Electron–phonon effects on the direct band gap in semiconductors: LCAO calculations

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Abstract

Using a perturbative treatment of the electron–phonon interaction, we have studied the effect of phonons on the direct band gap of conventional semiconductors. Our calculations are performed in the framework of the tight-binding linear combination of atomic orbitals (LCAO) approach. Within this scheme we have calculated the temperature and isotopic mass dependence of the lowest direct band gap of several semiconductors with diamond and zincblende structure. Our results reproduce the overall trend of available experimental data for the band gap as a function of temperature, as well as give correctly the mass dependence of the band gap on isotopic. A calculation of conduction band intervalley deformation potentials is also reported. Finally, calculated Debye–Waller factors are compared with X-ray and EXAFS experimental results.

1. Introduction

The energy bands of semiconductors exhibit large shifts with temperature at constant pressure. There are two effects contributing to these shifts: the thermal expansion of the lattice, related to the change of the electron energies with the volume, and the direct renormalization of band energies due to electron–phonon interactions [1].

The change of the direct band gap \( E_g \) with temperature can be written as

\[
\left( \frac{\partial E_g}{\partial T} \right)_p = \left( \frac{\partial E_g}{\partial T} \right)_{\text{EP}} + \left( \frac{\partial E_g}{\partial T} \right)_{\text{TE}},
\]

where the thermal expansion (TE) term can be expressed by

\[
\left( \frac{\partial E_g}{\partial T} \right)_{\text{TE}} = \left( \frac{\partial E_g}{\partial p} \right)_T \left( \frac{\partial \ln V}{\partial \ln V} \right)_T = -3\alpha B \left( \frac{\partial E_g}{\partial p} \right)_T \]

Here, \( \alpha = L^{-1}(\partial L/\partial T) \) is the linear expansion coefficient and the isothermal bulk modulus \( B = -V(\partial p/\partial V)_T \). The gap shifts induced by the thermal expansion are usually obtained from the experimental values of \( \alpha \), \( B \) and the variation of the gap with hydrostatic pressure, which can be directly measured in experiments under high pressure.

The effect of the electron–phonon interaction, on the other hand, implies the calculation of two types of processes: the Debye–Waller (DW) [2] and the self-energy (SE) terms [3]. These terms arise from perturbation theory up to second order and both are proportional to the time averaged square of the atomic displacement \( \mathbf{u} \), i.e. proportional to \( T \) at high temperatures. The DW term is related to the second derivative of the potential with respect to the atomic positions (two-phonon term) taken in first-order perturbation theory and is easier to evaluate. The SE
term contains the first derivative of the crystal potential (electron–one-phonon interaction) taken in second-order perturbation theory (emission and re-absorption of one phonon or vice versa). In order to obtain the SE term we have to sum over all intermediate states, i.e. we have to perform a tedious integration over k space. In many earlier calculations this term has been neglected since it was believed that the DW correction gives the most important contribution to the band gap shift with temperature. However, in recent years it has been increasingly recognized that one has to include both types of terms in order to calculate the correct variation of the band gap with temperature [1,4–7].

Until now, most of the published calculations of the temperature dependence of the band gap, as induced by the electron–phonon interaction, have been performed using the empirical pseudopotential method [5–10]. Although the results obtained with the pseudopotential approach reproduce, within a factor of two, the experimental values, the possibility to calculate the electron–phonon terms by using a tight-binding approach can help to model these terms in more complicated systems, like the zincblende-type copper halides [11,12]. In these compounds the strong hybridization of the cation d-electrons with the anion p-states, near the top of the valence band, complicates an efficient pseudopotential representation [13,14]. Although some work has been done with the pseudopotential formalism, introducing the d-orbitals in an ad hoc manner [11], the treatment of the d-electrons is more efficiently done in the tight-binding framework [14–16].

In this paper, we present a tight-binding calculation of the DW and SE contributions to the temperature dependence of the direct band gap of Ge and selected III–V and II–VI semiconductor compounds. Correspondingly, we have also calculated the dependence of the band gap on isotopic mass. Finally, we calculated within our approach the conduction band intervalley deformation potentials of a set of semiconductor compounds. Correspondingly, we have also calculated the dependence of the band gap on isotopic mass.

2. Method

2.1. LCAO-method: highlights

Although the linear combination of atomic orbitals (LCAO) method is widely known and used, we present here some details in order to illustrate the procedure used in our calculation. For a full description of the model, the interested readers are addressed to the appropriate literature, see for example Refs. [15,18]. In the LCAO method, the electronic wavefunction $\psi_{\kappa}(k)$ (k is the band index and k is the wavevector) is given in terms of Bloch-symmetrized atomic orbitals $\chi_{\mu\kappa k}$ ($\mu$ indicates the orbital and $\kappa$ the atomic specie):

$$\psi_{\kappa}(k) = \sum_{\mu,\kappa} c_{\mu\kappa} \chi_{\mu\kappa k}.$$  

where the eigenvector coefficients $c_{\mu\kappa}$ represent the contribution of the atomic orbital $\mu$ of atom $\kappa$ to a given band $n$ for a given k vector. In order to find the energy dispersion we have to solve the Schrödinger equation:

$$H\psi_{\kappa}(k) = E_{nk} \sum_{\mu,\kappa} c_{\mu\kappa} \chi_{\mu\kappa k}.$$  

Here, we multiply from the left by the function $\langle \chi_{\mu'\kappa' k} |$ and solve the eigenvalue equation:

$$\left[H_{\mu\mu'}^{\kappa\kappa'}(k) - E_{nk}\delta_{\mu'\mu}\delta_{\kappa'\kappa}\right] c_{\mu\kappa} = 0,$$  

where $H_{\mu\mu'}^{\kappa\kappa'}(k)$ are the matrix elements of the crystal Hamiltonian between Bloch sums, and $\delta_{\mu'\mu}\delta_{\kappa'\kappa}$ if the basis functions are orthogonal:

$$H_{\mu\mu'}^{\kappa\kappa'}(k) = \langle \chi_{\mu'\kappa' k} | H | \chi_{\mu\kappa k} \rangle, \quad \delta_{\mu'\mu}\delta_{\kappa'\kappa} = \langle \chi_{\mu'\kappa' k} | \chi_{\mu\kappa k} \rangle$$

and the function

$$\chi_{\mu\kappa k} = \frac{1}{\sqrt{N}} \sum_{I} e^{ik\cdot R_{\mu}} b_{\mu}(r - R_{\mu}).$$

must be a Fourier sum over all the unit cells I, since it represents an orbital function in a translational invariant medium. The functions $b_{\mu}(r - R_{\mu})$ are the atomic orbital functions of atoms localized at $R_{\mu} = I + R_{\mu}$, $R_{\mu}$ being the position of the atomic specie $\kappa$ from the origin of the unit cell.

To describe the diamond and zincblende crystal structures, we use a first-nearest-neighbors tight-binding approach with an orthogonal basis of five atomic orbitals, sp^3s^* per atom in the unit cell. This is the well known semi-empirical LCAO method, which was described by Slater and Koster [19]. Within this model, the sp^3 basis describes the valence band states, whereas the next highest s orbital (s*) is added in order to improve the description of the conduction bands [15,20]. This model has shown to give reasonable results in the calculation of the electronic structure of bulk materials [21,22], heterostructures [23,24] or surface states [25,26]. The model also provides reasonable values of electron deformation potentials [21,27]. Although we cannot guarantee a priori that the calculated variation of the energy gap with temperature or isotopic mass will be given correctly, we will show here that
our results are in good agreement with the experimental data. Spin–orbit effects are not considered in this work but its inclusion is straightforward. In this approach, the overlap matrix is taken as the unit matrix and the Hamiltonian matrix elements are

\[ H_{\mu \nu}(k) = \frac{1}{N} \sum_{\Omega} e^{-i\mathbf{R}_{\nu} \cdot \mathbf{r}} \left[ b_{\mu}(\mathbf{r} - \mathbf{R}_{\nu}) V(\mathbf{r} - \mathbf{R}_{\nu}) b_{\nu}(\mathbf{r} - \mathbf{R}_{\nu}) \right] d^3\mathbf{r}. \] (8)

where the potential can be centered at either \( \mathbf{R}_{\nu} \) or \( \mathbf{R}_{\mu} \), since only two-center integrals are considered (three-center integrals are usually negligible [28]). By choosing \( \Omega \) as the origin to perform the integral, and calling \( I' = I - \Omega \), the sum in \( I \) gives a factor of \( N \) since the overlap integral does not depend on \( \Omega \) and thus we can write

\[ H_{\mu \nu}(k) = \sum_{I'} e^{-i\mathbf{R}_{\nu} \cdot \mathbf{r}} V_{\mu \nu}(\mathbf{R}_{\nu}) \left[ b_{\mu}(\mathbf{r} - \mathbf{R}_{\nu}) b_{\nu}(\mathbf{r} - \mathbf{R}_{\nu}) \right] d^3\mathbf{r}, \] (9)

where \( \mathbf{R}_{\nu} = \mathbf{R}_{\mu} - \mathbf{R}_{\nu} \) are the four nearest neighbors of an atom located at \( \mathbf{R}_{\nu} \) (four possible values of \( I' \)) and the overlap integral \( V_{\mu \nu}(\mathbf{R}_{\nu}) \) depends only on the modulus of \( \mathbf{R}_{\nu} \) (and thus have the property \( V_{\mu \nu} = V_{\nu \mu}^* \)) [15]. These integrals are the well-known tight-binding matrix elements of the Hamiltonian that, in the zincblende compounds, can be defined by 13 parameters describing the interatomic interactions. We have six such on-site matrix elements (\( E_{\mu s}, E_{\mu p}, E_{\mu p'}, E_{\mu p'}, E_{\mu s}, \) and \( E_{\mu p} \)) and seven overlap parameters (\( V_{\mu s}, V_{\mu p}, V_{s p}, V_{s p'}, V_{s p'}, V_{s p}, \) and \( V_{p p} \)) in the first-nearest-neighbor approach. As discussed by Slater and Koster [19], the interatomic matrix elements are sums of products of two-center integrals with phase factors. In our interatomic matrix elements \( V_{\mu \nu}(\mathbf{R}_{\nu}) \), \( \mu \) and \( \nu \) represent the atomic orbitals \( s, p \) or \( s \), and \( k \) or \( k' \) the cation or anion. This matrix elements can be written as a function of the two-center atomic-like integrals \( V_{\mu \nu}^{\text{tot}}, V_{\mu \nu}^{\text{sp}}, V_{\mu \nu}^{\text{sp}}, \) and \( V_{\mu \nu}^{ss} \), and the direction cosines \( \cos(\theta_{\mu \nu}), \cos(\theta_{\mu \nu}), \cos(\theta_{\mu \nu}) \) of the vector \( \mathbf{R}_{\nu} = \mathbf{R}_{\nu} - \mathbf{R}_{\mu} \), the vector pointing from atom \( k \) to \( k' \). In the Slater and Koster tables [19] we find the interaction matrix elements given in terms of the two-center integrals:

\[ V_{\mu \nu}^{\text{tot}} = V_{\mu \nu}^{\text{tot}}, \quad V_{\mu \nu}^{\text{sp}} = \cos(\theta_{\mu \nu}) V_{\mu \nu}^{\text{sp}}, \]
\[ V_{\mu \nu}^{\text{sp}} = \cos(\theta_{\mu \nu}) V_{\mu \nu}^{\text{sp}} + [1 - \cos^2(\theta_{\mu \nu})] V_{\mu \nu}^{ss}, \] (10)
\[ V_{\mu \nu}^{ss} = \cos(\theta_{\mu \nu}) V_{\mu \nu}^{ss}. \]

The missing interatomic elements can be generated by cyclic permutations of \( x, y, \) and \( z \). By solving the eigenvalue problem (eigenvalue), we obtain the eigenvalues \( E_{\nu k} \) and the eigenvectors \( \xi_{\nu k} \) (in our case \( n = 1, 2, ..., 10 \)). We assume spin-degenerate bands: for simplicity spin–orbit coupling is not included. It has not been included in the pseudopotential calculations either.

2.2. Electron–phonon terms

Once the energy dispersion of the bands is known, we must obtain the correction to the energy \( E_{\nu k} \) due to electron–phonon interaction. The electronic interaction with all phonon branches is treated in perturbation theory. The potentials are expanded in a Taylor series around the equilibrium position \( \mathbf{u}_0 = 0 \), with the only leading terms retained. The corresponding shifts of the electronic levels are evaluated in second order perturbation theory. The zero order Hamiltonian, \( H_0 \), gives the unperturbed one-electron states |\( \phi_{\nu k}^0 \rangle \) and band energies \( E_{\nu k}^0 \).

Assuming small thermal displacements \( \mathbf{u} \) from their average positions \( \mathbf{R}_{\nu k} \), the potential energy can be expanded in a Taylor series as:

\[ V = V_0 + \sum_{\nu k} \frac{\partial V}{\partial \mathbf{R}_{\nu k}} \mathbf{u} - \frac{1}{2} \sum_{\nu' k' \nu k} \frac{\partial^2 V}{\partial \mathbf{R}_{\nu k} \partial \mathbf{R}_{\nu' k'}} \mathbf{u}_\nu \mathbf{u}_{\nu'}, \] (11)

where the first derivative refers to the gradient of the potential and the second derivative is a second order tensor (force parameters in lattice dynamics). Since only the potential energy depends on the atomic displacements, the Hamiltonian can be straightforwardly written as the unperturbed Hamiltonian \( H_0 \) plus two small terms, \( H^{(1)} \) and \( H^{(2)} \), linear and quadratic in the displacements, respectively:

\[ H = H_0 + H^{(1)} + H^{(2)}, \] (12)

corresponding to the second and third terms of Eq. (11).

Up to second order in perturbation theory

\[ E_{\nu k} = E_{\nu k}^0 + \left\langle \psi_{\nu k}^0 | H^{(1)} + H^{(2)} | \psi_{\nu k}^0 \right\rangle \]
\[ + \sum_{\nu' k'} \left\langle \psi_{\nu k}^0 | H^{(1)} + H^{(2)} | \psi_{\nu k}^0 \right\rangle \left\langle \psi_{\nu k}^0 | H^{(1)} + H^{(2)} | \psi_{\nu k}^0 \right\rangle, \] (13)

In first-order perturbation theory, only the term containing \( H^{(2)} \) contributes, since the correction due to \( H^{(1)} \), \( \left\langle \psi_{\nu k}^0 | H^{(1)} | \psi_{\nu k}^0 \right\rangle \) vanishes (the forces are zero at the equilibrium positions). In the second-order correction, only the terms in \( H^{(1)} \) provide quadratic terms in \( \mathbf{u}_\nu \); \( H^{(2)} \) twice or the combinations with \( H^{(1)} \) give higher order terms.
in \( u_{\mu} \), which are neglected. By using Eq. (11):
\[
E_{\mu k} = E_{\mu k}^0 + \sum_{k'k} \left\langle \psi_{\mu k}^0 \left| \frac{\partial^2 V}{\partial R_{\mu k} \partial R_{\mu k'}} \right| \psi_{\mu k}^0 \right\rangle 
+ \frac{1}{2} \sum_{k'k} \left( \frac{\partial^2 V}{\partial R_{\mu k} \partial R_{\mu k'}} \right)_{E_{\mu k}} |u_{\mu k}| u_{\mu k'}.
\]

An equivalent result is obtained using the Feynman–Hellman theorem, as has been elegantly shown by Baroni et al. [29]. The first correction in Eq. (14) is called Debye–Waller contribution; the second correction, the self-energy term, can be written as \( \Delta E_{\text{DW}} = \Delta E_{\text{DW}}^0 + \Delta E_{\text{SE}} \).

Fig. 1 shows the Feynman diagrams corresponding to these two terms. The DW term consists of the emission and absorption of a phonon in the same vertex (as corresponds to the second derivative of the potential vs. atomic displacement), while the SE term consists of the emission and successive absorption of a phonon, giving rise to the energy renormalization.

It is worth noting that these two terms are not zero even if the temperature is zero, due to the quantum factor \( \frac{1}{2} \) in the phonon distribution function. In other words, there is an energy correction even at zero temperature.

Our purpose is to write these matrix elements in terms of the overlap integrals or derivatives of the overlap integrals of our tight-binding Hamiltonian. The evaluation of the matrix element corresponding to the Debye–Waller contribution has been given in Appendix A. It can be written in terms of the second derivative of the overlap integrals \( V_{\mu\mu'}^{\mu\mu'} \):

\[
\left\langle \psi_{\mu k}^0 \left| \frac{\partial^2 V}{\partial R_{\mu k} \partial R_{\mu k'}} \right| \psi_{\mu k}^0 \right\rangle = \frac{1}{N} \sum_{\mu\mu' \rho\rho'} c_{\mu\rho\mu'} c_{\mu'\rho'} e^{\text{ik}(R_{\rho k'} - R_{\rho k})} \frac{\partial^2 V^\mu_{\mu'}^{\mu\mu'}}{\partial R_{\mu k} \partial R_{\mu k'}}.
\]

and we can write
\[
\Delta E_{\text{DW}} = \frac{1}{N} \sum_{\mu\mu' \rho\rho'} c_{\mu\rho\mu'} c_{\mu'\rho'} \sum_{k} e^{-i\mathbf{k} \cdot (R_{\rho k'} - R_{\rho k})} \frac{\partial^2 V_{\mu\mu'}^{\mu\mu'}}{\partial R_{\mu k} \partial R_{\mu k'}} \times |u_{\mu k}| u_{\mu k'}.
\]

Here, the atomic displacements can be written in the second quantization formalism, in terms of creation and annihilation operators. To emphasize that the displacements are real, let us write them as
\[
u_{\mu k} = \sum_{qk} \frac{-\hbar}{2NM_s \omega_{qk}} \left[ a_{qk\mu} e^{iqR_{\mu k}} + a^*_{qk\mu} e^{-iqR_{\mu k}} \right],
\]

where \( q \) and \( \omega \) represent phonon wavevector and frequency, \( \lambda \) denotes the phonon branches, \( a_{qk\mu} (a^*_{qk\mu}) \) the phonon annihilation (creation) operators, \( M_s \) the atomic mass of atom \( \kappa \) and \( \nu_{qk} \) the corresponding phonon polarization vector component.

If \( \langle \cdots n_{qk} \cdots \rangle \) represents the phonon eigenvector in the second quantization formalism, it is straightforward to show that
\[
\langle \cdots n_{qk} \cdots | u_{\mu k} u_{\mu k'} | \cdots n_{qk} \cdots \rangle = \frac{\hbar}{2NM_s M_c \omega_{qk}} \times \left( 2n_{qk} + 1 \right) \nu_{qk}^* \nu_{qk} e^{-iqR_{\mu k} + qR_{\mu k'}},
\]

where \( n_{qk} \) represents the number of phonons with wave vector \( q \) in branch \( \lambda \). Substituting in Eq. (16) gives
\[
\Delta E_{\text{DW}} = \sum_{\lambda} \sum_{\mu\mu' \rho\rho'} \sum_{k} c_{\mu\rho\mu'} c_{\mu'\rho'} \sum_{k} e^{\text{i\mathbf{k} \cdot (R_{\rho k'} - R_{\rho k})} \frac{\partial^2 V_{\mu\mu'}^{\mu\mu'}}{\partial R_{\mu k} \partial R_{\mu k'}} \times \frac{\hbar}{2NM_s M_c \omega_{qk}} \times \sum_{\lambda} \left( 2n_{qk} + 1 \right) \nu_{qk}^* \nu_{qk} e^{-i\mathbf{k} \cdot (R_{\rho k'} - R_{\rho k})}.
\]

where the sum in \( \Gamma \) and \( \kappa' \) is substituted by a sum in \( j_{\kappa} \) (all four \( j_{\kappa} \) atoms belong to the \( \kappa' \) atomic species), the four nearest neighbors of atom \( \kappa \) (\( \kappa = 1, 2 \) in diamond and zincblende structure) situated in the unit cell taken as the origin. Also, the sum in orbitals has been referred to \( \mu \), indicating that these are the orbitals belonging to the atoms surrounding the \( \kappa \) atomic species. If we wish to calculate the temperature gap variation, we must replace the number of phonons \( n_{qk} \) by the corresponding Bose–Einstein distribution function
\[
n_{qk} = \frac{1}{e^{\omega_{qk}/kB T} - 1},
\]

\( k_B \) being the Boltzmann constant. On the other hand, at the \( \Gamma \)-point, \( k = 0 \) and the expression becomes simpler.
The second term of Eq. (14) can be written as:

\[ \left\langle \phi_{i,k}^0 \frac{\partial V}{\partial R_{lk}} | \phi_{j,k}^0 \right\rangle = \frac{1}{N} \sum_{\mu \nu} \sum_{k} c_{\mu \nu}^* c_{\mu \nu} e^{-ik \cdot R_{lk}} \frac{\partial V_{\mu \nu}}{\partial R_{lk}} . \]  

(22)

The treatment of the self-energy term is more complex. The reason is that there is an intermediate electronic state which will lead to an integral over the whole BZ for the electronic states, while in the DW term only the \( k = 0 \) point contributes. In a similar way as in the DW case, the matrix element \( \left\langle \phi_{i,k}^0 | V | \phi_{j,k}^0 \right\rangle \) can be written as (see Appendix A):

\[ \left\langle \phi_{i,k}^0 | V | \phi_{j,k}^0 \right\rangle = 1/N \sum_{\mu \nu} \sum_{k} c_{\mu \nu}^* c_{\mu \nu} \frac{1}{4N} \left\langle \psi_{\mu,k}^0 | V | \psi_{\nu,k}^0 \right\rangle . \]

Here, again, we make use of Eq. (18), to obtain

\[ \Delta E_{HE} = \frac{1}{2} \sum_{n,k} \sum_{\mu \nu} \sum_{l \mu} \sum_{j \nu} \sum_{\ell \nu} \sum_{\lambda \mu} c_{\mu \nu}^* c_{\mu \nu} \frac{\hbar}{2M} \left( \sum_{\gamma} \sum_{\delta} \frac{\partial V_{\mu \nu}}{\partial R_{l \mu}} \left( \frac{\partial V_{\nu \lambda}}{\partial R_{\ell \nu}} \right) - \frac{\partial V_{\mu \nu}}{\partial R_{l \mu}} \frac{\partial V_{\lambda \mu}}{\partial R_{\ell \nu}} \right) \]

\[ \times e^{-i(k_{l \mu} R_{\ell \nu} - k_{\ell \nu} R_{l \mu})} \frac{E_{l \mu}^0 - E_{\ell \nu}^0}{E_{l \mu}^0 - E_{k \nu}^0} \]

\[ \times (2n_{k \delta} + 1) \epsilon_{k \nu} \epsilon_{\ell \gamma} \epsilon_{\mu \lambda} . \]

(23)

where \( j_{\nu} \) are the neighbors of \( \kappa \), \( j_{\lambda} \) is a second index of the neighbors of \( \kappa \) and, finally, \( j_{\mu} \) are the neighbors of \( j_{\kappa} \). The same notation is used for the \( \mu \), the orbital index. Again, if we refer to the \( T \) point, \( k = 0 \) and the above expression simplifies.

2.3. Derivatives of the overlap integrals

In the pseudopotential formalism, for example, the potential is expanded in terms of its Fourier components and the dependence on the amplitudes of Bloch phonons can be easily obtained [5]. In the tight-binding approach, however, the potential is unknown. The only parameters of the model are the overlap integrals \( V_{\mu \nu}^0 \), which, in the nearest neighbors approach, are assumed to depend on the distances through an expression of the type [15, 30]

\[ V_{\mu \nu}^0 (r) = V_{\mu \nu}^0 (r_0) \left( \frac{r_0}{r} \right)^n . \]

(25)

Taking \( n = 2 \) for all the orbitals involved in the matrix elements corresponds to the well known Harrison’s scaling law [15]. However, recent studies show that using somewhat different values for the exponents \( n \), depending on the orbitals being coupled, results in a better description of band structure related phenomena [30–33]. In the present work we have used the most reliable values found in the literature, as will be discussed in Section 4. They reproduce reasonably well the temperature dependence of the band gap in the semiconductors under consideration.

From Eq. (25), the first-order derivative of the overlap integrals becomes:

\[ \frac{\partial V_{\mu \nu}^0}{\partial \mu_{\lambda \kappa}} = -n \frac{\partial V_{\mu \nu}^0}{\partial R_{\lambda \nu}} R_{\lambda \nu} - R_{\lambda \nu}^0 \]

where \( \mu_{\lambda \kappa} = a_0 \sqrt{3}/4 \) is the equilibrium distance in the zincblende compounds, \( a_0 \) being the cubic lattice parameter. The second-order derivative results in the more complex expression:

\[ \frac{\partial^2 V_{\mu \nu}^0}{\partial \mu_{\lambda \kappa} \partial \mu_{\gamma \delta}} = -\frac{n \frac{\partial V_{\mu \nu}^0}{\partial \mu_{\lambda \kappa}}}{R_{\lambda \nu}^2} \frac{\partial V_{\lambda \mu}}{\partial R_{\gamma \delta}} + \left( \frac{n + 1}{R_{\lambda \nu}^2} \right) \left( R_{\lambda \nu} - R_{\lambda \nu}^0 \right) \left( R_{\kappa \mu} - R_{\kappa \mu}^0 \right) \]

where \( I \) is the identity matrix and \( \otimes \) represents the diadic product, which gives rise to a 3 x 3 matrix. In our approach, and without loss of generality, we take as origin the atom \( \kappa \) of the \( T \) point, \( k = 0 \) and the above expression simplifies.

Thus, from the dependence of the interatomic matrix elements on distance (Eqs. (26) and (27)), \( \Delta E_{HE}(T) \) can be evaluated following Eqs. (19) and (24). As we have already stressed, here we use values for the exponent \( n \), Eq. (25), which differ from Harrison’s value \( n = 2 \). Following the parametrization of Ref. [33], we use \( n_{ss} = 3.25, n_{sp} = 2.5, n_{pp} = 3.0 \), and \( n_{pp} = 1.5 \). In order to obtain the gap variation with \( T \) we have to calculate the contribution of electron–phonon interaction on both the conduction and valence bands.

The tight-binding Hamiltonian provides a set of electronic states to generate electron eigenvectors. But, in order to calculate the electron–phonon interaction we also need a reliable set of \( a_{\kappa k} \) and \( \epsilon_{\kappa k} \). We have used different lattice-dynamical models based on the parameters available in the literature for the different compounds we have selected. When different sets of parameters were available for a given component we chose the set that gives the best known eigenvectors at several high-symmetry points. A
common problem in lattice-dynamics calculations is that the parameters of the model are obtained from a minimization procedure where only eigenvalues (sometimes also sound velocities) at different high-symmetry points are used: There is no guarantee that the lattice dynamics obtained in this manner yields correct eigenvectors.

In the electron–phonon calculations we have used either the shell model (SM) [34–36], the rigid-ion model (RIM) [37–39] or the bond charge model (BCM) [40,41].

2.4. Thermal expansion

The thermal expansion correction to the gap variation can be straightforwardly calculated. The corrected gap \( E_g(T) \) is given, in terms of the gap at 0 K by:

\[
\Delta E_g(T)_{\text{TE}} = \int_0^T \left( \frac{\partial E_g}{\partial T} \right)_{\text{TE}} dT' = -3B \left( \frac{\partial E_g}{\partial p} \right) \int_0^T \alpha(T')dT'.
\]

(28)

The values \( \alpha = \alpha(T) \) can be calculated using the anharmonic lattice dynamics [42] or by interpolating and integrating numerically experimental data, when available. Here we have used the second option, since the main purpose of our calculations is to treat the electron–phonon interaction.

3. Results and discussion

3.1. Mean square displacements and displacement correlation function

The square of the displacements of a given atom can be calculated by taking \( \mathbf{l} = \mathbf{l}' \) and \( \mathbf{k} = \mathbf{k}' \) in Eq. (18) and performing the sum in \( \mathbf{q} \) and \( \lambda \). We must then take the thermal average by replacing the number of phonons \( n_{q\lambda} \) by the Bose–Einstein distribution functions [45]. The result is

\[
\langle u_l^2 \rangle = \frac{h}{N M_\lambda} \sum_{q\lambda} \frac{1}{\alpha_{q\lambda}} \left[ 2 n_{q\lambda} + 1 \right].
\]

(29)

In general, \( \langle u_l^2 \rangle \) depends on the phonon eigenvectors and provides a test for the semiempirical lattice-dynamics. The displacements, actually the Debye–Waller factor, can be obtained from X-ray diffraction data as a function of temperature (the so called temperature coefficients or temperature ellipsoids of crystallographers). Unfortunately, due to the lack of experimental results, the comparison with all our data is not always possible.

Table 1 shows calculations of \( \langle u_l^2 \rangle \) performed with different lattice-dynamics models for several diamond and zincblende-type semiconductors compared with available experimental data. As we can appreciate, our calculations

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* Ref. [43].

b This work.
Again, the phonon occupation number \( n \) corresponds to the data obtained with the SM, while the different atomic positions of the neighbors: while for the DCF we obtain a phase which accounts for the so called mean-square relative displacement (MSRD) along the line which joins the neighbor atom with the reference one. The MSRD \( \sigma_{\text{MSRD}}^2 \) is defined as [46,47]:

\[
\sigma_{\text{MSRD}}^2 = \langle \langle \hat{r} (\mathbf{u}_s - \mathbf{u}_e) \rangle^2 \rangle,
\]

where the atom at \( \mathbf{R}_s \) is taken as the origin and \( \hat{r} \) is a unit vector along \( \mathbf{R}_e - \mathbf{R}_s \). By expanding Eq. (30), we obtain three terms

\[
\sigma_{\text{MSRD}}^2 = \langle \langle \hat{r} \mathbf{u}_s \rangle^2 \rangle + \langle \langle \hat{r} \mathbf{u}_e \rangle^2 \rangle - 2 \langle \langle \hat{r} \mathbf{u}_s \rangle \langle \hat{r} \mathbf{u}_e \rangle \rangle).
\]

The first two terms are MSD (projected along \( \hat{r} \)), while the third term is called displacement correlation function (DCF), which really gives information on the difference of atomic displacements. The calculation of the DCF is a hard test of a lattice dynamics model. The model has to supply the right eigenvectors in modulus and sign in order to provide reasonable values of DCF, which is not always the case. The projected MSD can be easily calculated from Eq. (29)

\[
\langle \langle \mathbf{u}_s \rangle^2 \rangle = \frac{\hbar}{2N\hbar_0^2} \sum_{q}\sum_{k} \frac{1}{\omega_{qk}^2} \left[ \hat{r} \mathbf{q}_{k} \right]^2 \left[ n_{qk} + \frac{1}{2} \right],
\]

while for the DCF we obtain a phase which accounts for the different atomic positions of the neighbors:

\[
-2 \langle \langle \hat{r} \mathbf{u}_s \rangle \langle \hat{r} \mathbf{u}_e \rangle \rangle = -\frac{2\hbar}{2N\hbar_0^2} \sum_{q} \frac{1}{\omega_{qk}^2} \left( \hat{r} \mathbf{q}_{k} \right)^2 \left[ n_{qk} + \frac{1}{2} \right].
\]

Again, the phonon occupation number \( n_{qk} \) must be substituted by the Bose–Einstein function to calculate the displacements at a given \( T \).

We have calculated the MSRD in Ge by using the SM and the BCM. Both models give reasonable values of atomic displacements (in Table 1 only the SM results are given). Our calculations are compared with the MSRD obtained from EXAFS measurements [48,49] as a function of \( T \). In Fig. 2 we show the calculations, together with the experimental data, taken from Refs. [48,49]. The solid line corresponds to the data obtained with the SM, while the dashed line was obtained with the BCM. Our data agrees quite well with the experimental results, the difference between the models being negligible. The shift of the experimental data to higher values is due to dislocation and other defects (static inhomogeneities), which gives a temperature independent contribution [47,48].

Fig. 3 shows experimental data of EXAFS in GaSb obtained from Ref. [50], together with our calculations using the SM and BCM. The MSRD has been multiplied by two in order to compare directly with the data of Ref. [50]. Both models reproduce the experiment, within the uncertainty of the experimental points, which is larger than in the case of Ge. The sample used here seems to be of better quality than Ge, since the contribution of the static inhomogeneity is smaller.

### 3.2. Temperature dependence of \( \Delta E_g(T) \)

In this section we discuss the results obtained for the gap renormalization as a function of temperature for Ge, and some III–V and II–VI semiconductors. In Figs. 4–9 we show the results of our calculations and compare them with available experimental data. In all the figures, the full and/or open circles represent experimental values, the dotted line represents the thermal expansion (TE) contribution to \( \Delta E_g \), calculated using Eq. (2) and experimental data for \( \alpha \).
Fig. 3. Squared amplitude of projected relative displacements of GaSb atomic distance. The experimental values are from Ref. [50] (dots) and the solid (SM) and dashed (BCM) lines have been obtained with Eq. (30).

Fig. 4. Temperature dependence of $\Delta E_g$ for Ge. The experimental values [56] are represented by dots. The dotted line represents the thermal expansion contribution to the gap variation. The total contribution (TE + EP terms) to $\Delta E_g$ is represented by solid (SM) and dashed (BCM) lines.

### Table 2

<table>
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<th>$\Delta E_g(0)$ (renormalization)</th>
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<td>Experimental</td>
<td>Calculated</td>
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<td>GaAs</td>
<td>0.034$^d$</td>
<td>0.045$^b$</td>
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<td>InSb</td>
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<td>ZnS</td>
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<tr>
<td>CdTe</td>
<td>0.014$^j$</td>
<td>0.024$^g$</td>
</tr>
</tbody>
</table>

---

$^a$ Ref. [56].  
$^b$ Shell model calculations.  
$^c$ Bond charge model calculations.  
$^d$ Ref. [60].  
$^e$ Ref. [67].  
$^f$ Ref. [63].  
$^g$ Rigid ion model calculations.  
$^h$ Ref. [44].  
$^i$ Ref. [61].  
$^j$ Ref. [64].
The total contribution (TE + EP terms) to $\Delta E_g$ is represented by solid (SM or RIM) and dashed (BCM) lines. Table 2 displays the band gap renormalization due to electron–phonon interaction at 0 K and the slope of the curve (temperature coefficient of the gap) at high $T$. The zero-temperature gap renormalization has been obtained from the references given in the table by extrapolating the linear behavior found at high temperature to $T=0$ (for the discussion of this procedure, see Ref. [58]). Our calculated data are compared with experimental results.

Fig. 4 shows the calculated and measured values of $\Delta E_g(T)$ for Ge. The experimental data are from Ref. [56]. The contribution to $\Delta E_g$ in Ge has been calculated by using two different models for the dynamics, the SM (solid line) and the BCM (dashed line). For the SM we have used the parameters given in Ref. [35] and the BCM calculations have been done using the parameters given by Weber [40].

As can be appreciated in Fig. 4, the calculated shifts overestimate the experimental values of $\Delta E_g$, although those obtained using the BCM come closer to them. It is worth mentioning that the calculated $\Delta E_g(T)$, for both models, deviates from the experimental data by an amount similar to that found in early calculations [5]. Table 2 shows that both, the calculated linear temperature coefficient of the gap, and the gap renormalization, are overestimated by 45%. In spite of this, the overall trends of the calculations are in agreement with the measured values.

In a recent work, Lärrsen et al. have measured the variation of the excitonic gap of GaAs in the temperature range 4–60 K. In Fig. 5 we show their experimental data and the calculations obtained with two lattice-dynamics models under consideration, the SM (solid line) and the BCM (dashed line). The agreement with the experiment is excellent, especially for the SM calculations. The thermal expansion contribution is nearly negligible in this temperature range. At this point we would like to emphasize that there are no fitting parameters in these calculations. The input parameters are well known parameters which fit the phonon dispersion curves and the electronic band structure. The whole temperature range has also been studied (Fig. 6) and compared with the experimental data of Grilli et al. [60]. Our calculations are close to the experimental data in the whole temperature range, although the SM gives a somewhat better agreement.

In Fig. 7 we show the calculations for another III–V compound, InSb. The experimental data are from Ref. [62]. The calculations are also in good agreement with the experimental data, especially those performed using the SM
lattice-dynamics agree rather closely with the experiment. In Table 2 we can observe how the calculated ‘high temperature’ coefficient of the gap has nearly the same value as the experimental one. The calculated zero-temperature gap renormalization also agrees well with the experiment. The SM seems to provide better values for the electron–phonon interaction in the case of II–VI compounds.

We have also calculated the variation of the gap with temperature for a few II–VI compounds. Fig. 8 compares our calculations with the experimental data of Ref. [44] (dots) and Ref. [63] (open circles) for ZnSe. Our calculations were performed using the RIM for the lattice-dynamics [38]. We have found that the BCM (with the set of parameters found in the literature [41,59]) describes incorrectly the eigenvectors of the longitudinal phonons at the X-point. The calculations overestimate the experimental variation by 45%, like in the case of Ge (see Table 2).

Finally, Fig. 9 shows the results for CdTe. In this figure three experimental sets are displayed: the full circles are the measurements of Kim et al. [61], the open circles the ones obtained from Laurenti et al. [64] and the open triangles are some recent results of Fonthal et al. [65]. There are significant differences between different experimental data sets. The first two experimental results were fitted with a Varshni equation [63]. These fits lead to significantly different parameters. Kim et al. [61] used the values $\alpha = 4.5 \times 10^{-4}$ eV K$^{-1}$ and $\beta = 46$ K, while Laurenti et al. [64] used $\alpha = 3.25 \times 10^{-4}$ eV K$^{-1}$, $\beta = 78.2$ K for the parameters in that equation. The results of Fonthal et al. deviate significantly from Varshni’s expression, they are better fitted with a Manoogian–Wooley expression [66], i.e. even the gap dependence with temperature is different for the different experimental results. Our calculations (solid line), performed with the RIM [39], compare reasonably well with the measurements of Kim et al. [61], while they overestimate the data of Laurenti et al. [64].

In Table 2 we compare the calculated and experimental gap renormalization $\Delta E_g(T)$, and the linear temperature coefficient for Ge, GaAs, InSb, ZnS, ZnSe, ZnTe and CdTe. It is clear from the listed values that our calculated $\Delta E_g(T)$ are in good agreement with the extrapolated experimental values. The calculated linear temperature coefficient for InSb shows good agreement with the experimental value, while for ZnS and ZnTe our calculations overestimate, almost by a factor of two, the experimental values. Although our calculations, in general, show the correct trend of $\Delta E_g(T)$, there are noticeable discrepancies for some of the II–VI compounds, as we can appreciate in Table 2.
of the temperature effect, we can separate the dependence of the electron–phonon interaction. Actually, as in the case on the mass will affect the gap renormalization as account

$$\frac{\partial E_g}{\partial M} = E_{EP} + E_{TE}.$$  

The first term in the RHS of Eq. (35) represents the contribution of the electron–phonon interaction at constant volume, while the second term is the contribution from the change of lattice constant with the isotopic mass. This term has the same origin as the thermal expansion term, the ‘zero-point vibrations’, and it can be called a ‘zero-point thermal expansion’ contribution at 0 K. It can be written as

$$\left( \frac{\partial E_g}{\partial M} \right)_{TE} = -3B \left( \frac{\partial E_g}{\partial \ln a} \right) M \left( \frac{\partial \ln a}{\partial M} \right).$$  

In principle, the contribution of the factors in the RHS of Eq. (36) can be obtained in a similar way as for the calculations undertaken in Section 3.2. The lack of experimental data for the change of the lattice constant with isotopic mass, however, is an important handicap to generate reliable results for comparison with experimental values. Data on the lattice parameter with the mass were found for three of the compounds studied in this work: Ge, GaAs, and ZnSe.

The electron–phonon terms, on the other hand, have been calculated using the same scheme that we have used to calculate the temperature dependence of $E_g$. First, we set the temperature to zero. Then, we take the derivative of the gap with respect to the isotopic mass (actually we calculate the energy for three different values of isotopic mass and take the slope of the fitting straight line). Hence, these calculations contain no additional parameters. Table 3 lists the calculated derivatives of the gap with respect to isotopic mass for the compounds studied in this work. The sum of the volume renormalization (TE) and electron–phonon (EP) contributions, in the cases where the former is known, Refs. [51,52,68,69], is listed under ‘Total’. Agreement with experiment is quite reasonable. We also list in Table 3 the calculated values of $(\partial E_g/\partial M)_{T=0}$ given in Ref. [69]. The magnitude of the contribution arising from the volume renormalization has been estimated using the measured values for Ge [68] and the calculations based on empirical lattice-dynamics for GaAs and ZnSe [69]. Since we do not have information about the volume term for all the calculated compounds, we are unable to complete the list. However, we have listed the calculated EP term for all the compounds studied in this work. It is interesting to notice that the EP coefficient for In in InSb has negative sign, although small in absolute value.

Compared with the experimental values shown in Table 3, it is possible to observe that our total calculated values agree better for Ge and for ZnSe than for GaAs. For GaAs our calculated values represent almost 70% of the experimental ones. Comparison with the empirical pseudo-potential calculations of Garro et al. [69] shows that, while their calculations overestimate the measured values our calculations show better agreement.
3.4. Intervalley deformation potentials

In this section we will calculate the intervalley deformation potentials (DPs) by using the formalism developed in Section 2. The process which will be analyzed is the following: an electron at the bottom of the conduction band at the \( G \) point (initial state) is scattered by a phonon to the bottom of the conduction band at the X or L valleys (final state). The matrix element corresponding to this process can be written as:

\[
\langle k^q|n^q_l\rangle^1_lH(1)l_{k^nq_l} \quad (37)
\]

where \( H(1) \) is the first term in the Taylor expansion of the potential in the phonon displacement (see Eq. (12)). The Hamiltonian must contain only one creation or annihilation phonon operator. In the initial state, our electron has a Bloch wave function \( l_{k^n} \) and, in particular, the number of phonons with wavevector \( q \) in the branch \( l \) is \( n^q_l \):

After the absorption or emission of a phonon with wavevector \( q \) (branch \( l \)), the electron is in its final state, whose Bloch function can be written as \( l_{k^nq_l} \) and the number of phonons for this particular \( q \) vector and branch will increase (phonon emission) or decrease (phonon absorption) by one unit. This process satisfy well known selection rules[21,71].

Basically, the symmetry of the phonon which couples the two conduction bands must be included in the expansion of the direct product of the symmetry representations corresponding to the electron wave functions. At this point we have to keep in mind that the symmetry of electron and phonon wave functions can depend on the origin of the unit cell. For instance, in zincblende semiconductors, if we choose the anion at the origin of the unit cell, the electron \( X^1 \) symmetry is composed mainly of anion s wave function and cation p wave function. On the other hand, the \( X^3 \) electron wave function contains the p anion wave function and s cation wave function. However, if the origin is chosen at the cation, the role of \( X^1 \) and \( X^3 \) reverses [72]. We have chosen the anion at the origin, both in our tight-binding Hamiltonian and in the lattice-dynamics, to guarantee the fulfilment of the selection rules.

Since the transverse phonons have \( X^5 \) symmetry, they do not contribute to the scattering between the \( T^1 \) and \( X_{1,3} \) states [73]. The longitudinal acoustic and optic phonons (LA and LO) have \( X^1 \) and \( X^3 \) symmetry, respectively, and thus

### Table 3

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<th>Comp</th>
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<th>( \langle \partial E_p/\partial M \rangle_{TE} )</th>
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<tr>
<td>As</td>
<td>As</td>
<td>0.223(^a)</td>
<td>0.233(^b)</td>
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<td>CdTe</td>
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\(^a\) Shell model calculations.
\(^b\) Bond charge model calculations.
\(^c\) Ref. [69].
\(^d\) Ref. [68].
\(^e\) Values taken from Ref. [69].
\(^f\) Arsenic has only one stable isotope.
\(^g\) Rigid ion model calculations.
\(^h\) Ref. [70].

### Table 4

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</table>
they will contribute. If the anion is heavier than the cation, then the $X_1$ phonon mode has higher energy (LO) than the $X_2$ (LA). On the other hand, if the cation is heavier than the anion, the symmetry for the phonon modes is reversed. For the $\Gamma-L$ scattering, both the LA and LO phonons have $L_1$ symmetry and contribute to scattering processes at the lowest conduction $L$ band ($L_2$), whereas transverse phonon scattering (having $L_3$ symmetry) is forbidden [73].

We define the deformation potential (DP) constants $D(q,\lambda,k)$ for the scattering through emission or absorption of a phonon with wave vector $q$ and mode $\lambda$ as

$$|\langle k \pm q | H_2 | k \rangle| = \left( \frac{\hbar^2 N_{kq}}{2N_{0\lambda k}} \right)^{1/2} D(q,\lambda,k),$$  

(38)

$$D(q,\lambda,k) = \frac{\partial V}{\partial d} \tilde{\tilde{f}} \sum_{\sigma} \left\{ \frac{e^{2ikq}\delta d}{\sqrt{M_c/M}} - \frac{e^{-2kq}}{\sqrt{M_c/M}} \right\} e^{2ik(\sigma-k)\sigma},$$  

(39)

where $M$ is the mass of the unit cell, and the other quantities are defined in Section 2.2. In Eqs. (38) and (39) $D$ is in units of energy.

Table 4 contains the calculated DPs for $\Gamma-X$ and $\Gamma-L$ scattering. The values for $D_{\Gamma-X}$ are in the range of those reported in the literature [27,73]. The calculated DPs seem to be smaller than the experimental values, however, this fact has been also reported in the pseudopotential calculations performed by Zollner et al. [73] Table 4 shows the wrong symmetry at the $X$-point for InSb, ZnS, and CdTe. The anomalous signs for InSb are due to the dynamical model permutation of the LA and LO phonon modes at $X$. That is, although for InSb the anion is heavier than the cation, we have found that the calculated eigenvectors predict that the LA phonon mode will have cation character while the LO phonon mode will be of anion character. For ZnS, the cation is heavier than the anion, for this reason the LO phonon mode has $X_3$ symmetry while the LA mode has $X_1$ symmetry. The results for CdTe have a different origin. Here the reason is that the electronic $X$ states have opposite symmetry, compared with those of GaAs. In other words, the lower state has even parity (s-like character at the group-II atom), whereas the upper state has odd parity (p-like character at the group-II atom), as it has been show for other compounds, and from this fact the calculated IV DPs do not violate the selection rules. For the rest of the calculated compounds the calculated DPs obey the selection rules.

4. Conclusions

Using a perturbative treatment of the electron–phonon terms we have calculated, within the tight-binding approximation, the temperature and isotopic mass dependence of the direct band gap (at $k = 0$) in conventional group IV, III–V, and II–VI semiconductors. Our calculated temperature dependence of $\Delta E_g(T)$ compares reasonably well with recent measurements of GaAs, as well as for other III–V and II–VI semiconductor compounds. Within this approach, our calculated shift of $E_g$ with isotopic mass is predicted to be within 30% of the measured one. As a further application of our approach, we have calculated the intervalley deformation potentials for a series of semiconductors. In this way we show that our tight-binding Hamiltonian satisfies appropriate selection rules. We have found that the intervalley deformation potentials are in the range of the values reported in the literature.

Acknowledgments

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Appendix A

Let us write as $\langle \Psi_k^\mu | \delta^2 V/\delta u_{\mu} \partial u_{\nu} | \Psi_k^0 \rangle$ the matrix element corresponding to the second derivative of the potential. Our result must be given in terms of the derivatives of the overlap integrals of the potential, since these are the only known parameters in the tight-binding approach. The function of an electron with wave vector $k$ in the band $n$ (Bloch function) can be written, in the LCAO approximation, as:

$$\Psi_k^\mu = \frac{1}{\sqrt{N}} \sum_{nk} c_{n\mu} \sum_{\Delta} e^{ikR_\mu} b_n(r - R_{nk}).$$  

(A1)

Substituting in the expression of the matrix element $\langle \Psi_k^\mu | \delta^2 V/\delta u_{\mu} \partial u_{\nu} | \Psi_k^0 \rangle$ we have:

$$\langle \Psi_k^\mu | \delta^2 V/\delta u_{\mu} \partial u_{\nu} | \Psi_k^0 \rangle = \frac{1}{N} \sum_{\mu \nu \sigma \alpha} c_{n\mu n\nu}^* c_{n\nu n\alpha} \sum_{\Delta \Delta'} e^{-i(kR_{\mu\nu} - R_{\nu\alpha})}$$  

$$\times \int b_n^*(r - R_{\nu\alpha}) \left( \delta^2 V/\delta u_{\mu} \partial u_{\alpha} \right) b_n(r - R_{\mu\nu}) d^3r.$$  

(A2)

Since we are dealing with the unperturbed wave function $\Psi_k^0$, the matrix element of the derivative of the potential between two orbital functions can be written as the derivative of the overlap integral (the orbital functions do not depend on the displacement $u_\mu$ within the spirit of the tight-binding approximation [15]. All changes in atomic
positions appears simply as changes in the potential):
\[
\int b^*_\mu(r - R_{f,e}) \left( \frac{\partial^2 V}{\partial n_{\mu} \partial n_{\nu}} \right) b^{*\nu}_{\nu}(r - R_{f,e}) d^4r
\]
\[
= \frac{\partial^2}{\partial n_{\mu} \partial n_{\nu}} \int b^*_\mu(r - R_{f,e}) V b^{*\nu}_{\nu}(r - R_{f,e}) d^4r. \tag{A3}
\]

We are taking the derivative of the overlap integral between two atoms which obviously must be the situated at \(R_{\text{b}}\) and \(R_{f,e}\), i.e. \(\Gamma^f = \Gamma, \Gamma^e = \Gamma\)' and \(\hat{k}^f = \hat{k}\). In any other case the derivative vanishes. Thus
\[
\langle \Psi_{\text{b}} | \frac{\partial^2 V}{\partial n_{\mu} \partial n_{\nu}} | \Psi_{\text{b}} \rangle
\]
\[
= \frac{1}{N} \sum_{\mu \neq \nu} \kappa_{\mu} \kappa_{\nu} \kappa_{\mu \nu} \sum_{\Gamma} c^{-ik_{\mu} R_{f,e} - k_{\nu} R_{f,e}} \frac{\partial^2 V^{\kappa_{\mu} \kappa_{\nu}}}{\partial R_{\mu} \partial R_{\nu}}, \tag{A4}
\]
in agreement with the notation introduced in Eq. (8).

This complete Debye–Wallner term consists of the sum in the unit cells \(I\) and \(I'\) multiplied by the displacements.

By following the same procedure, we can obtain the matrix element corresponding to the first derivative of the potential:
\[
\langle \Psi_{\text{b}} | \frac{\partial V}{\partial R_{\mu}} | \Psi_{\text{b}} \rangle
\]
\[
= \frac{1}{N} \sum_{\mu \neq \nu} \kappa_{\mu} \kappa_{\nu} \kappa_{\mu \nu} \sum_{\Gamma} c^{-ik_{\mu} R_{f,e} - k_{\nu} R_{f,e}} \frac{\partial V^{\kappa_{\mu} \kappa_{\nu}}}{\partial R_{\mu}}
\times \int d^4r b^*_\mu(r - R_{f,e}) V b^{*\nu}_{\nu}(r - R_{f,e}) d^4r \tag{A5}
\]
\[
= \frac{1}{N} \sum_{\mu \neq \nu} \kappa_{\mu} \kappa_{\nu} \kappa_{\mu \nu} \sum_{\Gamma} c^{-ik_{\mu} R_{f,e} - k_{\nu} R_{f,e}} \frac{\partial V^{\kappa_{\mu} \kappa_{\nu}}}{\partial R_{\mu}}
+ \frac{1}{N} \sum_{\mu \neq \nu} \kappa_{\mu} \kappa_{\nu} \kappa_{\mu \nu} \sum_{\Gamma} c^{-ik_{\mu} R_{f,e} - k_{\nu} R_{f,e}} \frac{\partial V^{\kappa_{\mu} \kappa_{\nu}}}{\partial R_{\mu}}. \tag{A5}
\]

References