

# In Search of the Electron-Phonon Contribution to Total Energy

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The total energy is a fundamental characteristic of solids, molecules, and nanostructures. In most first-principles calculations of the total energy, the nuclear kinetic operator is decoupled from the many-body electronic Hamiltonian and nuclear potential, and the dynamics of the nuclei is reintroduced afterward. This two-step procedure introduced by Born and Oppenheimer (BO) is approximate. Energies beyond the electronic and vibrational (or phononic) main contributions might be relevant when small energy differences are important, such as when predicting stable polymorphs or describing the magnetic energy landscape. We clarify the different flavors of BO decoupling and give an exact formulation for the total energy in the basis of BO electronic wave functions. Then, we list contributions beyond the main ones that appear in a perturbative expansion in powers of  $M_0^{-1/4}$ , where  $M_0$  is a typical nuclear mass, up to sixth order. Some of these might be grouped and denoted as the electron-phonon contribution to total energy,  $E^{\text{elph}}$ , which first appears at fourth order. The electronic inertial mass contributes at sixth order. We clarify that the sum of the Allen-Heine-Cardona zero-point renormalization of eigenvalues over occupied states is not the electron-phonon contribution to the total energy but rather part of the phononic contribution. The computation of the lowest-order  $E^{\text{elph}}$  is implemented and shown to be small but non-negligible in the case of diamond (3.8 meV per atom) and GaN (9.7 meV per atom). We also estimate the electronic inertial mass contribution and the quasi-harmonic one for diamond. We confirm the size consistency of all computed terms.

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## I. INTRODUCTION

The total energy is a cornerstone of modern solid-state physics and quantum chemistry. It governs material stability [1], phase transitions [2], crystal structure predictions [3], and defect formation energies [4]. Importantly for this work, whether a compound can be synthesized, which of its polymorphs is observed, and how it behaves in an operating device are decided by energy differences of a few tens of meV per atom. This is the scale that governs the thermodynamic stability of the lithiated and delithiated phases of battery electrodes [5], the competition between polymorphs in thermoelectric [6] and photovoltaic [7] compounds, the formation energy of the point defects that limit the efficiency of solar absorbers and light emitters [4], and the relative stability of the wide- and ultrawide-band-gap semiconductors on which energy-efficient power

conversion and solid-state lighting rely [8]. It is also the scale on which the high-throughput screening that now drives the discovery of energy materials operates [9]: the energy above the convex hull used to decide whether a compound is likely to be synthesizable is itself of the order of a few tens of meV per atom [10]. At this level of accuracy, the usual (zero-point motion, anharmonicity, and the electron-phonon coupling) contributions to the total energy that are habitually discarded can no longer be assumed to be negligible. Among them, the direct contribution of electron-phonon contribution to the total energy has so far neither been unambiguously identified nor computed from first principles for solids, which is the purpose of the present work.

Density functional theory (DFT) is often the method of choice when computing the total energy of solids [11,12]. If the exact exchange-correlation functional were known, then for any system of nuclei and electrons, DFT would give the exact total electronic energy at any chosen set of fixed nuclear positions  $\{\mathbf{R}\}$ . An open question is how to obtain the exact total energy (i.e., electronic plus nuclear vibrational) for the ground state of such a system. Indeed, DFT rests on the Born-Oppenheimer (BO) decoupling of nuclear and electronic degrees of freedom [13,14].

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Often, the first-principles BO nuclear contribution is added to the electronic energy. Phononic (or vibrational) degrees of freedom are taken into account through Bose-Einstein statistics in the case of harmonic solids [15] or through the quasiharmonic approximation to obtain thermal expansion [16–18] or using effective interatomic force constants to include anharmonic (phonon-phonon) corrections [19–21]. However, the BO decoupling leaves out numerous contributions to the total energy beyond the dominant electronic (static nucleus) energy and the nuclear ones (phononic harmonic, quasiharmonic, or anharmonic contributions). So, one can wonder whether electron-phonon contributions to the total energy exist, how to characterize them, and how to compute them. As a justification for their approach, Born and Oppenheimer [13] relied on a perturbation expansion, using  $M_0^{-1/4}$  as a small parameter, where  $M_0$  is a typical nuclear mass. In the equilibrium BO geometry, the total energy is obtained for frozen nuclei, so it does not depend on  $M_0$ . The first-order contribution vanishes. The second-order contribution, scaling as  $M_0^{-1/2}$ , is the phononic contribution. The third-order correction also vanishes. Three additional corrections come at the fourth order, with  $M_0^{-1}$  scaling. Among these, two contributions are of the anharmonic phonon-phonon type and can nowadays be included in first-principles calculations of total energy [19–21].

In this work, we observe that the third fourth-order BO expansion correction, sometimes referred to as the diagonal Born-Oppenheimer correction (DBOC) [14,22,23] can be computed approximately (within DFT) for solids on the basis of the electron-phonon matrix elements. Thanks to recent advances in efficient calculations of electron-phonon interaction [24], mostly relying on density functional perturbation theory [15,25–29], electron-phonon matrix elements are readily available when computing electronic transport [30,31] or thermal transport [32,33] properties, superconductivity [34], polaron formation [35,36], or the temperature dependence of the band gap and its zero-point renormalization [37,38]. Several terms of even higher order in the small parameter  $M_0^{-1/4}$  fall into that category. All could be grouped as “electron-phonon contributions to the total energy.” It is expected that such contributions are small compared to electronic and phononic contributions, but they might be crucial for the study of defects and surfaces [39], magnetic configurations [40], chemical reactions and bonding [41], or accurate phase transitions [42] where small energy differences matter.

Given the recent advances in the computation of electron-phonon matrix elements, several recent works have also discussed electron-phonon contributions to total energy. In 2020, Allen [43] suggested that this contribution could be calculated using the ingredients available when electron-phonon band-gap renormalization calculations are performed. His approach is based on the summation over occupied states of partial Fan-Migdal and

Debye-Waller self-energies [44]. Recently, Paul *et al.* [45] have performed first-principles calculations based on this idea. They argued that such a formulation violates size consistency, in which the total energy would depend on the size of the unit cell. In the present work, we show that Allen’s formulation is well defined and size-consistent. Crucially, we also show that the approach proposed by Allen does not deliver the fourth-order  $M_0^{-1}$  electron-phonon contribution term but is already part of the second-order phononic  $M_0^{-1/2}$  contribution to the total energy and should not be added to total energy calculations.

We first present in Sec. II the BO Hamiltonian and approximations based on BO wave functions. We also derive an expression for the exact total energy that includes contributions beyond the BO wave functions. We then perform a detailed mass-scaling analysis of all the terms entering the total energy in Sec. III. From this mass-scaling analysis, we identify which terms are phononic contributions, Sec. IV, while the remaining ones are detailed in Sec. V. In particular, we identify the lowest-order electron-phonon contribution to the total energy. In Sec. S4 of Supplemental Material [46], the BO perturbation expansion is derived and expressed in normal mode coordinates. We then show in Sec. VI the extension to solids with practical formulas for implementation in first-principles software. In Sec. VII, we show that Allen’s energy is not the electron-phonon contribution to the total energy but a part of the phononic contribution to the total energy. We then recast in Sec. VIII Allen’s formula into the standard Allen-Heine-Cardona (AHC) [44,47] theory for band renormalization thanks to an identically null term. In Sec. IX, we present a detailed analysis of the energy terms at the phonon zone center, comparing a frozen-phonon approach and perturbation theory. We find excellent agreement for all terms, with differences below 0.5%. We show size consistency by computing the diamond band renormalization using the ABINIT code [48–51] and an interpolation of the perturbed potential, which includes dipole and quadrupole contributions [52,53]. We show that the same results are obtained between the primitive and a supercell of diamond when no crystal symmetries are used.

Finally, in Sec. X, we compute the (fourth order) electron-phonon contribution to the total energy and approximate the effect of electron mass rescaling (sixth order) for two allotropes of carbon: the stable cubic diamond, an ultrawide-band-gap semiconductor considered for high-power, high-temperature electronics and for thermal management [54], and the high-pressure metastable hexagonal diamond called lonsdaleite, which is typically found in meteorites. For both materials, we report their converged total energy with momentum integration. We compute the electron-phonon forces and the new equilibrium lattice parameters of diamond and the internal parameter of lonsdaleite due to quasiharmonic effects. All energies are reported per two atoms. At 0 K,

we find that diamond is 52.7 meV more stable than lonsdaleite with a negligible amount coming from the electron-phonon term. For both polymorphs, the electron-phonon contribution to the total energy is 7.6 meV, which is 2% of the phonon contribution. Finally, we examine in Sec. XI three polymorphs of GaN (wurtzite, zincblende, and rocksalt), a material at the heart of energy-efficient power conversion and solid-state lighting [8], and find a much larger electron-phonon contribution, reaching 19.5 meV in the stable wurtzite phase, which represents 13% of the phonon contribution, and 19.9 meV, i.e., 18%, in the high-pressure rocksalt phase.

Overall, in addition to clarifying Allen's work, the main findings of this manuscript are (i) an equation fulfilled by the exact total energy, Eq. (30), in which all electronic degrees of freedom are hidden in a self-energy; (ii) the derivation of all terms in a perturbation expansion series in terms of  $M_0^{-1/4}$  up to order 6 included; (iii) the identification of terms that do not come from the Born-Oppenheimer anharmonicity, including those arising from the vector potential, the electron-phonon coupling, mixed terms, and the renormalization of nuclear mass due to electronic inertial effects; (iv) a practical formula for the lowest-order electron-phonon contribution to the total energy within DFT; (v) its implementation in ABINIT; and (vi) the study of diamond and lonsdaleite as well as three polymorphs of GaN.

## II. BORN-OPPENHEIMER-BASED APPROXIMATIONS

We first consider finite systems. We will extend the theory to periodic crystals in Sec. VI. The total Hamiltonian of a system composed of electrons and nuclei can be expressed as [13,55]

$$\hat{\mathcal{H}}\{\mathbf{R}\} \equiv \hat{T}^N + \hat{H}^{\text{BO}}\{\mathbf{R}\}, \quad (1)$$

$$\hat{T}^N \equiv \sum_{\kappa\alpha} \frac{\hat{P}_{\kappa\alpha}^2}{2M_\kappa} = -\frac{1}{2} \sum_{\kappa\alpha} \frac{1}{M_\kappa} \frac{\partial^2}{\partial R_{\kappa\alpha}^2}, \quad (2)$$

where  $\{\mathbf{R}\}$  denotes the set of nuclear positions,  $\hat{T}^N$  is the nuclear kinetic operator,  $\hat{P}_{\kappa\alpha} \equiv -i\partial/\partial R_{\kappa\alpha}$  is the canonical momentum operator for nuclei, with  $M_\kappa$  being the mass of the nucleus  $\kappa$  and  $\alpha$  an index for Cartesian axes. Electronic coordinates are implicit, unlike the nuclear ones. Operators acting on the electronic part of the wave function space are denoted with a hat, whereas operators acting on the nuclear configuration part of the wave function space are denoted with an inverted hat. Both can be present, as in the total Hamiltonian  $\hat{\mathcal{H}}\{\mathbf{R}\}$ . The inverted hat is omitted for operators that are local in nuclear configuration space. The global Hamiltonian in Eq. (1) is written in calligraphic style, as are the forthcoming associated total energies,

which are independent of  $\{\mathbf{R}\}$ . Hartree atomic units are used throughout.

The BO Hamiltonian,  $\hat{H}^{\text{BO}}\{\mathbf{R}\}$ , is defined as

$$\hat{H}^{\text{BO}}\{\mathbf{R}\} \equiv \hat{H}^e\{\mathbf{R}\} + V^{\text{NN}}\{\mathbf{R}\}, \quad (3)$$

$$\hat{H}^e\{\mathbf{R}\} \equiv \hat{T}^e + \hat{V}^{\text{ee}} + \hat{V}^{\text{eN}}\{\mathbf{R}\}, \quad (4)$$

where  $\hat{H}^e\{\mathbf{R}\}$  is the electronic Hamiltonian,  $V^{\text{NN}}\{\mathbf{R}\}$  the bare nucleus-nucleus interaction,  $\hat{T}^e$  the electronic kinetic operator,  $\hat{V}^{\text{ee}}$  the electron-electron operator, and  $\hat{V}^{\text{eN}}\{\mathbf{R}\}$  the electron-nucleus operator. The Schrödinger equation associated with the total Hamiltonian is

$$\hat{\mathcal{H}}\{\mathbf{R}\}|\psi_i\{\mathbf{R}\}\rangle = \mathcal{E}_i|\psi_i\{\mathbf{R}\}\rangle, \quad (5)$$

with ground state labeled  $i = 0$ . The Schrödinger equation for the BO Hamiltonian is

$$\hat{H}^{\text{BO}}\{\mathbf{R}\}|\phi_j\{\mathbf{R}\}\rangle = E_j^{\text{BO}}\{\mathbf{R}\}|\phi_j\{\mathbf{R}\}\rangle, \quad (6)$$

with ground state for each configuration  $\{\mathbf{R}\}$  labeled  $j = 0$ . The wave function  $\psi_i$  is normalized when integrated over electronic  $\mathbf{r}$  and nuclear  $\mathbf{R}$  coordinates, while the BO wave function  $\phi_j$  is normalized for each nuclear configuration  $\{\mathbf{R}\}$  when integrated over electronic coordinates only. The Dirac bracket notation is used for the electronic degrees of freedom unless specified otherwise.

The denominations “Born-Oppenheimer Hamiltonian,” “Born-Oppenheimer wave function” and “Born-Oppenheimer eigenenergy” for quantities in Eqs. (3) and (6) are well established and consistent in the literature, but there is some confusion about the meanings of “Born-Oppenheimer approximation” and “adiabatic approximation” [56–61].

In many publications, these are used interchangeably, while in others, they have different meanings.

For example, in their 1972 publication, Ballhausen and Hansen [56] discuss various adiabatic approximations, including “Born-Oppenheimer,” “Born-Huang,” “Herzberg-Teller,” and “crude” based on wave functions of the type

$$|\psi_i\{\mathbf{R}\}\rangle = X_i\{\mathbf{R}\}|\zeta_i\{\mathbf{R}\}\rangle, \quad (7)$$

that is, a simple product of a configuration-dependent (normalized) function of the nuclear configuration only  $X_i\{\mathbf{R}\}$ , with a single normalized electronic wave function, also possibly configuration-dependent. The electronic wave functions in these schemes change smoothly with the configuration. However, beyond the different “adiabatic approximations” used by Ballhausen and Hansen, the recent “exact factorization” [60–62] approach also has the form of Eq. (7) but is exact in that case. Therefore, it is

not helpful to define the “*adiabatic approximation*” as being based on Eq. (7), which is too general.

Instead, if one considers that  $|\zeta_j\{\mathbf{R}\}\rangle$  is a BO wave function  $|\phi_j\{\mathbf{R}\}\rangle$ , a meaningful set of approximations follows. We start from the exact relation:

$$|\psi_i\{\mathbf{R}\}\rangle = \sum_j \chi_{ij}\{\mathbf{R}\} |\phi_j\{\mathbf{R}\}\rangle, \quad (8)$$

where the wave function  $\chi_{ij}\{\mathbf{R}\}$  defines the nuclear dynamics. This decomposition can always be done since for every configuration  $\{\mathbf{R}\}$ , the set of  $|\phi_j\{\mathbf{R}\}\rangle$  forms a complete orthonormalized basis. Normalization of  $|\psi_i\{\mathbf{R}\}\rangle$  combined with the electronic normalization of  $|\phi_j\{\mathbf{R}\}\rangle$  implies the following normalization condition on the  $\chi_{ij}\{\mathbf{R}\}$ , with respect to integration over  $\{\mathbf{R}\}$  configurations:

$$\sum_j \langle \chi_{ij}\{\mathbf{R}\} | \chi_{ij}\{\mathbf{R}\} \rangle_{\mathbf{R}} \equiv \sum_j \int d\{\mathbf{R}\} \chi_{ij}^*\{\mathbf{R}\} \chi_{ij}\{\mathbf{R}\} = 1, \quad (9)$$

where we introduce the notation  $\langle \cdot | \cdot \rangle_{\mathbf{R}}$  to indicate that we evaluate the scalar product by integrating functions over all nuclear configurations  $\{\mathbf{R}\}$ . Scalar products without such a subscript are implicitly only for electronic degrees of freedom.

We choose a reference configuration  $\{\mathbf{R}^{\text{ref}}\}$  and the associated reference BO wave function  $|\phi_j\{\mathbf{R}^{\text{ref}}\}\rangle$ . We impose unicity and that  $|\phi_j\{\mathbf{R}\}\rangle$  changes smoothly as a function of  $\{\mathbf{R}\}$  around  $\{\mathbf{R}^{\text{ref}}\}$ . We note that such an imposition might be difficult when there are degeneracies around  $\{\mathbf{R}^{\text{ref}}\}$  or when the BO wave function changes abruptly.

Moreover, the arbitrary phase of the BO wave function should be taken consistently to achieve smoothness. We also use the index  $j$  to label this set of BO wave functions, even beyond the neighborhood where the smoothness is established.

We will assume in Sec. III that  $\{\mathbf{R}^{\text{ref}}\}$  is the configuration of a (local or global) minimum of a BO hypersurface, denoted by  $\{\mathbf{R}_j^0\}$ , but such a restriction is not yet needed. For illustrative purposes, we present in Fig. 1 a specific case of a one-dimensional coordinate diagram with a ground-state BO hypersurface and two BO excited surfaces.

In the literature, there are several possible approximations to Eq. (8) in which only one term is kept. A first possible approximation consists of considering  $E_j^{\text{BO}}\{\mathbf{R}\}$  as an effective scalar potential for nuclear dynamics:

$$|\psi_i\{\mathbf{R}\}\rangle \approx \chi_{ij}^{\text{sca}}\{\mathbf{R}\} |\phi_j\{\mathbf{R}\}\rangle \quad (10)$$

$$\left( \tilde{T}^{\text{N}} + E_j^{\text{BO}}\{\mathbf{R}\} \right) \chi_{ij}^{\text{sca}}\{\mathbf{R}\} = \mathcal{E}_{ij}^{\text{sca}} \chi_{ij}^{\text{sca}}\{\mathbf{R}\}. \quad (11)$$

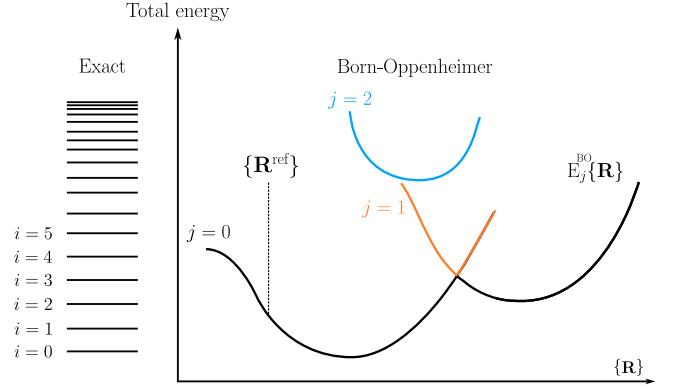


FIG. 1. Example of coordinate diagram for the BO energy hypersurfaces  $E_j^{\text{BO}}\{\mathbf{R}\}$  of the electronic ground state ( $j = 0$ ) and first- and second-excited states ( $j = 1$  and  $j = 2$ ). Eigenenergies of the total Hamiltonian are also shown, labeled with the  $i$  index. Unlike their wave functions, or the BO eigenenergies, they do not depend on the configuration of nuclei. The ground state of the total Hamiltonian has  $i = 0$  label. Usually, the corresponding wave functions will be made predominantly of the BO wave functions of one of the BO hypersurfaces, but there could be hybridized states. The chosen reference configuration is denoted by  $\{\mathbf{R}^{\text{ref}}\}$ . In this example, we present a specific case where the  $j = 0$  BO hypersurface has two minima, a global one and a local one, that might both be chosen to be the reference state  $\{\mathbf{R}_{j=0}^0\}$  in Sec. III. The  $j = 2$  BO hypersurface has one global minimum.

We refer to this approximation as the “*scalar potential*” approximation.

A second possible approximation, still using one term in Eq. (8), which we refer to as the “*optimal approximation*,” is based on choosing  $\chi_{ij}\{\mathbf{R}\}$  such that the expectation value of the Hamiltonian, Eq. (1), is stationary (minimal in the ground-state case). In that case, the nuclear wave function fulfills the following equation:

$$\left( \tilde{T}^{\text{N}} + E_j^{\text{BO}}\{\mathbf{R}\} + \sum_{\kappa\alpha} \frac{1}{2M_\kappa} \left[ 2B_{\kappa\alpha j}\{\mathbf{R}\} + 2A_{\kappa\alpha j}\{\mathbf{R}\} \tilde{P}_{\kappa\alpha} \right] \right) \times \chi_{ij}^{\text{opt}}\{\mathbf{R}\} = \mathcal{E}_{ij}^{\text{opt}} \chi_{ij}^{\text{opt}}\{\mathbf{R}\}, \quad (12)$$

with

$$A_{\kappa\alpha j}\{\mathbf{R}\} \equiv \left\langle \phi_j\{\mathbf{R}\} \left| -i \frac{\partial \phi_j}{\partial R_{\kappa\alpha}} \right| \right\rangle, \quad (13)$$

$$B_{\kappa\alpha j}\{\mathbf{R}\} \equiv -\frac{1}{2} \left\langle \phi_j\{\mathbf{R}\} \left| \frac{\partial^2 \phi_j}{\partial R_{\kappa\alpha}^2} \right| \right\rangle, \quad (14)$$

where the notation  $X_{\mathbf{R}}$  indicates that we take the derivative at the nuclear configuration  $\{\mathbf{R}\}$ . We also note that the presence of the terms  $A_{\kappa\alpha j}\{\mathbf{R}\}$  and  $B_{\kappa\alpha j}\{\mathbf{R}\}$  was observed by Born in 1951 (see Appendix VIII of Ref. [14]). However,  $A_{\kappa\alpha j}\{\mathbf{R}\}$  was then long ignored because it

disappears if the BO wave functions  $|\phi_j\{\mathbf{R}\}\rangle$  can be chosen to be real. Additionally, even if the BO wave functions are not real, there might be systems for which a choice of phase (gauge choice) in the relevant smoothness region yields vanishing  $A_{\kappa\alpha j}\{\mathbf{R}\}$ . This is usually possible for finite systems, except in certain cases. The first such case is related to the so-called *conical intersections* detailed in 1979 by Mead and Truhlar [63]. A conical intersection can appear if the reference BO hypersurface  $E_j^{\text{BO}}\{\mathbf{R}\}$  is not separated from the other BO hypersurfaces. However, if there is such a separation in the relevant region in the neighborhood of  $\{\mathbf{R}^{\text{ref}}\}$ , this problem can be neglected. A second exception arises if the Hamiltonian breaks the time-reversal symmetry. In this case,  $A_{\kappa\alpha j}\{\mathbf{R}\}$  will generally not vanish in a finite region around  $\{\mathbf{R}^{\text{ref}}\}$ , although it can be made to vanish for the chosen reference configuration. There has recently been interest in the presence of such a term, inducing chirality and/or angular momentum of phonons [64–70]. The  $A_{\kappa\alpha j}\{\mathbf{R}\}$  term is actually a Berry connection.

If  $A_{\kappa\alpha j}\{\mathbf{R}\}$  does not disappear, it is nevertheless possible to reformulate Eq. (12) so that  $A_{\kappa\alpha j}\{\mathbf{R}\}$  plays the role of a vector potential that modifies the nuclear momenta, giving

$$\left(\tilde{T}_j^{\text{vec}}\{\mathbf{R}\} + E_j^{\text{opt}}\{\mathbf{R}\}\right)\chi_{ij}^{\text{opt}}\{\mathbf{R}\} = \mathcal{E}_{ij}^{\text{opt}}\chi_{ij}^{\text{opt}}\{\mathbf{R}\}, \quad (15)$$

where  $\tilde{T}^{\text{N}}$  is replaced by

$$\tilde{T}_j^{\text{vec}}\{\mathbf{R}\} \equiv \sum_{\kappa\alpha} \frac{\left(\tilde{P}_{\kappa\alpha} + A_{\kappa\alpha j}\{\mathbf{R}\}\right)^2}{2M_{\kappa}}, \quad (16)$$

and  $E_j^{\text{BO}}\{\mathbf{R}\}$  is replaced by an “optimal” potential,

$$E_j^{\text{opt}}\{\mathbf{R}\} \equiv E_j^{\text{BO}}\{\mathbf{R}\} + E_j^{\text{DBOC}}\{\mathbf{R}\}. \quad (17)$$

The diagonal Born-Oppenheimer correction [14,22,23]  $E_j^{\text{DBOC}}\{\mathbf{R}\}$  is defined as

$$E_j^{\text{DBOC}}\{\mathbf{R}\} \equiv \sum_{\kappa\alpha} \frac{1}{M_{\kappa}} B_{\perp\kappa\alpha j}\{\mathbf{R}\}, \quad (18)$$

with

$$B_{\perp\kappa\alpha j}\{\mathbf{R}\} \equiv \frac{1}{2} \left\langle \frac{\partial \phi_j}{\partial R_{\kappa\alpha}} \middle| \hat{P}_{\perp j}^{\text{BO}}\{\mathbf{R}\} \middle| \frac{\partial \phi_j}{\partial R_{\kappa\alpha}} \right\rangle. \quad (19)$$

In Eq. (19), one has introduced  $\hat{P}_{\perp j}^{\text{BO}}\{\mathbf{R}\}$ , the projector on the space perpendicular to the  $j$ -BO manifold at configuration  $\{\mathbf{R}\}$ . It is a local operator in the nuclear configuration space, defined as follows:

$$\hat{P}_j^{\text{BO}}\{\mathbf{R}\} \equiv |\phi_j\{\mathbf{R}\}\rangle\langle\phi_j\{\mathbf{R}\}|. \quad (20)$$

The orthogonal projector is then

$$\hat{P}_{\perp j}^{\text{BO}}\{\mathbf{R}\} \equiv \hat{1}\{\mathbf{R}\} - \hat{P}_j^{\text{BO}}\{\mathbf{R}\}, \quad (21)$$

where  $\hat{1}\{\mathbf{R}\}$  is the unit operator in the electronic space. The presence of the projector in Eq. (19) removes the phase arbitrariness that is present in Eq. (14). In the literature dealing with phonon chirality [68], a simplified version of Eq. (15) is often encountered, where the vector potential is considered but not the DBOC term, see Sec. S1 of Supplemental Material [46]. As a historical note, the gauge-independent version of  $B$ , Eq. (19), was found after the 1979 work of Mead and Truhlar [63] while the gauge-dependent  $B$  term, Eq. (14), was known earlier.

Both approximations, Eqs. (11) and (15), to the exact Schrödinger equation, Eq. (5), have been referred to as “*adiabatic approximation*” and/or as “*Born-Oppenheimer approximation*” in the literature, with the following approximate total wave functions:

$$|\psi_i^{\text{sca}}\{\mathbf{R}\}\rangle = \chi_{ij}^{\text{sca}}\{\mathbf{R}\}|\phi_j\{\mathbf{R}\}\rangle, \quad (22a)$$

$$|\psi_i^{\text{opt}}\{\mathbf{R}\}\rangle = \chi_{ij}^{\text{opt}}\{\mathbf{R}\}|\phi_j\{\mathbf{R}\}\rangle. \quad (22b)$$

The introduction of the reference set of BO wave functions already allows one to obtain an exact representation of the total wave function, Eq. (8), as well as to define different adiabatic approximations, Eqs. (22a) and (22b), and it even yields a nuclear wave function equation that must be fulfilled by the exact eigenenergy.

For this purpose, we return to the exact wave function  $|\psi_i\{\mathbf{R}\}\rangle$ . The Hamiltonian Eq. (1) can be block-decomposed ( $2 \times 2$  decomposition) in the subspace spanned by the set of all  $|\phi_j\{\mathbf{R}\}\rangle$  for a chosen  $j$  value (but varying nuclear configurations) and its orthogonal complement. The first is left invariant upon application of  $\hat{P}_j^{\text{BO}}\{\mathbf{R}\}$  and the second is left invariant upon application of  $\hat{P}_{\perp j}^{\text{BO}}\{\mathbf{R}\}$ . This corresponds to the exact decomposition of the wave function,

$$|\psi_i\{\mathbf{R}\}\rangle = \chi_{ij}\{\mathbf{R}\}|\phi_j\{\mathbf{R}\}\rangle + |\mathcal{F}_i\{\mathbf{R}\}\rangle, \quad (23)$$

where  $|\mathcal{F}_i\{\mathbf{R}\}\rangle$  fulfills the constraint

$$\hat{P}_j^{\text{BO}}\{\mathbf{R}\}|\mathcal{F}_i\{\mathbf{R}\}\rangle = |0\{\mathbf{R}\}\rangle, \quad (24)$$

where  $|0\{\mathbf{R}\}\rangle$  is the null wave function in the electronic and nuclei space. The left-hand side of the Schrödinger equation, Eq. (6), can be moved to the right-hand side, and the Hamiltonian can be replaced by its expression in Eq. (1). The BO energy and Hamiltonian being diagonal in

this decomposition, the block decomposition delivers two equations:

$$\hat{\mathcal{P}}_j^{\text{BO}}\{\mathbf{R}\}(\check{T}^{\text{N}} + E_j^{\text{BO}}\{\mathbf{R}\} - \mathcal{E}_i)\chi_{ij}\{\mathbf{R}\}|\phi_j\{\mathbf{R}\}\rangle + \hat{\mathcal{P}}_j^{\text{BO}}\{\mathbf{R}\}\check{T}^{\text{N}}|\mathcal{F}_i\{\mathbf{R}\}\rangle = |\mathcal{O}\{\mathbf{R}\}\rangle, \quad (25a)$$

$$\hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}\}\check{T}^{\text{N}}\chi_{ij}\{\mathbf{R}\}|\phi_j\{\mathbf{R}\}\rangle + \hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}\}(\check{T}^{\text{N}} + \hat{H}^{\text{BO}}\{\mathbf{R}\} - \mathcal{E}_i)\hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}\}|\mathcal{F}_i\{\mathbf{R}\}\rangle = |\mathcal{O}\{\mathbf{R}\}\rangle. \quad (25b)$$

Let us first consider the second equation of this system. The action of  $\hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}\}\check{T}^{\text{N}}$  on a product of a nuclear wave function and a BO wave function can be rewritten in terms of a hybrid non-Hermitian operator,  $\check{T}_j^{\text{N}}\{\mathbf{R}\}$ , acting on the nuclear wave function only, which delivers its result in the full nuclear and electronic space:

$$\check{T}_j^{\text{N}}\{\mathbf{R}\}\chi_{ij}\{\mathbf{R}\} \equiv \hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}\}\check{T}^{\text{N}}\chi_{ij}\{\mathbf{R}\}|\phi_j\{\mathbf{R}\}\rangle, \quad (26)$$

which corresponds to

$$\check{T}_j^{\text{N}}\{\mathbf{R}\} \equiv \sum_{\kappa\alpha} \frac{\hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}\}}{2M_{\kappa}} \left[ -\left| \frac{\partial^2 \phi_j}{\partial R_{\kappa\alpha}^2} \right\rangle - 2i \left| \frac{\partial \phi_j}{\partial R_{\kappa\alpha}} \right\rangle \check{P}_{\kappa\alpha} \right]. \quad (27)$$

To treat the second term of the second equation in Eq. (25b), one introduces the Green's function of the full Hamiltonian, which is a function of a complex variable  $z$ . It is a nonlocal operator in nuclear configuration space, with kernel

$$\left[ \check{\mathcal{G}}(z) \right]_{\{\mathbf{R}_1, \mathbf{R}_2\}} \equiv \left[ \left( z - \check{\mathcal{H}}\{\mathbf{R}\} \right)^{-1} \right]_{\{\mathbf{R}_1, \mathbf{R}_2\}}. \quad (28)$$

Its restriction in the space orthogonal to the BO wave functions is defined by the following kernel

$$\begin{aligned} & \left[ \check{\mathcal{G}}_{\perp j}(z) \right]_{\{\mathbf{R}_1, \mathbf{R}_2\}} \\ & \equiv \hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}_1\} \left[ \left( z - \check{\mathcal{H}}\{\mathbf{R}\} \right)^{-1} \right]_{\{\mathbf{R}_1, \mathbf{R}_2\}} \hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}_2\}, \end{aligned} \quad (29)$$

with the term between parentheses defining a pseudoinverse, limited to that subspace. Although Green's function might not be defined for specific real  $z$  values above the ground-state energy  $z = \mathcal{E}_0$ , the restriction to the space orthogonal to the BO-wave functions removes this problem up to  $z$  being equal to the lowest excited-state BO eigenenergy. We also assume that  $z = \mathcal{E}_i$  is a value for which the projected Green's function  $\check{\mathcal{G}}_{\perp j}(z)$  exists.

Finally, we single out  $|\mathcal{F}_i\{\mathbf{R}\}\rangle$  in the second line of Eq. (25b) by applying  $\check{\mathcal{G}}_{\perp j}(\mathcal{E}_i)$  and inject it into the first line of Eq. (25a). After some algebraic manipulations, similar to those needed to go from Eq. (5) to Eq. (15), one deduces

$$\begin{aligned} & \left( \check{T}_j^{\text{vec}}\{\mathbf{R}\} + E_j^{\text{opt}}\{\mathbf{R}\} \right) \chi_{ij}\{\mathbf{R}\} \\ & + \int d\{\mathbf{R}'\} \left[ \check{\Sigma}_j(\mathcal{E}_i) \right]_{\{\mathbf{R}, \mathbf{R}'\}} \chi_{ij}\{\mathbf{R}'\} = \mathcal{E}_i \chi_{ij}\{\mathbf{R}\}, \end{aligned} \quad (30)$$

where

$$\left[ \check{\Sigma}_j(z) \right]_{\{\mathbf{R}_1, \mathbf{R}_2\}} \equiv \check{T}_j^{\text{N}, \dagger}\{\mathbf{R}_1\} \left[ \check{\mathcal{G}}_{\perp j}(z) \right]_{\{\mathbf{R}_1, \mathbf{R}_2\}} \check{T}_j^{\text{N}}\{\mathbf{R}_2\}. \quad (31)$$

The operator  $\check{\Sigma}_j(z)$  is an operator similar to the self-energy operators found in the context of many-body perturbation theory [71].

Importantly, Eq. (30) is an exact version of the approximate Eqs. (11) and (15) and focuses only on nuclear dynamics where all electronic degrees of freedom are condensed in the self-energy operator. The fact that the electronic degrees of freedom are completely hidden in Eq. (30), an exact reformulation of the Schrödinger equation, Eq. (5), before starting the mass-scaling perturbation expansion (see next section), is a key result of this work. Indeed, as a consequence, the self-energy operator will be shown to appear only for a large (actually sixth) power of the BO small parameter expansion. Thus, the hierarchy and categorization of terms in such BO expansion is easier to establish than in the initial BO approach, explaining why we are able to list all terms up to order 6 in the present work.

The Green's function of the full Hamiltonian fulfills a Dyson-type equation:

$$\begin{aligned} & \left[ \check{\mathcal{G}}_{\perp j}(z) \right]_{\{\mathbf{R}_1, \mathbf{R}_2\}} = \hat{\mathcal{G}}_{\perp j}^{\text{BO}}(z, \{\mathbf{R}_1\}) \\ & \times \left( [\hat{1}]_{\{\mathbf{R}_1, \mathbf{R}_2\}} + \check{T}^{\text{N}} \left[ \check{\mathcal{G}}_{\perp j}(z) \right]_{\{\mathbf{R}_1, \mathbf{R}_2\}} \right), \end{aligned} \quad (32)$$

where  $\hat{1}$  is the identity operator, and where  $\hat{\mathcal{G}}_{\perp j}^{\text{BO}}(z, \{\mathbf{R}\})$  is the BO Green's function, a local operator in nuclear configuration space, defined as

$$\hat{\mathcal{G}}_{\perp j}^{\text{BO}}(z, \{\mathbf{R}\}) \equiv \hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}\} \left( z - \hat{H}^{\text{BO}}\{\mathbf{R}\} \right)^{-1} \hat{\mathcal{P}}_{\perp j}^{\text{BO}}\{\mathbf{R}\}. \quad (33)$$

Inserting Eq. (32) into Eq. (31) can yield further approximate treatments. For example, motivated by the

inverse mass of nuclei that is present in  $\check{T}^N$ , one might neglect  $\check{T}^N \check{G}_{\perp j}$  with respect to  $\check{I}$  in Eq. (32). We will study this approximation in Sec. III on the basis of its mass-scaling behavior.

As a final comment in this section, let us now focus on the ground state. The variational freedom of the wave function Eq. (23) is complete, producing the lowest possible value of the energy of the Hamiltonian Eq. (1). Thus, restricting the trial wave function to the BO-wave-function subspace, which corresponds to the solution of Eq. (15), or, correspondingly, to the neglect of the self-energy in Eq. (30), must come with an increase in the energy such that  $\mathcal{E}_0 \leq \mathcal{E}_0^{\text{opt}}$ .

### III. MASS-SCALING ANALYSIS

In the original BO work [13], it is shown how to formulate a perturbation expansion around a minimum (global or local) of a chosen BO energy hypersurface with index  $j$ , taken as a reference configuration, when the nuclei masses are much larger than the electronic masses. The small parameter of this expansion is here denoted  $\lambda$ . Taking  $M_0$  as a characteristic nuclear mass, expressed in units of electronic mass, one defines relative nuclear masses

$$m_\kappa \equiv M_\kappa / M_0. \quad (34)$$

Then, the masses become  $\lambda$ -dependent and are scaled together,

$$M_\kappa(\lambda) = m_\kappa \lambda^{-4}. \quad (35)$$

For the value  $\lambda = \lambda_0 \equiv M_0^{-1/4}$ , the physical masses are recovered. We note that  $M_0^{-1/4}$  is small and at most 0.153 in the case of the hydrogen nucleus. The choice of Eq. (35) will be explained later by the observation that the average fluctuations of nuclear displacements with respect to a reference configuration chosen to be a local BO energy minimum  $\{\mathbf{R}_j^0\}$ , explicitly

$$\Delta R_{\kappa\alpha j} = R_{\kappa\alpha} - R_{\kappa\alpha j}^0, \quad (36)$$

are proportional to  $\lambda$  at the lowest order. Similarly, the average momenta are inversely proportional to  $\lambda$ . Also, when  $\lambda$  tends to zero, all masses become infinite, so that there is no nuclear dynamics.

The Schrödinger equation, Eq. (5), becomes

$$\check{\mathcal{H}}_\lambda\{\mathbf{R}\}|\psi_{i\lambda}\{\mathbf{R}\}\rangle = \mathcal{E}_{i\lambda}|\psi_{i\lambda}\{\mathbf{R}\}\rangle, \quad (37)$$

with a  $\lambda$ -dependent Hamiltonian replacing Eqs. (1) and (2),

$$\check{\mathcal{H}}_\lambda\{\mathbf{R}\} = \sum_{\kappa\alpha} \frac{\lambda^4 \check{p}_{\kappa\alpha}^2}{2m_\kappa} + \hat{H}^{\text{BO}}\{\mathbf{R}\}. \quad (38)$$

Quantities that depend on  $\lambda$  (wave functions, Hamiltonian, total energy, and Green's function) can be expanded in a Taylor series in  $\lambda$  as follows, generically:

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \mathcal{O}(\lambda^3), \quad (39a)$$

$$X^{(n)} = \frac{1}{n!} \frac{\partial^n X}{\partial \lambda^n} \Big|_{\lambda=0}. \quad (39b)$$

For  $\lambda = \lambda_0$ , the scaled Hamiltonian is equal to the original Hamiltonian so that the series

$$\mathcal{E}_{i\lambda_0} = \mathcal{E}_i^{(0)} + \lambda_0 \mathcal{E}_i^{(1)} + (\lambda_0)^2 \mathcal{E}_i^{(2)} + \mathcal{O}(\lambda_0^3) \quad (40)$$

delivers the exact total energy.

Quantities that depend on the nuclear coordinates (the wave functions, different potentials, Hamiltonians, and Green's functions) can also be expanded in another series, now considering atomic displacements, generically:

$$X\{\mathbf{R}\} = X_{j|0} + \sum_{\kappa\alpha} \frac{\partial X}{\partial R_{\kappa\alpha}} \Delta R_{\kappa\alpha j} + \frac{1}{2} \sum_{\substack{\kappa\alpha \\ \kappa'\alpha'}} \frac{\partial^2 X}{\partial R_{\kappa\alpha} \partial R_{\kappa'\alpha'}} \Delta R_{\kappa\alpha j} \Delta R_{\kappa'\alpha' j} + \mathcal{O}(\Delta \mathbf{R}_j^3), \quad (41)$$

where the  $j|0$  subscript of  $X_{j|0}$  indicates that the quantity  $X$  is evaluated at  $\{\mathbf{R}\} = \{\mathbf{R}_j^0\}$ . For conciseness, we also introduce a compact notation for the terms of such Taylor series:

$$X\{\mathbf{R}\} = X_{j|0} + X^{\{1\}} \cdot \Delta \mathbf{R}_j + X^{\{2\}} \cdot \Delta \mathbf{R}_j^2 + \mathcal{O}(\Delta \mathbf{R}_j^3), \quad (42a)$$

$$X^{\{n\}} \equiv \frac{1}{n!} \frac{\partial^n X}{\partial R_{\kappa_1 \alpha_1} \cdots \partial R_{\kappa_n \alpha_n} j|0}, \quad (42b)$$

$$\Delta \mathbf{R}_j^n \equiv \prod_{s=1}^n \Delta R_{\kappa_s \alpha_s j}, \quad (42c)$$

where the dot product in Eq. (42a) is defined as  $\cdot \equiv \sum_{\kappa_1 \alpha_1} \cdots \sum_{\kappa_n \alpha_n}$ . Curly brackets are used as superscripts in this notation, instead of the superscript parentheses of Eq. (39a). Being at the BO equilibrium positions, the first-order derivatives of the BO energy vanish so that

$$E_j^{\text{BO}}\{\mathbf{R}\} = E_{j|0}^{\text{BO}} + E_j^{\text{BO}\{2\}} \cdot \Delta \mathbf{R}_j^2 + \mathcal{O}(\Delta \mathbf{R}_j^3). \quad (43)$$

When considering only the second-order term in this expansion (curvature), the nuclear dynamics can be described by first solving the following auxiliary

( $\lambda$ -independent) multidimensional harmonic oscillator Hamiltonian,

$$\check{\mathfrak{H}}_j^{\text{ho}}\{\Delta\mathbf{R}\} \equiv \sum_{\kappa\alpha} \frac{\check{P}_{\kappa\alpha}^2}{2m_\kappa} + E_j^{\text{BO}\{2\}} \cdot \Delta\mathbf{R}_j^2, \quad (44)$$

with associated normalized nuclear eigenwavefunctions,  $\vartheta_{jj}$ , and eigenenergies  $\mathfrak{E}_{jj}^{\text{ho}}$ ,

$$\check{\mathfrak{H}}_j^{\text{ho}}\{\Delta\mathbf{R}\} \vartheta_{jj}\{\Delta\mathbf{R}\} = \mathfrak{E}_{jj}^{\text{ho}} \vartheta_{jj}\{\Delta\mathbf{R}\}, \quad (45)$$

where the subscript  $j$  (dotless  $j$ ) characterizes the nuclear state, considering the  $j$  BO hypersurface energy and curvature in the chosen reference configuration. The expression of the energy in terms of the nuclear state and the expansion around a (local or global) minimum is depicted in Fig. 2 for the specific  $j = 0$  BO hypersurface, for which one has to choose between two possible reference configurations. Importantly, the nuclear state index  $j$  starts at zero around each minimum  $\{\mathbf{R}_j^0\}$  of the  $j$  hypersurface. Both  $\check{\mathfrak{H}}_j^{\text{ho}}\{\Delta\mathbf{R}\}$  and  $\mathfrak{E}_{jj}^{\text{ho}}$  are denoted with a gothic calligraphy to indicate that they are related only to nuclear dynamics. Because  $\check{\mathfrak{H}}_j^{\text{ho}}$  is even with respect to a sign change of  $\Delta\mathbf{R}_j$ , its eigenfunctions are even or odd under such a sign change.

In Sec. S2 of Supplemental Material [46], we show that the Schrödinger equation, Eq. (37), is satisfied up to the

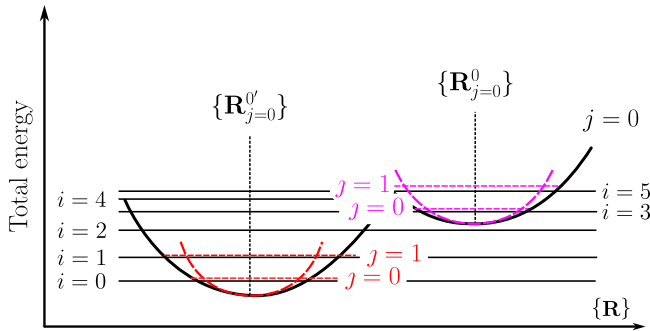


FIG. 2. Same coordinate diagram as Fig. 1, where we focus on the specific  $j = 0$  BO hypersurface (black curved line). This BO hypersurface presents here two minima denoted  $\{\mathbf{R}_{j=0}^0\}$  and  $\{\mathbf{R}_{j=0}^{0'}\}$ . The exact total energy  $\mathcal{E}_i$  (black horizontal line) of some level  $i$  is obtained from a series expansion considering one or the other reference configuration as the starting point, in the neighborhood of which the BO hypersurface is expanded to quadratic order (dashed parabola), defining an harmonic oscillator Hamiltonian. An eigenstate of this harmonic oscillator Hamiltonian is labeled with the index  $j$  (dotless- $j$ ). The corresponding eigenenergy is added to the reference BO energy, giving the red dashed horizontal line. The series expansion (red dash) maps the corresponding black energy level if the series converges.

second order (up2) in the displacements by the following wave function:

$$|\psi_{i\lambda}^{\text{up2}}\{\mathbf{R}\}\rangle \equiv N_\lambda \vartheta_{jj}\{\Delta\mathbf{R}_j/\lambda\} |\phi_j\{\mathbf{R}\}\rangle, \quad (46)$$

that has the form of Eq. (22b) and where we have associated the index  $i = (j, j)$  with a specific pair  $j$  and  $j$  where the index  $j$  is associated with the local minimum  $\mathbf{R}_j^0$  which best describes  $i$ . This association is possible when the  $\lambda$ -based expansion starting from the auxiliary harmonic oscillator Hamiltonian converges. This is exemplified by Fig. 2. The nuclear displacements are scaled by the inverse of  $\lambda$  in the first factor, which describes the nuclear dynamics, while they are not scaled in the second factor, which describes the electronic BO wave functions. In Sec. S2 of Supplemental Material [46], it is also shown that  $\mathcal{E}_i^{(2)} = \mathfrak{E}_{jj}^{\text{ho}}$ , so that

$$\mathcal{E}_{i\lambda} = E_{j\mathbf{0}}^{\text{BO}} + \lambda^2 \mathfrak{E}_{jj}^{\text{ho}} + \mathcal{O}(\lambda^3), \quad (47)$$

where the first term is independent of the characteristic mass and the second term scales as  $M_0^{-1/2}$ . In Eq. (47), the second-order energy is the vibrational correction with respect to a zero-order energy that depends on the index  $j$ .

Born and Oppenheimer [13] have analyzed anharmonic corrections, expanding  $E_j^{\text{BO}}\{\mathbf{R}\}$  beyond the second order in nuclear displacements, up to the fourth order in  $\lambda$ . We proceed with the analysis of the mass scaling of other corrections beyond those examined by them, up to the sixth order in  $\lambda$ . In order to do this, inspired by Eq. (46), we define scaled nuclear displacements with respect to the reference configuration and express the nuclear dynamics in terms of these. Explicitly,

$$\rho_{\kappa\alpha j} \equiv \Delta R_{\kappa\alpha j} / \lambda, \quad (48)$$

$$\check{\pi}_{\kappa\alpha} \equiv \lambda \check{P}_{\kappa\alpha}. \quad (49)$$

The associated notation for functions of the configuration argument is

$$X[\lambda \rho_j] \equiv X\{\mathbf{R}_j^0 + \lambda \rho_j\}, \quad (50)$$

with the shift by  $\mathbf{R}_j^0$  being taken into account and square brackets being used. The square bracket notation for functions that depend separately and explicitly on  $\lambda$  and  $\{\mathbf{R}\}$  does not follow the above simple correspondence and will be specified in their definition. In particular, we will favor a convention in which the dominant  $\lambda$  power is factored outside of such functions.

Importantly, the derivatives of the electronic BO wave functions present in  $A_{\kappa\alpha j}\{\mathbf{R}\}$ , Eq. (13), in  $B_{\perp\kappa\alpha j}\{\mathbf{R}\}$ , Eq. (19), as well as in  $\check{\mathcal{T}}_j^{\text{N}}\{\mathbf{R}\}$ , Eq. (27), remain derivatives in terms of nuclear configurations. This is due to the

expression of the second factor in Eq. (46), which is still expressed in nuclear configurations, not in scaled displacements. However, these functions are evaluated in the configuration expressed equivalently by  $\{\mathbf{R}\}$  or by  $[\lambda\boldsymbol{\rho}]$ . So, one has

$$A_{\kappa\alpha j}\{\mathbf{R}\} = A_{\kappa\alpha j}[\lambda\boldsymbol{\rho}_j] \quad (51)$$

$$B_{\perp\kappa\alpha j}\{\mathbf{R}\} = B_{\perp\kappa\alpha j}[\lambda\boldsymbol{\rho}_j]. \quad (52)$$

Also, referring to Eq. (27), we define

$$\lambda^3 \check{T}_{j\lambda}^N[\boldsymbol{\rho}_j] \equiv \lambda^3 \sum_{\kappa\alpha} \frac{\hat{P}_{\perp j}^{\text{BO}}[\lambda\boldsymbol{\rho}_j]}{2m_\kappa} \times \left[ -\lambda \left| \frac{\partial^2 \phi_j}{\partial R_{\kappa\alpha}^2} \right|_{[\lambda\boldsymbol{\rho}_j]} \right] - 2i \left| \frac{\partial \phi_j}{\partial R_{\kappa\alpha}} \right|_{[\lambda\boldsymbol{\rho}_j]} \check{\pi}_{\kappa\alpha}. \quad (53)$$

Transformed to the mass-scaled coordinates, the  $\lambda$ -dependent Hamiltonian, Eq. (38), becomes

$$\check{\mathcal{H}}_\lambda[\boldsymbol{\rho}_j] = \lambda^2 \check{T}^N[\boldsymbol{\rho}_j] + \hat{H}^{\text{BO}}[\lambda\boldsymbol{\rho}_j], \quad (54)$$

$$\check{T}^N[\boldsymbol{\rho}_j] = \sum_{\kappa\alpha} \frac{\check{\pi}_{\kappa\alpha}^2}{2m_\kappa}. \quad (55)$$

The corresponding Schrödinger equation is

$$\check{\mathcal{H}}_\lambda[\boldsymbol{\rho}_j]|\psi_{i\lambda}[\boldsymbol{\rho}_j]\rangle = \mathcal{E}_{i\lambda}|\psi_{i\lambda}[\boldsymbol{\rho}_j]\rangle. \quad (56)$$

We now examine the mass-scaling behavior of the different approximations presented in Sec. II. Similarly to Eqs. (22a) and (22b), we express the total wave function using scaled displacements  $[\boldsymbol{\rho}_j]$  instead of real-space coordinates:

$$|\psi_{i\lambda}[\boldsymbol{\rho}_j]\rangle = \chi_{jj\lambda}[\boldsymbol{\rho}_j]|\phi_j[\lambda\boldsymbol{\rho}_j]\rangle. \quad (57)$$

The optimal approximation of Eq. (15) becomes

$$\left( \lambda^2 \check{T}_{j\lambda}^{\text{vec}}[\boldsymbol{\rho}_j] + E_{j\lambda}^{\text{opt}}[\boldsymbol{\rho}_j] \right) \chi_{jj\lambda}^{\text{opt}}[\boldsymbol{\rho}_j] = \mathcal{E}_{i\lambda}^{\text{opt}} \chi_{jj\lambda}^{\text{opt}}[\boldsymbol{\rho}_j], \quad (58)$$

with

$$\check{T}_{j\lambda}^{\text{vec}}[\boldsymbol{\rho}_j] = \sum_{\kappa\alpha} \frac{(\check{\pi}_{\kappa\alpha} + \lambda A_{\kappa\alpha j}[\lambda\boldsymbol{\rho}_j])^2}{2m_\kappa}, \quad (59a)$$

$$E_{j\lambda}^{\text{opt}}[\boldsymbol{\rho}_j] = E_j^{\text{BO}}[\lambda\boldsymbol{\rho}_j] + \lambda^4 E_j^{\text{DBOC}}[\lambda\boldsymbol{\rho}_j], \quad (59b)$$

$$E_j^{\text{DBOC}}[\lambda\boldsymbol{\rho}_j] = \sum_{\kappa\alpha} \frac{1}{m_\kappa} B_{\perp\kappa\alpha j}[\lambda\boldsymbol{\rho}_j]. \quad (59c)$$

In the scalar approximation, one sets  $\lambda A_{\kappa\alpha j}[\lambda\boldsymbol{\rho}_j]$  and  $E_j^{\text{DBOC}}[\lambda\boldsymbol{\rho}_j]$  to zero, while keeping either of them leads to

alternative approximations, see Sec. S1 of Supplemental Material [46]. The exact equation for the energy  $\mathcal{E}_{i\lambda}$  of the full Hamiltonian, Eq. (56), is now expressed in terms of the self-energy, Eq. (30):

$$\left( \lambda^2 \check{T}_{j\lambda}^{\text{vec}}[\boldsymbol{\rho}_j] + E_{j\lambda}^{\text{opt}}[\boldsymbol{\rho}_j] \right) \chi_{jj\lambda}[\boldsymbol{\rho}_j] + \lambda^6 \int d[\lambda\boldsymbol{\rho}'_j] \{ \check{\Sigma}_{j\lambda}(\mathcal{E}_{i\lambda}) \}_{[\boldsymbol{\rho}_j, \boldsymbol{\rho}'_j]} \chi_{jj\lambda}[\boldsymbol{\rho}'_j] = \mathcal{E}_{i\lambda} \chi_{jj\lambda}[\boldsymbol{\rho}_j], \quad (60)$$

where

$$\{ \check{\Sigma}_{j\lambda}(z) \}_{[\boldsymbol{\rho}_j, \boldsymbol{\rho}'_j]} = \check{T}_{j\lambda}^{N, \dagger}[\boldsymbol{\rho}_j] \{ \check{\mathcal{G}}_{\perp j\lambda}(z) \}_{[\boldsymbol{\rho}_j, \boldsymbol{\rho}'_j]} \check{T}_{j\lambda}^N[\boldsymbol{\rho}'_j], \quad (61)$$

and

$$\{ \check{\mathcal{G}}_{\perp j\lambda}(z) \}_{[\boldsymbol{\rho}_j, \boldsymbol{\rho}'_j]} = \hat{P}_{\perp j}^{\text{BO}}[\lambda\boldsymbol{\rho}_j] \times \left\{ \left( z - \check{\mathcal{H}}_\lambda[\boldsymbol{\rho}_j] \right)^{-1} \right\}_{[\boldsymbol{\rho}_j, \boldsymbol{\rho}'_j]} \hat{P}_{\perp j}^{\text{BO}}[\lambda\boldsymbol{\rho}'_j]. \quad (62)$$

Referring to Eq. (32), the latter Green's function can equivalently be expressed in terms of the BO Green's function as

$$\{ \check{\mathcal{G}}_{\perp j\lambda}(z) \}_{[\boldsymbol{\rho}_j, \boldsymbol{\rho}'_j]} = \hat{G}_{\perp j}^{\text{BO}}(z, [\lambda\boldsymbol{\rho}_j]) \times \left( \{ \check{\mathcal{I}} \}_{[\boldsymbol{\rho}_j, \lambda\boldsymbol{\rho}'_j]} + \lambda^2 \check{T}^N[\boldsymbol{\rho}_j] \{ \check{\mathcal{G}}_{\perp j\lambda}(z) \}_{[\boldsymbol{\rho}_j, \boldsymbol{\rho}'_j]} \right), \quad (63)$$

and

$$\hat{G}_{\perp j}^{\text{BO}}(z, [\lambda\boldsymbol{\rho}_j]) = \hat{P}_{\perp j}^{\text{BO}}[\lambda\boldsymbol{\rho}_j] \left( z - \hat{H}^{\text{BO}}[\lambda\boldsymbol{\rho}_j] \right)^{-1} \hat{P}_{\perp j}^{\text{BO}}[\lambda\boldsymbol{\rho}_j]. \quad (64)$$

In Eq. (60), the reference BO energy  $E_{j0}^{\text{BO}}$  can be subtracted from both  $E_{j\lambda}^{\text{opt}}[\boldsymbol{\rho}_j]$  and  $\mathcal{E}_{i\lambda}$ , leaving quantities that are at least second order in  $\lambda$ . Such a second-order component can be used as a zeroth-order Hamiltonian to find the remaining expansion for  $\mathcal{E}_{i\lambda}$  and to find the wave function  $\chi_{jj\lambda}[\boldsymbol{\rho}_j]$ . Explicitly, from Eq. (60), one deduces

$$\check{\mathfrak{H}}_{j\lambda}[\boldsymbol{\rho}_j] \chi_{jj\lambda}[\boldsymbol{\rho}_j] = \mathfrak{E}_{jj\lambda} \chi_{jj\lambda}[\boldsymbol{\rho}_j], \quad (65)$$

with

$$\check{\mathfrak{H}}_{j\lambda}[\boldsymbol{\rho}_j] = \check{\mathfrak{H}}_j^{\text{ho}}[\boldsymbol{\rho}_j] + \Delta \check{\mathfrak{H}}_{j\lambda}[\boldsymbol{\rho}_j], \quad (66)$$

that includes the auxiliary harmonic oscillator Hamiltonian

$$\check{\mathfrak{H}}_j^{\text{ho}}[\rho_j] \equiv \sum_{\kappa\alpha} \frac{\check{\pi}_{\kappa\alpha}^2}{2m_\kappa} + E_j^{\text{BO}\{2\}} \cdot \rho_j^2, \quad (67)$$

and corrections to this auxiliary harmonic oscillator Hamiltonian

$$\begin{aligned} \Delta\check{\mathfrak{H}}_{j\lambda}[\rho_j] &\equiv \lambda \check{T}_j^{\text{vec}(1)}[\lambda\rho_j] + \lambda^2 T_j^{\text{vec}(2)}[\lambda\rho_j] \\ &\quad + \sum_{n=1} \lambda^n E_j^{\text{BO}\{n+2\}} \cdot \rho_j^{n+2} \\ &\quad + \lambda^2 E_j^{\text{DBOC}}[\lambda\rho_j] + \lambda^4 \check{\Sigma}_{j\lambda}(\mathcal{E}_{i\lambda}), \end{aligned} \quad (68)$$

where

$$\check{T}_j^{\text{vec}(1)}[\lambda\rho_j] \equiv \sum_{\kappa\alpha} \frac{\check{\pi}_{\kappa\alpha} A_{\kappa\alpha j}[\lambda\rho_j] + A_{\kappa\alpha j}[\lambda\rho_j] \check{\pi}_{\kappa\alpha}}{2m_\kappa} \quad (69)$$

$$T_j^{\text{vec}(2)}[\lambda\rho_j] \equiv \sum_{\kappa\alpha} \frac{(A_{\kappa\alpha j}[\lambda\rho_j])^2}{2m_\kappa}. \quad (70)$$

The eigenvalues in Eq. (65) are related to those in Eq. (60) by

$$\mathcal{E}_{i\lambda} - E_{j0}^{\text{BO}} = \lambda^2 \mathfrak{E}_{jj\lambda}. \quad (71)$$

In Eq. (68) and in later equations, the functions of the argument  $\lambda\rho_j$  are expanded using the notation of Eq. (42a) adapted to this argument:

$$X[\rho_j] = X_{j0} + X^{\{1\}} \cdot \rho_j + X^{\{2\}} \cdot \rho_j^2 + \mathcal{O}(\rho_j^3). \quad (72)$$

Without the corrections  $\Delta\check{\mathfrak{H}}_{j\lambda}$ , Eq. (65) reduces to the  $\lambda$ -independent equation

$$\check{\mathfrak{H}}_j^{\text{ho}}[\rho_j] \chi_{jj}^{\text{ho}}[\rho_j] = \mathfrak{E}_{jj}^{\text{ho}} \chi_{jj}^{\text{ho}}[\rho_j], \quad (73)$$

where identification with Eq. (45) shows that

$$\chi_{jj}^{\text{ho}}[\rho_j] = \vartheta_{jj}[\rho_j]. \quad (74)$$

Contributions with different powers of  $\lambda$  in  $\Delta\check{\mathfrak{H}}_{j\lambda}[\rho_j]$  can be ordered to understand the effect of  $\mathcal{O}(\lambda)$  and  $\mathcal{O}(\lambda^2)$  contributions on  $\mathfrak{E}_{jj\lambda}$ . Moreover, it is possible to fix the gauge of the BO wave function at the reference configuration, as well as its first-order derivative with respect to atomic displacements, such that  $A_{\kappa\alpha j}[\mathbf{0}] = 0$ . Hence  $\check{T}_j^{\text{vec}(1)}$  is  $\mathcal{O}(\lambda)$  and  $T_j^{\text{vec}(2)}$  is  $\mathcal{O}(\lambda^2)$ . The corrections to the harmonic oscillator Hamiltonian, Eq. (68) becomes

$$\begin{aligned} \Delta\check{\mathfrak{H}}_{j\lambda}[\rho_j] &\equiv \lambda E_j^{\text{BO}\{3\}} \cdot \rho_j^3 \\ &\quad + \lambda^2 \left( \check{T}_j^{\text{vec}(1)\{1\}} \cdot \rho_j + E_j^{\text{BO}\{4\}} \cdot \rho_j^4 + E_j^{\text{DBOC}}[\lambda\rho_j] \right) \\ &\quad + \sum_{n=3} \lambda^n \left( \check{T}_j^{\text{vec}(1)\{n-1\}} \cdot \rho_j^{n-1} + E_j^{\text{BO}\{n+2\}} \cdot \rho_j^{n+2} \right) \\ &\quad + \sum_{n=4} \lambda^n \left( T_j^{\text{vec}(2)\{n-2\}} \cdot \rho_j^{n-2} \right) + \lambda^4 \check{\Sigma}_{j\lambda}(\mathcal{E}_{i\lambda}). \end{aligned} \quad (75)$$

In this definition, the  $\lambda$  behavior of the first line is  $\mathcal{O}(\lambda)$ ,  $\mathcal{O}(\lambda^2)$  for the second line,  $\mathcal{O}(\lambda^3)$  for the third line, and  $\mathcal{O}(\lambda^4)$  for the fourth line. Note that the second, third, and fourth lines also contain contributions of higher orders because of the  $[\lambda\rho_j]$  argument of some of their terms or due to explicit higher  $n$  values in the summation.

As previously observed,  $\vartheta_{jj}$  is even or odd with respect to a change of sign of  $\rho_j$  (also changing the sign of the associated momentum). Moreover, all terms of  $\Delta\check{\mathfrak{H}}_{j\lambda}$  that are even with respect to such a sign change have an even  $\lambda$  exponent, while all terms that are odd with respect to such a sign change have an odd  $\lambda$  exponent. Due to these symmetry considerations, the  $\lambda$  expansion of the total energy turns out to have only even power terms.

The eigenenergy present in Eq. (65) is studied in Sec. S3 of Supplemental Material [46] and gives

$$\mathcal{E}_i^{(4)} = \mathcal{E}_i^{(4),\text{anh}} + \mathcal{E}_i^{(4),\text{vec}} + E_j^{\text{DBOC}}[\mathbf{0}], \quad (76)$$

with three components. The first one is the anharmonic term,

$$\begin{aligned} \mathcal{E}_i^{(4),\text{anh}} &= \langle \vartheta_{jj} | E_j^{\text{BO}\{4\}} \cdot \check{\rho}_j^4 | \vartheta_{jj} \rangle_{\rho_j} \\ &\quad + \langle \vartheta_{jj} | \left( E_j^{\text{BO}\{3\}} \cdot \check{\rho}_j^3 \right) \check{\mathfrak{G}}_{\perp jj}^{\text{ho}} \left( E_j^{\text{BO}\{3\}} \cdot \check{\rho}_j^3 \right) | \vartheta_{jj} \rangle_{\rho_j}, \end{aligned} \quad (77)$$

that is present in the expansion of the scalar approximation. In Eq. (77), we encounter averages of different operators for the eigenfunctions  $\vartheta_{jj}$  of the auxiliary harmonic oscillator Hamiltonian. Such averages are performed over the space of nuclear configurations. For convenience, we use the Dirac notation, whereas until now, the Dirac notation had been reserved for the integrations over the electronic configurations. In order to avoid any confusion, the subscript  $\rho_j$  is mentioned on the lower right-hand side of the average expression. Also in Eq. (77), the Green's function of the auxiliary harmonic oscillator Hamiltonian  $\check{\mathfrak{H}}_j^{\text{ho}}[\rho_j]$ , see Eq. (44), has been introduced. More precisely, we define

$$\check{\mathfrak{G}}_{\perp jj}(z) \equiv \check{\mathcal{P}}_{\perp \vartheta_{jj}} \left( z - \check{\mathfrak{H}}_j^{\text{ho}} \right)^{-1} \check{\mathcal{P}}_{\perp \vartheta_{jj}}, \quad (78)$$

with the term between parentheses being a pseudoinverse, limited to the subspace perpendicular to  $\vartheta_{jj}$ . The Green's

function evaluated at  $z = \mathfrak{G}_{jj}^{\text{ho}}$  is labeled with a “ho” superscript and used in Eq. (77),

$$\check{\mathfrak{G}}_{\perp jj}^{\text{ho}} \equiv \check{\mathfrak{G}}_{\perp jj}(\mathfrak{G}_{jj}^{\text{ho}}). \quad (79)$$

Because the Green’s function is nonlocal in nuclear configuration space, the nuclear configuration  $\rho_j$  present in  $\Delta\check{\mathfrak{S}}_{j\lambda}$ , Eq. (75), must be handled with care and becomes an operator in the context of the averages present in Eq. (77).

In addition to the anharmonic term already present in the scalar approximation, two terms are also present in Eq. (76): the vector one,

$$\mathcal{E}_i^{(4),\text{vec}} = \langle \vartheta_{jj} | \check{T}_j^{\text{vec}(1)\{1\}} \cdot \check{\rho}_j | \vartheta_{jj} \rangle_{\rho_j}, \quad (80)$$

and the DBOC one,

$$E_j^{\text{DBOC}}[\mathbf{0}] = \langle \vartheta_{jj} | E_j^{\text{DBOC}}[\mathbf{0}] | \vartheta_{jj} \rangle_{\rho_j}. \quad (81)$$

Now that we have established the mass scaling of the optimal and scalar approximations up to order 5, we can carry on our search for the electron-phonon contribution to the total energy. However, there is an intermediate question first: what is the *phonon* contribution to the total energy?

#### IV. WHAT IS THE PHONON CONTRIBUTION TO THE TOTAL ENERGY?

To identify terms that can be called electron-phonon contributions to the total energy, we first need to identify terms that can be called phonon contributions to the total energy. In the present context, we define the phonon contributions as those coming from the terms that are quadratic in scaled displacements and momenta, in line with the literature [13,14,56–61,72,73].

At first sight, the second-order contribution  $\mathcal{E}_i^{(2)} = \mathfrak{G}_{jj}^{\text{ho}}$  is precisely the phonon contribution, a solution of the auxiliary harmonic oscillator Hamiltonian for the nuclear dynamics, with the well-known  $M_0^{-1/2}$  scaling, in which case higher-order terms should not be labeled as phonon contributions. However, this choice has three drawbacks. The first concerns the electronic inertial mass, especially that of the core electrons. The core electrons follow the nuclei’s movement rigidly. Therefore, the mass of core electrons should be added to the bare nuclear mass in Eq. (2). The second drawback comes from the vector potential in Eq. (16).

In fact, in the classical equation of motion that stems from the harmonic approximation, a spatially homogeneous Berry curvature simply generates a force-velocity coupling, which does not prevent one from obtaining normal modes of vibrations with well-characterized frequencies [64–70].

The third drawback stems from the fact that the optimal geometry (the average expectation of the nuclear positions

for the exact wave function) is not exactly the one at the minimum of the BO hypersurface. The BO curvature at the optimal geometry will differ from the one at the BO geometry and would be better suited to define the phonon contribution to the total energy.

In these three cases, the contribution from phonons will not have a pure  $M_0^{-1/2}$  scaling. For example, the electronic inertial mass adds to the bare nuclear mass  $M_\kappa$  a  $n_{e\kappa}m_e$  correction, where  $n_{e\kappa}$  is the number of electrons moving with the nucleus  $\kappa$ , while  $m_e$  is the electronic mass (1 in atomic units). One can take such a modification into account by updating accordingly the value of  $m_\kappa$ , with a factor  $M_0^{-1}$ , that is  $\lambda^4$ . Coupled with the  $\lambda^2$  scaling of the phonon energy, one sees that this contribution should appear in a  $\lambda^6$  term in the perturbation expansion of Sec. III.

Indeed, the lowest-order  $\lambda$  contribution to the total energy by the self-energy operator  $\check{\Sigma}_{j\lambda}$  contains such an inertial electronic mass correction. Using Eqs. (53) and (61)–(64), we find

$$\check{\Sigma}_{j\lambda}(z) = \sum_{\kappa\alpha} \frac{1}{2} \check{\pi}_{\kappa\alpha} \Delta m_{\kappa\alpha, \kappa'\alpha'}^{\text{elm}, -1}(z) \check{\pi}_{\kappa'\alpha'} + \mathcal{O}(\lambda), \quad (82)$$

where

$$\Delta m_{\kappa\alpha, \kappa'\alpha'}^{\text{elm}, -1}(z) = \left\langle \frac{\partial \phi_j}{\partial R_{\kappa\alpha}} \left| \frac{2\hat{\mathcal{G}}_{\perp j}^{\text{BO}}(z, [\mathbf{0}])}{m_\kappa m_{\kappa'}} \right| \frac{\partial \phi_j}{\partial R_{\kappa'\alpha'}} \right\rangle_{\mathbf{0}} \quad (83)$$

is the correction to the inverse nuclear mass induced by the electronic inertia. Taking into account that this is only the lowest-order correction to the electronic mass, this expression matches the one obtained using the exact factorization technique, see Eqs. (13)–(15), and (B10) of Ref. [60]. We note that Eq. (82) is quadratic in the scaled momenta and does not depend on the scaled displacements  $\rho_j$ . Such a quadratic contribution can be transferred from  $\Delta\check{\mathfrak{S}}_{j\lambda}[\rho_j]$  as defined in Eq. (68) or (75) to  $\check{\mathfrak{S}}_{j\lambda}^{\text{ho}}[\rho_j]$  defined in Eq. (67) without changing the fact that the latter is a harmonic oscillator Hamiltonian. It simply becomes  $\lambda$ -dependent.

Similarly, quadratic contributions in the scaled displacements  $\rho_j$  can be transferred from  $\Delta\check{\mathfrak{S}}_{j\lambda}[\rho_j]$  to  $\check{\mathfrak{S}}_{j\lambda}^{\text{ho}}[\rho_j]$ , as well as mixed contributions that include the scaled momenta and scaled displacements, such as

$$\check{T}_j^{\text{vec}(1)\{1\}} \cdot \rho_j = \sum_{\kappa\alpha} \frac{1}{2m_\kappa} A_{\kappa\alpha j}^{\{1\}} \cdot (\check{\pi}_{\kappa\alpha} \rho_j + \rho_j \check{\pi}_{\kappa\alpha}). \quad (84)$$

Moreover, some contributions might be extracted from the terms in  $\Delta\check{\mathfrak{S}}_{j\lambda}[\rho_j]$  that are higher-order in the combined scaled displacements and scaled momenta, such as  $\lambda E_j^{\text{BO}\{3\}} \cdot \rho_j^3$ , and might be transferred to  $\check{\mathfrak{S}}_{j\lambda}^{\text{ho}}[\rho_j]$  in connection to a  $\lambda$ -dependent change of reference

configuration. These are so-called “quasiharmonic” contributions. Let us consider Eq. (77). Changing the reference configuration from  $\{\mathbf{R}_j^0\}$  to some nearby configuration  $\{\mathbf{R}^{\text{ref}}\}$  will increase the BO energy contribution to the total energy, with a dominant effect proportional to the square of the change of configuration. However, such a change of configuration might induce a linear change of  $\lambda E_j^{\text{BO}\{3\}} \cdot \check{\rho}_j^3 |\vartheta_{jj}\rangle_{\rho_j}$ , that is present twice in Eq. (77). The net result might be a gain in energy. This possibility is especially relevant when one examines the behavior of the optimized volume of the primitive cell. The standard BO approach starts from the volume that minimizes the BO energy. The derivative of the BO energy with respect to a volume change is zero. However, the zero-point energy of phonons creates a modification of this energy, which is incorporated in the total energy. The gradient of the zero-point energy of phonons with respect to a volume change will usually not vanish at the BO-optimized configuration. Hence, the reoptimized volume will be linear in the zero-point energy, that is  $\lambda^2$ . A  $\lambda^2$  change in volume will create a  $\lambda^4$  change in total energy.

It is possible to establish a BO expansion both with the BO-optimized configuration as a reference, as we have done until now, or with a  $\lambda$ -dependent optimized configuration as a reference, as obtained in such quasiharmonic approximation. Since the reference configuration changes, the terms of both series will not be identical, but the series summation gives the same final result.

However, some terms cannot be eliminated by modifying the parameters of the auxiliary harmonic oscillator: those of order lower than quadratic in scaled displacements and momenta, which come from the DBOC energy and the self-energy. They will be examined in the next section.

## V. REMAINING CONTRIBUTIONS TO THE TOTAL ENERGY

The Hamiltonian  $\Delta\check{\mathcal{H}}_{j\lambda}[\rho_j]$  includes the DBOC potential, which is order  $\mathcal{O}(\lambda^2)$  when developed in powers of the scaled displacement:

$$\lambda^2 E_j^{\text{DBOC}}[\lambda\rho_j] = \sum_{n=0} \lambda^{n+2} \left( E_j^{\text{DBOC}\{n\}} \cdot \rho_j^n \right). \quad (85)$$

The displacement-independent contribution to the total energy of Eq. (85) at the lowest order in  $\lambda$  is given in Eq. (81) and can be further evaluated since it does not depend on displacement. Using Eqs. (59c), (52), and (19):

$$E_j^{\text{DBOC}}[\mathbf{0}] = \sum_{\kappa\alpha} \left\langle \frac{\partial\phi_j}{\partial R_{\kappa\alpha}} \left| \frac{\hat{P}_{\perp j}^{\text{BO}}[\mathbf{0}]}{2m_\kappa} \right| \frac{\partial\phi_j}{\partial R_{\kappa\alpha}} \right\rangle. \quad (86)$$

The derivative of the wave function with respect to the displacement of a nucleus is a typical quantity present in the first-principles calculations of dynamical matrices and

phonons for solids [26,27,29]. Similarly, for molecules, the interatomic force constants are found from such calculations, as well as vibrational frequencies. The scalar product of such a quantity with excited electronic states delivers the electron-phonon (or electron-vibration) matrix elements, as shown later. As such, among all the contributions to the total energy that appear in the BO expansion, Eq. (86) is the lowest-order one that can be called an “*electron-phonon contribution to the total energy*” (or electron vibration).

Accordingly, one defines

$$\mathcal{E}_i^{(4),\text{elph}} \equiv E_j^{\text{DBOC}}[\mathbf{0}] \quad (87)$$

that is independent of the vibrational state. The next DBOC lowest-order contribution is linear in the scaled displacement,  $n = 1$  in Eq. (85). Being odd with respect to the inversion of  $\rho_j$ , its expectation value for the vibrational wave function  $\vartheta_{jj}$  vanishes. It will not contribute to first order in  $\Delta\check{\mathcal{H}}_{j\lambda}[\rho_j]$  but will contribute at the next order. This contribution might then be called an electron-phonon contribution to the total energy as well, albeit of higher order.

Finally, we have seen that the self-energy  $\check{\Sigma}_{j\lambda}(z)$  yields Eq. (82) at lowest order and corresponds to a mass renormalization of the Hamiltonian.

From the expression of  $\check{\mathcal{T}}_{j\lambda}^{\text{N}}[\rho_j]$ , Eq. (53), and its double use in the self-energy, Eq. (61), one sees that first- and second-order derivatives of the BO wave functions play an important role in the self-energy, which might also be referred to as an electron-phonon contribution to the total energy. Beyond the lowest-order contribution, Eq. (82), the next order brings one momentum operator multiplied by  $\lambda$ . Being odd with respect to the inversion of  $\rho_j$ , its expectation value for the dynamical wave function  $\vartheta_{jj}$  vanishes. The order 6 energy associated with the mass renormalization from Eq. (83) is  $\mathcal{E}_i^{(6),\text{elm}}$  and is given in Eq. (S27) of Sec. S3 of Supplemental Material [46].

Altogether, there are five groups of energy terms at order 6, see Sec. S3 of Supplemental Material [46], including an electron-phonon energy contribution,  $\mathcal{E}_i^{(6),\text{elph}}$ , the electronic inertial mass contribution,  $\mathcal{E}_i^{(6),\text{elm}}$ , terms associated with the vector potential (which is zero in materials with time-reversal symmetry),  $\mathcal{E}_i^{(6),\text{vec}}$ , anharmonic energy terms,  $\mathcal{E}_i^{(6),\text{anh}}$ , and mixed terms that involve anharmonic and vector potential contributions, as well as one anharmonic and an electron-phonon term,  $\mathcal{E}_i^{(6),\text{mix}}$ . This concludes our listing of all the energy contributions to the total energy up to order 6 in the mass scaling, and we present a summary of the terms in Table I. We now turn to the practical evaluation of the DBOC contribution to the total energy, which we will refer to as the *electron-phonon contribution* to the total energy.

TABLE I. Summary of all the energy terms up to order 6 in the mass scaling that contribute to the total energy. The main text contains expressions up to order 4, while Sec. S3 of Supplemental Material [46] presents those of order 6.

| Energy                                               | Equation | Mass-scaling             |
|------------------------------------------------------|----------|--------------------------|
| $\mathcal{E}_i^{(0)} = E_{ji}^{\text{BO}}$           | (43)     | $\mathcal{O}(\lambda^0)$ |
| $\mathcal{E}_i^{(2)} = \mathcal{G}_{jj}^{\text{ho}}$ | (45)     | $\mathcal{O}(\lambda^2)$ |
| $\mathcal{E}_i^{(4),\text{vec}}$                     | (80)     | $\mathcal{O}(\lambda^4)$ |
| $\mathcal{E}_i^{(4),\text{anh}}$                     | (77)     | $\mathcal{O}(\lambda^4)$ |
| $\mathcal{E}_i^{(4),\text{elph}}$                    | (87)     | $\mathcal{O}(\lambda^4)$ |
| $\mathcal{E}_i^{(6),\text{elph}}$                    | (S26)    | $\mathcal{O}(\lambda^6)$ |
| $\mathcal{E}_i^{(6),\text{elm}}$                     | (S27)    | $\mathcal{O}(\lambda^6)$ |
| $\mathcal{E}_i^{(6),\text{vec}}$                     | (S37)    | $\mathcal{O}(\lambda^6)$ |
| $\mathcal{E}_i^{(6),\text{anh}}$                     | (S39)    | $\mathcal{O}(\lambda^6)$ |
| $\mathcal{E}_i^{(6),\text{mix}}$                     | (S38)    | $\mathcal{O}(\lambda^6)$ |

## VI. SEMICONDUCTORS AND INSULATORS TREATED WITHIN DENSITY-FUNCTIONAL THEORY

In Sec. II, we introduced  $\phi_j\{\mathbf{R}\}$  as the many-body electronic wave function for a fixed nuclear configuration, in the Born-Oppenheimer approximation, see Eq. (6). Such a many-body wave function can only be computed in the simplest systems. In this section, one approximates it by a Slater determinant formed from the combination of density-functional theory (DFT) one-electron Kohn-Sham wave functions [74]. This approximation will allow us to compute  $E^{\text{DBOC}}$ . Moreover, the application to gapped periodic solids is considered. As mentioned in the previous section, the obtained results rely on nondegenerate perturbation theory, with an energy separation between the ground-state energy and the first excited-state energy. This justifies our consideration of gapped solids only. Modifications would be needed to deal with metallic periodic solids. We note that  $E^{\text{DBOC}}$  had already been investigated for small molecules by chemists [22,23], mostly based on the Hartree-Fock approximation, although some studies used configuration interaction many-body wave functions. In these studies, it has been established that this contribution cannot be neglected for accurate total energy calculations. For example, it was found that for the  $\text{CH}_2$  molecule, the value of this correction (0.11 kcal/mol) for the singlet-triplet splitting energy is larger than the relativistic correction to the same quantity.

For periodic solids, eigenfunctions are Bloch waves, consisting of a periodic part multiplied by a phase. A band index  $n$  and a crystalline momentum  $\mathbf{k}$  characterize each wave function  $\phi_{n\mathbf{k}}$ .

For simplicity, the spin index is not explicitly noted, and the summations over bands are to be understood as applying to bands and spin channels if the two spin channels are treated separately. The dependence on the nuclear configuration will not be explicitly noted for the wave functions, or the charge density, or for entities that depend on such configuration only indirectly through the wave functions or the density. The dependence on the configuration will be explicitly written for the BO energy and the Kohn-Sham eigenenergies throughout.

The ground-state Born-Oppenheimer DFT energy for solids includes [74] a kinetic energy term, a one-electron atomic potential energy term, the Hartree-exchange-correlation (Hxc) energy term, and a nucleus-nucleus interaction energy term, as follows:

$$E^{\text{BO}}\{\mathbf{R}\} = T + E^{\text{e-N}}\{\mathbf{R}\} + E^{\text{Hxc}} + E^{\text{NN}}\{\mathbf{R}\}, \quad (88)$$

where we now assume we are in the ground state  $j = 0$ . Therefore, the  $j$  index is omitted.

The DFT Kohn-Sham eigenenergies are obtained from the expectation value of the kinetic energy, one-electron nuclear potential, and Hxc potential operators for the Kohn-Sham wave functions.

$$\epsilon_{n\mathbf{k}}\{\mathbf{R}\} = \langle \phi_{n\mathbf{k}} | \hat{T} + \hat{V}^{\text{e-N}}\{\mathbf{R}\} + \hat{V}^{\text{Hxc}} | \phi_{n\mathbf{k}} \rangle, \quad (89)$$

where  $\hat{V}^{\text{e-N}}$  and  $\hat{V}^{\text{Hxc}}$  are periodic, and the Kohn-Sham wave functions are normalized to 1 in the unit cell. The one-electron nuclear potential can be considered in an all-electron, pseudopotential, or projector-augmented wave framework. In the latter two frameworks, the potential operator has local and nonlocal contributions. Also, the nucleus-nucleus energy includes an Ewald energy term from periodic positively charged particles placed in a negatively charged homogeneous background, but also possibly a pseudocore energy [75] for the pseudopotential and projector-augmented wave frameworks.

The ground-state Born-Oppenheimer DFT energy per unit cell can be written in terms of its eigenenergy component,  $E^{\text{e}}$ , plus other contributions, denoted  $E^{\text{other}}$ ,

$$E^{\text{BO}}\{\mathbf{R}\} = E^{\text{e}}\{\mathbf{R}\} + E^{\text{other}}\{\mathbf{R}\}, \quad (90)$$

with the eigenenergy component per unit cell being

$$E^{\text{e}}\{\mathbf{R}\} = \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \sum_n f_{n\mathbf{k}} \epsilon_{n\mathbf{k}}\{\mathbf{R}\}, \quad (91)$$

$\Omega^{\text{BZ}}$  is the Brillouin-zone volume and  $f_{n\mathbf{k}}$  is the Fermi-Dirac occupation function.

In this work, zero temperature is considered so that the occupation function is either 1 or 0, possibly for each of the spin channels. Moreover, for gapped solids, the occupation function for all energy bands below the gap

is 1 and 0 for bands above the gap. We therefore write Eq. (91) as

$$E^e\{\mathbf{R}\} = \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \sum_n^{\text{occ}} \varepsilon_{n\mathbf{k}}\{\mathbf{R}\}, \quad (92)$$

and the other contributions are

$$E^{\text{other}}\{\mathbf{R}\} = E^{\text{Hxc}} - V^{\text{Hxc}} + E^{\text{NN}}\{\mathbf{R}\}, \quad (93a)$$

$$V^{\text{Hxc}} = \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \sum_n^{\text{occ}} \langle \phi_{n\mathbf{k}} | \hat{V}^{\text{Hxc}} | \phi_{n\mathbf{k}} \rangle. \quad (93b)$$

Returning to the different orders of the Taylor expansion of the total ground-state energy, Eq. (40) becomes:

$$\mathcal{E}_\lambda = E_0^{\text{BO}} + \lambda^2 \mathcal{E}^{(2)} + \lambda^4 \mathcal{E}^{(4)} + \mathcal{O}(\lambda^5), \quad (94)$$

where one has to write expressions for the second-order and fourth-order energies in the case of DFT for a solid. The physical total energy is obtained with  $\lambda = \lambda_0$ . We then perform a transformation to normal mode coordinates, see Sec. S4 of Supplemental Material [46], and express the second-order contribution to the total energy per unit cell resulting from atomic vibrations (or phonons), Eq. (S53), as

$$E^{\text{ph}} \equiv \lambda_0^2 \mathcal{E}^{(2)} = \lambda_0^2 \mathfrak{E}_0^{\text{ho}} = \int_{\text{BZ}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \sum_\nu \frac{\omega_{\nu\mathbf{q}}}{2}, \quad (95)$$

where  $\omega_{\nu\mathbf{q}}$  is the phonon frequency for mode  $\nu$  and momentum  $\mathbf{q}$ .

The fourth-order contribution to the total energy due to the electron-phonon interaction from Eq. (S54) can be written in different ways. Considering normal mode derivatives of the wave functions yields

$$E^{\text{elph}} \equiv \lambda_0^4 \mathcal{E}^{(4),\text{elph}}, \quad (96a)$$

$$= \frac{1}{2} \int_{\text{BZ}} \frac{d\mathbf{k} d\mathbf{q}}{(\Omega^{\text{BZ}})^2} \sum_n^{\text{occ}} \sum_\nu \left\langle \frac{\partial \phi_{n\mathbf{k}}}{\partial \eta_{\nu\mathbf{q}}} \right| \hat{\mathcal{P}}_{\perp\text{occ},\mathbf{k}+\mathbf{q}}^{\text{BO}} \left| \frac{\partial \phi_{n\mathbf{k}}}{\partial \eta_{\nu\mathbf{q}}} \right\rangle, \quad (96b)$$

with a possible spin doubling in the unpolarized spin case and where  $\hat{\mathcal{P}}_{\perp\text{occ},\mathbf{k}+\mathbf{q}}^{\text{BO}}$  is the projector on the unoccupied states.

The relation between nuclei displacements  $\Delta R_{l\kappa\alpha}$  and normal mode amplitude  $\eta_{\nu\mathbf{q}}$ , in the case of periodic solids, is given by

$$\Delta R_{l\kappa\alpha} = \sum_\nu \eta_{\nu\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_l} U_{\nu\kappa\alpha\mathbf{q}}, \quad (97)$$

where  $\mathbf{R}_l$  is the lattice vector of the cell  $l$ , or alternatively, by

$$\Delta R_{l\kappa\alpha} = \sum_\nu \eta_{\nu\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_{l\kappa}} U_{\nu\kappa\alpha\mathbf{q}}, \quad (98)$$

where  $\mathbf{R}_{l\kappa}$  is the position vector of the atom  $\kappa$  in cell  $l$ . The phase difference between these two possibilities does not impact observables, as they cancel in the scalar product present in Eq. (96b).

Direct derivatives of wave functions with respect to the atomic displacements of a specific sublattice can also be used. Defining

$$\Delta R_{l\kappa\alpha} \equiv R_{\kappa\alpha\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_l}, \quad (99)$$

where  $R_{\kappa\alpha\mathbf{q}} = \sum_\nu \eta_{\nu\mathbf{q}} U_{\nu\kappa\alpha\mathbf{q}}$ , gives

$$E^{\text{elph}} = \frac{1}{2} \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \times \sum_n^{\text{occ}} \sum_{\kappa\alpha} \frac{1}{M_\kappa} \left\langle \frac{\partial \phi_{n\mathbf{k}}}{\partial R_{\kappa\alpha\mathbf{q}}} \right| \hat{\mathcal{P}}_{\perp\text{occ},\mathbf{k}+\mathbf{q}}^{\text{BO}} \left| \frac{\partial \phi_{n\mathbf{k}}}{\partial R_{\kappa\alpha\mathbf{q}}} \right\rangle. \quad (100)$$

A third possibility to express the fourth-order contribution to the total energy due to electron-phonon interaction relies on the usual electron-phonon matrix elements and a sum over unoccupied states. This expression reads

$$E^{\text{elph}} = \frac{1}{2} \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \times \sum_n^{\text{occ}} \sum_m^{\text{unocc}} \sum_\nu \frac{2\omega_{\nu\mathbf{q}} |g_{mn\nu}(\mathbf{k}, \mathbf{q})|^2}{(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}})^2}, \quad (101)$$

where  $g_{mn\nu}(\mathbf{k}, \mathbf{q}) = \langle \phi_{m\mathbf{k}+\mathbf{q}} | \Delta V_{\mathbf{q}\nu} | \phi_{n\mathbf{k}} \rangle$  are the electron-phonon matrix elements in which  $\Delta V_{\mathbf{q}\nu}$  is the first-order change to the Kohn-Sham potential induced by a phonon mode  $\nu$ . The first-order potential in the mode basis is expressed in terms of the movement of atoms  $\kappa$  in the Cartesian direction  $\alpha$  as

$$\Delta V_{\mathbf{q}\nu}(\mathbf{r}, \mathbf{r}') = \left[ \frac{1}{2\omega_{\nu\mathbf{q}}} \right]^{\frac{1}{2}} \sum_{\kappa\alpha} U_{\nu\kappa\alpha\mathbf{q}} \frac{\partial V(\mathbf{r}, \mathbf{r}')}{\partial R_{\kappa\alpha\mathbf{q}}}, \quad (102)$$

where the derivative with respect to the collective displacement amplitude  $R_{\kappa\alpha\mathbf{q}}$  of Eq. (99) is the lattice sum  $\partial/\partial R_{\kappa\alpha\mathbf{q}} = \sum_l e^{i\mathbf{q}\cdot\mathbf{R}_l} \partial/\partial R_{l\kappa\alpha}$ , and where the two arguments  $\mathbf{r}$  and  $\mathbf{r}'$  account for the nonlocality of the potential operator. In the ABINIT software, for the purpose of the present work, Eqs. (100) and (101) have been implemented. As mentioned earlier, the spin index is omitted, and the summations over bands are to be understood as being on bands and spin channels if the two spin channels are treated separately. In the spin-unpolarized case, the

summation might be done over the (non-spin-polarized) wave functions, and a factor of 2 might be included afterward.

## VII. ALLEN'S ELECTRON-PHONON CONTRIBUTION TO THE TOTAL ENERGY

In Ref. [43] and its erratum, Ref. [76], Allen proposed that the contribution from the electron-phonon interaction to the total energy could be computed from the same ingredients as for the zero-point renormalization of the electronic eigenenergies due to the electron-phonon interaction. Using the notation of the present paper, Eq. (4) of Ref. [76] becomes

$$E^{\text{Allen}} = \int \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \sum_n f_{n\mathbf{k}} \sum_{\nu} \left[ \langle \phi_{n\mathbf{k}} | \Delta_2 V_{\nu\mathbf{q}} | \phi_{n\mathbf{k}} \rangle + \sum_m \frac{|\langle \phi_{n\mathbf{k}} | \Delta V_{\nu\mathbf{q}} | \phi_{m\mathbf{k}+\mathbf{q}} \rangle|^2}{\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}}} (1 - f_{m\mathbf{k}+\mathbf{q}}) \right], \quad (103)$$

where the expression for the second-order potential  $\Delta_2 V_{\nu\mathbf{q}}$  can be found in Ref. [24] (there, it is denoted  $V_{\nu\mathbf{q}}^{(2)}$ ).

It is asserted in Ref. [76] that this expression has the same structure as the sum of the electron-phonon energy shifts  $\Delta\epsilon_{n\mathbf{k}}$  of the occupied states, but it differs from the latter because of the presence of the  $(1 - f_{m\mathbf{k}+\mathbf{q}})$  factor in Eq. (103).

For comparison, such shifts are written as

$$\Delta\epsilon_{n\mathbf{k}} = \int_{\text{BZ}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \sum_{\nu} \left[ \langle \phi_{n\mathbf{k}} | \Delta_2 V_{\nu\mathbf{q}} | \phi_{n\mathbf{k}} \rangle + \sum'_m \frac{|\langle \phi_{n\mathbf{k}} | \Delta V_{\nu\mathbf{q}} | \phi_{m\mathbf{k}+\mathbf{q}} \rangle|^2}{\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}}} \right], \quad (104)$$

where the prime indicates that the intraband contribution ( $m = n$ ) is omitted for  $\mathbf{q} = \mathbf{0}$ .

Interestingly, the  $(1 - f_{m\mathbf{k}+\mathbf{q}})$  factor can be suppressed from Eq. (103).

Indeed, due to the change of sign in the denominator  $\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}}$  upon the exchange between  $n\mathbf{k}$  and  $m\mathbf{k} + \mathbf{q}$ , one has

$$\int \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \sum'_{\nu nm} f_{n\mathbf{k}} \frac{|\langle \phi_{n\mathbf{k}} | \Delta V_{\nu\mathbf{q}} | \phi_{m\mathbf{k}+\mathbf{q}} \rangle|^2}{\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}}} f_{m\mathbf{k}+\mathbf{q}} = 0. \quad (105)$$

Thus, without any approximation,

$$E^{\text{Allen}} = \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \sum_n f_{n\mathbf{k}} \Delta\epsilon_{n\mathbf{k}}, \quad (106)$$

which at 0 K reduces to

$$E^{\text{Allen}} = \sum_n^{\text{occ}} \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega^{\text{BZ}}} \Delta\epsilon_{n\mathbf{k}}. \quad (107)$$

In a subsequent work [77], Varma *et al.* computed the right-hand side of Eq. (107) and argued that it approximates well Eq. (103), the electron-phonon contribution to the total energy. Like Allen, they did not mention that both quantities are equal. We also remark that the eigenvalue renormalization in Eq. (104) is expressed using the adiabatic approximation, but the nonadiabatic version of  $\Delta\epsilon_{n\mathbf{k}}$  should be used for infrared-active materials [37,78].

Let us proceed with the mass-scaling analysis of  $E^{\text{Allen}}$ . Relying on the analysis presented in Sec. III, in particular the fact that the fluctuations of nuclear displacements are proportional to  $\lambda$ , one finds that  $\Delta\epsilon_{n\mathbf{k}}$  scales as  $\lambda^2$ . Actually,  $\Delta V_{\nu\mathbf{q}}$  scales as  $\lambda$  and is present twice in Eq. (104), while  $\Delta_2 V_{\nu\mathbf{q}}$  scales like  $\lambda^2$ , see Eqs. (34) and (40) of Ref. [24]. Hence,  $E^{\text{Allen}}$  also scales as  $\lambda^2$ . It is of second order in the perturbation, not of fourth order.

However, the perturbation approach of the previous sections shows that the second-order term gives the phonon contribution to the total energy; no second-order contribution in  $\lambda$  can be called an electron-phonon contribution.

As we will show, this alleged electron-phonon contribution to the total energy is actually part of the phonon contribution to the total energy previously mentioned,  $E^{\text{ph}}$ .

Hence,  $E^{\text{Allen}}$  should not be added to  $E_0^{\text{BO}}$  and  $E^{\text{ph}}$ . The correct expressions for the lowest-order electron-phonon contribution to the total energy, if any,  $E^{\text{elph}}$ , are given by Eqs. (96a), (100), and (101).

To prove that  $E^{\text{Allen}}$  is a contribution to  $E^{\text{ph}}$  and not to  $\lambda_0^4 \mathcal{E}^{(4)}$ , we further start from Eqs. (1) and (2) of Ref. [37]:

$$\Delta\epsilon_{n\mathbf{k}} = \frac{1}{2} \sum_{\nu} \int_{\text{BZ}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \frac{1}{2\omega_{\nu\mathbf{q}}} \times \sum_{\kappa\alpha\kappa'\beta l} \frac{\partial^2 \epsilon_{n\mathbf{k}}}{\partial R_{0\kappa\alpha} \partial R_{l\kappa'\beta}} e^{i\mathbf{q}\cdot\mathbf{R}_l} U_{\nu\kappa\alpha\mathbf{q}}^* U_{\nu\kappa'\beta\mathbf{q}}. \quad (108)$$

This expression is inserted in Eq. (107) and combined with Eq. (92) to give

$$E^{\text{Allen}} = \frac{1}{2} \sum_{\nu} \int_{\text{BZ}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \frac{1}{2\omega_{\nu\mathbf{q}}} \times \sum_{\kappa\alpha\kappa'\beta l} \frac{\partial^2 E^e}{\partial R_{0\kappa\alpha} \partial R_{l\kappa'\beta}} e^{i\mathbf{q}\cdot\mathbf{R}_l} U_{\nu\kappa\alpha\mathbf{q}}^* U_{\nu\kappa'\beta\mathbf{q}}, \quad (109)$$

where the dependence of the electronic energy  $E^e$  on  $\phi$  and  $\{\mathbf{R}\}$  is omitted for conciseness.

In addition, the second-order derivative of the BO total energy is the interatomic force constant; see Eq. (S42), which extends for the periodic case to

$$\omega_{\nu\mathbf{q}}^2 = \sum_{\kappa\alpha\kappa'\beta l} \frac{\partial^2 E^{\text{BO}}}{\partial R_{0\kappa\alpha} \partial R_{l\kappa'\beta}} e^{i\mathbf{q}\cdot\mathbf{R}_l} U_{\nu\kappa\alpha\mathbf{q}}^* U_{\nu\kappa'\beta\mathbf{q}}. \quad (110)$$

This is the same expression as the second summation in Eq. (109) when  $E^e$  is replaced by  $E^{\text{BO}}$ . Dividing Eq. (110) by  $2\omega_{\nu\mathbf{q}}$  and inserting it into Eq. (95) gives

$$E^{\text{ph}} = \sum_{\nu} \int_{\text{BZ}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \frac{1}{2\omega_{\nu\mathbf{q}}} \times \sum_{\kappa\alpha\kappa'\beta l} \frac{\partial^2 E^{\text{BO}}}{\partial R_{0\kappa\alpha} \partial R_{l\kappa'\beta}} e^{i\mathbf{q}\cdot\mathbf{R}_l} U_{\nu\kappa\alpha\mathbf{q}}^* U_{\nu\kappa'\beta\mathbf{q}}. \quad (111)$$

The decomposition of the BO energy had been introduced in Eq. (90) and allows one to split the second-order phononic contribution to the total energy, delivering

$$E^{\text{ph}} = 2E^{\text{Allen}} + E^{\text{ph,other}}, \quad (112)$$

with

$$E^{\text{ph,other}} = \sum_{\nu} \int_{\text{BZ}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \frac{1}{2\omega_{\nu\mathbf{q}}} \times \sum_{\kappa\alpha\kappa'\beta l} \frac{\partial^2 E^{\text{other}}}{\partial R_{0\kappa\alpha} \partial R_{l\kappa'\beta}} e^{i\mathbf{q}\cdot\mathbf{R}_l} U_{\nu\kappa\alpha\mathbf{q}}^* U_{\nu\kappa'\beta\mathbf{q}}. \quad (113)$$

As announced,  $E^{\text{Allen}}$  is a contribution to  $E^{\text{ph}}$ . The factor of 2 in front of  $E^{\text{Allen}}$  in Eq. (112) might seem surprising. It comes from the fact that the zero-point energy of phonons includes both a kinetic energy and a potential energy contribution, which are actually equal, while the zero-point renormalization of eigenvalues, Eq. (108), does not include a kinetic contribution but contains the curvature of  $\varepsilon_{n\mathbf{k}}$ , which acts as a potential energy.

Therefore, Allen's energy defined in Ref. [76] is not an electron-phonon energy but a part of the phonon contribution to the total energy. We can inquire about the origin of the problem in Ref. [76]. Apparently, the issue stems from the use of an effective Hamiltonian, with separate electronic and phononic terms fixed *a priori*, to which an electron-phonon interaction is added, changing the total energy. As derived in the present work, following the BO approach, the first-principles BO-DFT phonons come from the BO curvature, *which already includes the electronic energy curvature*, in addition to nuclear-nuclear energy curvature, and Hartree and exchange-correlation corrections. Hence, phonons cannot be separated from electrons *a priori*, unlike in the effective Hamiltonian of Ref. [76].

## VIII. CONNECTION WITH THE ALLEN-HEINE-CARDONA THEORY

Despite  $E^{\text{Allen}}$  not being the desired electron-phonon interaction energy, one can nonetheless study it and examine its connection with the AHC theory of zero-point renormalization. Using Ref. [37],  $\Delta\varepsilon_{n\mathbf{k}}$  in Eq. (107) can be decomposed as

$$\Delta\varepsilon_{n\mathbf{k}} = \Delta\varepsilon_{n\mathbf{k}}^{\text{AHC}} + \Delta\varepsilon_{n\mathbf{k}}^{\text{NRIA}}, \quad (114)$$

where  $\Delta\varepsilon_{n\mathbf{k}}^{\text{AHC}}$  is obtained from the AHC theory [44,47] with the rigid-ion approximation [79] to describe the Debye-Waller term.  $\Delta\varepsilon_{n\mathbf{k}}^{\text{AHC}}$  has the following sum-over-state expression [37,80]:

$$\Delta\varepsilon_{n\mathbf{k}}^{\text{AHC}} = \sum_{\nu} \int_{\text{BZ}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \frac{1}{2\omega_{\nu\mathbf{q}}} \sum_{\kappa\alpha\kappa'\beta} \left[ U_{\nu\kappa\alpha\mathbf{q}}^* U_{\nu\kappa'\beta\mathbf{q}} \times \sum_m' \frac{g_{mn\kappa\alpha}^*(\mathbf{k}, \mathbf{q}) g_{mn\kappa'\beta}(\mathbf{k}, \mathbf{q})}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + i\eta} - \frac{1}{2} [U_{\nu\kappa\alpha\mathbf{q}}^* U_{\nu\kappa\beta\mathbf{q}} + U_{\nu\kappa'\alpha\mathbf{q}}^* U_{\nu\kappa'\beta\mathbf{q}}] \times \sum_m' \frac{g_{mn\kappa\alpha}^*(\mathbf{k}, \mathbf{\Gamma}) g_{mn\kappa'\beta}(\mathbf{k}, \mathbf{\Gamma})}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}} + i\eta} \right], \quad (115)$$

where  $\eta$  should be a positive infinitesimal in the AHC theory. In Eq. (115),  $g_{mn\kappa\alpha}(\mathbf{k}, \mathbf{q}) \equiv \langle \phi_{m\mathbf{k}+\mathbf{q}} | \Delta V_{\mathbf{q}\kappa\alpha} | \phi_{n\mathbf{k}} \rangle$  are the electron-phonon matrix elements expressed in the Cartesian basis,  $\Delta V_{\mathbf{q}\kappa\alpha}$  being obtained from  $\Delta V_{\mathbf{q}\nu}$ , Eq. (102), by removing both the  $[1/(2\omega_{\nu\mathbf{q}})]^{1/2}$  prefactor and the  $\sum_{\kappa\alpha} U_{\nu\kappa\alpha\mathbf{q}}$  summation. They are therefore exactly related to the mode-resolved matrix elements of Eq. (101) by

$$g_{mn\nu}(\mathbf{k}, \mathbf{q}) = \left[ \frac{1}{2\omega_{\nu\mathbf{q}}} \right]^{1/2} \sum_{\kappa\alpha} U_{\nu\kappa\alpha\mathbf{q}} g_{mn\kappa\alpha}(\mathbf{k}, \mathbf{q}), \quad (116)$$

the mode-dependent factors being kept explicit in Eq. (115). Beyond AHC,  $\eta$  would effectively describe the lifetime of the quasiparticle state [81]. In this work, without computing  $\eta$ , it is chosen to be 5 meV.

The non-rigid-ion approximation (NRIA)  $\Delta\varepsilon_{n\mathbf{k}}^{\text{NRIA}}$  terms in Eq. (114) have been shown to be small in solids [38,79].

Computing them requires the second-order derivative of the Hamiltonian, which is not available with the current DFPT implementation, that reads:

$$\Delta\varepsilon_{n\mathbf{k}}^{\text{NRIA}} = \sum_{\nu} \int_{\text{BZ}} \frac{d\mathbf{q}}{\Omega^{\text{BZ}}} \sum_{l\alpha\beta, \kappa \neq \kappa'} \frac{e^{-i\mathbf{q}\cdot\mathbf{R}_l}}{4\omega_{\nu\mathbf{q}}} U_{\nu\kappa'\beta\mathbf{q}}^* U_{\nu\kappa\alpha\mathbf{q}} \times \int d\mathbf{r} \phi_{n\mathbf{k}}^*(\mathbf{r}) \phi_{n\mathbf{k}}(\mathbf{r}) \frac{\partial^2 V^{\text{Hxc}}(\mathbf{r})}{\partial R_{0\kappa\alpha} \partial R_{l\kappa'\beta}}, \quad (117)$$

where  $V^{\text{Hxc}}(\mathbf{r})$  is the Hartree and exchange-correlation potential. Therefore, at the DFPT level, one cannot currently compute  $E^{\text{Allen}}$ , but only its AHC approximation,

$$E^{\text{Allen,AHC}} \equiv \sum_n^{\text{occ}} \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \Delta \varepsilon_{n\mathbf{k}}^{\text{AHC}}, \quad (118)$$

with possible spin doubling in the unpolarized case.

## IX. VALIDATION FOR DIAMOND AT THE PHONON ZONE CENTER

In this section, we compute different quantities mentioned in Secs. VI–VIII using diamond as an example and compare results from perturbation theory with those from finite differences (FD—frozen phonon approach). Although the numbers will first be obtained for a single wave vector at the zone center, the procedure is defined for a grid of wave vectors compatible with a supercell of the primitive cell.

Let  $N$  be the size ratio between the primitive cell and the supercell, the latter being commensurate with the former, and consider similarly that there are  $N$  allowed  $\mathbf{q}$  wave vectors that match periodic boundary conditions in the supercell.

We define  $E^{\text{BO,sup}}$ , the BO energy of the supercell, which will be evaluated with atoms collectively displaced from their equilibrium positions. Precisely, the atom labeled  $\kappa$  in the cell  $l$ , with equilibrium position  $\mathbf{R}_{l\kappa}^0$ , will be displaced by  $h$  times the eigendisplacement  $\mathbf{U}_{\nu\kappa\mathbf{q}}$ , modulated by the phase  $e^{-i\mathbf{q}\cdot\mathbf{R}_l}$ , giving the displaced position

$$\mathbf{R}_{l\kappa}(h) = \mathbf{R}_{l\kappa}^0 + h\mathbf{U}_{\nu\kappa\mathbf{q}}e^{-i\mathbf{q}\cdot\mathbf{R}_l}. \quad (119)$$

We refer the reader to Ref. [82], Eqs. (70) and (71), for the treatment of complex displacements using linear combinations of such displacements. The phonon frequencies are obtained using the following FD formulation:

$$\omega_{\nu\mathbf{q}}^2 = \frac{1}{Nh^2} \left( E^{\text{BO,sup}}[\{\mathbf{R}_{l\kappa}(h)\}] + E^{\text{BO,sup}}[\{\mathbf{R}_{l\kappa}(-h)\}] - 2E^{\text{BO,sup}}[\{\mathbf{R}_{l\kappa}^0\}] \right). \quad (120)$$

This FD value can be introduced in a discretized version of Eq. (95) to obtain  $E^{\text{ph}}$ . Alternatively,

$$E^{\text{ph}} = \sum_{\nu\mathbf{q}} \frac{1}{2\omega_{\nu\mathbf{q}}N^2h^2} \left( E^{\text{BO,sup}}[\{\mathbf{R}_{l\kappa}(h)\}] + E^{\text{BO,sup}}[\{\mathbf{R}_{l\kappa}(-h)\}] - 2E^{\text{BO,sup}}[\{\mathbf{R}_{l\kappa}^0\}] \right). \quad (121)$$

In this expression, one of the factors  $N$  comes from the number of  $\mathbf{q}$  vectors, while the other comes from the

reduction of  $E^{\text{BO,sup}}$  to the primitive cell. Similarly, the change in eigenvalues due to electron-phonon interaction can be computed with FD as

$$\Delta \varepsilon_{n\mathbf{k}} = \frac{1}{2N} \sum_{\nu\mathbf{q}} \frac{1}{2\omega_{\nu\mathbf{q}}} \frac{1}{h^2} \left( \varepsilon_{n\mathbf{k}}[\{\mathbf{R}_{l\kappa}(h)\}] + \varepsilon_{n\mathbf{k}}[\{\mathbf{R}_{l\kappa}(-h)\}] - 2\varepsilon_{n\mathbf{k}}[\{\mathbf{R}_{l\kappa}^0\}] \right). \quad (122)$$

Allen's total energy has two equivalent formulations using FD:

$$E^{\text{Allen}} = \frac{1}{2} \sum_{\nu\mathbf{q}} \frac{1}{2\omega_{\nu\mathbf{q}}N^2h^2} \left( E^{\text{e,sup}}[\{\mathbf{R}_{l\kappa}(-h)\}] + E^{\text{e,sup}}[\{\mathbf{R}_{l\kappa}(h)\}] - 2E^{\text{e,sup}}[\{\mathbf{R}_{l\kappa}^0\}] \right), \quad (123)$$

$$= \sum_n^{\text{occ}} \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \Delta \varepsilon_{n\mathbf{k}}, \quad (124)$$

with a possible spin doubling in the unpolarized case for the last equation. The remaining contribution is

$$E^{\text{ph,other}} = \sum_{\nu\mathbf{q}} \frac{1}{2\omega_{\nu\mathbf{q}}N^2h^2} \left( E^{\text{other,sup}}[\{\mathbf{R}_{l\kappa}(h)\}] + E^{\text{other,sup}}[\{\mathbf{R}_{l\kappa}(-h)\}] - 2E^{\text{other,sup}}[\{\mathbf{R}_{l\kappa}^0\}] \right). \quad (125)$$

Finally, Eq. (117) can also be computed using finite differences. We first define

$$\mathbf{R}_{l\kappa}(h_1, \kappa_1, h_2, \kappa_2) \equiv \mathbf{R}_{l\kappa}^0 + h_1\delta_{\kappa\kappa_1}\mathbf{U}_{\nu\kappa_1\mathbf{q}} + h_2\delta_{\kappa\kappa_2}\mathbf{U}_{\nu\kappa_2\mathbf{q}}e^{-i\mathbf{q}\cdot\mathbf{R}_l}, \quad (126)$$

and obtain

$$\Delta \varepsilon_{n\mathbf{k}}^{\text{NRIA}} = \sum_{\nu\mathbf{q}} \frac{1}{4\omega_{\nu\mathbf{q}}4N^2h^2} \sum_{l\kappa_1 \neq \kappa_2} \int_{\text{sup}} d\mathbf{r} \phi_{n\mathbf{k}}^*(\mathbf{r}) \phi_{n\mathbf{k}}(\mathbf{r}) \times \left\{ V^{\text{Hxc}}[\mathbf{R}_{l\kappa}(h, \kappa_1, h, \kappa_2)](\mathbf{r}) - V^{\text{Hxc}}[\mathbf{R}_{l\kappa}(h, \kappa_1, -h, \kappa_2)](\mathbf{r}) - V^{\text{Hxc}}[\mathbf{R}_{l\kappa}(-h, \kappa_1, h, \kappa_2)](\mathbf{r}) + V^{\text{Hxc}}[\mathbf{R}_{l\kappa}(-h, \kappa_1, -h, \kappa_2)](\mathbf{r}) \right\}, \quad (127)$$

where the two arguments of  $V^{\text{Hxc}}$  indicate that two nuclei are moved in the FD approach, and where the integral is performed in the supercell. This term gives the corresponding total energy:

$$E^{\text{Allen,NRIA}} \equiv \sum_n^{\text{occ}} \int_{\text{BZ}} \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \Delta \epsilon_{n\mathbf{k}}^{\text{NRIA}}, \quad (128)$$

with possible spin doubling in the unpolarized case.

In this section, we consider the  $\mathbf{q} = \Gamma$  case so that finite difference calculations can be performed only in the primitive cell. We will use the finite  $\mathbf{q}$  formulation in Sec. X. Calculations are performed with the ABINIT v10.4.5 software [48,49,51] with a 40 Ha plane-wave energy cutoff and a zone-centered  $8 \times 8 \times 8$   $\mathbf{k}$ -point grid. We rely on the generalized gradient approximation (GGA) PBE [83] exchange-correlation functional, with the carbon scalar-relativistic standard PBE pseudopotential from PSEUDOJOJO [84] v0.5. We compute a relaxed 6.7513 Bohr lattice parameter, slightly overestimating the 6.74 Bohr experimental value [85]. Diamond is a nonpolar material with a long-range quadrupole value of 2.46  $e$ Bohr [86]. We note that the calculation of the quadrupole tensor in solids from perturbation theory has so far only been implemented in the ABINIT software [49,87]. Since ABINIT v10.4.5, the calculation of the quadrupole tensor supports nonlinear core correction (NLCC) of pseudopotentials and has been used here. We obtain a quadrupole value of 2.502  $e$ Bohr using a  $16 \times 16 \times 16$   $\mathbf{k}$ -point grid.

This recent development is crucial because the use of a model core charge has been shown to be important [88] in the case of generalized gradient approximation pseudopotentials such as PBE. In fact, when the valence and core densities overlap, neglecting the core density results in an artificially large gradient of the density. We have numerically tested this effect for diamond and found that ignoring the NLCC leads to numerically unstable finite-difference calculations but is acceptable for perturbation theory. Unless specified otherwise, we use the above-mentioned pseudopotential which includes NLCC.

We start by verifying phonon frequencies computed by perturbation theory and finite difference (FD) in Table II using an  $8 \times 8 \times 8$   $\mathbf{k}$ -grid, since phonon frequencies will be used in later quantities. All finite-difference calculations are performed using Richardson extrapolation with Romberg order 4, starting from  $h = 2$ . We find that the triply degenerate optical modes agree within 0.013 meV between the density functional perturbation theory (DFPT) [15,26] and FD values. We then compute the phonon zone-center contribution to the zero-point renormalization (ZPR) of the valence band maximum (VBM) computed using FD and obtain 27.695 meV, close to the value of 28.428 meV from a prior study [79]. Since the VBM is triply degenerate in band indices and any linear combination is a valid one, we report the average value over the three bands. The same value cannot be directly computed using DFPT, as it requires a higher-order perturbation currently not available in first-principles software. However, it can be approximated using the RIA, which gives 23.806 meV, again in close agreement with the

TABLE II. Comparison for diamond between the finite difference (FD) and density functional perturbation theory (DFPT) for different quantities at  $\mathbf{q} = \Gamma$  and  $T = 0$  K, at the optimized BO lattice parameters. The  $\Delta \epsilon_{\Gamma}$  refers to the band zero-point renormalization of the triply degenerate valence band maximum,  $\Delta \epsilon_{\Gamma}^{\text{NRIA}}$  is the nonrigid ion approximation (NRIA), and  $\Delta \epsilon_{\Gamma}^{\text{AHC}}$  refers to the AHC theory using the rigid-ion approximation. The zeroth-order Born-Oppenheimer (BO) total energy  $E^{\text{BO}}$  is decomposed into its eigenenergy part  $E^e$  and the *other* terms  $E^{\text{other}}$ . The second-order contribution to total energy due to phonons is  $E^{\text{ph}}$ . It can be decomposed into half the electronic contribution  $E^{\text{Allen}}$ , and the rest  $E^{\text{ph,other}}$ . The electron-phonon part of the fourth-order contribution to total energy  $E^{\text{elph}}$  can be computed using DFPT. Energies are given per unit cell (two atoms). For total energies, we use an  $8 \times 8 \times 8$   $\mathbf{k}$ -point grid with symmetry, detailed in Table S2. Absolute total energy values depend on the choice of pseudopotential but relative energy differences are observables.

|                                                                     | Evaluation | Equation             | Energy (meV) |
|---------------------------------------------------------------------|------------|----------------------|--------------|
| $\omega_{\Gamma}$                                                   | DFPT       | (S42)                | 159.989      |
| $\omega_{\Gamma}$                                                   | FD         | (120)                | 160.002      |
| $\Delta \epsilon_{\Gamma}$                                          | FD         | (122)                | 27.695       |
| $\Delta \epsilon_{\Gamma}^{\text{NRIA}}$                            | FD         | (127)                | 3.894        |
| $\Delta \epsilon_{\Gamma} - \Delta \epsilon_{\Gamma}^{\text{NRIA}}$ | FD         | (122) – (127)        | 23.801       |
| $\Delta \epsilon_{\Gamma}^{\text{AHC}}$                             | DFPT       | (115)                | 23.806       |
| $E^{\text{BO}}$                                                     | DFT        | (90)                 | –327559.414  |
| $E^e$                                                               | DFT        | (91)                 | 10119.178    |
| $E^{\text{other}}$                                                  | DFT        | (90) – (91)          | –337678.592  |
| $E^{\text{ph}}$                                                     | DFPT       | (95), (S42)          | 240.040      |
| $E^{\text{ph}}$                                                     | FD         | (95), (120)          | 240.023      |
| $E^{\text{ph}}$                                                     | FD         | (120), (121)         | 240.003      |
| $E^{\text{Allen}}$                                                  | FD         | (123)                | –84.214      |
| $E^{\text{Allen}}$                                                  | FD         | (124)                | –84.214      |
| $E^{\text{ph,other}}$                                               | FD         | (95), (120) – 2(124) | 408.451      |
| $E^{\text{ph,other}}$                                               | FD         | (125)                | 408.466      |
| $E^{\text{Allen,NRIA}}$                                             | FD         | (128)                | 17.086       |
| $E^{\text{Allen}} - E^{\text{Allen,NRIA}}$                          | FD         | (124) – (128)        | –101.300     |
| $E^{\text{Allen,AHC}}$                                              | DFPT       | (118)                | –100.783     |
| $E^{\text{elph}}$                                                   | DFPT       | (100)                | 3.639        |
| $E^{\text{elph}}$                                                   | DFPT       | (101)                | 3.638        |

24.830 meV value from a previous study [79]. The neglected NRIA term can be computed using FD and then added to the RIA term, giving 27.700 meV, in very close agreement with the direct FD value. We note that the RIA is a good approximation for solids when integrated over  $\mathbf{q}$ -points [38,79]. As a technical note, it is possible in ABINIT to reduce the computational cost by using a reduced ratio between the radius of the  $\mathbf{G}$ -vector sphere that can be inserted in the real-space fast Fourier transform box and the  $\mathbf{G}$ -vector sphere used to represent the wave function.

However, we find here that it is crucial to use a ratio of 2 to have an exact density; see Sec. S5 of Supplemental Material [46].

Next, we report in Table II the zeroth-order BO total energy. Such total energy, provided as an output of a standard self-consistent DFT cycle, contains a core electron energy that is assumed constant and ignored via the use of a pseudopotential. Therefore, the total energy depends on the arbitrary choice of the pseudopotential. In contrast, the contribution from its eigenenergy component  $E^e$  is only weakly dependent on the choice of the pseudopotential, in a way similar to other predicted observables with DFT. We compute a value of 10.119 eV directly from the output of the ABINIT software and verify that it gives the same result as the direct sum over the occupied eigenvalues  $\sum_{n\mathbf{k}} \epsilon_{n\mathbf{k}} f_{n\mathbf{k}}$ . We then compute the second-order contribution to the total energy due to phonons and find a value of 240.040 meV using DFPT, which is less than 0.04 meV larger than the two FD results. We see that such a contribution is significantly lower than the  $E^e$  energy contribution.

To assess the eigenenergy contribution to that second-order energy, we compute the ZPR for all  $\mathbf{k}$ -points of a homogeneous  $8 \times 8 \times 8$   $\mathbf{k}$ -grid using crystal symmetry and report their values in Sec. S6 of Supplemental Material [46]. We find a close agreement between perturbation theory and FD, with a difference of less than 2.1 meV.

From its weighted summation, we find that the eigenenergy contribution to the second-order energy is  $-84.214$  meV, which amounts to over one-third of the total second-order contribution.

This value can be approximated via DFPT and the RIA, which gives  $-100.783$  meV, overestimating the true value by 20%. As mentioned earlier, we expect the RIA to improve when summing over dense  $\mathbf{q}$ -points grids.

Furthermore, we compute the electron-phonon contribution to the fourth-order total energy using DFPT,  $E^{\text{elph}}$ , Eq. (100), and obtain 3.639 meV. Alternatively, we can use Eq. (101) to compute the same quantity via the electron-phonon interaction matrix elements. As shown in Fig. 3, both result in the same value, but Eq. (101) requires a sum over empty states, which converges slowly. In the case of diamond, we need at least 300 bands to converge that formulation.

Such a small value is nearly 2 orders of magnitude smaller than the second-order contribution, which is expected given the  $M_0^{-1/2}$  scaling between each higher-even order term. Although small, this contribution could play a role in stabilizing one allotrope over another, especially in the case of magnetic materials that can have a very shallow energy landscape.

Finally, it was argued in Ref. [45] that the DFPT formulation of AHC zero-point renormalization,  $\Delta \epsilon_{n\mathbf{k}}^{\text{AHC}}$ , violates size consistency, whereby the total energy  $E^{\text{Allen,AHC}}$  would depend on the unit cell size. To show

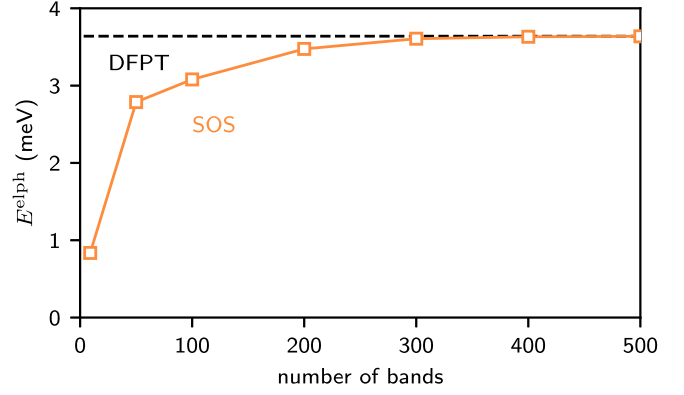


FIG. 3. Diamond fourth-order total energy contribution (per unit cell) computed using DFPT, Eq. (100), and with a sum-over-state (SOS) expression, Eq. (101). The  $\mathbf{k}$ -point grid used is  $8 \times 8 \times 8$  with only a single  $\mathbf{q} = \Gamma$  point.

the size consistency of Eq. (118), we simply need to prove the size consistency of  $\Delta \epsilon_{n\mathbf{k}}^{\text{AHC}}$ . For this, we compute the adiabatic zero-point renormalization using the rigid-ion approximation for the Debye-Waller term [79] and a Fourier interpolation of the perturbed potential [49,89]. We evaluate the diagonal [90] self-energy at the DFT eigenvalues (on-the-mass shell) and use a Sternheimer expression to replace the sum-over-state expression [37,80] and report the details in Sec. S7 of Supplemental Material [46]. We find excellent agreement, validating size consistency.

## X. DIAMOND AND LONSDALEITE ALLOTROPES

Having analyzed and compared the behavior of the theory and implementation in different cases, we now converge the various contributions to the total energies with phonon momentum  $\mathbf{q}$ .

In this case, we can no longer use FD methods, as the supercell size quickly becomes prohibitively large.

First, we remark that the various total energy calculations require dense phonon momentum  $\mathbf{q}$  grid samplings of the electron-phonon interaction, which can be computationally expensive. Two interpolation methods are often used to accurately and efficiently interpolate  $\mathbf{q}$ -dependent properties: the Wannier-Fourier interpolation of the electron-phonon matrix elements [91,92] and the Fourier interpolation of the perturbed potential [49,52,53].

Importantly, long-range electrostatics should be analytically removed and added back to ensure the accuracy of the interpolation [26,52,53,86,87,93–100].

To analyze the importance of the different terms, we compute these for another allotrope of diamond called *lonsdaleite* or *hexagonal diamond* [101] which forms naturally under high pressure and high temperature and is typically found in meteorite impacts. It crystallizes in the  $P6_3/mmc$  space group with four atoms per primitive cell.

TABLE III. Total energy contributions for diamond and lonsdaleite, at the BO-DFT optimized geometries, with a 40 Ha cutoff. The energies are reported per two atoms (diamond primitive cell). We also provide the band-by-band decomposition of  $E^{\text{elph}}$ . The total energy presented are computed at the BO atomic positions  $\{\mathbf{R}_0^0\}$  while  $\Delta E^{\text{QH}}$  is the total energy difference between the atomic position corresponding to the energy minimum of  $E^{\text{BO}} + E^{\text{ph}} + E^{\text{elph}} + E^{\text{elm}}$  and the same energy at  $\{\mathbf{R}_0^0\}$  (not computed for lonsdaleite).

| Total energy term                                                  | Diamond (meV) | Lonsdaleite (meV) |
|--------------------------------------------------------------------|---------------|-------------------|
| $E^{\text{BO}}$                                                    | -327559.414   | -327505.399       |
| $E^{\text{c}}$                                                     | 10119.178     | 9969.000          |
| $E^{\text{other}}$                                                 | -337678.592   | -337474.399       |
| $E^{\text{ph}}$                                                    | 358.685       | 357.381           |
| $E^{\text{Allen,AHC}}$                                             | -104.189      | -112.906          |
| $E^{\text{elph}}$                                                  | 7.600         | 7.608             |
| $E^{\text{elm}}$                                                   | -0.049        | -0.049            |
| $E_1^{\text{elph}}$                                                | 0.509         | 0.517             |
| $E_2^{\text{elph}}$                                                | 1.510         | 1.476             |
| $E_3^{\text{elph}}$                                                | 2.516         | 2.419             |
| $E_4^{\text{elph}}$                                                | 3.066         | 3.197             |
| $E^{\text{BO}} + E^{\text{ph}} + E^{\text{elph}} + E^{\text{elm}}$ | -327193.178   | -327140.459       |
| Relative difference                                                | -52.719       | 0                 |
| $\Delta E^{\text{QH}}$                                             | -2.11         | ...               |

We computed DFT-BO lattice parameters of  $a = 4.7477$  Bohr and  $c = 7.9011$  Bohr, slightly above the experimental lattice values of  $a = 4.743$  Bohr and  $c = 7.786$  Bohr [101]. Our computed fractional internal parameter is  $u = 0.374535$ . The volume per atom is similar for diamond and lonsdaleite, with  $38.465$  Bohr<sup>3</sup>/atom and  $38.560$  Bohr<sup>3</sup>/atom, respectively. We compute the quadrupole tensor of lonsdaleite integrated on a  $18 \times 18 \times 12$   $\mathbf{k}$ -point grid and obtain the nonequivalent values:  $Q_{\text{kyxx}} = -1.643$  e.Bohrs,  $Q_{\text{kzxx}} = -1.663$  e.Bohrs,  $Q_{\text{kxxz}} = -1.018$  e.Bohrs, and  $Q_{\text{kzzz}} = 2.775$  e.Bohrs. For diamond, we use a  $8 \times 8 \times 8$   $\mathbf{k}$ -point grid and a  $8 \times 8 \times 8$   $\mathbf{q}$ -point grid interpolated to a fine  $64 \times 64 \times 64$   $\mathbf{q}$ -grid. For lonsdaleite, we use a  $6 \times 6 \times 4$   $\mathbf{k}$ -point grid and a  $6 \times 6 \times 4$   $\mathbf{q}$ -point grid interpolated to a fine  $60 \times 60 \times 40$   $\mathbf{q}$ -grid.

Prior DFT calculations have reported that diamond is more stable than lonsdaleite by 2.6 kcal/mol [102]. As reported in Table III, we also find diamond to be more stable, but only by  $-54.015$  meV/(2 atoms), which corresponds to 0.6228 kcal/mol. We then study the second (phononic) and fourth-order (electron-phonon only) contributions to the total energy using DFPT and, in particular, the formulation of Eq. (100) for  $E^{\text{elph}}$ . We report in Fig. 4 the values of  $E^{\text{ph}}$ ,  $E^{\text{Allen,AHC}}$ , and  $E^{\text{elph}}$  as a function of momentum  $\mathbf{q}$ -grid integration.

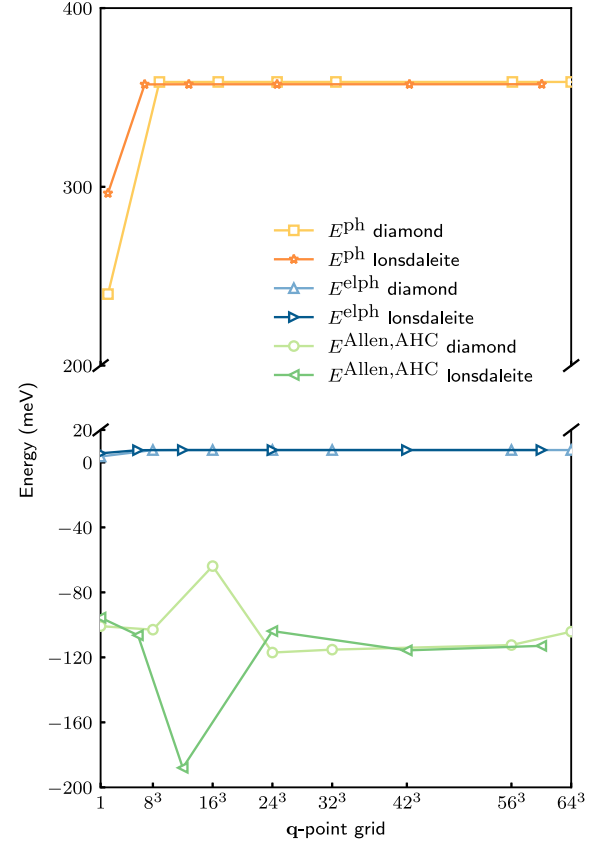


FIG. 4. Diamond and lonsdaleite convergence rates for the second- and electron-phonon fourth-order contributions to the total energy (per two atoms) with respect to  $\mathbf{q}$ -point grid integration. The  $\mathbf{k}$ -point grid used is  $8 \times 8 \times 8$  for diamond and  $6 \times 6 \times 4$  for lonsdaleite. In the case of lonsdaleite, the reported grid size corresponds to the first two numbers, e.g.,  $24^3$  means a  $\mathbf{q}$  grid of  $24 \times 24 \times 16$ .

We also integrate on  $\mathbf{k}$ -points using crystal symmetries and an  $8 \times 8 \times 8$  and  $6 \times 6 \times 4$  grids for diamond and lonsdaleite, respectively. We verify that increasing the  $\mathbf{k}$ -point grids changes the results by less than 1%.

Both  $E^{\text{ph}}$  and  $E^{\text{elph}}$  converge quickly with  $\mathbf{q}$ -point grids, but  $E^{\text{Allen,AHC}}$  requires very dense grids. This is not surprising, as this term is obtained by integrating the eigenvalue renormalization, a quantity that is known to converge slowly with phonon momentum grids [37,38].

We find the second-order energy  $E^{\text{ph}}$  per two atoms to be 358.7 and 357.4 meV for diamond and lonsdaleite, respectively. Interestingly, these values are very close, which is also the case for their  $E^{\text{Allen,AHC}}$  decomposition, with diamond having a value of  $-104.2$  meV while the lonsdaleite one is  $-112.9$  meV. Finally, we look at the fourth-order contribution and find that  $E^{\text{elph}}$  is similar in both cases, finding a value of 7.600 meV for diamond and 7.608 meV for lonsdaleite. In addition, and as expected, we see in Table III that the band decomposition of  $E^{\text{elph}}$  yields the largest contribution from the highest

energy bands. However, interestingly, the band-by-band differences between diamond and lonsdaleite are larger than the difference between their summed values, indicating band-structure differences between these two materials.

Overall, when accounting for phononic and electron-phonon interaction up to the fourth order, we find that lonsdaleite becomes a little more stable with respect to diamond than the straight BO value, going from  $-54.015 \text{ meV}/(2 \text{ atoms})$  to  $-52.719 \text{ meV}/(2 \text{ atoms})$ , which contributes marginally to explaining why lonsdaleite is stable and can be naturally observed. We remark that this stability will be modified at finite temperature, which is outside the scope of this study. Also, we did not compute the anharmonic fourth-order contribution to the total energy. We can still expect the relative difference to remain similar given the similarity in  $E^{\text{ph}}$  between the two materials.

We note that among all the  $\lambda^6$  order energy terms presented in Table I, the effect of the  $\mathcal{E}^{(6),\text{elm}}$  term given in Eq. (S27) can be easily computed, approximately, by renormalizing the  $E^{\text{ph}}$  term as

$$E^{\text{elm}} \equiv E^{\text{ph}} \left( \sqrt{\frac{M_{\kappa}}{M_{\kappa} + n_{e\kappa} m_e}} - 1 \right). \quad (129)$$

In this approximation, we consider the  $\Delta m_{\kappa\alpha,\kappa'\alpha'}^{\text{elm},-1}$  tensor to be diagonal and isotropic for each nucleus, with the value needed to fulfill the sum rule mentioned in Eq. (17) of Ref. [60], namely,  $n_{e\kappa} = 6$  for carbon nuclei. We report it in Table III and find the very small rounded value of  $-0.049 \text{ meV}$  for both allotropes, which therefore does not affect their relative stability.

We conclude this section by computing the forces and strain resulting from the addition of the phonon energy  $E^{\text{ph}}$ , electron-phonon energy  $E^{\text{elph}}$ , and electronic mass renormalization energy  $E^{\text{elm}}$  when the atoms are located at  $\{\mathbf{R}^0\}$ . Indeed, as already discussed at the end of Sec. IV, the  $\{\mathbf{R}^0\}$  atomic positions are at the BO minimum but might no longer be at the minimum of the modified energy hypersurface once the additional energy terms are included. This is indeed the case, as seen in Fig. 5: the diamond lattice parameter increases from 6.7513 to 6.7774 Bohr due to phonons (0.4% increase) and further to 6.7776 Bohr due to the electron-phonon interaction (0.8% of the phonon change). This term is known as zero-point lattice expansion [103]. We emphasize that this is a small but non-negligible increase that occurs at zero Kelvin and will be much larger with the temperature increase (thermal expansion). For lonsdaleite, a similar increase would occur, and we do not report it. However, in contrast to diamond, lonsdaleite has an internal parameter  $u$ , and we find in Fig. 5 a reduction of the internal parameter from 0.37459 to 0.37448. Moreover, the lowering of the energy

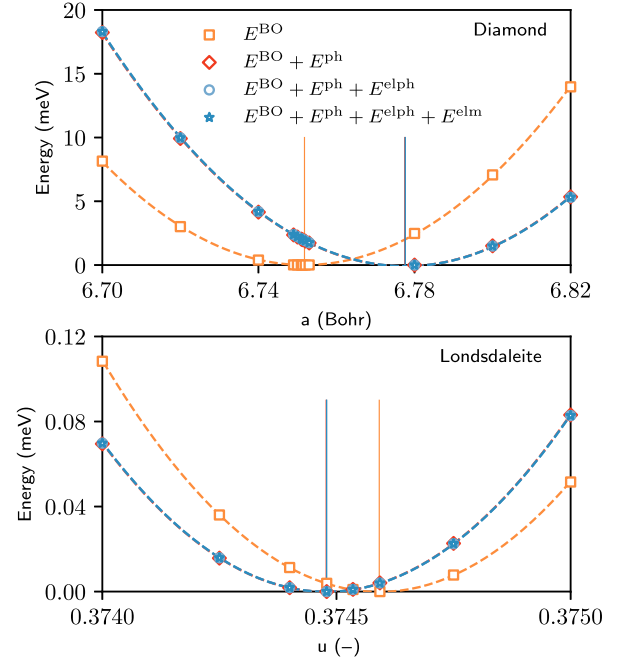


FIG. 5. Diamond energy dependence on the lattice parameter  $a$  and lonsdaleite energy dependence on the internal parameter  $u$ . All the energies are presented with their minimal value adjusted to 0. Vertical lines indicate the position of the energy minimum.

between the optimized atomic position and  $\{\mathbf{R}^0\}$  is the quasi-harmonic energy, defined (for the terms that we address in the present study) as

$$\Delta E^{\text{QH}} \equiv \min_{\{\mathbf{R}\}} (E^{\text{BO}} + E^{\text{ph}} + E^{\text{elph}} + E^{\text{elm}})_{\{\mathbf{R}\}} - (E^{\text{BO}} + E^{\text{ph}} + E^{\text{elph}} + E^{\text{elm}})_{\{\mathbf{R}^0\}}, \quad (130)$$

which gives a decrease of 2.1 meV due to the optimization of the volume of diamond and a negligible decrease for the optimization of the optimal internal parameter  $u$  of lonsdaleite.

Overall, we expect that computing these additional forces will bring the predictions of crystal structures closer to those obtained from cryogenic temperature measurements.

## XI. GALLIUM NITRIDE POLYMORPHS

We conclude by presenting an application to GaN, a material of considerable relevance for energy-related technologies. GaN is characterized by a high breakdown field, elevated thermal conductivity, and high electron mobility, making it a highly suitable candidate for high-power electronic devices [104–106]. In addition, GaN exhibits a large Seebeck coefficient and excellent thermal stability, which render it particularly promising for high-temperature thermoelectric applications [107].

Furthermore, GaN has been explored for use in thermal neutron and gamma radiation detection [108].

GaN crystallizes in three distinct polymorphs: (i) wurtzite ( $P6_3mc$ ), (ii) zincblende ( $F\bar{4}3m$ ), and (iii) rocksalt ( $Fm\bar{3}m$ ). Among these, the wurtzite phase is the thermodynamically stable and naturally occurring structure. The zincblende phase can be experimentally stabilized via epitaxial growth on cubic GaAs [001] substrates [109], whereas the rocksalt phase is accessible under high-pressure conditions [110].

We therefore also study the contribution of electron-phonon coupling to the total energy of the three polymorphs of GaN. We perform calculations with the ABINIT v10.6.5 software [51] with a 60 Ha plane-wave energy cutoff. We use the PBE [83] exchange-correlation functional, with the scalar-relativistic standard PBE pseudopotential from PSEUDODOJO [84] v0.5. We report relaxed lattice parameters, phonon frequencies at the zone center, and long-range parameters (Born effective charges, dynamical quadrupoles, and static dielectric constants) in Table IV. We used  $18 \times 18 \times 12$  (wurtzite) and  $16 \times 16 \times 16$  (zincblende and rocksalt)  $\mathbf{k}$ -point grids for the zone-center properties.

We first report in Table IV the zero-point renormalization (ZPR) of the VBM using the nonadiabatic AHC at  $\mathbf{k} = \Gamma$  and integrated on  $60 \times 60 \times 40$  (wurtzite) and  $64 \times 64 \times 64$  (zincblende and rocksalt)  $\mathbf{q}$ -point grids.

For wurtzite GaN, we obtain +89.7 meV, which underestimates the +101 meV value of Ref. [78]. For zincblende GaN, we compute +88.2 meV, in close agreement with the +85 meV value of Ref. [78].

The ZPR of the rocksalt phase was not reported before, and we obtain 100.8 meV. While Ref. [78] uses direct integration, we use Fourier interpolation of the perturbed potential, with long-range dipole and quadrupole included. Given the similar integration grids, a closer agreement could have been expected.

Next, we compute the total energy per two atoms by using the same  $\mathbf{q}$  grid and further integrate on  $6 \times 6 \times 4$  (wurtzite) and  $8 \times 8 \times 8$  (zincblende and rocksalt)  $\mathbf{k}$ -point grids.

We obtain similar phonon energies of 148.4 and 148.6 meV for the wurtzite and zincblende phases, and a significantly lower energy of 110.5 meV for the rocksalt phase, which is not stable under ambient conditions.

In contrast, we find that the electron-phonon contribution to the total energy is very similar for all three phases, with 19.5, 19.5, and 19.9 meV for wurtzite, zincblende, and rocksalt, respectively. Interestingly, this electron-phonon energy is much larger than that of diamond. It represents 13% of the phonon energy in the wurtzite and zincblende phases, and 18% in the rocksalt phase, a much larger fraction than the 2% obtained for diamond, highlighting the importance of including it in free-energy calculations.

TABLE IV. Computed properties of the three polymorphs of gallium nitride. Lattice parameters  $a$  (Bohr) and  $c$  (Bohr) and internal parameter  $u$ . Cartesian components of the dynamical dipole  $Z(e)$  and quadrupole  $Q(e \cdot \text{Bohrs})$  and dielectric tensor for GaN (only independent components are shown). For the zero-point renormalization of the valence band maximum (VBM), we used the same dense  $\mathbf{q}$ -point grids, and we are reporting the nonadiabatic results since it is a polar material.

|                                                     | Wurtzite                |         | Zincblende            |         | Rocksalt              |         |
|-----------------------------------------------------|-------------------------|---------|-----------------------|---------|-----------------------|---------|
|                                                     | Lattice                 |         |                       |         |                       |         |
| $a$                                                 | 6.083929                |         | 6.079468              |         | 5.704333              |         |
| $c$                                                 | 9.908288                |         |                       |         |                       |         |
| $u$                                                 | 0.376774                |         |                       |         |                       |         |
|                                                     | $\omega_{\Gamma}$ (meV) |         |                       |         |                       |         |
| TO                                                  | 16.909 ( $\times 2$ )   |         | 64.154 ( $\times 2$ ) |         | 25.317 ( $\times 2$ ) |         |
| LO                                                  | 39.599 ( $\times 1$ )   |         | 85.868 ( $\times 1$ ) |         | 76.626 ( $\times 1$ ) |         |
| LO                                                  | 62.273 ( $\times 1$ )   |         |                       |         |                       |         |
| TO                                                  | 65.098 ( $\times 1$ )   |         |                       |         |                       |         |
| TO                                                  | 65.967 ( $\times 2$ )   |         |                       |         |                       |         |
| TO                                                  | 81.478 ( $\times 1$ )   |         |                       |         |                       |         |
| LO                                                  | 86.539 ( $\times 1$ )   |         |                       |         |                       |         |
|                                                     | Ga                      | N       | Ga                    | N       | Ga                    | N       |
| $Z_{\kappa xx}$                                     | 2.6501                  | -2.6501 | 2.6977                | -2.6977 | 3.6828                | -3.6828 |
| $Z_{\kappa zz}$                                     | 2.7907                  | -2.7907 | 2.6977                | -2.6977 | 3.6828                | -3.6828 |
| $Q_{\kappa xyz}$                                    | 0                       | 0       | 5.5120                | -0.2266 | 0                     | 0       |
| $Q_{\kappa xxy}$                                    | 4.2840                  | -1.2165 | 0                     | 0       | 0                     | 0       |
| $Q_{\kappa xxz}$                                    | -2.6951                 | -0.0250 | 0                     | 0       | 0                     | 0       |
| $Q_{\kappa zxx}$                                    | -2.7603                 | -0.0725 | 0                     | 0       | 0                     | 0       |
| $Q_{\kappa zzz}$                                    | 5.7217                  | -0.4682 | 0                     | 0       | 0                     | 0       |
| $\epsilon_{xx}^{\infty}$                            | 5.9528                  |         | 6.1537                |         | 8.6461                |         |
| $\epsilon_{zz}^{\infty}$                            | 6.1396                  |         | 6.1537                |         | 8.6461                |         |
| Zero-point renormalization (meV)                    |                         |         |                       |         |                       |         |
| $\Delta \epsilon_{\Gamma, \text{VBM}}^{\text{AHC}}$ | 89.664                  |         | 88.236                |         | 100.813               |         |
| Total energy per two atoms (meV)                    |                         |         |                       |         |                       |         |
| $E^{\text{BO}}$                                     | -2364140.7397           |         | -2364131.8018         |         | -2363186.1091         |         |
| $E^{\text{ph}}$                                     | 148.404                 |         | 148.559               |         | 110.547               |         |
| $E^{\text{elph}}$                                   | 19.494                  |         | 19.484                |         | 19.942                |         |
| Total                                               | -2363972.8417           |         | -2363963.759          |         | -2363055.620          |         |
| Difference                                          | 0                       |         | 9.0827                |         | 917.222               |         |

We conclude by reporting on the cost of performing such calculations and the effect of the pseudopotential approximation.

Overall, the computational cost and scaling for these calculations are similar to those of multiple  $\mathbf{k}$ -point zero-point renormalization calculations. Indicatively, for our largest calculation on the fine grid of wurtzite GaN, the calculation took 34 h on 88 AMD EPYC 7742 cores with 8 GB of memory per core. Concerning the effect of the pseudopotential approximation, we find that our results are weakly sensitive to the number of valence electrons.

TABLE V. Pseudopotential dependence for wurtzite GaN using the PSEUDODOJO standard PBE and stringent tables. The standard pseudopotential includes  $3d^{10}4s^24p^1$  (Ga) and  $2s^22p^3$  (N) as valence electrons, while the stringent one includes  $3s^23p^63d^{10}4s^24p^1$  (Ga) and  $2s^22p^3$  (N) as valence electrons. For total energy calculations, we use a  $6 \times 6 \times 4$   $\mathbf{k}$ -point grid with a  $30 \times 30 \times 20$   $\mathbf{q}$ -point grid and report the energy per two atoms (meV).

|                   | Standard     | Stringent    |
|-------------------|--------------|--------------|
| $E^{\text{BO}}$   | -2364138.854 | -7040604.474 |
| $E^{\text{ph}}$   | 148.404      | 148.093      |
| $E^{\text{elph}}$ | 19.494       | 19.783       |

We compare results obtained with a Ga pseudopotential that includes  $3d^{10}4s^24p^1$  as valence electrons with one that includes the following semicore states:  $3s^23p^63d^{10}4s^24p^1$ . As can be seen in Table V, the BO total energy is very different due to the added electrons, but the phonon and electron-phonon contributions to the total energy are almost the same. This result stems from the denominator of Eq. (101), where semicore states have a negligible contribution to the total energy given their energy difference with unoccupied states. One can hypothesize that all-electron calculations will also yield similar results, or at least that the electron-phonon contribution from core electrons is insensitive to the chemical bonding.

## XII. CONCLUSIONS

In this work, we have examined which terms in the BO expansion might be called “*electron-phonon contribution to the total energy*.” The lowest-order possibility appears at fourth order in the small parameter of the Born-Oppenheimer expansion and scales as the inverse of the characteristic nuclear mass. This contribution, not yet computed from first principles for solids to our knowledge, might become relevant when addressing small energy differences between competing phases, magnetic configurations, defects, or surfaces. We actually derive all the contributions in the BO expansion up to the sixth order, even including the effect of time-reversal-symmetry breaking, with the appearance of a vector potential. We clarify that the expression proposed by Allen in 2020, which he called the electron-phonon contribution to the total energy, is in fact part of the second-order phonon contribution and should not be added independently. Building on this understanding, we derive and implement a correct expression for the fourth-order electron-phonon correction, which we show to be size-consistent and compatible with standard density-functional theory workflows. Our implementation is validated against finite-difference calculations or the sum-over-states formulation and applied to the case of diamond and its hexagonal polymorph, lonsdaleite. We find that although the fourth-order electron-phonon

contribution is small in absolute terms, it is non-negligible and on the order of several meV per atom. However, there is only a marginal difference between its values for the two allotropes. In contrast, we find a much larger contribution of the electron-phonon interaction to the total energy in GaN, amounting to 13% of the phonon energy in the stable wurtzite phase and up to 18% in the high-pressure rocksalt phase. Overall, this work provides a practical and accurate route to include the lowest-order electron-phonon contribution to the total energy in first-principles simulations, enabling more precise energy comparisons in systems where quantum lattice effects play a significant role, such as the wide- and ultrawide-band-gap semiconductors, battery electrodes, and thermoelectric compounds on which current energy technologies rely.

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## DATA AVAILABILITY

The data that support the findings of this article are openly available on the Materials Cloud Archive with the following Ref. [111].

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