBPT. From a physical point of view, this would mean that a fully quantistic approach is equivalent to treat the atoms semiclassically. Here, instead, we demonstrated that this is not true and the semiclassical TD-DFPT approach has no access to the phonon energy indetermination. To estimate the impact of the difference $\Omega_\lambda^{\rm CM} - \Omega_\lambda^{\rm QM}$ in realistic materials, let us compare the solution of Eq. (12) with Eq. (8a) in MgB_2, a paradigmatic material characterized by very large nonadiabatic effects [34]. We can safely assume that $\mathrm{Re}[\Pi_\lambda(-i\omega)] \sim \mathcal{P}(C_\lambda(-i\omega))$. It follows that we can rewrite the real part of Eq. (12) as

$$\left(\Omega_\lambda^{\rm QM}\right)^2 + \left(\gamma_\lambda^{\rm QM}\right)^2 = \left(\Omega_\lambda^{\rm CM}\right)^2. \tag{14}$$

Equation (14) is demonstrated analytically in Appendix F, and it represents another result of this paper. It provides an easy recipe to estimate the deviation of the TD-DFPT phonon energy from the MBPT result when the phonon acquires a finite width. First, we see that $\Omega_\lambda^{\rm CM} > \Omega_\lambda^{\rm QM}$, which means that the semiclassical phonon frequency is always larger than the MBPT one. More importantly, we can apply Eq. (14) to any material whose experimental phonon energies and widths have been either calculated or measured experimentally.

Indeed, if we suppose to use the *exact* MBPT self-energy, then $\Omega_\lambda^{\rm QM}$ ($\gamma_\lambda^{\rm QM}$) is, by definition, equal to the experimental frequency (width). So, we can use a slightly modified version of Eq. (14):

$$\Omega_\lambda^{\rm CM} = \sqrt{\left(\Omega_\lambda^{\rm exp}\right)^2 + \left(\gamma_\lambda^{\rm exp}\right)^2}. \tag{15}$$

In the case of MgB_2, we can apply Eq. (15) to the E_{2g} mode measured via Raman scattering by Ponoso and Streltsov in Ref. [33], whose energy (black line) and width (gray line) are reported as a function of the temperature in Fig. 2. We notice that at $T \sim 410$ K, $\gamma_{E_{2g}}^{\rm exp}$ reaches its maximum, 41.9 meV, which corresponds to ∼57% of the frequency (73.7 meV). In this case, Eq. (15) gives $\Omega_\lambda^{\rm CM} = 84.83$ meV, which corresponds to a 15% overestimation of the experimental value.

In Ref. [18], the DFPT approach has been applied to several conventional and layered metals, finding deviations of the experimental phonon frequencies from the adiabatic DFTP results ranging from ∼4.5% (CaC_6 at 300 K) to ∼24.5% (KC_8). These deviations are of the same order of magnitude of the $\Omega_\lambda^{\rm CM} - \Omega_\lambda^{\rm QM}$. This confirms that nonadiabatic effects cannot be described by TD-DFPT and impose the use of a fully quantistic approach.

V. CONCLUSIONS

In this paper, we proposed a time-dependent formulation of DFPT that extends the semiclassical phonon concept to the nonadiabatic regime. By solving exactly the integrodifferential equation which governs the atomic oscillations dynamics, we have demonstrated that phonon energies are purely real and that a semiclassical description has no access to the phonon energy indetermination.

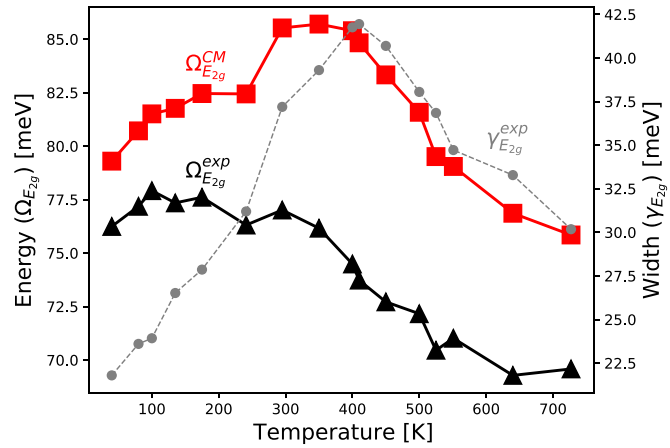

FIG. 2. MgB_2 experimental width ($\gamma_{E_{2g}}^{\rm exp}$, gray line, circles) and energy ($\Omega_{E_{2g}}^{\rm exp}$, black line, triangles) of the E_{2g} phonon mode as a function of the temperature [33] compared with the semiclassical TD-DFPT phonon energies ($\Omega_{E_{2g}}^{\rm CM}$, red line, boxes) calculated by means of Eq. (15) assuming that $\gamma_\lambda^{\rm exp} = \gamma_\lambda^{\rm QM}$. MgB_2 is well-known to manifest strong nonadiabatic effects that result in a phonon width that, at room temperature, is almost half the phonon energy. This very large width causes an equally large (15%) TD-DFPT overestimation of the phonon frequency.

Moreover, by comparing the TD-DFPT solution with the quasiphonon many-body picture, we derived a simple equation that allows us to estimate, even experimentally, the impact of the semiclassical phonon assumption. This method is applied to MgB_2 showing large (15% of the bare phonon frequency) overestimation of the experimental phonon energy when using TD-DFPT. This overestimation reflects the breakdown of the semiclassical picture. The final result is that the semiclassical DFTP phonon approach cannot describe nonadiabatic effects. In this case, a fully quantistic scheme is needed. The present results open several questions in many different fields of physics and call for further research on the impact of nonadiabatic effects on the atomic dynamics within and beyond the harmonic approximation.

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APPENDIX A: THE INITIAL HAMILTONIAN

The perturbed density functional theory (DFT) Hamiltonian has been introduced by several authors [11–16]. I take as

reference Eq. (24) of Ref. [11]:

$$\widehat{H} = \sum_i \epsilon_i \hat{c}_i^\dagger \hat{c}_i + \widehat{H}_{e-e} + \sum_\lambda \left[\frac{\omega_\lambda}{2} (\hat{u}_\lambda^\dagger \hat{u}_\lambda + \hat{p}_\lambda^\dagger \hat{p}_\lambda) + \left(\hat{\mathcal{L}}_\lambda + \sum_\mu \hat{\mathcal{Q}}_{\mu\lambda} \hat{\phi}_{+\mu} \right) \hat{\phi}_{+\lambda} \right] \tag{A1}$$

where $\hat{\mathcal{L}}_\lambda$, $\hat{\mathcal{Q}}_{\lambda\mu}$ are defined in Eq. (25) of Ref. [11].

As I am working within DFT the electron–electron interaction is replaced by the exact mean–field exchange–correlation potential, $\underline{\Delta V}^{Hxc}$.

In the present context we assume that the equilibrium positions the atoms are oscillating around are well described by the adiabatic DFPT, with negligible nonadiabatic corrections. Thanks to this assumption

$$\hat{\mathcal{L}}_\lambda = \sum_{ij} g^\lambda_{ji} \Delta\hat{\rho}_{ij}. \tag{A2}$$

Similarly we neglect second–order terms in Eq. (A1) in $\hat{\phi}_{s\lambda}$ which induces nonharmonic corrections to the atomic equation of motion. Thanks to this approximation

$$\hat{\mathcal{Q}}_{\lambda\mu} = -\frac{1}{2} C^{e-n}_{\lambda\mu}. \tag{A3}$$

We further assume $C^{e-n}_{\lambda\mu} \sim C^{e-n}_{\lambda\mu}\delta_{\lambda\mu}$.

By using Eqs. (A2)–(A3) in Eq. (A1) we obtain Eq. (2).

The notation used in Eq. (A1) is very general. The i label can represent any one–body quantum number. If we consider, for example, the electronic momentum $\mathbf{k}$ (bold symbols are vectors) Eq. (A1) turns into

$$\widehat{H} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \hat{c}^\dagger_{\mathbf{k}} \hat{c}_{\mathbf{k}} + \sum_{\lambda\mathbf{q}} \left[\frac{\omega_{\mathbf{q}\lambda}}{2} (\hat{u}^\dagger_{\mathbf{q}\lambda} \hat{u}_{\mathbf{q}\lambda} + \hat{p}^\dagger_{\mathbf{q}\lambda} \hat{p}_{\mathbf{q}\lambda}) + \sum_{\mathbf{k}} \left(g^\lambda_{\mathbf{q}} \hat{u}_{\mathbf{q}\lambda} + V^{Hxc}_{\mathbf{q}} \right) \hat{c}^\dagger_{\mathbf{k}} \hat{c}_{\mathbf{k}-\mathbf{q}} \right]. \tag{A4}$$

From Eq. (A4), the very same procedure described in the main text leads to

$$C_{\mathbf{q}\lambda}(z) = -\mathrm{i} g^\lambda_{\mathbf{q}} \tilde{g}^\lambda_{-\mathbf{q}} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}} - f_{\mathbf{k}+\mathbf{q}}}{z - \mathrm{i}(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}})}. \tag{A5}$$

See, for example, Eq. (A5) is equivalent to Eq. (145) of Ref. [12]. In a similar way band indexes can be added. The derivation of the main text will not depend on the specific notation used as it is completely agnostic of the underling one–body representation.

APPENDIX B: EQUATIONS OF MOTION FOR THE ELECTRONIC AND BOSONIC OPERATORS

The Hamiltonian defined in Eq. (2) induces a dynamics of all operators, electronic and atomic. These equations have been recently reviewed in Refs. [11,14,15]. The second–order time derivative of the displacement is

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2} \hat{u}_\lambda(t) = \omega_\lambda \left(\Pi^{st}_\lambda - \omega_\lambda \right) \hat{u}_\lambda(t) - \omega_\lambda \sum_{ij} g^\lambda_{ji} \Delta\hat{\rho}_{ij}(t), \tag{B1}$$

while the equation of motion for the density matrix is

$$i \frac{\mathrm{d}}{\mathrm{d}t} \hat{\rho}_{ij}(t) = -\Delta\epsilon_{ij} \hat{\rho}_{ij}(t) + \sum_\lambda \left[\underline{\hat{\rho}}(t), \underline{g}^\lambda \hat{u}_\lambda(t) \right]_{ij} + \left[\underline{\hat{\rho}}(t), \underline{\Delta V}^{Hxc}[\rho(t)] \right]_{ij} \tag{B2}$$

Eqs. (B1)–(B2) completely solve the many–body problem and produce the equations governing the classical atomic motion as an approximation.

APPENDIX C: ELECTRON–PHONON INTERACTION DYNAMICAL DRESSING

The role of V^{Hxc} in Eq. (B2) is to screen the electron–phonon interaction g^λ_{ji}. In order to see it we observe that [35]

$$\underline{\Delta V}^{Hxc}[\rho](t) = \int \mathrm{d}\tau\, t' \underline{\underline{f}}^{Hxc}(t-\tau) \delta\underline{\rho}(\tau) = \sum_\lambda \int \mathrm{d}\tau\, t' \underline{\underline{f}}^{Hxc}(t-\tau) \underline{\underline{\chi}}(\tau - t') \underline{g}^\lambda u_\lambda(t'), \tag{C1}$$

with $\underline{\underline{\chi}}$ the tensorial reducible response function and $\underline{\underline{f}}^{Hxc}$ the Hartree plus exchange–correlation kernel, defined as $\frac{\delta \underline{V}^{Hxc}[\rho](t)}{\delta\rho(t')}$. The single underlined quantities are matrices ($\underline{M}_{ij}$) while the doubly underlined are tensors ($\underline{\underline{M}}_{ij}$) in the electron–hole pairs space. If we now plug Eq. (C1) in Eq. (B2) and take the average of both terms we get

$$\underline{g}^\lambda u_\lambda(t) + \underline{\Delta V}^{Hxc}[\rho(t)] = \sum_\mu \int \mathrm{d}t' \left[\underline{\underline{\delta}} \delta_{\lambda\mu} \delta(t-t') + \int d\tau \underline{\underline{f}}^{Hxc}(t-\tau) \underline{\underline{\chi}}(\tau - t') \right] \underline{g}^\mu u_\mu(t') \sim \int \mathrm{d}t' \underline{\underline{\varepsilon}}^{-1}(t-t') \underline{g}^\lambda u_\lambda(t'). \tag{C2}$$

In Eq. (C2) it appears the TD–DFT inverse test–electron [14] dielectric matrix, $\underline{\underline{\varepsilon}}^{-1}(t-t')$, and I have neglected the $\lambda \neq \mu$ terms.

If we now use Eq. (C2) in Eq. (B2) we get

$$\Delta\underline{\rho}(t) = \int \mathrm{d}t' \underline{\underline{\chi}}(t-t') \underline{g}^\lambda u_\lambda(t'), \tag{C3}$$

that corresponds to the TD–DFT Kubo equation. If we now use the Källén–Lehmann spectral representation of $\underline{\underline{\chi}}(t-t')$ [32] we can expand Eq. (C3) over the poles (E_I) and residuals ($\underline{\underline{\chi}}^I$) of $\underline{\underline{\chi}}$:

$$\rho_{ij}(t) = \sum_I \left[\underline{\underline{\chi}}^I \underline{g}^\lambda\right]_{ij} \int dt' e^{iE_I(t-t')} u_\lambda(t'), \tag{C4}$$

From Eq. (C4) it follows that the effect of the time–dependent exchange–correlation DFT potential is to replace the independent particle energies with the poles of the full TD–DFT response function. Again, Eq. (C4) does not lead to any change in the main derivations of the work where, for simplicity, we use the static screening approximation and write

$$\rho_{ij}(t) \approx \tilde{g}^\lambda_{ij} \int dt' e^{i\Delta\epsilon_{ij}(t-t')} u_\lambda(t'), \tag{C5}$$

with $\underline{\tilde{g}}^\lambda \sim \underline{\underline{\varepsilon}}^{-1}(\omega=0)\underline{g}^\lambda$.

APPENDIX D: ON THE LAPLACE AND FOURIER TRANSFORMATIONS OF THE DIFFERENTIAL OPERATOR

The Laplace and Fourier transformations are, apparently, very similar:

$$g^f(\omega) = \int_0^\infty e^{i\omega t} g(t) dt, \tag{D1a}$$

$$g^l(\omega) = \int_0^\infty e^{-\omega t} g(t) dt. \tag{D1b}$$

In Eq. (D1) I have assumed $g(t)=0$ when $t<0$, which is the case of a classical pendulous displaced from the equilibrium position at $t=0$.

The Fourier transformation is not listed among the solvers of the integro–differential Volterra equation [27,30] and the reason is simple. If we apply Eq. (D1a) to the differential operator ($\frac{d^2}{dt^2}$) we get

$$\int_0^\infty e^{i\omega t} \frac{d^2u_\lambda(t)}{dt^2} dt = e^{i\omega t} \frac{du_\lambda(t)}{dt}\Big|_0^\infty - i\omega\Big[e^{i\omega t} u_\lambda(t)\Big|_0^\infty - i\omega u^f_\lambda(\omega)\Big], \tag{D2}$$

with $u^f_\lambda(\omega)$ the Fourier transformation of $u(t)$. From Eq. (D2) it is evident that in order for the differential operator to be Fourier transformable we do need to impose the condition $\frac{du_\lambda(t)}{dt}|_{t=\infty} = u_\lambda(t=\infty) = 0$. Therefore, the Fourier transformation can be used if and only if it is assumed from the beginning that the solution will decay in time.

This a peculiar property of the Volterra equation: if we start from the sub–space of function that decay for $t\to\infty$ the solution will decay as well even if at the end of the derivation we extend the initial sub–space of functions to the entire space.

APPENDIX E: REGULARIZATION OF THE LAPLACE TRANSFORMATION OF THE TIME–DEPENDENT DFPT KERNEL

We now notice that $C_\lambda(i\Delta\epsilon_{km}) = \infty$ for any $\Delta\epsilon_{km}$. This means that $u_\lambda(z)$ is ill defined when z approaches the electron–hole energies. However let's rewrite $C_\lambda(\omega)$ as

$$C_\lambda(\omega) = (-i)\frac{\sum_J R^\lambda_J \prod_{I\neq J}(\omega - i\Delta\epsilon_I)}{\prod_I(\omega - i\Delta\epsilon_I)}, \tag{E1}$$

with $I=(i,j)$ and $R_I = g^\lambda_{ji}\tilde{g}^\lambda_{ij}\Delta f_{ij}$. If we now use Eq. (E1) to rewrite $u_\lambda(z)$ we get

$$\frac{u_\lambda(z)}{(zu^0_\lambda + v^0_\lambda)} = \left[z^2 - \omega_\lambda\left(C^{e-n}_\lambda - \omega_\lambda\right) + \omega_\lambda C_\lambda(z)\right]^{-1} = \frac{\prod_I(\omega - i\Delta\epsilon_I)}{\left[z^2 - \omega_\lambda\left(C^{e-n}_\lambda - \omega_\lambda\right)\right]\prod_I(\omega - i\Delta\epsilon_I) - i\omega_\lambda \sum_J R^\lambda_J \prod_{I\neq J}(\omega - i\Delta\epsilon_I)}. \tag{E2}$$

From Eq. (E2) it follows that, if we use $\Delta\epsilon_{km} \to \Delta\epsilon_K$ we get

$$u_\lambda(i\Delta\epsilon_K) = \frac{i}{\omega_\lambda}\frac{0}{R^\lambda_K \prod_{I\neq K} i(\Delta\epsilon_K - \Delta\epsilon_I)} = 0. \tag{E3}$$

This means that the points $z = i\Delta\epsilon_K$ can be safely excluded from the complex plane integral as they do not give any contribution. This implies that we can replace $C_\lambda(z)$ with its *Cauchy principal value*, $C_\lambda(z) \to \mathcal{P}[C_\lambda(z)]$ which leads to a well defined Bromwhich integral.

APPENDIX F: SOLUTION OF THE TD–DFPT AND MBPT FIXED–POINT EQUATIONS

Let's start from the TD–DFPT and MBPT equations for the phonon energy and width:

$$z^2 + \omega^2_\lambda + \omega_\lambda \Delta C_\lambda(z) = 0, \tag{F1a}$$

$$\omega^2 - \omega^2_\lambda + \omega_\lambda C^{e-n}_\lambda - \omega_\lambda \Pi_\lambda(-i\omega) = 0. \tag{F1b}$$

We now rotate the Laplace equation to the imaginary axis $z \to -\mathrm{i}\omega$ so that the first equation becomes:

$$-\omega^2 + \omega_\lambda^2 + \omega_\lambda \Delta C_\lambda(-\mathrm{i}\omega) = 0. \tag{F2}$$

We now introduce a quasiphonon form of the energy dependence of C_λ and $\Pi_\lambda - C_\lambda^{e-n}$:

$$\Pi_\lambda(-\mathrm{i}\omega) - \omega_\lambda C_\lambda^{e-n} \sim \alpha_\lambda \frac{\omega^2}{\omega_\lambda} + \mathrm{i}\beta_\lambda \omega, \tag{F3}$$

with α_λ and β_λ to constants that can be easily defined by comparing Eq. (F3) with the analytic expression of Π_λ.

We now assume $\Delta C_\lambda(-\mathrm{i}\omega) \approx \mathcal{P}[\Pi_\lambda(-\mathrm{i}\omega) - C_\lambda^{e-n}]$. This is a very good approximation as the phonon self–energy and the TD–DFPT kernel have a very similar analytic form. If we define Ω_λ^{CM} the solution of Eq. (F2), from Eq. (F3) it follows that

$$\left(\Omega_\lambda^{CM}\right)^2 = \frac{\omega_\lambda^2}{1-\alpha_\lambda}. \tag{F4}$$

Similarly if we define $\Omega_\lambda^{QM} + \mathrm{i}\gamma_\lambda^{QM}$ the solution of Eq. (F1b) we get

$$\left(\Omega_\lambda^{QM}\right)^2 - \left(\gamma_\lambda^{QM}\right)^2 = \left(\Omega_\lambda^{CM}\right)^2 - \frac{\beta_\lambda \gamma_\lambda^{QM} \omega_\lambda}{1-\alpha_\lambda}, \tag{F5a}$$

$$\gamma_\lambda^{QM} = \frac{\beta_\lambda \omega_\lambda}{2(1-\alpha_\lambda)}. \tag{F5b}$$

If we now replace Eq. (F5b) in Eq. (F5a) we get

$$\left(\Omega_\lambda^{QM}\right)^2 + \left(\gamma_\lambda^{QM}\right)^2 = \left(\Omega_\lambda^{CM}\right)^2. \tag{F6}$$

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