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Direct evaluation of the isotope effect within the framework of density functional theory for superconductors

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Abstract

Within recent developments of density functional theory, its numerical implementation and of the superconducting density functional theory is nowadays possible to predict the superconducting critical temperature, T_c , with sufficient accuracy to anticipate the experimental verification. In this paper we present an analytical derivation of the isotope coefficient within the superconducting density functional theory. We calculate the partial derivative of T_c with respect to atomic masses. We verified the final expression by means of numerical calculations of isotope coefficient in monatomic superconductors (Pb) as well as polyatomic superconductors (CaC_6). The results confirm the validity of the analytical derivation with respect to the finite difference methods, with considerable improvement in terms of computational time and calculation accuracy. Once the critical temperature is calculated (at the reference mass(es)), various isotope exponents can be simply obtained in the same run. In addition, we provide the expression of interesting quantities like partial derivatives of the deformation potential, phonon frequencies and eigenvectors with respect to atomic masses, which can be useful for other derivations and applications.

Keywords: isotope effect, CaC_6 , superconductivity, SCDFT

1. Introduction

The discovery of isotope effect (IE) in superconductors, that is the variation of the superconducting critical temperature (T_c) upon isotope substitution of the constituent atoms of the material, has had a fundamental historical role. In fact, after

its discovery on mercury [1, 2] and the theoretical work of Fröhlich [3] on the interaction energy between electrons and lattice vibrations, Bardeen [4] concluded that *the superconducting state arises from the interaction of electrons with lattice vibrations*. This stimulated the theoretical investigation bringing to the formulation of the first microscopic theory of the superconducting phase by Bardeen, Cooper and Schrieffer (BCS) [5]. Among other merits, BCS theory predicts the isotope effect. In particular, it finds that the critical temperature scales as $T_c \sim M^{-\gamma}$ with M the atomic mass and γ , the isotope



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coefficient, equal to $\frac{1}{2}$. Although, this is the results of the many approximations within BCS theory, the prediction was qualitatively confirmed for many superconductors (Zn, Cd, Sn, Hg, Pb, Tl) [6]. However, the observation of reduced isotope effect ($\gamma < \frac{1}{2}$) in many materials (Ru, Os, Mo) [6] posed more stringent limits in a microscopic theory of superconductivity.

Beyond its historical importance, the measure of isotope effect also represents a key experimental tool in the study of superconductivity. Generally, IE is considered a measure of the phonon contribution on the electron pairing and its lack, as a possible indication of other pairing mechanisms. For example, in recent years, IE played a fundamental role confirming phonon mediated superconductivity in SH_3 [7], MgB_2 [8] and in CaC_6 [9], and several studies of isotope shifts on T_c have been carried in almost all known cuprates [10] and iron-superconductors [11].

Strictly speaking the value of the isotope coefficient has only a relative importance, without a reliable theory that interprets it. In fact, isotope coefficient is a ‘number’ that in principle contains *all* the relevant physics of the normal (non superconducting) phase and its final value can hinder peculiar and interesting effects like anharmonic contribution to explain the inverse isotope effect in superconducting Palladium–Hydride compounds [12]. On the contrary, even without anharmonic contributions, its final value accounts for *all* the interactions responsible for the superconducting phase: electron–phonon, Coulomb interactions, spin fluctuations, etc. A theory able to predict the isotope coefficient *must* be able to deal with all these relevant interactions.

The density functional theory for superconductors [13–15] (SCDFT) accounts for all these interactions and its predicting power have been successfully tested since 2005 achieving a complete first-principles description of the superconducting state [16–18], including all the relevant normal state effects and the most relevant pairing mechanisms [14, 19–23].

The implementation of the method allowed the *ab initio* calculation of many properties of real superconductors [15, 24–30] under different conditions [21, 31–34], and several predictions [35–42]. Among the others, the predicted isotope coefficients for simple metals [15, 43], allowed to highlight the origin of reduced isotope effect, underlining the need of a consistent treatment of electron–phonon and *renormalized* Coulomb electron–electron interaction which ultimately depends on the phonon frequency range.

Due to its fundamental importance, the straightforward comparison with the experiments and to complete the formulation of the SCDFT, in this paper we present an analytical derivation of the isotope coefficient within the SCDFT. This new approach will allow to obtain isotope coefficient as a post-processing with a considerable gain in terms of computational time and precision. In addition, the analytical calculation of partial derivatives of the interaction functionals gives access to many interesting quantities like derivative of deformation potential, phonon frequencies and eigenvectors with respect to atomic masses.

In the following we present the analytical derivation of IE (section 2) then, we performed the partial derivatives (section 3)

and then present a numerical implementation and discuss results on Pb and CaC_6 (section 4)

2. The isotope exponent

2.1. Basic definitions

Considering a superconductor with critical temperature T_c , the isotope effect is described by the dependence of T_c on the mass of the constituent atoms. In the case of one-atom per unit cell:

$$T_c \sim M^{-\gamma} \quad (1)$$

where M is the atomic mass. In case of several atoms per unit cell, this can be generalized to

$$T_c \sim \prod_{\alpha} M_{\alpha}^{-\gamma_{\alpha}} \quad (2)$$

or making use of a reference mass, M_0 , with reference critical temperature, T_c^0 :

$$T_c/T_c^0 = \prod_{\alpha} (M_{\alpha}/M_{\alpha}^0)^{-\gamma_{\alpha}}. \quad (3)$$

For small changes in the mass we obtain

$$T_c/T_c^0 \approx 1 - \sum_{\alpha} \gamma_{\alpha} (M_{\alpha}/M_{\alpha}^0 - 1) \quad (4)$$

or

$$T_c \approx T_c^0 - \sum_{\alpha} T_c^0/M_{\alpha}^0 \gamma_{\alpha} (M_{\alpha} - M_{\alpha}^0). \quad (5)$$

The partial isotope-coefficient, γ_{α} , can be obtained from

$$\gamma_{\alpha} = -\frac{M_{\alpha}^0}{T_c^0} \frac{\delta T_c}{\delta M_{\alpha}}, \quad (6)$$

or, if we introduce the critical inverse temperature $\beta_c = 1/(k_B T_c)$,

$$\gamma_{\alpha} = \frac{M_{\alpha}^0}{\beta_c^0} \frac{\delta \beta_c}{\delta M_{\alpha}}. \quad (7)$$

2.2. Dependence of the critical temperature on the masses

Within the SCDFT [14, 15] the superconducting critical temperature is determined by the linearized gap equation (lin. gap. equation) (refer to [14, 15] for the meaning of the symbols)⁸:

$$\Delta_k = -\mathcal{Z}_k \Delta_k - \frac{1}{2} \sum_{k'} \mathcal{K}_{kk'} \frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}} \Delta_{k'}. \quad (8)$$

The interaction kernel, $\mathcal{K}_{kk'}$, contains the sum of two contributions: the electron–phonon (el–ph) interaction ($\mathcal{K}_{kk'}^{\text{ph}}$) and the Coulomb electron–electron (el–el) interaction ($\mathcal{K}_{kk'}^{\text{el}}$).

First, we rewrite the linearized gap equation as a matrix equation with a symmetric kernel:

⁸ The following equation is identical to equation (5) of [15]. The only differences are: (i) use of the composite index (k, k') instead of $(n\mathbf{k}, n'\mathbf{k}')$, (ii) linearization near T_c , where $E_k \simeq \xi_k$.

$$\tilde{\Delta}_k = \sum_{k'} \mathcal{M}_{kk'} \tilde{\Delta}_{k'} \quad (9)$$

where

$$\tilde{\Delta}_k = \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k}} \Delta_k \quad (10)$$

$$\mathcal{M}_{kk'} = -Z_k \delta_{kk'} - \frac{1}{2} \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k}} [\mathcal{K}_{kk'}^{\text{ph}} + \mathcal{K}_{kk'}^{\text{el}}] \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}}}. \quad (11)$$

The linearized gap equation is only valid at the critical temperature, or equivalently β_c , which enters the equation via the kernel \mathcal{M} , which also depends—through the el–ph matrix elements [14, 15]—on the nuclear masses.

In order to calculate the dependence of β_c on the nuclear masses, we first rewrite the lin. gap equation as an eigenvalue equation, so that it is valid for all temperatures.

$$\sum_{k'} \mathcal{M}_{kk'} \tilde{\Delta}_{k'} = \lambda(\beta) \tilde{\Delta}_k. \quad (12)$$

The critical temperature is then defined by the lowest eigenvalue being equal to unity

$$\lambda(\beta_c) = 1. \quad (13)$$

Since the eigenvalue equation (12) depends separately on β and on the spectral function, also the eigenvalue λ^9 depends (independently) both on β and the masses M_α , while β_c depends, on the masses M_α through equation (13).

We now take the derivative of equation (13) with respect to the masses:

$$\frac{\partial \lambda}{\partial M_\alpha} + \frac{\partial \lambda}{\partial \beta} \Big|_{\beta=\beta_c} \frac{\partial \beta_c}{\partial M_\alpha} = 0. \quad (14)$$

From this we obtain:

$$\frac{d\beta_c}{dM_\alpha} = - \frac{\frac{\partial \lambda}{\partial M_\alpha}}{\frac{\partial \lambda}{\partial \beta}}. \quad (15)$$

Next, we need to calculate the partial derivatives of the eigenvalue λ . To this end we take the partial derivatives of equation (12) with respect to β and M_α .

Using the normalization of Δ (for each β),

$$\sum_k \tilde{\Delta}_k^* \tilde{\Delta}_k = 1 \quad (16)$$

we get

$$\lambda = \sum_{kk'} \tilde{\Delta}_k^* \mathcal{M}_{kk'} \tilde{\Delta}_{k'}. \quad (17)$$

Again, due to the normalization, we find

$$\frac{\partial \lambda}{\partial X} = \sum_{kk'} \tilde{\Delta}_k^* \frac{\partial \mathcal{M}_{kk'}}{\partial X} \tilde{\Delta}_{k'}. \quad (18)$$

This leads us to the desired result:

$$\frac{d\beta_c}{dM_\alpha} = - \frac{\sum_{kk'} \tilde{\Delta}_k^* \frac{\partial \mathcal{M}_{kk'}}{\partial M_\alpha} \tilde{\Delta}_{k'}}{\sum_{kk'} \tilde{\Delta}_k^* \frac{\partial \mathcal{M}_{kk'}}{\partial \beta} \tilde{\Delta}_{k'}} =: - \frac{A}{B} \quad (19)$$

⁹ Not to be confused with the electron–phonon parameter.

that, from the definition in equation (7) is proportional to the partial isotope coefficient.

3. Partial derivatives of the kernels

In order to calculate equation (19), we need to evaluate the partial derivatives of the interaction kernels with respect to the atomic masses (M_α) and inverse temperature (β), which represent the main part of the present paper.

From equation (11) we find

$$\frac{\partial \mathcal{M}_{kk'}}{\partial M_\alpha} = -\delta_{kk'} \frac{\partial Z_k}{\partial M_\alpha} - \frac{1}{2} \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k}} \frac{\partial \mathcal{K}_{kk'}^{\text{ph}}}{\partial M_\alpha} \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}}} \quad (20)$$

$$\begin{aligned} \frac{\partial \mathcal{M}_{kk'}}{\partial \beta} = & -\delta_{kk'} \frac{\partial Z_k}{\partial \beta} - \frac{1}{2} \left[\sqrt{\frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k}} \frac{\partial (\mathcal{K}_{kk'}^{\text{ph}} + \mathcal{K}_{kk'}^{\text{el}})}{\partial \beta} \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}}} \right. \\ & \left. + \frac{(\mathcal{K}_{kk'}^{\text{ph}} + \mathcal{K}_{kk'}^{\text{el}}) \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}}}}{4 \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k}} \cosh(\frac{\beta}{2} \xi_k)^2} + \frac{\sqrt{\frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k}} (\mathcal{K}_{kk'}^{\text{ph}} + \mathcal{K}_{kk'}^{\text{el}})}{4 \sqrt{\frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}}} \cosh(\frac{\beta}{2} \xi_{k'})^2} \right] \end{aligned} \quad (21)$$

where we used that the electronic contribution (\mathcal{K}^{el}) does not depend on the nuclear masses.

So, for the numerator and denominator of equation (19) we obtain:

$$\begin{aligned} A = & \sum_{kk'} \tilde{\Delta}_k \frac{\partial \mathcal{M}_{kk'}}{\partial M_\alpha} \tilde{\Delta}_{k'} = - \sum_k \frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k} \frac{\partial Z_k}{\partial M_\alpha} |\Delta_k|^2 \\ & - \frac{1}{2} \sum_{kk'} \Delta_k^* \frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k} \frac{\partial \mathcal{K}_{kk'}^{\text{ph}}}{\partial M_\alpha} \frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}} \Delta_{k'} \end{aligned} \quad (22)$$

$$\begin{aligned} B = & \sum_{kk'} \tilde{\Delta}_k \frac{\partial \mathcal{M}_{kk'}}{\partial \beta} \tilde{\Delta}_{k'} = - \sum_k \frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k} \frac{\partial Z_k}{\partial \beta} |\Delta_k|^2 \\ & - \frac{1}{2} \sum_{kk'} \left[\Delta_k^* \frac{\tanh(\frac{\beta}{2} \xi_k)}{\xi_k} \frac{\partial (\mathcal{K}_{kk'}^{\text{ph}} + \mathcal{K}_{kk'}^{\text{el}})}{\partial \beta} \frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}} \Delta_{k'} \right. \\ & \left. + \Re \frac{\Delta_k^* (\mathcal{K}_{kk'}^{\text{ph}} + \mathcal{K}_{kk'}^{\text{el}}) \frac{\tanh(\frac{\beta}{2} \xi_{k'})}{\xi_{k'}} \Delta_{k'}}{2 \cosh(\frac{\beta}{2} \xi_k)^2} \right]. \end{aligned} \quad (23)$$

3.1. Analytical derivatives

In order to calculate the above terms, we need to perform partial derivatives of the renormalization term (Z_k) and of interaction kernel ($\mathcal{K}_{kk'}^{\text{ph}}$) with respect to both nuclear masses (M_α) and inverse temperature (β). In this work we adopt the kernels (density functionals) of [14]¹⁰:

$$Z_k = \frac{1}{\tanh(\frac{\beta}{2} \xi_k)} \sum_{k'} \sum_{\lambda q} |g_{kk'}^{\lambda q}|^2 [J(\xi_k, \xi_{k'}, \Omega_{\lambda q}) + J(\xi_k, -\xi_{k'}, \Omega_{\lambda q})] \quad (24)$$

¹⁰ In [14] the Coulomb interaction $\mathcal{K}_{kk'}^{\text{el}}$ was considered in the Thomas–Fermi approximation. However, the formalism is equally valid for any other type of screening as the RPA [20, 27, 82], therefore with respect to [14] we drop here the TF label of \mathcal{K}^{el} .

$$\mathcal{K}_{kk'}^{\text{ph}} = \frac{2}{\tanh(\frac{\beta}{2}\xi_k)\tanh(\frac{\beta}{2}\xi_{k'})} \sum_{\lambda\mathbf{q}} |g_{kk'}^{\lambda\mathbf{q}}|^2 [I(\xi_k, \xi_{k'}, \Omega_{\lambda\mathbf{q}}) - I(\xi_k, -\xi_{k'}, \Omega_{\lambda\mathbf{q}})] \quad (25)$$

$$\mathcal{K}_{kk'}^{\text{el}} = v_{kk'}. \quad (26)$$

The partial derivative with respect to β does not pose relevant problems, because the temperature is present only within the Fermi and Bose factors, which have a clear analytical expression. The complete expression of the partial derivatives of \mathcal{Z}_k and $\mathcal{K}_{kk'}^{\text{ph}}$ with respect to β is reported in appendix A.

3.1.1. The kernel derivatives. The partial derivatives with respect to the masses of the kernels are more involved. They can be cast as:

$$\begin{aligned} \frac{\partial \mathcal{Z}_k}{\partial M_\alpha} &= \frac{1}{\tanh(\frac{\beta}{2}\xi_k)} \sum_{k'} \sum_{\lambda\mathbf{q}} \frac{\partial |g_{kk'}^{\lambda\mathbf{q}}|^2}{\partial M_\alpha} [J(\xi_k, \xi_{k'}, \Omega_{\lambda\mathbf{q}}) \\ &+ J(\xi_k, -\xi_{k'}, \Omega_{\lambda\mathbf{q}})] \\ &+ \frac{1}{\tanh(\frac{\beta}{2}\xi_k)} \sum_{k'} \sum_{\lambda\mathbf{q}} |g_{kk'}^{\lambda\mathbf{q}}|^2 \\ &\left[\frac{\partial J(\xi_k, \xi_{k'}, \Omega_{\lambda\mathbf{q}})}{\partial \Omega_{\lambda\mathbf{q}}} + \frac{\partial J(\xi_k, -\xi_{k'}, \Omega_{\lambda\mathbf{q}})}{\partial \Omega_{\lambda\mathbf{q}}} \right] \frac{\partial \Omega_{\lambda\mathbf{q}}}{\partial M_\alpha} \quad (27) \end{aligned}$$

$$\begin{aligned} \frac{\partial \mathcal{K}_{kk'}^{\text{ph}}}{\partial M_\alpha} &= \frac{2}{\tanh(\frac{\beta}{2}\xi_k)\tanh(\frac{\beta}{2}\xi_{k'})} \\ &\sum_{\lambda\mathbf{q}} \frac{\partial |g_{kk'}^{\lambda\mathbf{q}}|^2}{\partial M_\alpha} [I(\xi_k, \xi_{k'}, \Omega_{\lambda\mathbf{q}}) - I(\xi_k, -\xi_{k'}, \Omega_{\lambda\mathbf{q}})] \\ &+ \frac{2}{\tanh(\frac{\beta}{2}\xi_k)\tanh(\frac{\beta}{2}\xi_{k'})} \sum_{\lambda\mathbf{q}} |g_{kk'}^{\lambda\mathbf{q}}|^2 \\ &\times \left[\frac{\partial I(\xi_k, \xi_{k'}, \Omega_{\lambda\mathbf{q}})}{\partial \Omega_{\lambda\mathbf{q}}} - \frac{\partial I(\xi_k, -\xi_{k'}, \Omega_{\lambda\mathbf{q}})}{\partial \Omega_{\lambda\mathbf{q}}} \right] \frac{\partial \Omega_{\lambda\mathbf{q}}}{\partial M_\alpha} \quad (28) \end{aligned}$$

$$\frac{\partial \mathcal{K}_{kk'}^{\text{el}}}{\partial M_\alpha} = 0. \quad (29)$$

The above expressions involve the calculation of the derivative of the both phonon frequencies and electron–phonon coupling constant with respect to the atomic masses, which we afford in the next section.

3.1.2. Derivatives of the phonon frequencies. For a mode λ at wavevector \mathbf{q} the polarization vectors $\zeta_{\alpha\mu}^{\lambda\mathbf{q}}$ (with α the atom index and μ the cartesian coordinate) and phonon-frequencies $\Omega_{\lambda\mathbf{q}}$ are determined as eigenvectors and eigenvalues of the dynamical matrix [44]:

$$\sum_{\alpha'} \frac{C_{\alpha\mu, \alpha'\mu'}(\mathbf{q})}{\sqrt{M_\alpha M_{\alpha'}}} \zeta_{\alpha'\mu'}^{\lambda\mathbf{q}} = \Omega_{\lambda\mathbf{q}}^2 \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \quad (30)$$

where each matrix element

$$C_{\alpha\mu, \alpha'\mu'}(\mathbf{q}) = \sum_i e^{-i\mathbf{q}\mathbf{R}_i} \frac{\partial^2 E}{\partial R_{\alpha i}^\mu \partial R_{\alpha' i}^{\mu'}} \quad (31)$$

does not depend on the nuclear masses (the sum is over the atoms of the crystal at cell position \mathbf{R}_i , with respect the reference cell \mathbf{R}_0).

From equation (30), and using, again, the (mass-independent) normalization of the eigenvectors we obtain (see appendix B for the details of the calculations):

$$\frac{\partial \Omega_{\lambda\mathbf{q}}}{\partial M_\alpha} = - \frac{\sum_\mu \zeta_{\alpha\mu}^{\lambda\mathbf{q}*} \zeta_{\alpha\mu}^{\lambda\mathbf{q}}}{2M_\alpha} \Omega_{\lambda\mathbf{q}}. \quad (32)$$

3.1.3. Derivatives of the coupling constants. The electron–phonon coupling constants are given by the matrix element of the derivative of the self-consistent potential ($V_{\lambda\mathbf{q}}(\mathbf{r})$) with respect to the phonon mode λ at wave-vector \mathbf{q} between electron wavefunctions at wavevectors \mathbf{k} and $\mathbf{k}' = \mathbf{k} + \mathbf{q}$:

$$g_{kk'}^{\lambda\mathbf{q}} = \int d^3r \varphi_k^*(\mathbf{r}) V_{\lambda\mathbf{q}}(\mathbf{r}) \varphi_{k'}(\mathbf{r}). \quad (33)$$

The self-consistent potential can be written as [45]:

$$V_{\lambda\mathbf{q}}(\mathbf{r}) = V_{\lambda\mathbf{q}}^0(\mathbf{r}) + \int d^3r' \int d^3r'' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}') \right) \chi(\mathbf{r}', \mathbf{r}'') V_{\lambda\mathbf{q}}^0(\mathbf{r}'') \quad (34)$$

where $\chi(\mathbf{r}, \mathbf{r}')$ is the full response function, and

$$V_{\lambda\mathbf{q}}^0(\mathbf{r}) = \sum_{\alpha, i, \mu} \frac{Z_\alpha}{\sqrt{2M_\alpha \Omega_{\lambda\mathbf{q}}}} e^{i\mathbf{q}\mathbf{R}_i} \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \left(\frac{\partial}{\partial R_{\alpha i}^\mu} \frac{1}{|\mathbf{r} - \mathbf{R}_{\alpha i}|} \right) \quad (35)$$

the derivative of the bare potential. Since the full response function is not explicitly known, the response equation (34) is normally rewritten as

$$V_{\lambda\mathbf{q}}(\mathbf{r}) = V_{\lambda\mathbf{q}}^0(\mathbf{r}) + \int d^3r' \int d^3r'' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}') \right) \chi_0(\mathbf{r}', \mathbf{r}'') V_{\lambda\mathbf{q}}(\mathbf{r}'') \quad (36)$$

which involves only the Kohn–Sham response function ($\chi_0(\mathbf{r}', \mathbf{r}'')$), which is explicitly known, but it has to be solved self-consistently with respect to $V_{\lambda\mathbf{q}}(\mathbf{r})$.

In order to calculate the partial derivative of the coupling constant with respect to the masses we need to calculate the partial derivative of the potential, $\frac{\partial V_{\lambda\mathbf{q}}(\mathbf{r})}{\partial M_\alpha}$ as

$$\begin{aligned} \frac{\partial V_{\lambda\mathbf{q}}(\mathbf{r})}{\partial M_\alpha} &= \int d^3r' \int d^3r'' (\delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}'') \\ &+ \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}') \right) \chi(\mathbf{r}', \mathbf{r}'')) \frac{\partial V_{\lambda\mathbf{q}}^0(\mathbf{r}'')}{\partial M_\alpha}. \quad (37) \end{aligned}$$

We write $V_{\lambda\mathbf{q}}^0(\mathbf{r})$ as:

$$V_{\lambda\mathbf{q}}^0(\mathbf{r}) = \sum_{\alpha, \mu} \frac{Z_\alpha}{\sqrt{2M_\alpha \Omega_{\lambda\mathbf{q}}}} \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \tilde{V}_{\alpha\mu; \mathbf{q}}^0(\mathbf{r}) \quad (38)$$

with

$$\tilde{V}_{\alpha\mu; \mathbf{q}}^0(\mathbf{r}) = \sum_i e^{i\mathbf{q}\mathbf{R}_i} \left(\frac{\partial}{\partial R_{\alpha i}^\mu} \frac{1}{|\mathbf{r} - \mathbf{R}_{\alpha i}|} \right). \quad (39)$$

The same change of basis can be applied to $V^{\lambda\mathbf{q}}(\mathbf{r})$:

$$V^{\lambda\mathbf{q}}(\mathbf{r}) = \sum_{\alpha, \mu} \frac{Z_\alpha}{\sqrt{2M_\alpha \Omega_{\lambda\mathbf{q}}}} \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \tilde{V}_{\alpha\mu; \mathbf{q}}(\mathbf{r}). \quad (40)$$

Thus equation (34) can be written as:

$$\begin{aligned} \tilde{V}_{\alpha\mu;\mathbf{q}}(\mathbf{r}) = & \int d^3r' \int d^3r'' (\delta(\mathbf{r} - \mathbf{r}')\delta(\mathbf{r}' - \mathbf{r}'')) \\ & + \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}') \right) \chi(\mathbf{r}', \mathbf{r}'') \tilde{V}_{\alpha\mu;\mathbf{q}}^0(\mathbf{r}'). \end{aligned} \quad (41)$$

This form of the displacement potential now allows us to take the derivatives with respect to the nuclear masses *without* additional solutions of the response equation, since the response screening is performed on potentials which do not depend on the masses, and the eigenvectors, frequencies, etc are pulled outside the response function.

Therefore,

$$\frac{\partial V_{\lambda\mathbf{q}}}{\partial M_\alpha} = \sum_\mu \left[-\frac{Z_\alpha}{2M_\alpha\Omega_{\lambda\mathbf{q}}\sqrt{2M_\alpha\Omega_{\lambda\mathbf{q}}}} (\Omega_{\lambda\mathbf{q}} + M_\alpha \frac{\partial\Omega_{\lambda\mathbf{q}}}{\partial M_\alpha}) \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \tilde{V}_{\alpha\mu;\mathbf{q}}(\mathbf{r}) \right] + \quad (42)$$

$$+ \sum_\mu \left[\sum_{\alpha'} \frac{Z_{\alpha'}}{\sqrt{2M_{\alpha'}\Omega_{\lambda\mathbf{q}}}} \frac{\partial\zeta_{\alpha'\mu}^{\lambda\mathbf{q}}}{\partial M_\alpha} \tilde{V}_{\alpha'\mu;\mathbf{q}}(\mathbf{r}) \right]. \quad (43)$$

At this point we only need the derivative of the phonon frequencies and eigenvectors with respect to the masses, which are explicitly calculated in appendices B and C. At this point, we transform also the matrix element through

$$g_{kk'}^{\lambda\mathbf{q}} = \sum_{\alpha,\mu} \frac{Z_\alpha}{\sqrt{2M_\alpha\Omega_{\lambda\mathbf{q}}}} \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \tilde{g}_{kk'}^{\alpha\mu;\mathbf{q}} \quad (44)$$

with

$$\tilde{g}_{kk'}^{\alpha\mu;\mathbf{q}} = \int d^3r \varphi_k^*(\mathbf{r}) \tilde{V}_{\alpha\mu;\mathbf{q}}(\mathbf{r}) \varphi_{k'}(\mathbf{r}). \quad (45)$$

Using equations (42) in (44) and including the derivatives obtained in appendices B and C, we obtain:

$$\frac{\partial g_{kk'}^{\lambda\mathbf{q}}}{\partial M_\alpha} = \sum_\mu \left[-\frac{Z_\alpha}{\sqrt{2M_\alpha\Omega_{\lambda\mathbf{q}}}} \left(\frac{1 - \frac{1}{2} \sum_{\mu_1} \zeta_{\alpha\mu_1}^{\lambda\mathbf{q}*} \zeta_{\alpha\mu_1}^{\lambda\mathbf{q}}}{2M_\alpha} \right) \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \tilde{g}_{kk'}^{\alpha\mu;\mathbf{q}} - \sum_{\alpha'} \frac{1}{2M_\alpha} \frac{Z_{\alpha'}}{\sqrt{2M_{\alpha'}\Omega_{\lambda\mathbf{q}}}} \sum_{\lambda' \neq \lambda} \frac{(\Omega_{\lambda\mathbf{q}}^2 + \Omega_{\lambda'\mathbf{q}}^2) \sum_{\mu_1} \zeta_{\alpha\mu_1}^{\lambda'\mathbf{q}*} \zeta_{\alpha\mu_1}^{\lambda\mathbf{q}}}{\Omega_{\lambda'\mathbf{q}}^2 - \Omega_{\lambda\mathbf{q}}^2} \zeta_{\alpha'\mu}^{\lambda'\mathbf{q}} \tilde{g}_{kk'}^{\alpha'\mu;\mathbf{q}} \right] \quad (46)$$

Since the eigenvectors of the dynamical matrix form a unitary matrix, the $\tilde{g}_{kk'}^{\alpha\mu;\mathbf{q}}$ can also be generated from the first-principles calculated $g_{kk'}^{\lambda\mathbf{q}}$ through the transformation

$$\tilde{g}_{kk'}^{\alpha\mu;\mathbf{q}} = \frac{1}{Z_\alpha} \sum_\lambda \zeta_{\alpha\mu}^{\lambda\mathbf{q}*} \sqrt{2M_\alpha\Omega_{\lambda\mathbf{q}}} g_{kk'}^{\lambda\mathbf{q}}. \quad (47)$$

Finally, the required derivative of the modulus squared is

$$\frac{\partial}{\partial M_\alpha} |g_{kk'}^{\lambda\mathbf{q}}|^2 = g_{kk'}^{\lambda\mathbf{q}*} \left(\frac{\partial}{\partial M_\alpha} g_{kk'}^{\lambda\mathbf{q}} \right) + \left(\frac{\partial}{\partial M_\alpha} g_{kk'}^{\lambda\mathbf{q}*} \right) g_{kk'}^{\lambda\mathbf{q}} \quad (48)$$

and this completes our derivation of equation (7). The complete analytic expression of the isotope coefficients is clearly very complicated and we are not able to extract exact features from it, as an upper limit for the isotope coefficients. However it can be easily evaluated numerically for any given material.

4. Implementation and test cases: Pb and CaC₆

We test the validity of the analytical approach by direct tests with usual finite difference method (FDM). In this last case, in order to calculate γ_α we need to calculate the critical temperature for two different isotopic masses of the same α -atom. The two approaches must give the *same* result.

Evaluation of γ_α (equation (7)), requires the calculation of the one-electron energies near the Fermi level (ξ_k), phonon frequencies ($\Omega_{\lambda\mathbf{q}}$), the phonon eigenvectors ($\zeta_{\alpha\mu}^{\lambda\mathbf{q}}$) and electron-phonon matrix elements ($g_{kk'}^{\lambda\mathbf{q}}$). All these quantities have been calculated within density functional theory perturbation theory [44, 46–48] using a pseudopotential implementation [49]. In addition, we solved the gap equation to find T_c and obtain the values of Δ_k sufficiently close to T_c (where the gap vanishes by definition)¹¹. Thus, the main steps of the calculation can be summarized as: (i) calculate the el-ph matrix elements and phonons frequencies and eigenvectors on a regular grid for the electron wave-vector (\mathbf{k}) and phonon wave-vectors (\mathbf{q}) in the Irreducible Brillouin zone. (ii) Obtain Δ_k on a non-uniform [15] mesh of \mathbf{k} and \mathbf{k}' near the Fermi level and solve the superconducting gap equation to find the value of T_c . (iii) Calculate γ_α using the same non-uniform mesh.

4.1. Superconducting lead

The superconducting properties of Pb are quite well understood [50–52], however a renewed attention has been devoted to then many peculiarities of its superconducting phase, both theoretically [43, 53–55] and experimentally [56].

Pb crystallizes in a fcc lattice and its Fermi surface is composed of three sheets arising from the Pb p -orbitals; at 7.2 K it becomes superconductor showing a multigap superconductivity [43].

The calculation was performed using norm-conserving pseudopotential [57] with 32 Ry of energy cutoff. Converged Brillouin zone integration of the charge density was achieved with 26³ Monkhorst–Pack (MP) [58] grid. Phonon frequencies and electron-phonon matrix elements are calculated on a 8³ MP \mathbf{q} grid and 26³ MP \mathbf{k} grid. The self-consistent gap equation was solved on a non-uniform \mathbf{k} -mesh in the IBZ of 6000 (500) points for bands crossing (not crossing) the Fermi level. The results are identical to those reported in [43] and not discussed here. We focus, instead, on the isotope effect. First, we determine the isotope coefficient calculating the critical temperature T_c^1 and T_c^2 for two different isotopic masses,

¹¹ As general rule we decided to choose any temperature in which Δ_k^2 becomes linear with T . The BCS-type second order phase transition requires that near T_c the superconducting gap may be expressed as $\Delta \sim (1 - \frac{T}{T_c})^{\frac{1}{2}}$. Anyway, we always verified that this last choice ensures that γ does not depend on the temperature.

$M_1 = 207.21$ and $M_2 = 208$ respectively. Thus γ is obtained as:

$$\gamma = \frac{1 - T_c^2/T_c^1}{M_1/M_2 - 1} = 0.47 \pm 0.01.$$

The error bar accounts for the indeterminacy in the determination of T_c .

Application of the analytical procedure, using the same sets of k and q points, gives $\gamma = 0.48$. The experimental value is 0.48 ± 0.01 [59, 60]. The agreement is excellent.

In principle, the only value that can be compared with the experimental one, is the one obtained in the same conditions, that is, with a finite variation of the isotopic mass. The analytical derivation, assumes an infinitesimal variation around the reference mass. However, the dependence of γ on the reference mass itself is weak and irrelevant for practical purposes.

5. Graphite intercalated compound: CaC₆

The second example we want to discuss is the isotope effect in CaC₆ compound. This system (and in general the class of intercalated graphites [61]) has been theoretically very well characterized [27, 39, 62–68] and theory is overall in good agreement with most of the experimental evidence: electronic [69, 70], phononic [71–74], coupling [75, 76] and superconducting properties [28, 71, 75–79], with few exceptions [9, 80].

CaC₆ represents a stringent test for our analytic derivation. In fact, the multi-atom case is far from trivial, as it accounts for many different interaction between different masses. In order to be consistent with calculations of [65], we used the same computational details. Even in this case, our analytical procedure reproduces (within 0.01) the finite-difference values (obtained as described in the case of Pb). In particular, we find $\gamma_{Ca} = 0.24$ and $\gamma_C = 0.26$. These values in agreement with previous estimations [63, 65] outline the important role played by both C and Ca atoms in the superconducting phase transition and the high coupling of low energy Ca phonons, in agreement with recent ARPES measurements [70]. However the Ca isotope coefficient disagrees with the values measured in [9], that estimates a value between 0.4 and 0.56. This point, remains up to now unresolved [81].

6. Conclusions

This paper presents a development of the superconducting density functional theory presented in [14, 15]. We derived an analytical expression of the isotope coefficient in the framework of SCDFT which has many advantages with respect to the finite difference method. In particular: (i) in the finite difference method, a numerically stable value of γ , requires an evaluation of T_c with a high enough accuracy (less than 1%). This is a formidable task by itself. In fact, close to T_c the self-consistent gap is approaching zero, making the self-consistency very difficult and time consuming to achieve. In addition, in order to obtain a reliable estimate of T_c the calculation of the superconducting gap has to be performed for many different temperatures close to T_c . In case of multiband and polyatomic systems this procedure can represent a serious limitation. The advantage of the analytical approach is that it does not require extra self-consistent solutions of the gap equation. (ii) The determination of γ needs (at least) two independent calculations of T_c for two different atomic masses. The new approach needs only one calculation of T_c at the reference mass. (iii) In case of polyatomic systems, evaluation of γ_α for each species is an independent calculation. In the analytical approach γ_α is calculated within the same run for each atomic species (α). Therefore the overall calculation of isotope coefficients is reduced by a factor $2 \times N_{scf} \times N_s$, where N_{scf} is the number of self-consistent cycles in the solution of the gap equation and N_s the number of atomic species in the system.

We want to underline that the present analytical approach (even if at the moment rather complicated) is suitable to analyze the dependence of the isotope coefficients on many different normal states properties (electron eigen-energies, phonon frequencies and eigenvectors, superconducting gap, Coulomb potentials, etc.).

In conclusion, the present formulation of the isotope effect, completes the formal derivation of SCDFT. As for the BCS formulation, we were able to derive an analytical expression of isotope effect. This allows a relevant time-saving, higher accuracy with respect to the usual numerical calculation and an analytical framework to analyze the computational results.

Appendix A. Partial derivatives of interaction kernels with respect β

The partial derivative of \mathcal{Z}_k and $\mathcal{K}_{kk'}^{\text{ph}}$ with respect to β are defined as:

$$\begin{aligned} \frac{\partial \mathcal{Z}_k}{\partial \beta} = & -\frac{\xi_k}{2 \sinh(\frac{\beta}{2} \xi_k)^2} \sum_{k'} \sum_{\lambda \mathbf{q}} |g_{kk'}^{\lambda \mathbf{q}}|^2 [J(\xi_k, \xi_{k'}, \Omega_{\lambda \mathbf{q}}) + J(\xi_k, -\xi_{k'}, \Omega_{\lambda \mathbf{q}})] \\ & + \frac{1}{\tanh(\frac{\beta}{2} \xi_k)} \sum_{k'} \sum_{\lambda \mathbf{q}} |g_{kk'}^{\lambda \mathbf{q}}|^2 \left[\frac{\partial J}{\partial \beta}(\xi_k, \xi_{k'}, \Omega_{\lambda \mathbf{q}}) + \frac{\partial J}{\partial \beta}(\xi_k, -\xi_{k'}, \Omega_{\lambda \mathbf{q}}) \right] \end{aligned} \quad (\text{A.1})$$

$$\begin{aligned} \frac{\partial \mathcal{K}_{kk'}^{\text{ph}}}{\partial \beta} = & -\frac{1}{2} \frac{\xi_k \sinh(\beta \xi_{k'}) + \xi_{k'} \sinh(\beta \xi_k)}{\sinh(\frac{\beta}{2} \xi_k)^2 \sinh(\frac{\beta}{2} \xi_{k'})^2} \sum_{\lambda \mathbf{q}} |g_{kk'}^{\lambda \mathbf{q}}|^2 [I(\xi_k, \xi_{k'}, \Omega_{\lambda \mathbf{q}}) - I(\xi_k, -\xi_{k'}, \Omega_{\lambda \mathbf{q}})] \\ & + \frac{2}{\tanh(\frac{\beta}{2} \xi_k) \tanh(\frac{\beta}{2} \xi_{k'})} \sum_{\lambda \mathbf{q}} |g_{kk'}^{\lambda \mathbf{q}}|^2 \left[\frac{\partial I}{\partial \beta}(\xi_k, \xi_{k'}, \Omega_{\lambda \mathbf{q}}) - \frac{\partial I}{\partial \beta}(\xi_k, -\xi_{k'}, \Omega_{\lambda \mathbf{q}}) \right] \end{aligned} \quad (\text{A.2})$$

$$\frac{\partial \mathcal{K}_{kk'}^{\text{el}}}{\partial \beta} = 0. \quad (\text{A.3})$$

According to [14, 15], the function I is defined as:

$$I(\xi_1, \xi_2, \Omega) = f_\beta(\xi_1) f_\beta(\xi_2) n_\beta(\Omega) \left[\frac{e^{\beta \xi_1} - e^{\beta(\xi_2 + \Omega)}}{\xi_1 - \xi_2 - \Omega} - \frac{e^{\beta \xi_2} - e^{\beta(\xi_1 + \Omega)}}{\xi_1 - \xi_2 + \Omega} \right] \quad (\text{A.4})$$

and J as:

$$J(\xi_1, \xi_2, \Omega) = \tilde{J}(\xi_1, \xi_2, \Omega) - \tilde{J}(\xi_1, \xi_2, -\Omega) \quad (\text{A.5})$$

and

$$\tilde{J}(\xi_1, \xi_2, \Omega) = -\frac{f_\beta(\xi_1) + n_\beta(\Omega)}{\xi_1 - \xi_2 - \Omega} \left[\frac{f_\beta(\xi_2) + f_\beta(\xi_1 - \Omega)}{\xi_1 - \xi_2 - \Omega} - \beta f_\beta(\xi_1 - \Omega) f_\beta(\Omega - \xi_1) \right]. \quad (\text{A.6})$$

In the following sections we will derive analytical expression of the derivative of I and J with respect to β .

A.1. Derivative of I with respect to β

We rewrite I term defined in (A.4) as

$$I(\xi_1, \xi_2, \Omega) = \underbrace{f_\beta(\xi_1) f_\beta(\xi_2) n_\beta(\Omega)}_A \left[\underbrace{e^{\beta \xi_1} \frac{1 - e^{-\beta(\xi_1 - \xi_2 - \Omega)}}{\xi_1 - \xi_2 - \Omega}}_{B_1} - \underbrace{e^{\beta \xi_2} \frac{1 - e^{\beta(\xi_1 - \xi_2 + \Omega)}}{\xi_1 - \xi_2 + \Omega}}_{B_2} \right]. \quad (\text{A.7})$$

We use

$$\frac{\partial f_\beta(\xi)}{\partial \beta} = -\xi f_\beta(\xi) (1 - f_\beta(\xi)) \quad (\text{A.8})$$

$$\frac{\partial n_\beta(\Omega)}{\partial \beta} = -\Omega n_\beta(\Omega) (1 + n_\beta(\Omega)) \quad (\text{A.9})$$

$$\frac{\partial e^{\beta \xi}}{\partial \beta} = \xi e^{\beta \xi} \quad (\text{A.10})$$

to find

$$\frac{\partial A}{\partial \beta} = -A [\xi_1 (1 - f_\beta(\xi_1)) + \xi_2 (1 - f_\beta(\xi_2)) + \Omega (1 + n_\beta(\Omega))] \quad (\text{A.11})$$

$$\frac{\partial B_1}{\partial \beta} = \xi_1 B_1 + e^{\beta(\xi_2 + \Omega)} \quad (\text{A.12})$$

$$\frac{\partial B_2}{\partial \beta} = \xi_2 B_2 - e^{\beta(\xi_1 + \Omega)} \quad (\text{A.13})$$

and from that

$$\begin{aligned} \frac{\partial}{\partial \beta} I(\xi_1, \xi_2, \Omega) &= \frac{\partial A}{\partial \beta} (B_1 - B_2) + A \left(\frac{\partial B_1}{\partial \beta} - \frac{\partial B_2}{\partial \beta} \right) \\ &= -I [\xi_1 (1 - f_\beta(\xi_1)) + \xi_2 (1 - f_\beta(\xi_2)) + \Omega (1 + n_\beta(\Omega))] \end{aligned} \quad (\text{A.14})$$

$$+ A \left(\xi_1 B_1 - \xi_2 B_2 + e^{\beta(\xi_2 + \Omega)} + e^{\beta(\xi_1 + \Omega)} \right). \quad (\text{A.15})$$

A.2. Derivative of J with respect to β

From (A.5) we just need to calculate the partial derivative of $\tilde{J}(\xi_1, \xi_2, \Omega)$ with respect to β :

$$\begin{aligned} \frac{\partial}{\partial \beta} \tilde{J}(\xi_1, \xi_2, \Omega) &= \frac{\xi_1 f_\beta(\xi_1)(1 - f_\beta(\xi_1)) + \Omega n_\beta(\Omega)(1 + n_\beta(\Omega))}{\xi_1 - \xi_2 - \Omega} \\ &\quad \times \left[\frac{f_\beta(\xi_2) - f_\beta(\xi_1 - \Omega)}{\xi_1 - \xi_2 - \Omega} - \beta f_\beta(\xi_1 - \Omega) f_\beta(\Omega - \xi_1) \right] \\ &\quad - \frac{f_\beta(\xi_1) + n_\beta(\Omega)}{\xi_1 - \xi_2 - \Omega} \\ &\quad \times \left[\frac{-\xi_2 f_\beta(\xi_2)(1 - f_\beta(\xi_2)) + (\xi_1 - \Omega) f_\beta(\xi_1 - \Omega)(1 - f_\beta(\xi_1 - \Omega))}{\xi_1 - \xi_2 - \Omega} \right. \\ &\quad \left. + f_\beta(\xi_1 - \Omega) f_\beta(\Omega - \xi_1) \right] \\ &\quad \times \left[1 - \beta(\xi_1 - \Omega) f_\beta(\Omega - \xi_1) - \beta(\Omega - \xi_1) f_\beta(\xi_1 - \Omega) \right]. \end{aligned} \quad (\text{A.16})$$

Appendix B. Partial derivative of phonon frequencies with respect to atomic masses

From equation (30) we can write:

$$\frac{\partial \Omega_{\lambda \mathbf{q}}^2}{\partial M_{\alpha''}} = \sum_{\alpha \mu, \alpha' \mu'} \zeta_{\alpha \mu}^{\lambda \mathbf{q}*} \frac{\partial}{\partial M_{\alpha''}} \frac{C_{\alpha \mu, \alpha' \mu'}(\mathbf{q})}{\sqrt{M_\alpha M_{\alpha'}}} \zeta_{\alpha' \mu'}^{\lambda \mathbf{q}} \quad (\text{B.1})$$

$$= -\frac{1}{2M_{\alpha''}} \sum_{\alpha \mu, \alpha' \mu'} \zeta_{\alpha \mu}^{\lambda \mathbf{q}*} (\delta_{\alpha, \alpha''} + \delta_{\alpha', \alpha''}) \frac{C_{\alpha \mu, \alpha' \mu'}(\mathbf{q})}{\sqrt{M_\alpha M_{\alpha'}}} \zeta_{\alpha' \mu'}^{\lambda \mathbf{q}} \quad (\text{B.2})$$

$$= -\frac{1}{2M_{\alpha''}} \left(\sum_{\mu, \alpha' \mu'} \zeta_{\alpha'' \mu}^{\lambda \mathbf{q}*} \frac{C_{\alpha'' \mu, \alpha' \mu'}(\mathbf{q})}{\sqrt{M_{\alpha''} M_{\alpha'}}} \zeta_{\alpha' \mu'}^{\lambda \mathbf{q}} + \sum_{\alpha \mu, \mu'} \zeta_{\alpha \mu}^{\lambda \mathbf{q}*} \frac{C_{\alpha \mu, \alpha'' \mu'}(\mathbf{q})}{\sqrt{M_\alpha M_{\alpha''}}} \zeta_{\alpha'' \mu'}^{\lambda \mathbf{q}} \right) \quad (\text{B.3})$$

$$= -\frac{\sum_{\mu} \zeta_{\alpha'' \mu}^{\lambda \mathbf{q}*} \zeta_{\alpha'' \mu}^{\lambda \mathbf{q}}}{M_{\alpha''}} \Omega_{\lambda \mathbf{q}}^2 \quad (\text{B.4})$$

and

$$\frac{\partial \Omega_{\lambda \mathbf{q}}}{\partial M_\alpha} = \frac{1}{2\Omega_{\lambda \mathbf{q}}} \frac{\partial \Omega_{\lambda \mathbf{q}}^2}{\partial M_\alpha} = -\frac{\sum_{\mu} \zeta_{\alpha \mu}^{\lambda \mathbf{q}*} \zeta_{\alpha \mu}^{\lambda \mathbf{q}}}{2M_\alpha} \Omega_{\lambda \mathbf{q}} \quad (\text{B.5})$$

which ultimately have to be inserted in equation (42).

Appendix C. Partial derivative of the phonon eigenvectors

We will use perturbation theory in order to calculate the partial derivative of the phonon eigenvectors.

First, we linearize the dynamical matrix in terms of the masses:

$$\frac{C_{\alpha \mu, \alpha' \mu'}(\mathbf{q})}{\sqrt{M_\alpha M_{\alpha'}}} = \frac{C_{\alpha \mu, \alpha' \mu'}(\mathbf{q})}{\sqrt{M_\alpha^0 M_{\alpha'}^0}} - \frac{1}{2M_{\alpha''}^0} \left(\delta_{\alpha, \alpha''} \frac{C_{\alpha \mu, \alpha' \mu'}(\mathbf{q})}{\sqrt{M_\alpha^0 M_{\alpha'}^0}} + \delta_{\alpha', \alpha''} \frac{C_{\alpha \mu, \alpha' \mu'}(\mathbf{q})}{\sqrt{M_\alpha^0 M_{\alpha'}^0}} \right) (M_{\alpha''} - M_{\alpha''}^0) \quad (\text{C.1})$$

and then we will calculate the derivative as:

$$\begin{aligned}
\frac{\partial \zeta_{\alpha\mu}^{\lambda\mathbf{q}}}{\partial M_{\alpha''}} &= -\frac{1}{2M_{\alpha''}^0} \sum_{\lambda' \neq \lambda} \zeta_{\alpha\mu}^{\lambda'\mathbf{q}} \frac{\sum_{\alpha_1\mu_1, \alpha_2\mu_2} \zeta_{\alpha_1\mu_1}^{\lambda'\mathbf{q}} * \left(\delta_{\alpha_1\alpha''} \frac{C_{\alpha_1\mu_1, \alpha_2\mu_2}(\mathbf{q})}{\sqrt{M_{\alpha_1}^0 M_{\alpha_2}^0}} + \delta_{\alpha_2\alpha''} \frac{C_{\alpha_1\mu_1, \alpha_2\mu_2}(\mathbf{q})}{\sqrt{M_{\alpha_1}^0 M_{\alpha_2}^0}} \right) \zeta_{\alpha_2\mu_2}^{\lambda\mathbf{q}}}{\Omega_{\lambda'\mathbf{q}}^2 - \Omega_{\lambda\mathbf{q}}^2} \\
&= -\frac{1}{2M_{\alpha''}^0} \sum_{\lambda' \neq \lambda} \zeta_{\alpha\mu}^{\lambda'\mathbf{q}} \frac{\left(\sum_{\mu_1, \alpha_2\mu_2} \zeta_{\alpha''\mu_1}^{\lambda'\mathbf{q}} * \frac{C_{\alpha''\mu_1, \alpha_2\mu_2}(\mathbf{q})}{\sqrt{M_{\alpha''}^0 M_{\alpha_2}^0}} \zeta_{\alpha_2\mu_2}^{\lambda\mathbf{q}} + \sum_{\alpha_1\mu_1, \mu_2} \zeta_{\alpha_1\mu_1}^{\lambda'\mathbf{q}} * \frac{C_{\alpha_1\mu_1, \alpha''\mu_2}(\mathbf{q})}{\sqrt{M_{\alpha_1}^0 M_{\alpha''}^0}} \zeta_{\alpha''\mu_2}^{\lambda\mathbf{q}} \right)}{\Omega_{\lambda'\mathbf{q}}^2 - \Omega_{\lambda\mathbf{q}}^2} \\
&= -\frac{1}{2M_{\alpha''}^0} \sum_{\lambda' \neq \lambda} \zeta_{\alpha\mu}^{\lambda'\mathbf{q}} \frac{(\Omega_{\lambda\mathbf{q}}^2 + \Omega_{\lambda'\mathbf{q}}^2) \sum_{\mu_1} \zeta_{\alpha''\mu_1}^{\lambda'\mathbf{q}} * \zeta_{\alpha''\mu_1}^{\lambda\mathbf{q}}}{\Omega_{\lambda'\mathbf{q}}^2 - \Omega_{\lambda\mathbf{q}}^2}. \tag{C.2}
\end{aligned}$$

Appendix D. Derivative of the deformation potential

Substituting (C.2) and (B.5) in (42), we obtain

$$\begin{aligned}
\frac{\partial V_{\lambda\mathbf{q}}}{\partial M_{\alpha}} &= \sum_{\mu} \left[-\frac{Z_{\alpha}}{2M_{\alpha}\Omega_{\lambda\mathbf{q}}\sqrt{2M_{\alpha}\Omega_{\lambda\mathbf{q}}}} \left(\Omega_{\lambda\mathbf{q}} - \frac{1}{2} \sum_{\mu_1} \zeta_{\alpha\mu_1}^{\lambda\mathbf{q}} * \zeta_{\alpha\mu_1}^{\lambda\mathbf{q}} \Omega_{\lambda\mathbf{q}} \right) \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \tilde{V}_{\alpha\mu;\mathbf{q}}(\mathbf{r}) \sum_{\alpha'} \frac{Z_{\alpha'}}{\sqrt{2M_{\alpha'}\Omega_{\lambda\mathbf{q}}}} \frac{\partial \zeta_{\alpha'\mu}^{\lambda\mathbf{q}}}{\partial M_{\alpha}} \tilde{V}_{\alpha'\mu;\mathbf{q}}(\mathbf{r}) \right] \\
&= \sum_{\mu} \left[-\frac{Z_{\alpha}}{\sqrt{2M_{\alpha}\Omega_{\lambda\mathbf{q}}}} \left(\frac{1 - \frac{1}{2} \sum_{\mu_1} \zeta_{\alpha\mu_1}^{\lambda\mathbf{q}} * \zeta_{\alpha\mu_1}^{\lambda\mathbf{q}}}{2M_{\alpha}} \right) \zeta_{\alpha\mu}^{\lambda\mathbf{q}} \tilde{V}_{\alpha\mu;\mathbf{q}}(\mathbf{r}) \right. \\
&\quad \left. - \sum_{\alpha'} \frac{1}{2M_{\alpha}} \frac{Z_{\alpha'}}{\sqrt{2M_{\alpha'}\Omega_{\lambda\mathbf{q}}}} \sum_{\lambda' \neq \lambda} \frac{(\Omega_{\lambda\mathbf{q}}^2 + \Omega_{\lambda'\mathbf{q}}^2) \sum_{\mu_1} \zeta_{\alpha\mu_1}^{\lambda'\mathbf{q}} * \zeta_{\alpha\mu_1}^{\lambda\mathbf{q}}}{\Omega_{\lambda'\mathbf{q}}^2 - \Omega_{\lambda\mathbf{q}}^2} \zeta_{\alpha'\mu}^{\lambda'\mathbf{q}} \tilde{V}_{\alpha'\mu;\mathbf{q}}(\mathbf{r}) \right]. \tag{D.1}
\end{aligned}$$

Appendix E. Derivatives with respect to Ω

We consider again $I(\xi_1, \xi_2, \Omega)$:

$$\frac{\partial A}{\partial \Omega} = -\beta A (1 + n_{\beta}(\Omega)) \tag{E.1}$$

$$\frac{\partial B_1}{\partial \Omega} = e^{\beta\xi_1} \left[\frac{1 - e^{-\beta(\xi_1 - \xi_2 - \Omega)}}{(\xi_1 - \xi_2 - \Omega)^2} - \frac{\beta e^{-\beta(\xi_1 - \xi_2 - \Omega)}}{\xi_1 - \xi_2 - \Omega} \right] \tag{E.2}$$

$$\frac{\partial B_2}{\partial \Omega} = -e^{\beta\xi_2} \left[\frac{1 - e^{\beta(\xi_1 - \xi_2 + \Omega)}}{(\xi_1 - \xi_2 + \Omega)^2} + \frac{\beta e^{\beta(\xi_1 - \xi_2 + \Omega)}}{\xi_1 - \xi_2 + \Omega} \right] \tag{E.3}$$

$$\begin{aligned}
\frac{\partial I}{\partial \Omega} &= -\beta (1 + n_{\beta}(\Omega)) I + A \left[e^{\beta\xi_1} \left(\frac{1 - e^{-\beta(\xi_1 - \xi_2 - \Omega)}}{(\xi_1 - \xi_2 - \Omega)^2} - \frac{\beta e^{-\beta(\xi_1 - \xi_2 - \Omega)}}{\xi_1 - \xi_2 - \Omega} \right) \right. \\
&\quad \left. + e^{\beta\xi_2} \left(\frac{1 - e^{\beta(\xi_1 - \xi_2 + \Omega)}}{(\xi_1 - \xi_2 + \Omega)^2} + \frac{\beta e^{\beta(\xi_1 - \xi_2 + \Omega)}}{\xi_1 - \xi_2 + \Omega} \right) \right] \tag{E.4}
\end{aligned}$$

$$\frac{\partial}{\partial \Omega} J(\xi_1, \xi_2, \Omega) = \frac{\partial}{\partial \Omega} \tilde{J}(\xi_1, \xi_2, \Omega) + \frac{\partial}{\partial \Omega} \tilde{J}(\xi_1, \xi_2, -\Omega) \tag{E.5}$$

with

$$\begin{aligned}
\frac{\partial}{\partial \Omega} \tilde{J}(\xi_1, \xi_2, \Omega) &= \left[-\frac{f_{\beta}(\xi_1) + n_{\beta}(\Omega)}{(\xi_1 - \xi_2 - \Omega)^2} + \frac{\beta n_{\beta}(\Omega)(1 + n_{\beta}(\Omega))}{\xi_1 - \xi_2 - \Omega} \right] \\
&\quad \times \left[\frac{f_{\beta}(\xi_2) - f_{\beta}(\xi_1 - \Omega)}{\xi_1 - \xi_2 - \Omega} - \beta f_{\beta}(\xi_1 - \Omega) f_{\beta}(\Omega - \xi_1) \right] - \frac{f_{\beta}(\xi_1) + n_{\beta}(\Omega)}{\xi_1 - \xi_2 - \Omega} \\
&\quad \times \left[\frac{f_{\beta}(\xi_2) - f_{\beta}(\xi_1 - \Omega)}{(\xi_1 - \xi_2 - \Omega)^2} + \frac{\beta f_{\beta}(\xi_1 - \Omega) f_{\beta}(\Omega - \xi_1)}{\xi_1 - \xi_2 - \Omega} \right. \\
&\quad \left. - \beta^2 f_{\beta}(\xi_1 - \Omega) f_{\beta}(\Omega - \xi_1) (f_{\beta}(\Omega - \xi_1) - f_{\beta}(\xi_1 - \Omega)) \right]. \tag{E.6}
\end{aligned}$$

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