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Strain-induced birefringence in GaAs

Raynolds, James Edward, Ph.D.

The Ohio State University, 1994

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300 N. Zeeb Rd.
Ann Arbor, MI 48106

STRAIN-INDUCED BIREFRINGENCE IN GaAs

DISSERTATION

Presented in Partial Fulfillment of the Requirement for
the Degree of Doctor of Philosophy in the Graduate
School of The Ohio State University

by

JAMES E. RAYNOLDS, B.S., M.S.

* * * * *

The Ohio State University

1994

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To My Family and Friends

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CHAPTER I

Introduction and Background

The focus of this work is the accurate *first principles* calculation of the photoelastic tensor in the zinc-blende semiconductor GaAs. These calculations, which demand the highly-accurate convergence of a small difference of two large quantities, led to the confrontation of integrals over highly-oscillatory and sharply-peaked integrands in the Brillouin zone. The characterization of these pathological integrals and the resulting development of novel Brillouin zone integration techniques has led to a better understanding of the physics of the photoelastic effect in GaAs. In particular, for photon frequencies below the fundamental band gap (the only frequency range considered), the major source of the frequency dispersion is seen to arise from a tiny region of the Brillouin zone which comprises less than 2% of the zone volume. The sampling of this all-important “critical region” of the Brillouin zone, in which much cancellation takes place, is almost entirely missed by all but the highest-density meshes, which supercomputer resources will allow, when traditional sampling methods are used. An analytical investigation into the origin of the numerical difficulties, using second-order $\vec{k} \cdot \vec{p}$ theory, has been carried out with the result that the sharp-peaked nature of the integrand is explained as a consequence of the direct band gap at the zone center, and the oscillations as being due to the structure of the energy bands and wavefunctions in the neighborhood of the zone center. The oscillations are characterized in terms of spherical-harmonic expansions and analytical expressions for the expansion coefficients are presented in the form

of power series in k . Comparisons are made between spherical-harmonic expansion coefficients which are numerically-projected from our *ab initio* results and the analytical forms with favorable results demonstrating that the $\vec{k} \cdot \vec{p}$ theory provides a satisfactory description of the small- k behavior of the Brillouin zone integrands.

1.1 Overview of the thesis

Chapter 1 reviews aspects of the classical theory of light-propagation in a dispersive material, introducing the dielectric tensor and the concept of strain-induced birefringence and its corresponding susceptibility – the photoelastic tensor – followed by a summary of the major results of the thesis.

Chapter 2 presents a detailed review of our *ab initio* methods based on the density-functional theory in a plane wave-pseudopotential context. The computational solution of the ground-state problem is reviewed followed by a discussion of pseudopotentials. Difficulties with the density-functional theory with regard to the calculation of excited-state properties, in particular the calculation of band gaps in semiconductors, are discussed and their resolution in the context of the quasiparticle *GW* theory are considered. Optical response theory in the scissors operator formalism, which overcomes the difficulties of the band gap problem and allows for highly accurate calculations of dielectric functions in semiconductors is presented. The procedure by which local-field effects are included in our self-consistent procedure are also explained.

In Chapter 3, the effects of applied strains in terms of the symmetry properties of the Brillouin zone integrals which give rise to the dielectric and photoelastic

tensors are discussed. Kleinman's internal strain parameter ζ in the context of [111] strains is also discussed.

One of the major difficulties of this project, the accurate integration of highly oscillatory, sharply-peaked functions in the Brillouin zone is discussed in chapter 4. A detailed discussion of the means by which these pathological integrands were characterized and the novel integration methods which were developed to achieve extremely accurate results for these integrals is presented.

Chapter 5 presents the results of our calculations in comparison with experimental measurements. Dramatic improvement of the frequency-dispersion of the photoelastic tensor as well as significant corrections to the static value is obtained using our new integration methods. Detailed convergence studies and comparisons between the numerical and analytical characterization of the Brillouin zone integrands are also presented.

Chapter 6 summarizes the dissertation and suggests possible directions for future research.

1.2 Propagation of light in a material

Light propagating through a medium is described by Maxwell's displacement field $\vec{D}$ which is related to the macroscopic field $\vec{E}$ through the relation:

$$\vec{D}(\vec{r}, t) = \vec{E}(\vec{r}, t) + 4\pi\vec{P}(\vec{r}, t), \quad (1.1)$$

where $\vec{P}(\vec{r}, t)$ is the induced macroscopic polarization of the electrons in the material due to the electric field $\vec{E}(\vec{r}, t)$.

Linear response theory assumes a linear relationship between the macroscopic field and the induced polarization

$$P_i(\vec{q}, \omega) \equiv \frac{\varepsilon_{ij}(\vec{q}, \omega) - \delta_{ij}}{4\pi} E_j(\vec{q}, \omega), \quad (1.2)$$

where we sum over repeated indicies and have expressed the fields as Fourier expansions

$$\vec{E}(\vec{r}, t) = \int d^3q \int d\omega \vec{E}(\vec{q}, \omega) e^{i(\vec{q} \cdot \vec{r} - \omega t)}, \quad (1.3)$$

$$\vec{D}(\vec{r}, t) = \int d^3q \int d\omega \vec{D}(\vec{q}, \omega) e^{i(\vec{q} \cdot \vec{r} - \omega t)}, \quad (1.4)$$

and expressed the relationship, Eq. (1.2), in terms of the Fourier components of the fields. Equation (1.2) constitutes the definition of the dielectric function $\varepsilon_{ij}(\vec{q}, \omega)$. Since $\vec{P}$ and $\vec{E}$ are vectors, the dielectric function is a second-rank tensor.

It must be emphasized that the fields $\vec{E}$ and $\vec{D}$ are macroscopic quantities which are to be thought of as macroscopic averages of the corresponding microscopic fields $\vec{E}_{micro}$, and $\vec{D}_{micro}$. The microscopic $\vec{E}_{micro}$, for example is a sum of the external field $\vec{E}_{ext}$ and an induced field $\vec{E}_{ind}$ which will, in general, contain rapid variations on the atomic scale. This microscopic field is what is actually responsible for the polarization of the medium. The proper quantum mechanical treatment of polarization^{1,2,3} which starts with the assumption of a linear relationship between the *microscopic* fields leads to corrections to macroscopic dielectric function of Eq. (1.2). The discussion of these so-called *local-field corrections* will be deferred for the present. Assume for now that we know the macroscopic dielectric function $\varepsilon_{ij}(\vec{q}, \omega)$.

We will consider only the long wave, or in other words $\vec{q} \rightarrow 0$, limit of Eq. (1.2) and from now on drop the $\vec{q}$ variable when writing the dielectric function. Explicitly we write $\varepsilon_{ij}(\vec{q}, \omega) \rightarrow \varepsilon_{ij}(0, \omega) \equiv \varepsilon_{ij}(\omega)$. This is not such a severe restriction since

light with the wavelength of visible light and longer is still well approximated by the $\vec{q} \rightarrow 0$ assumption, that is we assume that the wavelength of the incident light is much greater than the lattice constant $\lambda \gg a$.

In situations in which the linear-response or dielectric-tensor description is adequate, the description of light propagation is completely determined by using Eqs. (1.1) and (1.2) in conjunction with Maxwell's equations, once the dielectric function is specified. By writing the dielectric tensor with respect to the principal axes $\hat{x}_1, \hat{x}_2$, and $\hat{x}_3$, a diagonal form is obtained giving three components $\varepsilon_{xx} \equiv \varepsilon_1$, $\varepsilon_{yy} \equiv \varepsilon_2$ and $\varepsilon_{zz} \equiv \varepsilon_3$. These, in turn, lead to the indices of refraction, defined as $n_i \equiv \sqrt{\varepsilon_i}$. The index of refraction n_i gives the velocity of a plane polarized light wave, $v_i = c/n_i$, traveling with its displacement vector $\vec{D}$ aligned parallel to the direction $\hat{x}_i$. For any given direction of propagation, two plane polarized waves can exist whose $\vec{D}$ -vectors are situated perpendicular to one another and lie in the plane normal to the direction of propagation.

A simple way to find the index of refraction for one of these waves is to construct the *indicatrix*.⁴ The indicatrix is an ellipsoid of revolution which is defined to be the locus of points satisfying the equation

$$\frac{x_1^2}{n_1^2} + \frac{x_2^2}{n_2^2} + \frac{x_3^2}{n_3^2} = 1, \quad (1.5)$$

where x_1, x_2 and x_3 are coordinates defined relative to the principle axes $\hat{x}_1, \hat{x}_2$, and $\hat{x}_3$. To find the index of refraction for any wave, one draws a line from the origin to a point P on the surface of the indicatrix, chosen such that the line OP coincides with the propagation direction of the wave. A plane perpendicular to the line OP and passing through the origin O is then constructed. The section of this plane which lies inside the indicatrix is an elliptical region with semi-axes OA

and OB . The $\vec{D}$ -vectors of the two waves with propagation direction OP lie in the plane perpendicular to OP , and are oriented along the semi-axes OA and OB . The indices of refraction are given by lengths OA and OB respectively.

Much can be learned about the dielectric function and of the resulting wave propagation, as determined by the indicatrix construction, by appealing to symmetry arguments. It must be remembered, however, that although the dielectric function is a tensor, the index of refraction is not, and therefore symmetry arguments are to be applied to the dielectric tensor before the indicatrix is constructed.

For an isotropic material or a material with cubic symmetry the dielectric function is isotropic, that is $\varepsilon_1 = \varepsilon_2 = \varepsilon_3$, and the resulting indicatrix is a sphere. In such a material, waves expanding outward from a point source would comprise two coincident spherical wavefronts.

A *uniaxial* crystal is one in which the dielectric tensor has two of its principal components equal and one unequal, for example: $\varepsilon_1 = \varepsilon_2 \neq \varepsilon_3$. The corresponding indicatrix would be constructed with the refractive indices $n_1 = n_2 \equiv n_o \neq n_3 \equiv n_e$. One finds that for any direction of propagation, the two resulting waves have refractive indices n_o and n_F , where n_F is a value between n_e and n_o . If the direction of propagation coincides with the principal axis $\hat{x}_3$, the two waves have equal refractive indices n_o . Waves expanding from a point source in such a material form two surfaces, one of which is a sphere (the wave with index of refraction n_o), and is generally referred to as the *ordinary wave*. The other one, which is called the *extraordinary wave*, is a surface of revolution about the axis of symmetry (i.e. $\hat{x}_3$) touching the the ordinary wave at the axis of symmetry.

A crystal which has all three principal components of the dielectric tensor unequal, $\varepsilon_1 \neq \varepsilon_2 \neq \varepsilon_3$, is said to be *biaxial*. The origin of the name, bi-axial, can be seen from the indicatrix construction in which there are two preferred directions in which both waves have the same index of refraction, as opposed to the situation in a uniaxial crystal in which there is only one such preferred direction. The resulting wave surfaces for light expanding from a point source in such a material are somewhat more complicated than those found in the case of a uniaxial crystal.⁴

1.3 The photoelastic effect

Lowering the point-group symmetry of a cubic crystal through the application of some external influence, such as stress or a uniform static electric or magnetic field, reduces the symmetry constraints on the dielectric tensor and the crystal can become uniaxial or biaxial depending on the relationship between the direction of the applied influence and the symmetry axes of the unstrained crystal. In a zinc-blende crystal such as GaAs, a strain (stress) along the $[001]$, or $[111]$ direction is said to be a *uniaxial strain*. In either case, the strain direction becomes the preferred (uniaxial) direction and is identified with the principal axis ($\hat{x}_3$ in the notation of the previous section). By symmetry, strains along $[100]$, $[010]$ and $[001]$ are equivalent.

Crystals under strain are said to exhibit the *photoelastic effect*, which means that applied strains induce changes in the dielectric function of the material which can be expressed as linear functions of the applied strain. Changes in the optical properties of the crystal are expressed in terms of the indicatrix, as discussed in the

preceding section. If we rewrite Eq. (1.5) as

$$B_{ij}x_ix_j = 1 \quad (1.6)$$

where $B_{ij} \equiv \partial E_i / \partial D_j$, then the change in the indicatrix induced by stress is written

$$\delta B_{ij} = \pi_{ijk\ell} \sigma_{k\ell}. \quad (1.7)$$

We are assuming the convention that repeated indices are summed. In the above equation $\sigma_{k\ell}$ is a second rank tensor representing the applied stress and $\pi_{ijk\ell}$ called the *piezo-optic* tensor⁵ (using the nomenclature of Ref. 4). Written in terms of the dielectric function, Eq. (1.7) becomes

$$\delta(\varepsilon_{ij}^{-1}) = \pi_{ijk\ell} \sigma_{k\ell}. \quad (1.8)$$

Using the relation between stress and strain

$$\sigma_{k\ell} = c_{k\ell rs} \mu_{rs}, \quad (1.9)$$

where μ_{rs} is the strain and $c_{k\ell rs}$ are the *stiffness constants*, Eq. (1.8) becomes

$$\delta(\varepsilon_{ij}^{-1}) = p_{ijk\ell} \mu_{k\ell}, \quad (1.10)$$

where $p_{ijk\ell}$ defined by

$$p_{ijk\ell} = \pi_{ijrs} c_{rsk\ell}, \quad (1.11)$$

is called the *photoelastic tensor*. In general thirty-six components must be specified for a complete knowledge of $p_{ijk\ell}$. The use of symmetry, however, allows us to specify various relations between different components of $p_{ijk\ell}$, and in cases of high symmetry there are very few independent components. The cubic classes $m\bar{3}$ and 23 , for example, require one to specify only three and four components respectively.

The zinc-blende structure, which will be of primary interest in our study of GaAs, has the point group symmetry $43m$, and the tensor $p_{ijk\ell}$ can be written in the form

$$p_{ijk\ell} = \begin{pmatrix} p_{11} & p_{12} & p_{12} & 0 & 0 & 0 \\ p_{12} & p_{11} & p_{12} & 0 & 0 & 0 \\ p_{12} & p_{12} & p_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & p_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & p_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & p_{44} \end{pmatrix}. \quad (1.12)$$

where an abbreviated notation has been used. The notation used above^{4,6} is convenient in that it allows one to simplify the use of tensor operations by writing them as matrix multiplications. The fact that the tensor $p_{ijk\ell}$ is symmetric in the pairs of indices ij and $k\ell$, is used to allow the replacement $11 \rightarrow 1$, $22 \rightarrow 2$, $33 \rightarrow 3$, $23, 32 \rightarrow 4$, $13, 31 \rightarrow 5$, $12, 21 \rightarrow 6$. The symmetric property of the first and second indices of $p_{ijk\ell}$ follows because the strain tensor is symmetric and, since we are neglecting absorption and static magnetic fields, so is the dielectric tensor. The tensor p is then written as

$$p_{\alpha\beta} \equiv p_{ijk\ell}, \quad (1.13)$$

with similar definitions for the tensors σ, c , and $\delta(\varepsilon^{-1})$. Unfortunately this handy notation comes at the price of including some, sometimes-confusing, factors of two as in definition

for π

$$\begin{aligned} \pi_{\alpha\beta} &= \pi_{ijk\ell} \text{ for } \alpha, \beta = 1, 2, 3; \\ \pi_{\alpha\beta} &= 2\pi_{ijk\ell} \text{ for } \alpha, \beta = 4, 5, 6, \end{aligned} \quad (1.14)$$

and similarly for μ . These factors of two arise to avoid double counting that would arise because of the fact that each of the indices $\alpha = 4, 5, 6$ is a compression of *two* indices, whereas the indices $\alpha = 1, 2, 3$ are compressions from single indices.

The matrix for the photoelastic tensor (Eq. (1.12)) is diagonalized to yield the eigenvalues $p_{11} + 2p_{12}$, $p_{11} - p_{12}$ and p_{44} which are singly-, doubly-, and triply-degenerate respectively. The corresponding eigenvectors represent 1) hydrostatic strain (uniform expansion or compression), 2) volume-conserving strain along a cubic four-fold axis (which can be thought of as a compression (expansion) along $[001]$, $[010]$ or $[100]$, followed by a hydrostatic expansion (compression) which returns the crystal to its original volume) and 3) a volume-conserving strain along a bonding direction $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[11\bar{1}]$ or $[\bar{1}11]$.

In practice, the theorist calculates the *strain*-induced changes in the dielectric function and uses Eq. (1.10) to obtain the photo-elastic tensor, while the experimentalist measures *stress*-induced changes and uses Eq. (1.8) or a similar relation (see footnote 5) to determine the piezo-optic tensor. Theory and experiment can then be compared using Eq. (1.11). In fact the tensors p , π and c can be simultaneously diagonalized. In the cubic systems we find the following simple scalar relations:⁷

$$\begin{aligned} p_{1111} + 2p_{1122} &= (\pi_{1111} + 2\pi_{1122})(c_{1111} + 2c_{1122}) \\ p_{1111} - p_{1122} &= (\pi_{1111} - \pi_{1122})(c_{1111} - c_{1122}) \\ p_{1212} &= \pi_{1212}c_{1212}. \end{aligned} \tag{1.15}$$

1.4 Photoelastic tensor: *ab initio* calculations

The independent components of the photoelastic tensor are calculated, using the relations presented in this section, by taking finite differences of various com-

ponents of the dielectric tensor calculated for a strained crystal in the presence of strain. This concludes the introduction to the photoelastic tensor.

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CHAPTER II

Calculational Methods

2.1 Hohenberg-Kohn-Sham density-functional theory

Optical response functions are calculated using perturbation theory on the electronic ground states obtained in the context of “Density-Functional” (DFT) theory. The so-called “Density-Functional” formalism is an approach to the quantum-mechanical many-body problem that is based on the proof¹ that all of the ground state properties of an electronic system can be determined once the single-particle density is known. In this theory knowledge of the many-body wave-function is not needed. Hohenberg and Kohn¹ proved that, for a system of electrons in the presence of an external potential (e.g., the potential due to the ions in a solid), the ground state is a unique *universal* functional of the single-particle density distribution; the functional being *universal* in that it depends only on the density and not on the external potential. They also proved that the minimum value of this “energy-functional” is obtained for the correct ground state density. The proof of these theorems assumes that the ground state is nondegenerate, and that the particular density distribution in question can be generated by some external potential. Actually the argument can be formulated in a way which doesn’t require these (somewhat restrictive) assumptions.^{2,3}

Kohn and Sham⁴ then went on to develop a practical calculation scheme based on the results of Hohenberg-Kohn.¹ The Kohn-Sham (KS) scheme is based on the following separation of the total-energy functional:

$$E[n] = T_o[n] + \frac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d\vec{r} n(\vec{r}) V_{ext}(\vec{r}) + E_{xc}[n], \quad (2.1)$$

where $T_o[n]$ is the kinetic energy of a non-interacting (electron-electron interactions excluded) system having the same density distribution $n(\vec{r})$ as the physical system. The second term is the classical electrostatic electron-electron energy of a system with density $n(\vec{r})$. The third term represents the interaction of the electrons with an external potential $V_{ext}(\vec{r})$ (e.g., the potential due to the ions in a solid). By writing the total energy in this way we have implicitly defined the quantity $E_{xc}[n]$ which is called the “exchange-correlation” energy. The fact that the first term in Eq.(2.1) is the kinetic energy of a “non-interacting” system – not the kinetic energy of the fully-interacting *physical* system – implies that the difference is contained in $E_{xc}[n]$. Likewise $E_{xc}[n]$ contains the difference between the *physical* electron-electron interaction energy – defined in terms of the two-particle density matrix (to be given shortly) – and the energy given by the second term in Eq. (2.1).

The reason for introducing the KS energy separation is that it leads to a set of local Schrödinger-like equations that can be solved self-consistently. The method is formally exact, however, the exact density functional for $E_{xc}[n]$ is not known and therefore approximations must be made for the “exchange-correlation” energy: $E_{xc}[n]$.

2.2 The Kohn-Sham equations

The derivation of the Kohn-Sham equations⁴ is based on a comparison between an interacting system (electron-electron interactions included) in an external potential $V_{ext}(\vec{r})$, and a noninteracting system (electron-electron interactions excluded) in an external potential $V(\vec{r})$. Taking the functional derivative of the total-energy functional given by equation Eq. (2.1) subject to the constraint of constant particle number gives:

$$\frac{\delta}{\delta n(\vec{r})} = \frac{\delta T_o}{\delta n(\vec{r})} + V_{ext}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} = \mu, \quad (2.2)$$

for the interacting system, and

$$\frac{\delta E[n]}{\delta n(\vec{r})} = \frac{\delta T_o}{\delta n(\vec{r})} + V(\vec{r}) = \mu, \quad (2.3)$$

for the noninteracting system. The constant μ is the Lagrange multiplier associated with the constraint of constant particle number.

Formally the problems are identical if we make the assignment:

$$V(\vec{r}) = V_{ext}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}. \quad (2.4)$$

By correspondence with the noninteracting problem, the solution is obtained by solving the Schrödinger equation for non-interacting particles:

$$\left(-\frac{1}{2}\nabla^2 + V(\vec{r}) \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \quad (2.5)$$

in the presence of the self-consistent potential of Eq. (2.4). The density is then constructing as:

$$n(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2, \quad (2.6)$$

and a self-consistent procedure is used such that Eq. (2.4) will be satisfied. The system of equations represented by Eq. (2.5) – with the potential given by Eq. (2.4) and the density given by Eq. (2.6) – are called the Kohn-Sham (KS) equations. The eigenvalues of the KS equations are to be interpreted not as single particle energies but as Lagrange multipliers with no other physical significance. This follows from that fact that the total energy is not simply a sum of the eigenvalues.

2.3 One-particle and two-particle densities

The density (also called the “one-particle density”) of particles at position $\vec{r}$ is defined as:

$$n(\vec{r}) \equiv P_1(\vec{r}) \equiv N \prod_{i=2}^N \int d\vec{r}_i \Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N). \quad (2.7)$$

The normalization is chosen so that this function behaves like a true density and integrates to the total number of particles N . The two-particle density is defined as:

$$P_2(\vec{r}, \vec{r}') \equiv N(N-1) \prod_{i=3}^N \int d\vec{r}_i \Psi^*(\vec{r}, \vec{r}', \vec{r}_3, \dots, \vec{r}_N) \Psi(\vec{r}, \vec{r}', \vec{r}_3, \dots, \vec{r}_N), \quad (2.8)$$

and is the number of pairs of particles in the system having one particle at position $\vec{r}$ and another at position $\vec{r}'$. Spin labels have been suppressed in the above definitions. The density is actually a sum of two terms: one for each possible value of spin; and the two particle density is a sum of four terms. It follows from these definitions that the expectation values of one- and two-particle operators can be written in terms of integrals involving the one- and two-particle densities, respectively.

2.4 Exchange and correlation

Since we are dealing with an interacting system, the two-particle density is not simply a product of the one-particle densities as it would be for a system of classical non-interacting particles, thus the motion of the particles is “correlated”. Electrons tend to avoid each other for two reasons: 1) the anti-symmetry of the wave-function keeps electrons of like spin apart and, 2) the Coulomb repulsion tends to keep all electrons apart; consequently the interaction energy is reduced. These are generally called “exchange” and “correlation” effects respectively.

In order to characterize the depletion of charge at a point $\vec{r}'$ due to the presence of an electron at $\vec{r}$, a “hole” function is defined as:

$$h(\vec{r}, \vec{r}') = \frac{P_2(\vec{r}', \vec{r})}{n(\vec{r})} - n(\vec{r}'). \quad (2.9)$$

The concept of the “hole-function” is central to the understanding of exchange-correlation potentials. The “hole-function” satisfies the following important sum rule:

$$\int d\vec{r}' h(\vec{r}, \vec{r}') = -1. \quad (2.10)$$

This sum rule holds in general despite the fact that an explicit form for the hole function is not known for an interacting system. The validity of the sum rule can be seen as follows. 1) The first term in Eq. (2.9) is the density distribution of the remaining $N - 1$ particles, given that one is known to be at position $\vec{r}$. This term must then integrate to $N - 1$.

2) The second term: the total density, must integrate to N . Combining these results yields Eq. (2.10).

For convenience the pair-correlation function is defined implicitly in terms of the hole function:

$$h(\vec{r}, \vec{r}') = n(\vec{r}')[g(\vec{r}, \vec{r}') - 1]. \quad (2.11)$$

Although the quantity $E_{xc}[n]$ defined in the KS separation contains kinetic as well as potential energy, an exact *formal* expression for $E_{xc}[n]$ is known in terms of a similar “hole” function (called the exchange-correlation hole) that also obeys the above sum rule. This is given as:

$$E_{xc}[n] = \frac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r})h_{xc}(\vec{r}, \vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|}, \quad (2.12)$$

where the “hole” function ($h_{xc}(\vec{r}, \vec{r} - \vec{r}')$) is given by:

$$h_{xc}(\vec{r}, \vec{r} - \vec{r}') \equiv n(\vec{r}') \int_0^1 d\lambda [g_\lambda(\vec{r}, \vec{r}') - 1]. \quad (2.13)$$

This expression is obtained by formally “switching on” the Coulomb interaction from zero strength (i.e. $\lambda = 0$: noninteracting system) to full strength ($\lambda = 1$: fully interacting system). It must be emphasized that this expression is useful for determining general properties of $E_{xc}[n]$ and for making approximations but it cannot be used for calculating $E_{xc}[n]$ since the pair correlation functions are not known explicitly.

2.5 The local density approximation

The “local density approximation” (LDA) as introduced by Kohn and Sham⁴ assumes that if we know the exchange correlation energy per particle in a homogeneous electron gas as a function of density, this quantity can be used to find the exchange-correlation energy in an inhomogeneous system by simply multiplying this

function (evaluated at the local density) by the local density and integrating over the volume of the system as:

$$E_{xc}[n] \equiv \int d^3\vec{r} n(\vec{r}) \epsilon_{xc}(n(\vec{r})). \quad (2.14)$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy of a system of electrons with *uniform* density n . The functional form originally proposed by Kohn and Sham⁴ for $E_{xc}[n]$ was obtained by 1) using the “exchange-only” hole function for a uniform electron gas in the exact expression for $E_{xc}[n]$ and, 2) using a local-density expression for the correlation energy of a paramagnetic electron gas of uniform density derived by Wigner.⁵ The “exchange-only” hole function is obtained from the definition of the hole function assuming that the wave-function is a Slater determinant of plane-waves.

There have been many improvements to the parameterization of the LDA including

1) formulae based on the results of many-body perturbation theory as applied to the homogeneous electron gas,^{6,7,8} and 2) parameterizations^{9,10} based on the Monte Carlo calculations of Ceperley and Alder.¹¹ The LDA has also been generalized to contain explicit spin dependence: the local spin density (LSD) approximation, for the description of systems with unequal numbers of spin up and spin down electrons. It is now generally believed^{12,13,14} that for inhomogeneous systems it is not possible to completely specify $E_{xc}[n]$ entirely in terms of the local density alone and therefore most of the improvements to $E_{xc}[n]$ in the past ten years have been based on attempts to go beyond the LDA.

Despite these caveats, the LDA is widely used in practice and gives remarkably good results for the calculation of many properties of atoms molecules and solids.¹²

The fact that the LDA does so well is attributed to the existence of the sum rule on the exchange-correlation hole, Eq. (2.10), and the fact that the exchange-correlation energy depends not on the detailed structure of the exchange-correlation hole but only on a spherical average, see Eq. (2.12).¹⁵ One of the most popular LDA functionals is the parameterization given by Perdew and Zunger¹⁰ of Ceperley and Alder's¹¹ results for the uniform electron gas.

2.6 Implementation: plane waves and pseudopotentials

All calculations to be discussed in this thesis are based on an implementation of the Density-Functional theory using the LDA in a plane wave basis. The electron-ion interaction is represented using ab-initio norm-conserving pseudopotentials^{16–18} in the separable form of Kleinman and Bylander.¹⁹ Details of the pseudopotential construction and of the Kleinman-Bylander form will be presented shortly. The following is a brief description of the plane wave/pseudopotential formalism for the ground state of a system of electrons in an external potential (e.g. the ground state of a semi-conductor or insulator). This derivation assumes a general semi-local pseudopotential^{16,17,18,20} and closely follows the derivation of Ihm, Zunger, and Cohen.²¹ By semi-local we mean local in the spatial coordinate r about an ionic center, but non-local in the angular-momentum quantum number l projected about the same ionic center. The notation of reference 21 will be used with the trivial exception that they worked in Rydberg units and the following will be in Hartree units.

Using Hartree energy units, the total energy of a system of electrons and ions is given by

$$E_{total} = T + V + \int E_{xc}(r) d^3r. \quad (2.15)$$

The total electronic kinetic energy (ions are assumed to be fixed) is

$$T = \frac{1}{2} \sum_i \psi_i^*(\vec{r}) (-\nabla^2) \psi_i(\vec{r}) d^3r, \quad (2.16)$$

and V is given by

$$V = \sum_{i,\mu,\ell} \int \psi_i^*(\vec{r}) U_{ps,\ell}(\vec{r} - \vec{R}_\mu) \hat{P}_\ell \psi_i(\vec{r}) d^3r + \frac{1}{2} \int \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' + \frac{1}{2} \sum_{\mu \neq \nu} \frac{Z^2}{|\vec{R}_\mu - \vec{R}_\nu|} \quad (2.17)$$

In these equations $\psi_i(\vec{r})$ is the pseudo-wavefunction representing a valence electron with quantum numbers: $i \equiv \{n, \vec{k}_i\}$. The sum over i represents a sum over the filled valence states and all allowed k -points. The charge density which represents the valence electrons is given by $\rho(\vec{r}) = \sum_i \psi_i(\vec{r})^* \psi_i(\vec{r})$, which is the analog of Eq. (2.6) in the pseudopotential scheme. Z is the ionic valence and $\vec{R}_\mu$ is an ionic position vector. The first term in Eq. (2.17) represents the energy of interaction between the valence electrons and the ion core (nucleus plus core electrons). The core is represented by the semi-local pseudo-potential as:

$$V_{ps} = \sum_\ell U_{ps,\ell}(\vec{r}) \hat{P}_\ell, \quad (2.18)$$

with $\hat{P}_\ell$ projecting the angular-momentum component ℓ on the valence pseudowavefunction. The second term in (2.17) is the electron-electron interaction energy and the last term is the ion-ion interaction energy. Equation (2.15) is equivalent to Eq. (2.1) and therefore the KS equations in this representation are:

$$\left(-\frac{1}{2} \nabla^2 + \sum_{\mu,\ell} U_{ps,\ell}(\vec{r} - \vec{R}_\mu) \hat{P}_\ell + \frac{1}{2} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \mu_{xc}(\vec{r}) \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \quad (2.19)$$

with,

$$\mu_{xc}(\vec{r}) = \frac{\delta E_{xc}(\vec{r})}{\delta \rho(\vec{r})}. \quad (2.20)$$

The LDA implies $E_{xc}(\vec{r}) \equiv \rho(\vec{r})\epsilon_{xc}(\rho(\vec{r}))$, where $\epsilon_{xc}(\rho)$ is the exchange-correlation energy per particle in a system with uniform density ρ . In our calculations $\epsilon_{xc}(\rho)$ and $\mu_{xc}(\rho)$ are given as parameterizations⁹ of Ceperly and Alder's data¹¹ for the uniform electron gas.

One principle advantage of using a plane wave basis is that the kinetic energy operator is diagonal in reciprocal space. Pseudopotentials are used on the assumption that the dominant physics is due to the valence electrons.

Assuming that the external potential is periodic as in a crystalline solid:

$$V_{ext}(\vec{r} + \vec{a}) = V_{ext}(\vec{r}), \quad (2.21)$$

where $\vec{a}$ is one of the primitive lattice translation vectors, implies that the electron pseudo-wavefunctions must obey Bloch's theorem

$$\psi_i(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n,\vec{k}}(\vec{r}), \quad (2.22)$$

where $u_{n,\vec{k}}(\vec{r})$ is a periodic function, i.e.,

$$u_{n,\vec{k}}(\vec{r} + \vec{a}) = u_{n,\vec{k}}(\vec{r}). \quad (2.23)$$

Because of the periodicity of the function of Eq. (2.23) the pseudowavefunction $\psi_i(\vec{r})$ can be written as an expansion in planewaves as:

$$\psi_{n,\vec{k}_i}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}_i + \vec{G}} e^{i(\vec{k}_i + \vec{G}) \cdot \vec{r}}. \quad (2.24)$$

For convenience of notation every quantity in reciprocal space will be written with the same symbol as the corresponding real-space quantity but with a reciprocal

space argument. For example, the pseudo-wavefunction expansion coefficient is written as:

$$C_{\vec{k}_i+\vec{G}} \equiv \psi(\vec{k}_i + \vec{G}). \quad (2.25)$$

Similarly the Coulomb interaction $V_{Coul}(\vec{r} - \vec{r}')$, the charge density $\rho(\vec{r})$ and the exchange-correlation potential $\mu_{xc}(\vec{r})$ are written in reciprocal space as $V_{Coul}(\vec{G})$, $\rho(\vec{G})$ and $\mu_{xc}(\vec{G})$ respectively, the Coulomb potential having the explicit form:

$$V_{Coul}(\vec{G}) = \frac{4\pi\rho(\vec{G})}{G^2}. \quad (2.26)$$

Using this result, the third term in Eq. (2.17) becomes:

$$\frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' = \frac{1}{2} \Omega \sum_{\vec{G}} V_{Coul}(\vec{G}) \rho(\vec{G}), \quad (2.27)$$

where Ω is the total crystal volume. The atomic volume will be defined as $\Omega_{at} = \Omega/N$ where N is the number of atoms.

To write the pseudopotential term each plane wave in the expansion is decomposed in terms of spherical harmonics and spherical Bessel functions and translational invariance is invoked. Thus the first term in Eq. (2.17) becomes:

$$\begin{aligned}
& \sum_{i,\mu,\ell} \int \psi_i^*(\vec{r}) U_{ps,\ell}(\vec{r} - \vec{R}_\mu) \hat{P}_\ell \psi_i(\vec{r}) d^3r \\
&= \Omega \sum_{i,\ell,\vec{G},\vec{G}'} \psi^*(\vec{k}_i + \vec{G}) \psi(\vec{k}_i + \vec{G}') \sum_{\mu} \frac{\exp[i(\vec{G}' - \vec{G}) \cdot \vec{R}_\mu]}{N} \\
&\times (1/\Omega_{at}) \int \exp[-i(\vec{k}_i + \vec{G}) \cdot \vec{r}] U_{ps,\ell}(\vec{r}) \hat{P}_\ell \exp[i(\vec{k}_i + \vec{G}') \cdot \vec{r}] d^3r \\
&= \Omega \sum_{i,\ell,\vec{G},\vec{G}'} \psi^*(\vec{k}_i + \vec{G}) \psi(\vec{k}_i + \vec{G}') S(\vec{G} - \vec{G}') U_{ps,\ell,\vec{k}_i+\vec{G},\vec{k}_i+\vec{G}'} \quad (2.28)
\end{aligned}$$

In the above, $S(\vec{G}-\vec{G}')$ is the structure factor and $U_{ps,\ell,\vec{k}_i+\vec{G},\vec{k}_i+\vec{G}'}$ is the generalized non-local form factor given by:

$$\begin{aligned}
U_{ps,\ell,\vec{k}_i+\vec{G},\vec{k}_i+\vec{G}'} &= (1/\Omega_{at}) \int \exp[-i(\vec{k}_i + \vec{G}) \cdot \vec{r}] U_{ps,\ell}(\vec{r}) \hat{P}_\ell \exp[i(\vec{k}_i + \vec{G}') \cdot \vec{r}] d^3r \\
&= (1/\Omega_{at})(2\ell + 1)4\pi \int U_{ps,\ell}(\vec{r}) j_\ell(|\vec{k}_i + \vec{G}|r) j_\ell(|\vec{k}_i + \vec{G}'|r) \\
&\times P_\ell(\cos \gamma) r^2 dr. \quad (2.29)
\end{aligned}$$

with

$$\cos \gamma = \frac{[(\vec{k}_i + \vec{G}) \cdot (\vec{k}_i + \vec{G}')]}{|\vec{k}_i + \vec{G}| |\vec{k}_i + \vec{G}'|}. \quad (2.30)$$

In Eq. (2.29) j_ℓ are spherical Bessel functions and P_ℓ are Legendre polynomials. The pseudopotentials are assumed to be spherically symmetric.

The nonlocal form factor as expressed in Eq. (2.29) is not very computationally efficient. To illustrate, suppose there are n planewaves ($\vec{G}$'s) and m k -points. The form of Eq. (2.29) implies that $mn(n+1)/2$ integrals must be computed. In practice, however, we need only compute mn integrals if we employ the Kleinman-Bylander¹⁹ separable form for $U_{ps,\ell,\vec{k}_i+\vec{G},\vec{k}_i+\vec{G}'}$.

Care must be taken when Eq. (2.17) is numerically evaluated since each term taken alone is divergent, as can be seen for example upon inspection of the reciprocal space expression for the Coulomb interaction (Eq (2.26)). This divergence which arises in the $\vec{G} \rightarrow 0$ limit is due to the long-range character of the Coulomb interaction.

Consider first the pseudopotential term in Eq. (2.17). The long-range character of the each pseudopotential component goes as $U_{ps}(\vec{r}) \sim -Z/r$ for large r , with no dependence on ℓ . The lack of ℓ dependence can be understood upon examination of the radial Schrödinger equation, in which the repulsive angular momentum dependent term dies off as $1/r^2$. For convenience we define a local pseudopotential which has the above mentioned long-range behavior: $U_{ps}(\vec{r}) \sim -Z/r$. The total pseudopotential is then written as:

$$\sum_{\ell} U_{ps,\ell}(\vec{r}) \hat{P}_{\ell} = U_{ps}(\vec{r}) + \sum_{\ell} (U_{ps,\ell}(\vec{r}) - U_{ps}(\vec{r})) \hat{P}_{\ell} = U_{ps}(\vec{r}) + \sum_{\ell} U'_{ps,\ell}(\vec{r}) \hat{P}_{\ell}. \quad (2.31)$$

Written in this way, all of the non-local terms, $U'_{ps,\ell}$, are convergent. We will see shortly that the divergent piece, $U_{ps}(\vec{G} = 0)$ will cancel with other terms in Eq. (2.17). Substituting the rewritten form of Eq. (2.31), into Eq. (2.28) gives:

$$\begin{aligned} \sum_{i,\mu,\ell} \int \psi_i^*(\vec{r}) U_{ps,\ell}(\vec{r} - \vec{R}_{\mu}) \hat{P}_{\ell} \psi_i(\vec{r}) d^3r \\ = \Omega \left(\sum_{\vec{G}} S(\vec{G}) U_{ps}(\vec{G}) \rho(\vec{G}) + \sum_{i,\ell,\vec{G},\vec{G}'} \psi_i^*(\vec{k}_i + \vec{G}) \psi_i(\vec{k}_i + \vec{G}') \right. \\ \left. \times S(\vec{G} - \vec{G}') U'_{ps,\ell,\vec{k}_i+\vec{G},\vec{k}_i+\vec{G}'} \right), \end{aligned} \quad (2.32)$$

with the first term on the left arising from the local part of the pseudopotential.

Using Eq. (2.32), the KS equations of Eq. (2.19) in reciprocal space take the following form:

$$\sum_{\vec{G}'} [(\vec{k}_i + \vec{G}')^2 \delta_{\vec{G}\vec{G}'} + V_{\vec{G}\vec{G}'}^i] \psi(\vec{k}_i + \vec{G}') = \epsilon_i \psi(\vec{k}_i + \vec{G}), \quad (2.33)$$

with

$$\begin{aligned} V_{\vec{G}\vec{G}'}^i = V_{Coul}(\vec{G}' - \vec{G}) + \mu_{xc}(\vec{G}' - \vec{G}) + S(\vec{G}' - \vec{G}) \Big[U_{ps}(\vec{G}' - \vec{G}) \\ + \sum_{\ell} U'_{ps,\ell,\vec{k}_i+\vec{G},\vec{k}_i+\vec{G}'} \Big]. \end{aligned} \quad (2.34)$$

The KS equations have thus been cast in the form of a matrix eigenvalue problem which can be solved by direct diagonalization. The procedure to be followed would be to first set the divergent terms $U_{Coul}(0)$ and $U_{ps}(0)$ equal to zero (which is equivalent to a constant energy shift) and solve Eq. (2.34). The calculations to be presented in this thesis actually employ a more sophisticated scheme called the Conjugate Gradient method²² which is an iterative scheme for solving Eq. (2.34).

The correct total energy for the system, which properly accounts for the cancellation of all divergent pieces, is then constructed as follows. Combining Eqs. (2.15), (2.27) and (2.32) gives:

$$\begin{aligned} E_{total} = \Omega \Big(\frac{1}{2} \sum_{i,\vec{G}} |\psi(\vec{k}_i + \vec{G})|^2 (\vec{k}_i + \vec{G})^2 + \frac{1}{2} \sum_{\vec{G}} V_{Coul}(\vec{G}) \rho(\vec{G}) + \sum_{\vec{G}} \rho(\vec{G}) \epsilon_{xc}(\vec{G}) \\ + \sum_{\vec{G}} S(\vec{G}) U_{ps}(\vec{G}) \rho(\vec{G}) + \sum_{i,\ell,\vec{G},\vec{G}'} \psi^*(\vec{k}_i + \vec{G}) \psi(\vec{k}_i + \vec{G}') \\ \times S(\vec{G} - \vec{G}') U'_{ps,\ell,\vec{k}_i+\vec{G},\vec{k}_i+\vec{G}'} \Big). \end{aligned} \quad (2.35)$$

A simpler form is obtained by rewriting in terms of the electronic eigenvalues as:

$$E_{total} = \sum_i \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r d^3 r'$$

$$\begin{aligned}
& + \int \rho(\vec{r})[\epsilon_{xc}(\vec{r}) - \mu_{xc}(\vec{r})]d^3r + \frac{1}{2} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z^2}{|\vec{R}_\mu - \vec{R}_\nu|} \\
& = \sum_i \epsilon_i - \Omega \left[\frac{1}{2} \sum_{\vec{G}} V_{Coul}(\vec{G}) \rho(\vec{G}) + \sum_{\vec{G}} \rho(\vec{G}) (\epsilon_{xc}(\vec{G}) - \mu_{xc}(\vec{G})) \right] \\
& + \frac{1}{2} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z^2}{|\vec{R}_\mu - \vec{R}_\nu|}
\end{aligned} \tag{2.36}$$

Equation (2.36) was obtained by multiplying Eq. (2.19) on the left by $\psi^*(\vec{r})$, integrating over $\vec{r}$ and summing over i . The result is then substituted into Eq. (2.15). Of course, we must still handle the divergences of $V_{Coul}(0)$, $U_{ps}(0)$ and

$$\frac{1}{2} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z^2}{|\vec{R}_\mu - \vec{R}_\nu|}.$$

Consider first the pseudopotential energy expanded in a formal power series in $|\vec{G}|$:

$$U_{ps}(\vec{G}) = \frac{-4\pi Z}{\Omega_{at} G^2} + \alpha_1 + (\text{higher order terms}), \tag{2.37}$$

with constant piece given by

$$\alpha_1 = \lim_{\vec{G} \rightarrow 0} \left[U_{ps}(\vec{G}) + (4\pi Z / \Omega_{at} G^2) \right] = (1/\Omega_{at}) \int [U_{ps}(\vec{r}) + Z/r] d^3r. \tag{2.38}$$

The first term in Eq. (2.37) is the divergent piece associated with the pseudopotential which will be canceled. There is no term in $1/\vec{G}$. If there were such a term it would lead to a divergent total energy and would thus be unphysical. The pseudopotential would have to be chosen such that no $1/G$ term arises. The authors in reference 21 mention the Simons-Bloch pseudopotential²³ as an example of a pseudopotential which gives rise to the unphysical $1/\vec{G}$ term.

The charge density in reciprocal space $\rho(\vec{G})$ must be expanded since it appears with two of the divergent pieces in the combinations $V_{Coul}(\vec{G})\rho(\vec{G})$ and $U_{ps}(\vec{G})\rho(\vec{G})$.

The charge density is expanded as:

$$\rho(\vec{G}) = Z/\Omega_{at} + \beta G^2 + (\text{higher order terms}) \quad (2.39)$$

The constant β is written as:

$$\beta = \lim_{\vec{G} \rightarrow 0} \frac{1}{4\pi} \left(V_{Coul}(\vec{G}) - \frac{4\pi Z}{\Omega_{at} G^2} \right) = \frac{1}{4\pi\Omega} \int \int \frac{[\rho(\vec{r}) - Z/\Omega_{at}]}{|\vec{r} - \vec{r}'|} d^3r d^3r', \quad (2.40)$$

where Eq. (2.26) has been used. This constant β would be difficult to evaluate numerically but fortunately such an evaluation is unnecessary since it doesn't appear in the final expression for the total energy.

Lastly, assuming the system to be electrostatically neutral, the divergent piece of the ion-ion interaction energy per atom can be separated out as:²⁴

$$\frac{1}{2} \sum_{\nu}' \frac{Z^2}{|\vec{R}_{\nu}|} = \gamma_{Ewald} + \frac{1}{2} \lim_{\vec{G} \rightarrow 0} \frac{4\pi Z^2}{\Omega_{at} G^2}, \quad (2.41)$$

with

$$\gamma_{Ewald} \equiv \frac{1}{2} \sum_{\nu}' \frac{Z^2}{|\vec{R}_{\nu}|} - \frac{1}{2} \lim_{\vec{G} \rightarrow 0} \frac{4\pi Z^2}{\Omega_{at} G^2} = \frac{1}{2} \left(\frac{1}{2} \sum_{\nu}' \frac{Z^2}{|\vec{R}_{\nu}|} - \frac{1}{\Omega_{at}} \int \frac{Z^2}{r} d^3r \right). \quad (2.42)$$

The prime on the summation indicates that the $\vec{R}_{\nu} = 0$ term is excluded. Finally, using Eq.'s (2.26), (2.37), (2.39), and (2.41), the divergent pieces can be handled, giving

$$\begin{aligned} \lim_{\vec{G} \rightarrow 0} \Omega_{at} \left[\frac{1}{2} V_{Coul}(\vec{G}) \rho(\vec{G}) + U_{ps}(\vec{G}) \rho(\vec{G}) \right] + \frac{1}{2} \sum_{\nu}' \frac{Z^2}{|\vec{R}_{\nu}|} \\ = \lim_{\vec{G} \rightarrow 0} \left[\frac{\Omega_{at}}{2} \frac{4\pi [Z/\Omega_{at} + \beta G^2]^2}{G^2} + \Omega_{at} \left(\frac{-4\pi Z}{\Omega_{at} G^2} + \alpha_1 \right) \left(\frac{Z}{\Omega_{at}} + \beta G^2 \right) \right. \\ \left. + \frac{1}{2} \frac{4\pi Z^2}{\Omega_{at} G^2} \right] + \gamma_{Ewald} = \alpha_1 Z + \gamma_{Ewald}, \end{aligned} \quad (2.43)$$

as the energy per atom arising from the divergent pieces. The final expression for the total energy per atom is then given by

$$\begin{aligned}
 E_{total}/N = \frac{1}{N} \sum_i \epsilon_i - \frac{1}{2} \Omega_{at} \sum_{\vec{G} \neq 0} V_{Coul}(\vec{G}) \rho(\vec{G}) \\
 + \Omega_{at} \sum_{\vec{G}} \rho(\vec{G}) [\epsilon_{xc}(\vec{G}) - \mu_{xc}(\vec{G})] + \alpha_1 Z + \gamma_{Ewald} \quad (2.44)
 \end{aligned}$$

Once again, the procedure is to solve Eq. (2.33) self-consistently with $U_{ps}(0)$ and $V_{Coul}(0)$ set to zero then the total energy is formed as in Eq. (2.44).

2.7 Pseudopotentials

Electronic-structure calculations using plane wave basis sets would be prohibitively costly without the use of pseudopotentials, since extremely large numbers of plane waves would be needed to represent the rapidly oscillating tightly-bound electronic core states. Instead, the core states are omitted from the calculation and the all-electron potential felt by the valence electrons is replaced by a “pseudopotential” which mimics the effects of the core states and is chosen to be smooth and shallow in the core region. The valence wavefunction must be replaced by the pseudowavefunction which is the eigenfunction of the Hamiltonian containing the pseudopotential.

Extensive reviews of pseudopotential theory and of the methods for fitting pseudopotentials (empirical pseudopotentials) to experimental data were given by Cohen and Heine²⁵, and Heine and Weaire²⁶.

The working assumption when using pseudopotentials is that for many physical situations of interest (e.g., the chemistry of covalent bonding in molecules and the physics of the valence and conduction electrons in a solid) the core electrons play a relatively minor role. The core states are largely unchanged in going from an isolated atom to a solid, their primary role being the enforcement of the orthogonality between the core and valence states. For this reason it is reasonable to make the approximation that the core states *are* fixed (called the “frozen core approximation”). In other words, the core states of the ion in a solid are assumed to be *the same* as they are in an isolated atom. A pseudopotential constructed using the

results of a quantum-mechanical calculation for an atom, which also works well in other environments, such as a molecule or solid, is said to be “transferable”.

The early pseudopotentials (empirical pseudopotentials) were constructed by representing the total potential felt by an electron by a few terms in a Fourier expansion.^{25,26} The parameters in the expansion were then adjusted to give results in agreement with experiments such as Fermi Surface, Phonon, and Optical measurements.

2.8 Pseudopotentials in the OPW context

Pseudopotentials were theoretically justified by Phillips and Kleinman²⁰ in 1959 in the context of the orthogonalized plane-wave (OPW) method.²⁷ While the Phillips-Kleinman pseudopotentials are not very convenient to use and are not the most accurate pseudopotentials available, their method of pseudopotential construction, which follows, is an instructive example of the general ideas behind pseudopotential use.

The OPW method assumes that the core functions are well localized on the atomic sites and are best represented by tight-binding wavefunctions. In contrast, the valence electrons are fairly delocalized and can be well represented by a plane wave expansion in the interstitial regions. OPW functions, which are used to represent the valence electrons, are plane wave functions which have been constructed to be orthogonal to the core states which are presumed known. An OPW is written as a plane wave plus a sum of core states (see Ref. 28 p. 206) as:

$$\langle \vec{r} | \phi_{\vec{k}} \rangle = e^{i\vec{k} \cdot \vec{r}} + \sum_c b_c \langle \vec{r} | \psi_{\vec{k}}^c \rangle. \quad (2.45)$$

By forcing the OPW to be orthogonal to the core states, that is

$$\langle \psi_{\vec{k}}^{c*} | \phi_{\vec{k}} \rangle = 0, \quad (2.46)$$

we obtain the coefficients b_c as:

$$b_c = -\langle \psi_{\vec{k}}^{c*} | e^{i\vec{k} \cdot \vec{r}} \rangle \quad (2.47)$$

In the above expressions, $\langle \vec{r} | \psi_{\vec{k}}^c \rangle$ is a Bloch sum of the conduction state “ c ” on all of the ions, and the resulting OPW’s are of the Bloch form. The exact wavefunction for a valence state is then written as a superposition of OPW’s,

$$|\psi_{\vec{k}}\rangle = \sum_{\vec{G}} C_{\vec{G}} |\phi_{\vec{k}+\vec{G}}\rangle. \quad (2.48)$$

If we define the plane wave part of Eq. (2.48) as:

$$\langle \vec{r} | \phi_{\vec{k}}^v \rangle = \sum_{\vec{G}} C_{\vec{G}} e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}, \quad (2.49)$$

and use Eqs. (2.45), (2.47) and (2.49) in Eq. (2.48), we can write the exact valence eigenstate as:

$$|\psi_{\vec{k}}^v\rangle = |\phi_{\vec{k}}^v\rangle - \sum_c |\psi_{\vec{k}}^c\rangle \langle \psi_{\vec{k}}^{c*} | \phi_{\vec{k}}^v \rangle \quad (2.50)$$

The exact valence wavefunction $|\psi_{\vec{k}}^v\rangle$ must satisfy the Schrödinger equation

$$H|\psi_{\vec{k}}^v\rangle = \epsilon_{\vec{k}}^v |\psi_{\vec{k}}^v\rangle, \quad (2.51)$$

so if we act on the left of Eq. (2.50) with H we obtain

$$H|\phi_{\vec{k}}^v\rangle - \sum_c \langle \psi_{\vec{k}}^{c*} | \phi_{\vec{k}}^v \rangle H|\psi_{\vec{k}}^c\rangle = \epsilon_{\vec{k}}^v \left(|\phi_{\vec{k}}^v\rangle - \sum_c \langle \psi_{\vec{k}}^{c*} | \phi_{\vec{k}}^v \rangle |\psi_{\vec{k}}^c\rangle \right). \quad (2.52)$$

Now using the fact that the conduction states satisfy the Schrödinger equation

$$H|\psi_{\vec{k}}^c\rangle = \epsilon_{\vec{k}}^c |\psi_{\vec{k}}^c\rangle, \quad (2.53)$$

leads to the following effective Schrödinger equation for the plane wave part, $|\phi_k^v\rangle$, of

Eq. (2.48)

$$(H + \hat{V})|\phi_k^v\rangle = \epsilon_k^v|\phi_k^v\rangle, \quad (2.51)$$

where the action of the operator $\hat{V}$ defined as:

$$\hat{V}|\psi\rangle = \sum_c (\epsilon_k^v - \epsilon_k^c) \langle \psi_k^{c*} | \psi \rangle |\psi_k^c\rangle. \quad (2.55)$$

The eigenstate $|\psi_k^v\rangle$ of equation (2.54) is called the *pseudowavefunction* and has the same eigenvalue as the true valence wavefunction $|\phi_k^v\rangle$. The *pseudopotential* (call it V^{pseudo}) is defined as the effective potential associated with the pseudowavefunction in Eq. (2.54). In other words

$$H + \hat{V} \equiv -\frac{\hbar^2}{2m} \nabla^2 + V^{pseudo}. \quad (2.56)$$

It was hoped that by working with the pseudowavefunction and pseudopotential that a computational savings could be obtained since the pseudowavefunction would not contain all of the core-region oscillations that are in the true wavefunction, and fewer plane wave would be needed to represent the pseudowavefunction than would be needed for the full valence wavefunction. The OPW method of Phillips and Kleinman was used^{29,30} to calculate band structures for Si and a few other semiconductors.

Despite the formal elegance of the Phillips-Klienman construction there are several problems. 1) The pseudopotential so constructed is non-local in $\vec{r}$ making it computationally more expensive to use than one which is local in $\vec{r}$. 2) It is energy-dependent implying that certain quantum mechanical theorems are not

obeyed by the pseudohamiltonian such as the orthogonality of pseudowavefunctions corresponding to different eigenvalues.²⁸ 3) The distribution of valence electronic charge is incorrect¹⁷ since outside of the core region the true valence wavefunction and the pseudowavefunction have the same shape but different amplitudes.

2.9 Norm-conserving pseudopotentials

The “modern era” of pseudopotential theory began with the introduction of ab-initio “norm-conserving” pseudopotentials by Hamann, Schlüter, and Chiang.¹⁶ Norm-conservation was first introduced by Topp and Hopfield³¹ for use with an empirical model potential for Na. In the method of Hamann, Schlüter, and Chiang,¹⁶ the potential felt by a valence electron, with given angular momentum component ℓ , obtained from an all-electron calculation using density-functional theory, is modified within some core radius, R_c , to be a smooth potential approaching the origin of the radial coordinate with zero slope. Outside of R_c , the potential is the self-consistent potential which is obtained from an “all-electron” calculation. The modified potential is then used in the Schrödinger equation to solve for the valence state. The adjustable parameters use to modify the “all-electron” potential are varied to reproduce the exact eigenvalue for the valence state. The “pseudowavefunction” so obtained is then further modified to enforce the constraint that the pseudowavefunction is normalized (conservation of charge) and has the correct analytic form for small r . The Schrödinger equation is then inverted to solve for the pseudopotential. The pseudowavefunction must, of course, be nodeless in order to permit the inversion. The pseudopotential thus constructed is local in the radial coordinate, energy independent, and angular momentum *dependent*. These

potentials, which are sometimes characterized as *semi-local* can be written as:

$$V_{ps} = \sum_{\ell} U_{ps,\ell}(\vec{r}) \hat{P}_{\ell}, \quad (2.18)$$

with $\hat{P}_{\ell}$ projecting the angular-momentum component ℓ on the valence pseudowavefunction.

By construction, 1) norm-conserving pseudopotentials give, in the case of a single atom, the correct electronic charge distribution outside the core region and the correct integrated charge in the core region. Also, 2) the pseudopotential and all-electron potentials are identical outside of the core radius R_c . Generally these two features are what is meant by “norm-conserving.”

Also, it has been shown^{16,31,32} that if the pseudopotential is norm-conserving then the logarithmic derivatives (with respect to the radial coordinate) of the pseudowavefunction will be correctly reproduced for some energy range about the eigenvalue, and since the logarithmic derivatives are related to the scattering phase shifts,³³ this gives one the hope that the norm-conserving pseudopotential will correctly describe scattering states when it is used in a solid-state environment, i.e. will be transferable. The logarithmic derivatives of the pseudowavefunction, at a given radius R , are related to the total charge contained within a sphere of radius R as:^{16,31,32}

$$-2\pi \left[(r\phi)^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \phi \right]_R = 4\pi \int_0^R \phi^2 r^2 dr. \quad (2.57)$$

This says that if one has two different pseudowavefunctions ϕ_1 and ϕ_2 obtained from the pseudopotentials v_1 and v_2 and these pseudowavefunctions have the same integrated charge-density inside some cutoff radius R (defined by $\phi_1(R) = \phi_2(R)$) then the energy variation of the scattering phase shifts (around some value ϵ) for

these two pseudowavefunctions will be the same. A pseudopotential is said to be “transferable” if it leads to accurate results in an environment which is different than the one in which it was constructed (e.g., an atomic pseudopotential in a solid-state environment).

Issues of transferability and some recent attempts at improved pseudopotential construction are discussed in Refs. 34, 35, 36, 37, 38 and 39.

Bachelet, Hamann and Schlüter¹⁷ used the procedure of Hamann, Schlüter and Ching¹⁶ to construct and tabulate pseudopotentials for all of the elements from H to Pu. For the heavy atoms relativistic calculations were used to construct pseudopotentials for the two spin-orbit coupling possibilities $j = \ell + 1/2$ and $j = \ell - 1/2$ using a method developed by Kleinman.⁴⁰

Hamann generalized the method of norm-conserving pseudopotential construction⁴¹ to avoid difficulties, encountered using the previous procedure, such as the need to use ionized configurations to calculate pseudopotentials for (weakly bound) angular momentum states not found in the ground state of the atom.

All of the calculations to be described in this thesis use Hamann’s generalized pseudopotentials,⁴¹ and employ the Kleinman-Bylander¹⁹ separable form.

2.10 Kleinman and Bylander’s separable form

The norm-conserving pseudopotentials discussed previously have the property that they are of a semi-local form (local in variable $\vec{r}$ but non-local in the ℓ variable)

$$V_{ps} = \sum_{\ell} U_{ps,\ell}(\vec{r}) \hat{P}_{\ell} = \sum_{\ell,m} |Y_{\ell m}\rangle U_{ps,\ell}(\vec{r}) \langle Y_{\ell m}|. \quad (2.58)$$

where the projection operator has been written as

$$\hat{P}_\ell = \sum_m |Y_{\ell m}\rangle \langle Y_{\ell m}|. \quad (2.59)$$

The $Y_{\ell m}$'s are spherical harmonics. A matrix element of this operator between two plane wave states $|\vec{k}\rangle$ and $|\vec{k}'\rangle$ gives rise to integrals of the form:

$$\int j_\ell(kr) U_{ps,\ell}(r) j_\ell(k'r) P_\ell(\cos \theta_{\vec{k}\vec{k}'}) r^2 dr, \quad (2.60)$$

where j_ℓ is a spherical Bessel function and $P_\ell(\cos \theta_{\vec{k}\vec{k}'})$ is a Legendre polynomial of the angle between the wavevectors $\vec{k}$ and $\vec{k}'$. The form of Eq. (2.60) implies that for each ℓ one has to compute $mn(n+1)/2$ integrals if there are n plane waves in the pseudowavefunction expansion at m k -points in the Brillouin zone. For most applications this would be a prohibitively large number of integrals to compute.

To circumvent this difficulty, Kleinman and Bylander¹⁹ found a way to write the semi-local pseudopotential of Eq. (2.58) in a fully *non-local* form. The non-local form is computationally advantageous since matrix elements of the non-local operator are of a separable form, that is, the analog of the right side of Eq. (2.60) is written as a product of integrals each of which involves only one k -vector. Using this form reduces the number of integrals that need to be computed from $n(n+1)/2$ to mn .

Kleinman and Bylander's procedure is as follows. Add and subtract an arbitrary local function in Eq. (2.58)

$$V = V_L(r) + \sum_{\ell,m} |Y_{\ell m}\rangle \delta U_\ell \langle Y_{\ell m}|, \quad (2.61)$$

where

$$\delta U_\ell(r) \equiv U_{ps,\ell}(r) - V_L(r). \quad (2.62)$$

Now by defining

$$\Phi_{\ell m}(\vec{r}) = \phi_{\ell}(r)Y_{\ell m}(\theta, \phi), \quad (2.63)$$

the non-local form

$$V_{\ell}^{NL}(r) = \sum_{\ell m} \frac{|\delta U_{\ell}(\Phi^0)_{\ell m}\rangle \langle (\Phi^0)_{\ell m} \delta U_{\ell}|}{\langle (\Phi^0)_{\ell m} | \delta U_{\ell} | (\Phi^0)_{\ell m} \rangle}, \quad (2.64)$$

can be written in place of the semi-local term, V_{ℓ}^{SL} , in Eq. (2.61). The functions $(\Phi^0)_{\ell m}$ are the pseudo-eigenfunctions corresponding to the semi-local potential V_{ℓ}^{SL} .

As was shown by Kleinman and Bylander¹⁹ this operator gives the same result when acting on a pseudo eigenfunction $(\Phi^0)_{\ell m}$ as does the semi-local operator. The fact that the results are different for the non-local and semi-local operators, when acting on a state which is not an eigenstate, as is the case when the pseudopotential is used in a different environment, can be used to improve transferability through an appropriate choice of the local potential $V_L(r)$

One drawback of the use of this form of separable potential is the possible existence of spurious eigenstates (see footnote 10 in Ref. 19). These spurious states, sometimes called “ghost states”, which have the signature of having extremely low, unphysical eigenvalues, have been analyzed by Gonze et al.^{42,43} These authors have provided a prescription for eliminating ghost states through proper adjustment of certain pseudopotential parameters such as the core cutoff radius. Generally, however, we have found that simply changing the choice of the local potential used to construct the Kleinman Bylander non-local operator is sufficient to eliminate ghost states.

2.11 The band gap problem: “GW” theory

The density-functional formalism^{1,4} is a formally exact theory of the ground state of an interacting system of electrons in an external potential. In order to apply this theory to real systems, however, one must make approximations to the exchange-correlation energy E_{xc} and its functional-derivative – the exchange-correlation potential. The most common approximation used in practice is the local-density approximation (LDA)⁴ which allows for a practical procedure for calculating ground-state properties.

While the single-particle wave functions lead to accurate ground-state densities,^{44,45,46,47} the eigenvalues have no direct physical significance but arise in the theory as lagrange multipliers which assure conservation of particle number. The eigenvalues do, however, form a discrete spectrum and it is attractive to interpret them as single-particle excitation energies. Fairly good results are obtained for metals⁴⁶, when this procedure is adopted, but for semiconductors, the results are disappointing leading to errors in calculated band gaps of up to 50%.^{47,48} Band gaps are always underestimated with the LDA.

Often the local-density approximation to the exchange-correlation energy is blamed for the poor results in the calculated band gaps, and attempts have been made to devise better exchange-correlation potentials in hopes of solving the so called “band gap problem”.

Some of the first attempts to improve on the LDA involved incorporating corrections depending on the gradients of the density^{1,4}. Since that time, many gradient-corrected density functionals have been proposed^{44,49,50,51,52,53,54} which, in many cases, have led to better ground-state properties, but excitation energies are seen to be marginally improved at best.

Other attempts include self-interaction corrections^{55,56} and density-functionals based on model dielectric functions,^{57,58,59,60,61,62}. None of these attempts, however, have lead to a definitive solution to the band gap problem.

Quite a different viewpoint was taken by Perdew and Levy⁶³ and Sham and Schlüter⁶⁴ who demonstrated that even if the *exact* density-functional were known, the band gap would still not be correctly given by the difference of Kohn-Sham eigenvalues between the highest occupied and lowest unoccupied states due to discontinuities in the exchange-correlation and kinetic energy functionals. These discontinuities are examined in detail by Sham and Schlüter⁶⁵ and Lannoo, Schlüter and Sham.⁶⁶

Currently the most accurate calculations of band gaps in semiconductors and insulators have been obtained using the *GW* theory of Hedin and Lundqvist,^{61,67,68,69,70,71,72,73,74,75,76,77,78} This theory starts from Dyson's equation^{61,67}

$$(T + V_{ion} + V_h)\psi_{n,k}(\vec{r}) + \int d^3r' \Sigma(\vec{r}, \vec{r}', E_{n,k}^{qp})\psi_{n,k}(\vec{r}') = E_{n,k}^{qp}\psi_{n,k}(\vec{r}), \quad (2.1)$$

where the terms in Eq. (2.1) are the kinetic energy, the ionic potential, the Hartree potential, and the electron self-energy operator respectively. Exchange and correlation effects are contained in Σ . In this theory, excitation energies are given as the poles of the self-energy operator.

The so called *GW* approximation,^{61,67} which allows for practical calculations, is obtained by assuming the following form for the self-energy operator

$$\Sigma(\vec{r}, \vec{r}'; E) = \frac{i}{2\pi} \int d\omega \epsilon^{-i\delta\omega} G(\vec{r}, \vec{r}'; E - \omega) W(\vec{r}, \vec{r}'; \omega), \quad (2.2)$$

where G is the dressed Green's function, W is the dynamically screened Coulomb interaction and δ is a positive infinitesimal. One drawback of this theory is that prior knowledge of the frequency and wave number dependent dielectric function is required in order to obtain the screened Coulomb interaction.

2.12 Important consequences of *GW* theory

The *ab initio* calculations to be presented in this dissertation are based on the density-functional theory in the LDA but make use of two important results of *GW* theory as applied to semiconductors namely, 1) the quasiparticle wave functions obtained using *GW* theory are extremely well approximated by LDA wave functions and, 2) the quasiparticle band structure of *GW* theory can be obtained fairly accurately by invoking a rigid upward shift of the conduction bands obtained using LDA. This shifting of the LDA conduction bands has been called the “scissors operator” in the literature. On the first point, Hybertsen and Louie found better than 99.9% overlap between quasiparticle and LDA wave functions⁷¹ and on the second point, Godby, Schlüter and Sham carried out detailed investigations of the validity of “scissors operator” and found it to be accurate to within 0.1eV in silicon and to within 0.2eV in GaAs.⁷⁶

2.13 Optical response: time-dependent perturbation theory

The calculations to be presented use the linear-response methods of Levine and Allan.^{79,80,81,82,83} This theory, which includes local-field corrections (to be discussed), is based on an approach to linear response, in the context of density-functional theory, which has been called the time-dependent local-density approximation (TDLDA),^{84,85,86,87} or more recently, simply density-functional perturbation theory.^{88,89} In this theory the induced charge density arises in response to the self-consistent field of the external plus Coulomb and exchange correlation potentials.

The induced number density is written as

$$\delta n(\vec{r}; \omega) = \int d^3 r' \chi_0(\vec{r}, \vec{r}'; \omega) \phi^{scf}(\vec{r}'; \omega). \quad (2.3)$$

The self-consistent field $\phi^{scf}(\vec{r}'; \omega)$, is given in terms of the external field $\phi^{ext}(\vec{r}'; \omega)$ as

$$\phi^{scf}(\vec{r}'; \omega) = \phi^{ext}(\vec{r}'; \omega) + \phi^C(\vec{r}'; \omega) + \phi^{xc}(\vec{r}'; \omega), \quad (2.4)$$

where

$$\phi^C(\vec{r}'; \omega) = e^2 \int d^3 r' \frac{\delta n(\vec{r}'; \omega)}{|\vec{r} - \vec{r}'|}, \quad (2.5)$$

is the induced Coulomb potential and

$$\phi^{xc}(\vec{r}'; \omega) = \left. \frac{\delta V_{xc}(\vec{r})}{\delta n(\vec{r})} \right|_{n(\vec{r})=n_0(\vec{r})} \delta n(\vec{r}; \omega), \quad (2.6)$$

is the induced exchange-correlation potential. The independent-particle susceptibility is given as

$$\chi_0(\vec{r}, \vec{r}'; \omega) = \sum_{ij} (f_i - f_j) \frac{\psi_i^*(\vec{r}) \psi_j(\vec{r}) \psi_j^*(\vec{r}') \psi_i(\vec{r}')}{\epsilon_i + \hbar\omega - \epsilon_j + i\eta}, \quad (2.7)$$

where the f_i are occupation factors (0 or 1), η is a positive infinitesimal and the sum is over all single-particle states (taken to be the LDA eigenstates).

We apply this theory to crystalline solid, where the self-consistent potential, induced charge density and wave functions have the Bloch form

$$\phi^{scf}(\vec{r}; \omega) = \Omega_0^{-1} e^{i\vec{q} \cdot \vec{r}} \tilde{\phi}^{scf}(\vec{r}; \omega), \quad (2.8)$$

$$\delta n(\vec{r}; \omega) = \Omega_0^{-1} e^{i\vec{q} \cdot \vec{r}} \tilde{n}(\vec{r}; \omega) \quad (2.9)$$

$$\psi_{n\vec{k}}(\vec{r}) = (N\Omega_0)^{-1/2} e^{i\vec{q} \cdot \vec{r}} \langle \vec{r} | n, \vec{k} \rangle$$

where $\tilde{\phi}^{scf}(\vec{r}; \omega)$, $\tilde{n}(\vec{r}; \omega)$ and $\langle \vec{r} | n, \vec{k} \rangle$ have the periodicity of the lattice, Ω_0 is the unit cell volume and N is the number of unit cells in the crystal. The periodic part of the induced charge density is obtained using Eq. (2.3) as

$$\tilde{n}(\vec{r}; \omega) = \Omega_0 \int_{BZ} d^3k \sum_{n\pm}^{occ} \langle n, \vec{k} | \vec{r} \rangle \langle \vec{r} | (e_{n,\vec{k}} \pm \hbar\omega - H_{\vec{k}+\vec{q}})^{-1} \tilde{\phi}^{scf}(\omega) | n, \vec{k} \rangle, \quad (2.10)$$

where the operator $\tilde{\phi}^{scf}(\omega)$ is defined as

$$\tilde{\phi}^{scf}(\omega) = \Omega_0^{-1} \int_0 d^3r |\vec{r}\rangle \tilde{\phi}^{scf}(\vec{r}; \omega) \langle \vec{r}|,$$

$\Omega_0 = \Omega_0/(2\pi)^3$ and the $\vec{k} \cdot \vec{p}$ Hamiltonian $H_{\vec{k}}$ is given in LDA by

$$H_{\vec{k}+\vec{q}}^{LDA} = \frac{1}{2}(\vec{p} + \vec{k})^2 + V_{\vec{k}}. \quad (2.11)$$

The sum in Eq. (2.10) is over occupied states and the potential $V_{\vec{k}}$ is a non-local pseudopotential. Optical response is calculated by assuming a long-wave external potential $\phi^{ext}(\vec{r}) = \phi_0 e^{i\vec{q} \cdot \vec{r}}$ with $\vec{q} \rightarrow 0$ and the $\vec{k} \cdot \vec{p}$ Hamiltonian $H_{\vec{k}+\vec{q}}$ is expanded for small $\vec{q}$.

2.14 Local-field effects

We distinguish between long-wave and short-wave contributions to the induced charge density $\tilde{n}(\vec{r}; \omega)$. By definition, the long-wave component is that which gives rise to a non-zero average of $\tilde{n}(\vec{r}; \omega)$ over a unit cell and the short-wave piece is the rest.

If we assume a long-wave external potential $\phi^{ext}(\vec{r}) = \phi_0 e^{i\vec{q} \cdot \vec{r}}$, (i.e., $\tilde{\phi}^{ext}(\vec{r}) = \phi_0$) and expand Eq. (2.10) to first-order in $\vec{q}$, a non-vanishing $\tilde{n}(\vec{r}; \omega)$ is obtained ($\tilde{n}(\vec{r}; \omega)$ vanishes to zeroth order in $\vec{q}$). This response, so obtained, has short-wave character (the long-wave response to the long-wave potential vanishes to this order in $\vec{q}$). The long-wave potential thus induces a short-wave charge density which in turn induces a short-wave potential. This short-wave potential is the “local-field”. Also to the same order in $\vec{q}$ there is a long-wave response to the short-wave potential, which is obtained by assuming a potential of the Bloch form in Eq. (2.10), expanding to first order in $\vec{q}$ and integrating over the unit cell.

Lastly, a non-vanishing long-wave response to a long-wave potential is obtained by expanding the $\vec{k} \cdot \vec{p}$ Hamiltonian to second order in $\vec{q}$. Expressions for the long- and short-wave induced densities were presented by Levine and Allan.⁸¹

Ultimately we are interested in the long-wave number-density induced by the long-wave perturbation, which has two contributions: 1) the direct contribution induced to second order in $\vec{q}$ and 2) the indirect or “local-field” contribution which is the long-wave response to the short-wave potential which was induced by the long-wave external potential.

2.15 The dielectric function

The dielectric function relates the self-consistent potential to the external potential as

$$\phi^{scf}(\omega) = \varepsilon^{-1}(\omega) \phi^{ext}(\omega). \quad (2.12)$$

We may also write this in terms of the macroscopic susceptibility χ_0 as

$$\phi^{scf} = \sum_{n=0}^{\infty} (v\chi_0)^n \phi^{ext} \quad (2.13)$$

where $v = 4\pi e^2/q^2$ is the Coulomb interaction, and the macroscopic susceptibility relates the long-wave component of the self-consistent charge-density $(\delta\tilde{n}^{SCF})^{long}$ to the external potential as

$$(\delta\tilde{n}^{SCF})^{long} = \chi_0 \tilde{\phi}^{ext}. \quad (2.14)$$

Summing the geometric series of Eq. (2.13) gives

$$\varepsilon^{-1} = (I - v\chi_0)^{-1}, \quad (2.15)$$

implying

$$\varepsilon = (I - v\chi_0). \quad (2.16)$$

The dielectric function is computed by calculating $(\delta\tilde{n}^{SCF})^{long}$ as the sum of the direct and indirect pieces (as discussed in the previous section), and Eq. (2.16) is evaluated using Eq. (2.14).⁸¹

2.16 Scissors operator

As discussed previously, results of *GW* calculations indicate that a rigid upward shift of the conduction bands produces a good approximation to the quasiparticle

band structure. Levine and Allan demonstrated, however, that it is incorrect to simply shift all band gaps which arise in the LDA optical response formulae.^{79,80,81}

Their theory begins by adding the scissors operator $\Sigma_{\vec{k}}$ to the $\vec{k} \cdot \vec{p}$ Hamiltonian

$$H_{\vec{k}} = \frac{1}{2}(\vec{p} + \vec{k})^2 + V_{\vec{k}} + \Sigma_{\vec{k}}, \quad (2.17)$$

where

$$\Sigma_{\vec{k}} = \Delta_{\vec{k}} P_{c\vec{k}}. \quad (2.18)$$

In Eq. (2.18), $\Delta_{\vec{k}}$ is the scissors shift and $P_{c\vec{k}}$ is the projection operator onto the conduction bands. Even if a rigid shift is used, the scissors operator has k -dependence due to the projection operator $P_{c\vec{k}}$.

Levine and Allan showed that inclusion of the scissors operator is equivalent to making the Ward-identity replacement

$$\vec{p} \rightarrow (\epsilon_{n\vec{k}} - H_{\vec{k}}^{LDA})^{-1} (\epsilon_{n\vec{k}} - H_{\vec{k}}^{LDA}) \vec{p}$$

in LDA optical response formulae. For example the static, long-wave number density induced by a long-wave perturbation, in the scissors operator formalism, is given by

$$\begin{aligned} \Omega_0^{-1} \int_0 d^3r \delta \tilde{n}(\vec{r}, 0) &= 2\phi_0 \Omega_0 \int_{BZ} d^3k \sum_n^{occ} \langle n\vec{k} | H_1^{LDA} (\epsilon_{n\vec{k}} - H_{\vec{k}}^{LDA})^{-1} \\ &\quad \times (\epsilon_{n\vec{k}} - H_{\vec{k}})^{-1} (\epsilon_{n\vec{k}} - H_{\vec{k}}^{LDA})^{-1} H_1^{LDA} | n\vec{k} \rangle, \end{aligned} \quad (2.19)$$

where $H_1^{LDA} \equiv \nabla_{\vec{k}} \cdot H_{\vec{k}}^{LDA}$. Note that only one of the three energy denominators has been shifted $H_{\vec{k}}^{LDA} \rightarrow H_{\vec{k}}$.

The use of this theory has produced results for the dielectric function which are in agreement with experiments to within a few percent in contrast to previous LDA results which were, in some cases, in error by 10% to 20%.^{79,80,81} This concludes the discussion of our calculational methods.

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CHAPTER III

Symmetry and strain

3.1 Definitions

The photoelastic tensor is defined in terms of a linear relation between the applied strain and the resulting changes in the dielectric tensor and can be viewed as the lowest order term in a series expansion in powers of the strain. As such, the calculation must be sensitive enough to be able to resolve small changes induced in the dielectric function by small applied strains. In addition, one must verify that the linear relation does, in fact, hold for the strains used in the calculations. Fortunately, our calculations are extremely sensitive and we were able to use very small strains which easily satisfied the linear-in-strain relation. For example, changes in the valence bands at the Γ -point resulting from the application of volume-non-conserving strains along the $[001]$ direction were found to follow a linear relation for most of the range of strains from $\delta a/a = 0.04\%$ to $\delta a/a = 5\%$, where a is the lattice constant, as shown in Fig. 3.1. “Volume-non-conserving”, in the previous sentence, means that the crystal is compressed along the $[001]$ direction keeping the unit-cell lengths in the $[100]$ and $[010]$ directions fixed.

Fig. 3.1 Bandgaps at $k = 0$ as a function of tetragonal ([001]) strain. Appendix B gives a detailed discussion of strain-effects at $k = 0$, in particular, the deformation potential b_{gap} , is determined from this plot as $b_{gap} = (-2/3)(\text{slope of } E_4(0) - E_1(0))$ (see appendix B), where $E_4(0)$ is the strain-dependent, $k = 0$, lowest conduction band and $E_1(0)$, $E_2(0)$ and $E_3(0)$ are the strain-dependent, $k = 0$, highest valence bands.

For the plot of the $k = 0$ band gaps vs. strain, Fig. 3.1, the slopes are found to obey relations predicted by $\vec{k} \cdot \vec{p}$ theory¹ (see appendix B). In particular two valence bands (E_2 and E_3) increase in energy relative to the conduction band (E_4) with positive strain while the remaining band (E_1) decreases with the ratio of the slope for the single band to that for the group of two bands given by -2 . The deformation potential b_{gap} , is determined from this plot as $b_{gap} = (-2/3)(\text{slope of } E_4(0) - E_1(0)) = -1.69 \text{ eV}$ (see appendix B).

To minimize any errors due to non-linearities we used the smallest strains possible while still maintaining a good signal-to-noise ratio, the noise being the numerical error in the calculated dielectric function. We chose $\delta a/a = 0.0004$, which gives, for changes in the dielectric function, a signal-to-noise ratio greater than 100, for the smallest strain-induced changes which came from the volume-conserving [001] and volume-conserving [111] strains. Whenever the term “volume-conserving” is encountered it means a(n) compression (expansion) along one direction, say along [001] for instance, followed by a compensating expansion (compression) in the plane normal to the axis of the initial strain. The strain tensors in each case are traceless and these strains are also referred to as “shear” strains.

We used the same small value of $\delta a/a$ in all of the strains considered. For hydrostatic strain this means a change in the unit cell lengths in each of the x , y , and z directions by the amount $\delta a/a = 0.0004$. For strain in the [111] direction this means a change in all lengths, $\delta \ell/\ell = 0.0004$, measured along the [111] direction followed by a volume restoring change in the plane normal to the [111] direction.

Based on the study of energy bands vs. strain for the volume-non-conserving [001] strains, it is assumed that the chosen values of $\delta a/a = 0.0004$ for hydro-

static strain, and $\delta\ell/\ell = 0.0004$ for [111] also produce strains which satisfy the linear-strain assumption. The reasoning is as follows. Consider the [001] volume non-conserving strain that was used for the energy band study mentioned above. The volume-non-conserving strain can be decomposed into two contributions: 1) a hydrostatic (uniform) strain and 2) a volume-conserving (traceless strain tensor) strain. Explicitly we write:

$$\mu = \frac{\delta a}{a} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \frac{\delta a}{3a} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{\delta a}{3a} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \quad (3.1)$$

where the first term is the hydrostatic contribution and the second is the [001] volume-conserving piece. Let us now estimate the volume change implied by the hydrostatic contribution corresponding to the largest ($\delta a/a = 5\%$) strain considered. Each dimension of the unit cell would be changed by an amount $0.05/3$ leading to an overall volume change given by

$$\frac{\delta V}{V} = 0.05. \quad (3.2)$$

This is to be compared with the volume change obtained when $\delta a/a = 0.0004$ is used to study the effects of hydrostatic strain on the dielectric function

$$\frac{\delta V}{V} = 3(0.0004) = 0.0012, \quad (3.3)$$

a volume change which is roughly a factor of 40 smaller. This is certainly in the linear regime! Keep in mind that even with this *tiny* strain, the resulting change in the calculated dielectric function is still more than 1000 times larger than the numerical error. The hydrostatic strains produce changes in the dielectric tensor that are generally about an order of magnitude larger than the volume conserving strains.

As for the shear strains, in both of the $[001]$ and $[111]$ volume-conserving cases, the changes in the dielectric function are smaller than the corresponding hydrostatic-induced changes and are believed to be, if anything, in *better* agreement with the assumption of linear strains. Also, the analytic structure of the theory representing small strain-induced changes suggest that all three ways of straining give very similar changes.^{1,2} From this we conclude that if our applied strains are small enough to induce linear changes for hydrostatic and $[001]$ strains then they are also small enough for strains in the $[111]$ direction. We can be content to study only these three strains since we can calculate all of the needed tensor components with only these.

As we saw in section 1.3 of chapter 1, the three eigenvalues, $p_{11} + 2p_{12}$, $p_{11} - p_{12}$ and p_{44} , of the photoelastic tensor correspond to the strain eigenvectors representing hydrostatic, $[001]$ volume-conserving and $[111]$ volume-conserving strains respectively. In the language of group theory, these strains are reducible representations of the point group of the unstrained crystal ($43m$ for zinc-blende). The hydrostatic strain,

$$\frac{\delta a}{a} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (3.4)$$

is fully symmetric and corresponds to the Γ_1 symmetry. The character for the irreducible Γ_1 representation is 1 and therefore the eigenvalue $p_{11} + 2p_{12}$ is singly degenerate. The $[001]$ shear strain

$$\frac{\delta a}{3a} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad (3.5)$$

has the symmetry Γ_{12} and leads to a two-fold degeneracy of the eigenvalue $p_{11} - p_{12}$. Lastly the $[111]$ shear strain

$$\mu = \frac{\delta\ell}{3\ell} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}, \quad (3.6)$$

has symmetry Γ'_{25} and leads to the three-fold degenerate p_{44} .

Let us consider the expressions for the the various photoelastic tensor components in detail.

3.2 Hydrostatic strain: $p_{11} + 2p_{12}$

Writing the hydrostatic strain of Eq. (3.4) as a “sixvector”, using the compressed notation introduced in section 1.3 of chapter 1, gives

$$[\mu] = \frac{\delta a}{a} (1, 1, 1, 0, 0, 0)^T, \quad (3.7)$$

which is then multiplying on the left with the photoelastic tensor written in matrix form gives

$$\delta[\varepsilon^{-1}] = [p][\mu] = \frac{\delta a}{a} (p_{11} + 2p_{12}, p_{11} + 2p_{12}, p_{11} + 2p_{12}, 0, 0, 0)^T. \quad (3.8)$$

The changes on the left-hand side are obtained by taking finite differences of the strained and unstrained dielectric function as

$$\delta[\varepsilon^{-1}] = \frac{\delta a}{a} \begin{pmatrix} p_{11} + 2p_{12} & 0 & 0 \\ 0 & p_{11} + 2p_{12} & 0 \\ 0 & 0 & p_{11} + 2p_{12} \end{pmatrix}. \quad (3.9)$$

Since the changes in all three diagonal components are the same, we can write the expression for $p_{11} + 2p_{12}$ in terms of any one of them, say the zz component, as

$$p_{11} + 2p_{12} = -\frac{1}{\delta a/a} \left(\frac{\varepsilon_{zz} - \varepsilon_{zz}^0}{(\varepsilon_{zz}^0)^2} \right), \quad (3.10)$$

where ε_{zz}^o is the unstrained value of the zz component of the dielectric function and we have made the approximation

$$\frac{1}{\varepsilon_{zz}^2} \approx \frac{1}{(\varepsilon_{zz}^o)^2}. \quad (3.11)$$

3.3 [001] shear strain: $p_{11} - p_{12}$

The volume-conserving [001] strain of Eq. (3.5) is written as a sixvector as

$$[\mu] = \frac{\delta a}{3a}(-1, -1, 2, 0, 0, 0)^T, \quad (3.12)$$

and is then multiplied on the left by the photoelastic tensor in matrix form to yield

$$\delta[\varepsilon^{-1}] = \frac{\delta a}{3a} \begin{pmatrix} p_{12} - p_{11} & 0 & 0 \\ 0 & p_{12} - p_{11} & 0 \\ 0 & 0 & -2(p_{12} - p_{11}) \end{pmatrix}. \quad (3.13)$$

As in the case of the hydrostatic strain, we obtain the eigenvalue $p_{12} - p_{11}$, in terms of the difference between strained and unstrained components of the dielectric tensor. By subtracting two of the strained dielectric tensor components, such as ε_{xx} and ε_{zz} we can eliminate the dependence on the unstrained quantities. Forming the combination $\varepsilon_{zz}^{-1} - \varepsilon_{xx}^{-1}$, using Eq. (3.13) and solving for the eigenvalue $p_{11} - p_{12}$ gives

$$p_{11} - p_{12} = -\frac{\varepsilon_{zz} - \varepsilon_{xx}}{(\varepsilon^o)^2 \delta a / a}, \quad (3.14)$$

where we have used the approximation

$$\frac{1}{\varepsilon_{xx}^2} \approx \frac{1}{\varepsilon_{zz}^2} \approx \frac{1}{(\varepsilon_{zz}^o)^2} \equiv \frac{1}{(\varepsilon^o)^2}. \quad (3.15)$$

This equation, which depends only on quantities evaluated for the strained crystal, is convenient for investigating properties of the Brillouin-zone integrals involved since only one calculation rather than two need be done.

3.4 [111] shear strain: p_{44}

The last strain that we consider is the volume-conserving strain along [111] which is given by Eq. (3.6). Written as a sixvector this strain is

$$[\mu] = \frac{\delta\ell}{3\ell}(0, 0, 0, 2, 2, 2)^T, \quad (3.16)$$

which when multiplied on the left by the photoelastic tensor gives

$$\delta[\varepsilon^{-1}] = \frac{2\delta\ell}{3\ell} \begin{pmatrix} 0 & p_{44} & p_{44} \\ p_{44} & 0 & p_{44} \\ p_{44} & p_{44} & 0 \end{pmatrix}. \quad (3.17)$$

The calculation can be simplified somewhat if we choose to write this tensor in terms of the principal axes, which for this case, are defined such that the z -axis, call it $\hat{z}'$, lies along the [111] strain axis of the cubic system. The other two axes, $\hat{x}'$ and $\hat{y}'$, are chosen to lie in a plane normal to the $\hat{z}'$ and be orthogonal to each other. In this system, the matrix of Eq. (3.17) becomes diagonal and assumes the form

$$\delta[(\varepsilon')^{-1}] = \frac{2\delta\ell}{3\ell} \begin{pmatrix} -p_{44} & 0 & 0 \\ 0 & -p_{44} & 0 \\ 0 & 0 & +2p_{44} \end{pmatrix}. \quad (3.18)$$

We write p_{44} in terms of quantities evaluated entirely with respect to the strained crystal

$$p_{44} = -\frac{\varepsilon_{zz} - \varepsilon_{xx}}{2(\varepsilon^o)^2\delta\ell/\ell}, \quad (3.19)$$

as was done for the $p_{11} - p_{12}$ component.

3.5 Internal strain relation: ζ

The [111] strain is slightly more complicated than the other two in that the [111] bond is no longer equivalent to the other three [111], $[\bar{1}\bar{1}1]$ and $[1\bar{1}\bar{1}]$ bonds. In this

case, the relative positions the two fcc sublattices, which comprise the zinc-blende structure, are no longer constrained by symmetry and, in general, a structural relaxation occurs. The internal strain parameter ζ was defined by Kleinman^{3,4} in such a way so that for $\zeta = 0$ there is no relaxation and all atomic positions are changed according to $\vec{r}_{final} = (\mathbf{1} + \mu)\vec{r}_{initial}$. For a volume conserving [111] strain, as considered in Eq. (3.6), this implies bond-lengths $(\sqrt{3}a/4)(1 + 2\eta/3)$ for the [111] direction and $(\sqrt{3}a/4)(1 - 2\eta/6)$ for the $[\bar{1}\bar{1}\bar{1}]$, $[1\bar{1}\bar{1}]$ and $[11\bar{1}]$ directions. For $\zeta = 1$, a relaxation occurs in such a way so that all of the bond-lengths are the same and assume their original unstrained length $(\sqrt{3}a/4)$. If we assume that the unstrained [111] bond is directed from the origin to the point $(a/4)(1, 1, 1)$ then the relaxation corresponding to $\zeta = 1$ is a shift of the atom at position $(a/4)(1 + 2\eta/3)(1, 1, 1)$, which corresponds to $\zeta = 0$, by the amount $\vec{d} = -(a/6)(\eta, \eta, \eta)$.

Let the two fcc sublattices of the unstrained zinc-blende structure be comprised of atoms of type A and type B . Choose the unit cell to be spanned by the position vectors of four atoms of type B

$$\begin{aligned}\vec{r}_0 &= (0, 0, 0) \\ \vec{r}_1 &= (a/2)(0, 1, 1) \\ \vec{r}_2 &= (a/2)(1, 0, 1) \\ \vec{r}_3 &= (a/2)(1, 1, 0),\end{aligned}\tag{3.20}$$

and let the basis be the position vector

$$\vec{b} = (a/4)(1, 1, 1)\tag{3.21}$$

which indicates the position of an atom of type A . This basis vector can be written in terms of the position vectors for the B atoms as

$$\vec{b} = \tau(\vec{r}_1 + \vec{r}_2 + \vec{r}_3) \quad (3.22)$$

with $\tau = 1/4$. Under an arbitrary strain, μ , the position vectors for the B atoms are changed as

$$\vec{r}_i^{final} = (\mathbf{1} + \mu)\vec{r}_i^{initial}. \quad (3.23)$$

For hydrostatic and $[001]$ strains, the A atom moves according to Eq. (3.22) with $\tau = 1/4$. If however, a $[111]$ strain is applied, then the B atoms still move as Eq. (3.23) but now the A atom is allowed to relax and its final position is given by Eq. (3.22) but now with τ given by

$$\tau = \frac{1}{4} \left(1 - \frac{2\zeta\eta}{3(1+\eta)} \right), \quad (3.24)$$

as is shown in section 3.6. Equation (3.24) holds for both volume conserving and volume non-conserving strains.

Some representative values of ζ for GaAs are 0.48 (Calc. Ref. 4), 0.6 (Calc. Ref. 5) and 0.76 (Exp. Ref. 6). We have calculated the strain parameter $\zeta = 0.517$ which is in agreement with the ab-initio calculations of Gironcoli, Baroni, and Resta⁷ who predict $\zeta = 0.528$.

Our calculation of ζ is performed by calculating the interatomic force vs. ζ and finding the ζ which eliminates the force. These calculations were performed with volume non-conserving strains so as to be able to determine the volume dependence of $\zeta = \zeta(V)$. Averaging the results for expansion and contraction gives $\zeta(V)$ at the unstrained volume while taking the difference leads to volume derivatives of ζ . The

experimental lattice constant was used to obtain the unstrained volume and lengths along the [111] were changed by $\delta\ell/\ell = \pm 0.004$. We express the volume dependence of ζ in terms of the logarithmic derivative of ζ with respect to the lattice constant as

$$\begin{aligned} \frac{d \ln \zeta}{d \ln a} &= \frac{3V}{\zeta(V)} \frac{d\zeta}{dV} \\ &= \frac{3V}{\zeta(V)} \left(\frac{\zeta(V + \Delta V) - \zeta(V - \Delta V)}{2\Delta V} \right). \end{aligned} \quad (3.25)$$

At the experimental lattice constant we obtain

$$\frac{d \ln \zeta}{d \ln a} \approx -15. \quad (3.26)$$

The fact that ζ can take on a range of values tells us that the interactions between the atoms cannot be described simply in terms of two-body potentials. If the energy of interaction depended only on bond-lengths then we would find $\zeta = 1$ always, since for $\zeta = 1$ the bond-lengths would all be equal. On the other hand suppose only bond-angles mattered. In this case the relaxation parameter would always take on the value $\zeta = -1/2$, as this is the value of ζ which yields equal bond-angles.

Stillinger and Weber proposed empirical potentials which include three-body as well two-body interactions^{8,9} and emphasized that two-body interactions alone would be insufficient to stabilize the diamond and zinc-blende structures. We can make an estimate of the relaxation parameter ζ by using potentials of the Stillinger-Weber form, which have been optimized to describe liquid and solid GaAs,¹⁰ and minimizing the energy of atoms in the strained crystal with respect to bond-length and bond-angle, i.e. with respect to ζ .

Consider once again the unit cell, which in the unstrained crystal, consists of four atoms of type B at the vertices of a tetrahedron and one atom of type A at the center. This unit cell is described by Eqs. (3.20) and (3.21) for the unstrained crystal and by Eqs. (3.22), (3.23) and (3.24) in the crystal in the presence of $[111]$ strain with relaxation. We have sufficient information to determine the bond-lengths and bond-angles using the aforementioned equations. From these we can determine the energy with respect to the parameter ζ .

Assume a quadratic energy function of bond-length and bond-angle of the form:

$$E(dl, d\theta) = A \sum_i \left(\frac{d\ell_i}{\ell} \right)^2 + B \sum_j \left(\frac{d\theta_j}{\theta} \right)^2. \quad (3.27)$$

The bond-length change along the $[111]$ direction is given by

$$d\ell_1 = \eta \ell \left(1 - \frac{2\zeta}{3} \right), \quad (3.28)$$

while along the $[1\bar{1}1]$, $[11\bar{1}]$ and $[1\bar{1}\bar{1}]$ directions the bond-length changes are given by

$$d\ell_2 = d\ell_3 = d\ell_4 = \frac{\eta \ell (1 + 2\zeta)}{9}. \quad (3.29)$$

Three bond-angles increase by the amount

$$d\theta_{102} = d\theta_{103} = d\theta_{104} = \sqrt{8} \frac{(1 + 2\zeta)}{9}, \quad (3.30)$$

while the three remaining bond-angles $d\theta_{203}$, $d\theta_{204}$, $d\theta_{304}$, decrease by the same amount. The notation in the above equations means that the central atom is denoted by 0, the atom along $[111]$ by 1 and the remaining three by 2, 3, and 4. Using Eq.'s (3.28), (3.29) and (3.30) in Eq. (3.27) gives

$$E(dl, d\theta) = \eta^2 A \left[\left(1 - \frac{2\zeta}{3} \right)^2 + \frac{3}{81} \left(1 + 2\zeta \right)^2 \right] + \eta^2 B \left[\frac{16}{27} \frac{1}{\theta^2} \left(1 + 2\zeta \right)^2 \right],$$

where A and B are obtained by expanding the empirical Stillinger-Weber potentials about the equilibrium bond-length and bond-angle. Minimizing $E(dl, d\theta)/\eta^2$ with respect to ζ gives

$$\zeta = \left(\frac{1 - (2/\theta^2)(B/A)}{1 + (4/\theta^2)(B/A)} \right),$$

for the optimal ζ . Using the parameters appropriate to GaAs¹⁰ we find $B/A = 0.15016$ which leads to $\zeta = 0.78807$, a value larger than our calculated ζ by roughly a factor of 3/2. It is possible that this slightly higher value of ζ is due to neglect next-nearest neighbor interactions when using the empirical potentials.

3.6 Implementation of [111] strain

Some details regarding the atomic coordinates required for the implementation of the [111] strains including the relaxation defined by Kleinman's ζ will now be provided. Imagine a volume non-conserving strain along the [111] direction with no relaxation. This simply means that all lengths measured along the [111] direction are rescaled as

$$\ell_{final} = (1 + \eta)\ell_{initial}, \quad (3.31)$$

where

$$\eta \equiv \frac{\delta\ell}{\ell}, \quad (3.32)$$

is a negative scalar for compressions and is positive for expansions. In the conventional cubic coordinate system the strain tensor would be written

$$\mu = \frac{\eta}{3} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}. \quad (3.33)$$

Changes in lengths measured along any given direction $\hat{\ell}$, are obtained as

$$\frac{\delta\ell}{\ell} = \hat{\ell}^T \cdot \mu \cdot \hat{\ell}. \quad (3.34)$$

For the $[111]$ direction

$$\hat{\ell} \equiv \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}.$$

Eq. (3.34) implies length changes $\delta\ell/\ell = \eta$ as promised. Equivalently this can be seen by writing the strain tensor with respect to the principal axes $\{\hat{x}', \hat{y}', \hat{z}'\}$

$$\mu' = \eta \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (3.35)$$

where $\hat{z}'$ lies along $[111]$.

In an unstrained zinc-blende structure consisting of atoms of type A and B , each atom of type A can be viewed as sitting at the center of a tetrahedron with four atoms of type B at the vertices. Let us define the origin to be the point at which the atom of type A sits. In this system, assuming the AB bond-length to be given by ℓ , the coordinates of the four B atoms are given by

$$\begin{aligned} \vec{r}_1 &= \ell(0, 0, 1) \\ \vec{r}_2 &= \ell\left(0, \frac{2\sqrt{2}}{3}, -\frac{1}{3}\right) \\ \vec{r}_3 &= \ell\left(\frac{\sqrt{6}}{3}, -\frac{\sqrt{2}}{3}, -\frac{1}{3}\right) \\ \vec{r}_4 &= \ell\left(-\frac{\sqrt{6}}{3}, -\frac{\sqrt{2}}{3}, -\frac{1}{3}\right) \end{aligned} \quad (3.36)$$

Note that these vectors are expressed in terms of a coordinate system in which the $[111]$ direction of the conventional cubic system coincides with the $-\hat{z}$ direction. Under the volume non-conserving strain of Eq. (3.33), the z -components in Eqs. (3.36) are modified as $\ell \rightarrow \ell(1 + \eta)$ for $\vec{r}_1$ and $-\ell/3 \rightarrow -\ell/3(1 + \eta)$ for $\vec{r}_2, \vec{r}_3$ and $\vec{r}_4$. The $[111]$ bond-length is $\ell(1 + \eta)$. If we now permit relaxation this bond-length changes to $\ell(1 + \eta - \zeta^*)$. One must be careful to realize at this point that the internal strain parameter defined here, ζ^* , is **not** the same as Kleinman's ζ .

Actually we will see that $\zeta = (3/2)\zeta^*$. The difference lies in the fact that the volume *non*-conserving strain that we have considered here contains a hydrostatic contribution which doesn't contribute to the relaxation.

In the presence of relaxation the B atoms do not change their relative positions: only the A atom moves with respect to the B atoms. For this reason, let us adopt a new coordinate system in which the atom at $\vec{r}_1$ is the origin and atom A is written relative to the position vectors of the B atoms at $\vec{r}_2$, $\vec{r}_3$ and $\vec{r}_4$. Let the new position vectors be denoted by $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ as

$$\begin{aligned}\vec{b}_1 &= \vec{r}_2 - \vec{r}_1 \\ \vec{b}_2 &= \vec{r}_3 - \vec{r}_1 \\ \vec{b}_3 &= \vec{r}_4 - \vec{r}_1.\end{aligned}\tag{3.37}$$

Now write the position vector for the A atom as

$$\vec{r}_A = \tau \vec{b}_1 + \tau \vec{b}_2 + \tau \vec{b}_3.\tag{3.38}$$

Using Eq. (3.37) in Eq. (3.38) gives

$$\vec{r}_A = (0, 0, -4\tau\ell(1 + \eta)).\tag{3.39}$$

Since we have defined the bond-length, in the presence of relaxation, to be

$$\ell(1 + \eta - \zeta^*),\tag{3.40}$$

we arrive at an expression for the parameter τ , which defines the position of the A atom relative to the B atoms, in terms of the relaxation parameter ζ^* as

$$\tau = \frac{1}{4} \left(1 - \frac{\zeta^* \eta}{1 + \eta} \right).\tag{3.41}$$

The parameter τ is, of course, independent of the choice of coordinate system. With the replacement $\zeta^* = (2/3)\zeta$ it will be valid also for volume-conserving strains.

We now show that the relaxation parameter ζ^* , defined above, is related to Kleinman's ζ by $\zeta = (3/2)\zeta^*$. The volume non-conserving strain of Eq. (3.33) (which for convenience is written in terms of the conventional cubic coordinate system) is decomposed as a sum of a hydrostatic and a volume-conserving contribution

$$\mu = \frac{\eta}{3} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} = \frac{\eta}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{\eta}{3} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}, \quad (3.42)$$

where the first term is the hydrostatic piece and the second is the volume-conserving piece. Using Eq. (3.34) to determine length changes along [111] we arrive at

$$\ell_{final} = \ell_{initial} \left(1 + \frac{\eta}{3} + \frac{2\eta}{3} \right), \quad (3.43)$$

where the second term comes from the hydrostatic contribution and the third comes from the volume conserving piece. The relaxation of the [111] bond comes only from the volume conserving contribution since the hydrostatic strain doesn't lower the symmetry and thus cannot contribute to the relaxation. The net result is that Kleinman's ζ is defined only in terms of the last term in Eq. (3.43) as

$$\ell_{final} = \ell_{initial} \left(1 + \frac{\eta}{3} + \frac{2\eta(1 - \zeta)}{3} \right). \quad (3.44)$$

Equating Eq. (3.44) with Eq. (3.40) gives

$$\zeta = (3/2)\zeta^*. \quad (3.45)$$

Using Eq. (3.45) in Eq. (3.41) gives the correct form for the parameter τ as

$$\tau = \frac{1}{4} \left(1 - \frac{2\zeta\eta}{3(1 + \eta)} \right), \quad (3.46)$$

where ζ is the conventional internal strain parameter as defined by Kleinman.³

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CHAPTER IV

Numerical integration methods

4.1 Problems with k -point sampling

The calculation of the photoelastic effect in GaAs presented a difficult convergence problem which arose out of the need to accurately sample sharply-peaked, highly-oscillatory integrands over a tiny region of the Brillouin-zone centered about the Γ -point. Standard k -point integration methods were insufficient, and an alternate approach was required. This chapter presents details of the methods used to characterize the integrands and correctly perform the integrals.

As discussed in section 1.3, the photoelastic tensor components are obtained by taking differences of the dielectric function calculated in the presence of various strains. Since the strain-induced changes are very small in comparison to the unstrained dielectric function, we were faced with a difficult signal-to-noise problem. Levels of accuracy which are entirely acceptable for the calculation of the dielectric function are woefully inadequate for calculating the photoelastic tensor.

The behavior of the frequency-dependent photoelastic tensor is dominated by “critical points,”^{1,2,3} which are points in k -space at which the joint density of states becomes singular, i.e., points where $\nabla_{\vec{k}} \cdot (E_c(\vec{k}) - E_v(\vec{k})) = 0$. For photon energies (frequencies) below the fundamental gap, the most important critical point is the

Γ -point ($\vec{k} = 0$). This point is largely responsible for the frequency dispersion of the photoelastic tensor and becomes increasingly important as the fundamental gap is approached. The static limit is dominated by the average of the integral over the entire zone. Nonetheless, we will see that even in the static limit the Γ -point contribution makes up to a 50% correction.

In our theory, the frequency-dependent dielectric function, in the long-wave limit, is proportional to:

$$\varepsilon_{ij}(\vec{q} = 0, \omega) - 1 \propto \sum_n^{occ} \sum_m^{unocc} \int d^3\vec{k} \frac{\langle n\vec{k} | p_i | m\vec{k} \rangle \langle m\vec{k} | p_j | n\vec{k} \rangle}{(E_{n\vec{k}} - E_{m\vec{k}})^2 ((E_{m\vec{k}} - E_{n\vec{k}} + \Delta) - \omega^2)}. \quad (4.1)$$

where Δ is the self-energy correction. The photoelastic tensor components are obtained by subtracting integrals of the form of Eq. (4.1) and, as such, can themselves be written as integrals. If the resulting integrals for the photoelastic tensor were to be written in terms of energy, through a change of variables, then the joint density of states would appear as the Jacobian of the transformation and we would more easily see points or regions where $\nabla_{\vec{k}} \cdot (E_c(\vec{k}) - E_v(\vec{k})) = 0$ as being important. In terms of k -space quantities, what we find is that the integrand is 1) sharply-peaked as we approach $\vec{k} = 0$ radially (see Fig. 4.1) , 2) highly-oscillatory as a function of the angular coordinates at a given radius k (see Figs. 5.10 and 5.11), and 3) thousands of times larger in magnitude at the Γ -point than the average over the zone. By sharply-peaked we mean that most of the action occurs in a *tiny* region of the zone yet makes order-one contributions to the effect. The Γ -point region, making such a substantial contribution, comprises less than 2% of the zone volume and is completely missed by a special k -point mesh of the density corresponding to 60 special points (see Fig. 4.1).

Fig. 4.1 Integrands for the unstrained dielectric function (○) and the photoelastic tensor (●) plotted as functions of k along the [111] direction in k -space; each exhibiting a peak at $k = 0$. The curves are normalized to unity at $k = 0$. The positions of the nearest two mesh points of a 60-point mesh are indicated by the black triangles demonstrating that the 60-point mesh completely misses the peaks. The integrand for the photoelastic tensor has a similar shape as the one for the unstrained dielectric but the ratio of the $k = 0$ value to that at the first mesh point is an order of magnitude larger.

Qualitatively, the dominant oscillations in the integrand are due to the behavior of the matrix elements (see $k \cdot p$ appendix) and the large magnitude of the integrand near Γ is due to the small energy denominator in equations such as Eq. (4.1), resulting from the small direct band gap at $\vec{k} = 0$.

It must be kept in mind that the sharply-peaked and highly-oscillatory character of the integrands for the photoelastic tensor is *also found in the integrand for the unstrained dielectric function* of Eq. (4.1). In the case of the unstrained dielectric function, however, the Γ -point region has a much smaller weight in the integral but is still significant, accounting for roughly a 1% correction. The difference in the case of the photoelastic tensor is that we are considering strain-induced *changes* and we find very large changes coming from the Γ -point region making it imperative to have an accurate treatment of this region.

At this point one might guess that the best thing to do is to simply increase density of the sampling mesh until convergence is obtained. The problem with this approach is that it would simply be too costly. The calculation of the integrand at each k -point requires roughly 1 CPU second, on the Cray Y-MP, per frequency if local field corrections are not included and 10 CPU seconds per frequency with local fields. A uniform mesh of k -points with a density large enough to correctly integrate all of the oscillations in the Γ -point region would require roughly 500,000 points in the full zone which corresponds to 31,250 in the irreducible zone for a crystal strained along [001] and 62,500 in the irreducible zone for a crystal strained along [111]. Obviously using such large numbers of points is out of the question even using the most powerful computers available. The above estimates are to be contrasted with the fact that most modern electronic-structure calculations for

insulators are adequately performed using typically fewer than a hundred points in the irreducible zone.

Fortunately things are not nearly as dismal as they might seem from the estimates made above. What saves us is the fact that as one moves away from the Γ -point, the characteristic wavelength of the oscillations becomes progressively longer allowing one to effectively use an integration mesh which is much less dense than is needed near Γ . Despite the good fortune of having the Γ -point pathology well localized, one must not underestimate the numerical challenge presented by the integral over the rest of the zone, which, in the final analysis, required several thousand points in the irreducible zone and pushed our computing resources to their limits.

To understand the necessity and effectiveness of the integration techniques which were ultimately used, one must gain an appreciation for the enormity of the numerical difficulties which were encountered. Since the methods used were extremely demanding computationally, it must be realized that they were arrived at and implemented only after it was determined that simpler methods would simply not do.

To give an example of the computational price that had to be paid, consider that to fully converge our results required up to 12,000 CPU seconds per frequency, and files as large as 500 Megabytes had to be saved between runs. To fully characterize the photoelastic tensor below the fundamental gap required roughly eight to ten frequencies per component and each of the three tensor components required calculations to be performed at both compressive and extensive strains for each frequency. Calculations were performed in the unstrained geometry of each symmetry,

for at least one frequency, to verify consistency, and the runs using hydrostatic strain required a calculation at zero strain as well as the expansion and compression. Thus to calculate $p_{11} + 2p_{12}$ required three calculations per frequency as opposed to only two calculations per frequency which were needed for the $p_{11} - p_{12}$ and p_{44} components. Of course, all of the above estimates are only for the production runs which generated the final converged results. It is estimated that at least four or five times as much effort went into characterizing the integrand and determining the accuracy of the integration method.

Before entering into a discussion of the integration techniques and systematic convergence studies, let us look at some of the ways which were used to characterize the integrand.

4.2 Investigations of Brillouin-zone integrands

The integrands associated with the Brillouin-zone integrals for the photoelastic tensor become singular as the frequency of light approaches the band gap corresponding to resonant absorption. Our theory is valid only for frequencies below the fundamental gap, but the singularity must be handled correctly as it is responsible for the frequency dispersion and to a lesser extent the static value of the photoelastic tensor.

Since there is a direct gap at $\vec{k} = 0$ in GaAs, what we see in k -space for a given frequency is that the integrand is peaked at $\vec{k} = 0$ and becomes stronger as the frequency is increased becoming singular at the band gap. This is the reason why the Γ -point region becomes more important as the frequency is increased.

The first indication that there was a problem with standard k -space integration techniques came by realizing that the LDA band gap at the nearest k -points in a 60 k -point mesh is given by 1.1 eV while the gap at $\vec{k} = (0, 0, 0)$ is 0.5 eV. This variation of 0.6 eV in the bandgap over a small range of k , although small, is significant since it appears in denominators of our k -space integrands. As mentioned in the previous paragraph, the errors are even more pronounced for non-zero frequencies.

The nearest k -points surrounding the Γ -point using a 60 k -point mesh are given by $(2\pi/a)(\pm 0.0625, \pm 0.0625, \pm 0.0625)$ and enclose a cubic region of volume $0.002(2\pi/a)^3$ which accounts for slightly less than 0.05% of the entire zone volume.

For errors made in the sampling of the Γ -point region to matter, the integrand must be sufficiently larger in this region than over the rest of the zone since the Γ -point region is so small. As was mentioned in the previous section, the photoelastic tensor is determined by subtracting two integrals which differ primarily due to contributions from the Γ -point region, and as such, the calculation of the photoelastic tensor represents just such a case in which the integrands are much larger in the Γ -point region than they are throughout the rest of the zone and give appreciable contributions despite the small integration volume.

A further complication that was found is that the integrand has considerable variation, as a function of the angular variables, at a given radius k . For small k , the dominant oscillations come from the matrix elements, but as k increases, variations due to the non-parabolicity of the energy bands also lead to angular variations. What is needed, therefore, is a systematic means of characterizing the integrands. These means are provided by spherical-harmonic expansions of the integrand on

spherical meshes of points and plane wave expansion of the integrand on uniform cubic grids of points throughout the zone.

4.3 Plane wave expansions: Fourier transforms

Fourier transforms of the integrand evaluated on uniform cubic grids of points are used to characterize the ability of standard “special k -point” techniques to correctly represent the integrand. By examining the highest Fourier components as we go from a given integration mesh to one with a higher density of points, we obtain an indication as to whether or not we are capturing all of the action.

For a given mesh density, if we see a smooth fall off of the Fourier components we are led to believe that our mesh is capturing all of the dominant oscillations. Of course we have to be careful if there is a localized feature, as there is in this problem, because if the mesh is not sufficiently dense, it might be the case that the integrand is fairly well behaved at every sampling point and yet the localized feature is completely missed. Luckily, since we know where the localized feature is, we can choose a mesh that is sufficiently dense to start with so that the nearest point is roughly in the region where the action is. The standard “special” k -point sets which contain 28, 60 and 110 points in the irreducible zone for an unstrained zinc-blende structure have their closest-to-the-origin points given by $(2\pi/12a)(\pm 1, \pm 1, \pm 1)$, $(2\pi/16a)(\pm 1, \pm 1, \pm 1)$ and $(2\pi/20a)(\pm 1, \pm 1, \pm 1)$ respectively. These closest points satisfy the requirement that they are close enough to the origin to begin to pick up the high-frequency components in the Γ -point region but as we will see, these meshes are only useful for characterizing the integrand and have densities which are far too small to accurately represent the integrands.

For any given k -space mesh containing N points there are N corresponding Fourier components. We are expanding a function defined in k -space in terms of a plane wave expansion

$$f(\vec{k}) = \frac{1}{N} \sum_{\vec{R}} f(\vec{R}) e^{i\vec{k} \cdot \vec{R}}, \quad (4.2)$$

where the vectors $\{\vec{R}\}$ are the reciprocal lattice vectors of the *of the reciprocal space*, or in other words, the direct lattice vectors, and N is the total number of $\vec{R}$ -vectors in the expansion. This expansion only assumes the periodicity of the reciprocal lattice $f(\vec{k} + \vec{G}) = f(\vec{k})$. The Fourier components $f(\vec{R})$ are obtained by inverting Eq. (4.2) as

$$f(\vec{R}) = \sum_{\vec{k}} f(\vec{k}) e^{-i\vec{k} \cdot \vec{R}}. \quad (4.3)$$

The k -space function $f(\vec{k})$ in our calculation is defined only for the first Brillouin-zone which is a polyhedron in the shape of a cube of length $4\pi/a$ with the corners cut off by the eight equivalent planes $[(\pi/a)(1,1,1)]$. For simplicity we extend the domain of $f(\vec{k})$ to include the second Brillouin-zone (the cube corners) by translating through reciprocal lattice vectors from the first zone. By doing this we obtain a cubic region in k -space as well as R -space simplifying the sums in Eqs. (4.2) and (4.3).

The Fourier transform of our k -space function is displayed as a plot of $|f(\vec{R})|$ as a function of the magnitude $|\vec{R}|$. Figures 4.2, and 4.3 present the Fourier transform of the k -space integrand associated with the photoelastic tensor for GaAs and Si (60 points in the irreducible zone) respectively.

In Figs. 4.2 and 4.3, we see an abrupt, step-function-like drop-off above a certain $|\vec{R}|$. This is because considered as a function of $|\vec{R}|$, the Fourier transform

is only correctly represented for $|\vec{R}| < R_c$ where R_c is the radius of a sphere in R -space which can be inscribed inside the cube of R -vectors. If a certain mesh is dense enough to correctly represent the k -space function $f(\vec{k})$ then the Fourier transform dies off before reaching the R_c cutoff. Thus, if as we go from one mesh to a more dense one, we see the step-function drop-off go away, then we can say that we have reached convergence of the function $f(\vec{k})$.

From the similarity of Figs. 4.2 and 4.3 it might appear that the 60-point mesh is inadequate for both GaAs and Si, whereas in fact Si is well represented by the 60-point mesh. The difference in the Brillouin zone integrands for GaAs and Si—a strong peak localized near $k = 0$ in the case of GaAs whereas there is no such peak in the $k = 0$ band gap of Si—is not easily detectable by examining the Fourier transform (real-space transform of k -space integrand) which tells us nothing about the location of k -space features especially near Γ .

The primary importance of Fourier transform data is its use in connection with the “masking-function” (to be discussed in section 4.14). The masking function is used to suppress contributions coming from the small- k region of the uniform grid. To ensure that the masking procedure doesn’t introduce any spurious oscillations into the integrand, the Fourier transform for the masked integrand is compared with that of the unmasked integrand. What is found is that the magnitude of all of the Fourier transform components are suppressed slightly and none are augmented, indicating that the masking procedure does not introduce but rather eliminates some of the oscillations of the integrand as desired. The masking function and its use will be discussed in detail in section 4.14.

Fig. 4.2 Magnitude of the Fourier transform of the k -space integrand associated with the static photoelastic tensor for GaAs, sampled with a 60-point uniform k -point mesh (60 k -points in the irreducible zone). What is plotted is the magnitude of Eq. (4.3). Direct-space lattice vectors (the transform variables of the k -space integrand) measured in units of the lattice constant. Note that no data is presented for direct-space lattice vectors larger in magnitude than $10.1a$ (a = lattice constant), which direct space lattice vector corresponds to the smallest spacing of the k -space sampling mesh. With a finer k -space mesh there would be more Fourier transform data, that is, larger direct lattice vectors corresponding to Fourier components with smaller wavelengths. Note the similarities between GaAs (this figure) and Si (Fig. 4.3). The 60-point mesh is not fine enough to resolve the striking differences between

the photoelastic integrand for GaAs and that for Si which difference occurs in the near- Γ region.

Fig. 4.3 Magnitude of the Fourier transform of the k -space integrand associated with the static photoelastic tensor for Si, sampled with a 60-point uniform k -point mesh (60 k -points in the irreducible zone). What is plotted is the magnitude of Eq. (4.3) Direct-space lattice vectors (the transform variables of the k -space integrand) measured in units of the lattice constant. See Fig. 4.2 for comparisons.

4.4 Fourier interpolation

Fourier interpolation provides a more direct way of ascertaining the accuracy of the cubic-mesh description of the function $f(\vec{k})$ than is provided by the Fourier transform, which is somewhat abstract and doesn't tell us anything about the topography of the k -space function. Fourier interpolation provides an approximation to the function $f(\vec{k})$, call it $\hat{f}(\vec{k})$, at *every* point in the Brillouin zone based on the known values of the function $f(\vec{k}_j)$ on the set of uniformly-spaced points $\{\vec{k}_j\}$. This approximate function is then compared with the *exact* function, as determined by direct sampling, to yield information as to how and where in k -space the uniform-grid representation breaks down.

To obtain the Fourier interpolating function $\hat{f}(\vec{k})$ we start with the plane wave expansion of the k -space function

$$f(\vec{k}) = \frac{1}{N} \sum_{\ell} f(\vec{R}_{\ell}) e^{i\vec{k} \cdot \vec{R}_{\ell}}, \quad (4.4)$$

where once again the vectors $\{\vec{R}_{\ell}\}$ are direct-space vectors. The expression for $f(\vec{R}_{\ell})$ given by Eq. (4.3), evaluated at the particular k -space mesh points $\{\vec{k}_j\}$

$$f(\vec{R}_{\ell}) = \sum_{\vec{k}_j} f(\vec{k}_j) e^{-i\vec{k}_j \cdot \vec{R}_{\ell}}, \quad (4.5)$$

is substituted into the plane wave expansion of Eq. (4.4) evaluated at an *arbitrary* k -point $\vec{k}$. The formal expression for the interpolation function, so obtained, is given by

$$\hat{f}(\vec{k}) = \frac{1}{N} \sum_{\vec{k}_j \in \{\vec{k}^{large}\}} f(\vec{k}_j) \sum_{\vec{R}_{\ell}} e^{i\vec{R}_{\ell} \cdot (\vec{k} - \vec{k}_j)}, \quad (4.6)$$

where $\{\vec{k}^{large}\}$ is the set of k -points comprising the first and second Brillouin zones, and N is the total number of direct-lattice vectors which, incidentally, is the same as the number of k -points in $\{\vec{k}^{large}\}$.

The sum over the direct-lattice vectors $\vec{R}_\ell$, can be performed analytically to yield the interpolating function as a sum over the k -space function at each cubic mesh point multiplied by a simple function involving sines and cosines. The interpolating function naturally reduces exactly to the known function $f(\vec{k}_j)$ when evaluated at one of the cubic mesh points:

$\hat{f}(\vec{k}_j) \equiv f(\vec{k}_j)$. The result is

$$\hat{f}(\vec{k}) = \frac{1}{N} \sum_{\vec{k}_j \in \{\vec{k}^{large}\}} f(\vec{k}_j) \prod_{\sigma=x,y,z} \left[\cos[N\pi(k_\sigma - k_{j\sigma})/2] + \frac{\sin[(N-1)\pi(k_\sigma - k_{j\sigma})/2]}{\sin[\pi(k_\sigma - k_{j\sigma})/2]} \right], \quad (4.7)$$

which is the cubic-mesh representation of the function $f(\vec{k})$ at an arbitrary point. In the above equation the k 's are the Cartesian coordinates of the k -points. Regions where the function, $\hat{f}(\vec{k})$, differs significantly from the true function, $f(\vec{k})$, require special treatment. The Fourier-interpolating function of Eq. (4.7) is crucial to understanding the interplay between the cubic-mesh description and the spherical-mesh description, which will be used in the Γ -point region where the cubic-mesh description breaks down. The interpolating-function is also the key to a systematic evaluation of the convergence of our integration method.

Considering one term in the sum in Eq. (4.7), we recognize the function given by the product of square brackets as a sharply peaked function of $\vec{k}$ which is centered around the k -point $\vec{k}_j$ and has nodes at all of the other k -points. The amplitude decreases quickly with increasing distance from $\vec{k}_j$ and there are no nodes between $\vec{k}_j$'s. This leads us to the explanation of why we sum over $\vec{k}_j \in \{\vec{k}^{large}\}$ which is a

cubic region in k -space and comprises the first *and* second Brillouin zones. If we had used only the points in the first zone, the interpolating function would have twice as many nodes, incorrectly placing one, in particular, at the Γ -point.

The sums over the direct-lattice vectors are performed as follows. One first constructs $f(\vec{k}_j)$ defined on the region $\{\vec{k}^{large}\}$, using the periodicity of k -space to obtain $f(\vec{k}_j)$ in the second zone from the values in the first zone. The direct lattice $\vec{R}_\ell$, is then taken as the reciprocal-lattice of the k -space lattice as is usual. The plane waves in Eq. (4.6) factor and the sums over $\vec{R}_{\ell\sigma}$ for the three Cartesian directions $\sigma = x, y, z$, can then be performed separately leading to the three products in Eq. (4.7). Explicitly we use the identity

$$\sum_{n=-N/2}^{N/2} w_n e^{i n \theta} \equiv \cos[N\theta/2] + \frac{\sin[(N-1)\theta/2]}{\sin[\theta/2]}, \quad (4.8)$$

where N is taken to be even, and the weights are given by $w_n = 1$ for all n except at the end points where $w_{\pm N/2} = 1/2$.

4.5 Special k -points: cubic meshes

The cubic meshes discussed above arise from a fairly standard method for constructing a Brillouin-zone integration scheme. The term “special k -points” is a term which is used fairly loosely and implies that the so-called special k -point set has been constructed in a “special” way so as to satisfy various theorems of numerical integration. The goal is to construct a set of integration points which will *exactly* integrate a number N , of the basis functions which are used to expand the function. Surprisingly, for integrating functions in k -space, the integration mesh turns out simply to be a uniform grid of points. Monkhorst and Pack⁴ demonstrated that

an optimal integration mesh could be constructed by laying down uniformly-spaced points which are given by the prescription

$$\vec{k} = \ell_1 \vec{b}_1 + \ell_2 \vec{b}_2 + \ell_3 \vec{b}_3, \quad (4.9)$$

where the $\vec{b}_i$ are the primitive basis vectors of the reciprocal lattice defined by $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$, in terms of the primitive vectors $\vec{a}_i$ of the direct lattice of the crystal. The relative coordinates ℓ_i are given by $\ell_i = (2i-1)/2N$ with $i = 1, 2, \dots, N$ and form a simple-cubic mesh of N^3 points in the ℓ -space. The underlying direct lattice in a zinc-blende crystal is of the Face-Centered Cubic (FCC) form implying a Body-Centered Cubic (BCC) lattice in reciprocal space. The Monkhorst and Pack construction of Eq. (4.9), therefore, leads to a BCC lattice of k -points in the first Brillouin-zone for the optimal k -space integration mesh. As we will see, their method must be modified somewhat when we wish to investigate a crystal whose symmetry has been lowered by strain.

Any function defined in the Brillouin-zone must obey the same point group as the direct lattice. This can easily be seen by applying a symmetry operator to any arbitrary k -space function, call it $g(\vec{k})$. We can expand $g(\vec{k})$ in plane waves as follows

$$g(\vec{k}) = \sum_{\vec{R}} f(\vec{R}) e^{i\vec{k} \cdot \vec{R}} \quad (4.10)$$

by appealing to the periodicity of k -space. Any point group operation applied to the direct lattice vectors $\vec{R}$ must leave any k -space function invariant. Now we use the following property of the dot product

$$\vec{k} \cdot (S_\sigma \vec{R}) = (S_\sigma^{-1} \vec{k}) \cdot \vec{R} \quad (4.11)$$

to show that invariance of the point-group element S_σ acting on $\vec{R}$ implies invariance of S_σ^{-1} acting on $\vec{k}$ as

$$\begin{aligned}
 g(\vec{k}) &= \sum_{\vec{R}} f(\vec{R}) e^{i\vec{k} \cdot \vec{R}} \\
 &= \sum_{\vec{R}} f(\vec{R}) e^{i\vec{k} \cdot (S_\sigma \vec{R})} \\
 &= \sum_{\vec{R}} f(\vec{R}) e^{(S_\sigma^{-1} \vec{k}) \cdot \vec{R}}.
 \end{aligned} \tag{4.12}$$

Group theory tells us that all of elements S_σ^{-1} are in the group and that it doesn't matter what order we take when applying the symmetry operations. Therefore, the direct and reciprocal spaces, must have the *same* point group.

Let us consider what this implies for the Monkhorst-Pack k -point mesh of Eq. (4.9). For an unstrained zinc-blende structure, the direct lattice is an FCC lattice, and, as mentioned previously, the mesh generated by Eq. (4.9) is a BCC lattice in k -space and a simple-cubic lattice in ℓ -space (that is, the relative coordinates of Eq. (4.9)). If we apply the point-group operations we find that, in addition to the BCC points all, of the “holes” in between the BCC points are mapped onto and what results is not a BCC lattice anymore but rather a *simple-cubic* lattice in k -space, which can equivalently be thought of as an FCC lattice in ℓ -space. Keep in mind that there are really only *two* spaces to consider: the direct and the reciprocal space, and that the ℓ -space and k -space are just two equivalent ways of describing the reciprocal space.

There is seemingly a contradiction here as to which mesh, BCC or simple cubic, in k -space, gives the optimal integration scheme, whereas in fact both meshes give *exactly* the same results for a crystal with cubic symmetry. The answer to this

minor mystery is discovered when we consider the *irreducible Brillouin-zones* (IBZ) associated with each of the two meshes. The IBZ for a given set of k -points is the smallest set of points in the Brillouin-zone (the full Brillouin-zone) which cannot be mapped onto itself by the point-group operations. One only needs to calculate the function in the IBZ and apply the point-group operations to obtain the function over the full-zone. This naturally leads to the simplification that Brillouin-zone integrals are performed over the IBZ then symmetrization, by applying the point-group operations, yields the integral over the full zone. Considering the function in the IBZ allows a great savings in practical calculations as well as providing the answer to the riddle posed at the beginning of this paragraph. In short, the IBZ for the BCC lattice in k -space is *identical* to the one for the simple-cubic lattice in k -space.

It is important to remember that the discussion of the previous paragraph was considered only with the situation of an *unstrained* crystal, and when we consider as *strained* crystal we must start with the mesh that has the proper symmetry, in other words, the simple-cubic mesh in k -space. The way the IBZ is constructed in the strained situation is to start with the simple-cubic mesh in k -space and use the point-group operations compatible with the lowered symmetry (assuming we are excluding hydrostatic strain for the moment) to define the IBZ. In general, the IBZ will be larger in the strained situation than in the unstrained, and in contrast to the unstrained situation the IBZ will be *different* depending on whether the BCC or simple-cubic lattice is used to construct the IBZ.

The message of this subsection is that uniform simple-cubic meshes of integration points are used because they allow one to accurately integrate the largest

number of plane waves. In fact, using a uniform cubic mesh of points, one can exactly integrate *twice* as many basis functions as there are k -points in the mesh — N sines and N cosines for N mesh points. As long as a plane wave expansion gives a good description of the function to be integrated, a cubic mesh gives the best approximation to the integral. As we will see, the integrands associated with the photoelastic tensor can be described by a plane wave expansion, on a sufficiently dense cubic mesh, everywhere in the Brillouin zone except for a small, important region near the Γ -point in which the function will be represented using spherical-harmonic expansions, radius by radius in k , on meshes of points which lie on concentric spherical shells.

4.6 Spherical-harmonic expansions

The $l = m = 0$ coefficient of the spherical-harmonic expansion for small k leads to the radial function which represents the spherical average of the integrand at any given radius and as such describes the surviving contributions to the integral after all cancellations have been properly handled. The higher expansion coefficients characterize the angular variations.

The integrals that we will be concerned with give rise to tensor functions (the dielectric tensor, the photoelastic tensor) and therefore we must concern ourselves with the symmetry properties of the integrands as functions of the variable $\vec{k}$. To provide consistency checks of our results as well as saving computational effort, we use group theory to place constraints on the various coefficients in our expansions. When expanding a scalar function of $\vec{k}$, such as the trace of the integrand associated with the dielectric function, various coefficients can be shown to vanish

due to the presence of certain point group symmetry elements. For example, invariance under the operation of a four-fold rotation about the z-axis implies that expansion coefficients $C_{\ell,m}$ vanish for all values of m except those in the sequence $m = 0, 4, 8, \dots$. If we are considering a crystal which has cubic symmetry, and we eliminate all coefficients which are forbidden, what remains is an expansion in the so-called “cubic-harmonics”, that is, basis functions which are invariant under the cubic point-group.

Since we will be considering situations with lower-than-cubic symmetry — the crystal in the presence of uniaxial strains — we start with the spherical-harmonics and use group theory to eliminate various expansion coefficients. The spherical-harmonic expansion is also a natural choice for use when doing the integrals because of the convenience of writing the three-dimensional integral over a spherical region in terms of a one-dimensional integral over the radial function of k which is written in terms of the coefficient $C_{0,0}(k)$.

Often we will be concerned with the characterization and convergence of individual components of the dielectric function which, when expanded in spherical-harmonics, have more allowed coefficients than would a scalar function in the same crystal. For example, the values $m = 2, 6, \dots$ are forbidden when considering a scalar function of $\vec{k}$ but *are* allowed in the expansion of, for example, the integrand associated with the xx component of the dielectric function $\varepsilon_{xx}(\vec{k})$. Let us now consider some of the constraints which are imposed by symmetry on the spherical-harmonic expansions.

4.7 Spherical-harmonic expansions and symmetry

Two symmetries which are possessed by both scalar and tensor functions of $\vec{k}$ in our theory are inversion and reality. We are considering only the real-part of the dielectric function (the imaginary part vanishes below the fundamental band gap) and strain-induced changes thereof. For this reason, we are only interested in spherical-harmonic expansions of real functions of $\vec{k}$. The inversion symmetry, $\vec{R} \rightarrow -\vec{R}$, which is excluded from the point-group of a zinc-blende structure, is allowed in k -space, $\vec{k} \rightarrow -\vec{k}$, as a result of time-reversal symmetry. In particular, time-reversal gives us

$$\langle \vec{r} | n, \vec{k} \rangle = \langle \vec{r} | n, -\vec{k} \rangle^*, \quad (4.13)$$

and

$$E_{n\vec{k}} = E_{n-\vec{k}}. \quad (4.14)$$

Using the above two equations and the odd parity of the matrix elements $\langle n\vec{k} | p_i | m\vec{k} \rangle$ shows that the integrand of Eq. (4.1) obeys the inversion symmetry.

The spherical-harmonics are given by

$$Y_{\ell m}(\theta, \phi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi} \frac{(n-m)!}{(n+m)!}} P_{\ell m}(\cos \theta) e^{im\phi}. \quad (4.15)$$

Using the following properties of the Associated Legendre polynomials

$$P_{\ell, m}(-x) = (-1)^{n+m} P_{\ell, m}(x), \quad (4.16)$$

and

$$P_{\ell, -m}(x) = (-1)^m \frac{(n-m)!}{(n+m)!} P_{\ell, m}(x), \quad (4.17)$$

leads to

$$Y_{\ell, m}(\theta - \pi, \phi + \pi) = (-1)^{\ell} Y_{\ell, m}(\theta, \phi), \quad (4.18)$$

and

$$Y_{\ell,-m}(\theta, \phi) = (-1)^m Y_{\ell,m}^*(\theta, \phi). \quad (4.19)$$

Now consider the effect of inversion on the spherical-harmonics. In spherical coordinates (k, θ, ϕ) , the inversion operation implies the following substitution $(k, \theta, \phi) \rightarrow (k, \pi - \theta, \phi + \pi)$. Expanding an arbitrary function $f(\theta, \phi)$ in spherical-harmonics

$$f(\theta, \phi) = \sum_{\ell,m} C_{\ell,m} Y_{\ell,m}(\theta, \phi), \quad (4.20)$$

and requiring it to be invariant under inversion $f(\theta, \phi) = f(\pi - \theta, \phi + \pi)$, leads to the following constraint on the expansion coefficients

$$C_{\ell,m} = (-1)^\ell C_{\ell,m}, \quad (4.21)$$

where we have used Eq. (4.18). In order to satisfy Eq. (4.21) we must have

$$C_{\ell,m} = 0 \text{ for } \{\ell = 1, 3, 5, 7, \dots\}. \quad (4.22)$$

Imposing reality $f(\theta, \phi) = f^*(\theta, \phi)$, and using Eq. (4.19) gives

$$C_{\ell,m} = (-1)^m C_{\ell,-m}^*. \quad (4.23)$$

Using Eq. (4.23) allows us to eliminate the sum over the negative values of m and write the expansion of $f(\theta, \phi)$ as

$$\begin{aligned} f(\theta, \phi) &= 2Re \sum_{\ell} ' \sum_{m=0}^{\ell} C_{\ell,m} Y_{\ell,m}(\theta, \phi) \\ &= 2 \sum_{\ell} ' \sum_{m=0}^{\ell} \left(C_{\ell,m}^r Y_{\ell,m}^r(\theta, \phi) - C_{\ell,m}^i Y_{\ell,m}^i(\theta, \phi) \right) \end{aligned} \quad (4.24)$$

where the superscripts r , and i have been used to indicate the real and imaginary parts of the spherical-harmonics and the expansion coefficients as $Y_{\ell,m} = (Y_{\ell,m}^r +$

$iY_{\ell,m}^i$) and $C_{\ell,m} = (C_{\ell,m}^r + iC_{\ell,m}^i)$, and the prime on the ℓ -summation means that we only consider even ℓ .

A further simplification of the expansion of Eq. (4.24) can be made if we choose the coordinate system in such a way so that the mirror symmetry $\hat{y} \rightarrow -\hat{y}$ holds. The crystal under hydrostatic and [001] strain have the $\hat{y} \rightarrow -\hat{y}$ symmetry in the conventional coordinate system. For the [111] strain, if we place the $\hat{z}'$ axis along the [111] direction, the $\hat{x}'$ and $\hat{y}'$ axes can be chosen so that $y' = -y'$ holds. When the coordinate system is chosen as described above, the function $f(\theta, \phi)$ obeys the symmetry

$$f(\theta, \phi) = f(\theta, -\phi) \quad (4.25)$$

which eliminates the second term in Eq. (4.24) because of the fact that $Y_{\ell,m}^i(\theta, \phi) \propto \sin(m\phi)$ and is thus odd in ϕ . For simplicity we will, from now on, write the expansion of $f(\theta, \phi)$ as

$$f(\theta, \phi) = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\ell} C_{\ell,m} Y_{\ell,m}(\theta, \phi), \quad (4.26)$$

where we only consider real expansion coefficients ($2C_{\ell,m}^r \rightarrow C_{\ell,m}$) and we have the understanding that there are restrictions on the allowed values of ℓ and m , and that we are only considering the real part of the spherical-harmonic

$$Y_{\ell,m}^r(\theta, \phi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi} \frac{(n-m)!}{(n+m)!}} P_{\ell,m}(\cos \theta) \cos(m\phi). \quad (4.27)$$

Up to this point we have made no restrictions on the allowed values of m . If we consider a two-fold rotation around the z -axis, $f(\theta, \phi) = f(\theta, \phi + \pi)$ (of course this excludes the case of [111] strain) we obtain

$$C_{\ell,m} = \cos(m\pi) C_{\ell,m} \quad (4.28)$$

which vanishes for odd values of m .

To summarize the results so far, any scalar or tensor function of $\vec{k}$, written with respect to an appropriately chosen coordinate system, can be expanded, for fixed magnitude k , as in Eq. (4.26) where the $C_{\ell,m}$'s are real, the $Y_{\ell,m}(\theta, \phi)$ is the real-part of the spherical-harmonic, the sum is only over positive m , and there are certain restrictions on the allowed values of ℓ and m . The ℓ 's are restricted to take on only even integers and for the case of a crystal under [001] or hydrostatic strain (also unstrained) the values of m are restricted likewise to be only even. All of what has been said so far applies equally well to tensor as well as scalar functions. The scalar functions obey more symmetry relations giving the further restriction $\ell, m = \{0, 4, 8, 12, \dots\}$. For the [111] case the result is $\ell, m = \{0, 6, 12, \dots\}$ whereas for tensor functions we only have the restriction $\ell, m = \{0, 3, 6, 9, \dots\}$. The full function of $\vec{k}$ is recovered by allowing the $C_{\ell,m}$'s to be functions of k .

4.8 Tensor vs. scalar functions of $\vec{k}$

Let us now consider the difference between tensor and scalar functions with regard to the point-group symmetry operations. Let us define the operator S as follows

$$|\vec{k}'\rangle = S^{-1}|\vec{k}\rangle, \quad (4.29)$$

where $\vec{k}'$ is obtained from $\vec{k}$ through the point group operation S^{-1} . Considered as an active rotation, both vectors are written in terms of the same coordinate system. We denote the unit vectors of this system by $\{\hat{k}_1, \hat{k}_2, \hat{k}_3\}$. In terms of

components, the relation of Eq. (4.29) is given as

$$\langle \hat{k}_i | \vec{k}' \rangle = k'_i = \langle \hat{k}_i | S^{-1} | \vec{k} \rangle = \sum_j \langle \hat{k}_i | S^{-1} | \hat{k}_j \rangle k_j = \sum_j S_{ij}^{-1} k_j. \quad (4.30)$$

The above results are equivalent to making a passive rotation, that is, a rotation of the basis vectors by

$$|\hat{k}'_i\rangle = S|\hat{k}_i\rangle. \quad (4.31)$$

Any vector $\vec{v}$ transforms like the vector $\vec{k}$ as

$$v'_i = \sum_j S_{ij}^{-1} v_j. \quad (4.32)$$

Likewise every index of a tensor transforms according to Eq. (4.32), that is, the tensor transforms like a product of k -vectors. In particular, a second-rank tensor τ_{ij} transforms according to

$$\tau'_{ij} = \sum_p \sum_q S_{ip}^{-1} S_{jq}^{-1} \tau_{pq}. \quad (4.33)$$

Scalar functions of position transform according to

$$f(\vec{k}') = \langle \vec{k}' | f \rangle = \langle \vec{k} | S | f \rangle = \langle (S^{-1} \vec{k}) | f \rangle = f(S^{-1} \vec{k}). \quad (4.34)$$

In other words, the scalar functions are simply evaluated at the rotated point and the constraint on the spherical-harmonic expansion is obtained by requiring $f(\vec{k}') = f(\vec{k})$. Tensor functions of $\vec{k}$ transform according to Eq. (4.33) with the argument evaluated at the rotated point

$$\tau'_{ij}(\vec{k}') = \sum_p \sum_q S_{ip}^{-1} S_{jq}^{-1} \tau_{p,q}(S^{-1} \vec{k}). \quad (4.35)$$

For scalar functions in the presence of hydrostatic strain (or unstrained) or [111] strain, the operation of a rotation about the z -axis by $\pi/2$ leads to the constraint

$$C'_{\ell,m} = \cos(m\pi/2) C_{\ell,m}, \quad (4.36)$$

which vanishes for all m except those in the sequence $m = \{0, 4, 8, 12, \dots\}$. This relation does not necessarily hold if we are considering a second-rank tensor function of $\vec{k}$ such as the dielectric function. As we see, the relation of Eq. (4.36) holds only for the zz component of a second-rank tensor. To see why this is so, consider the integrand associated with the dielectric function

$$\varepsilon(\vec{k}) = \begin{pmatrix} \varepsilon_{xx}(\vec{k}) & \varepsilon_{xy}(\vec{k}) & \varepsilon_{xz}(\vec{k}) \\ \varepsilon_{yx}(\vec{k}) & \varepsilon_{yy}(\vec{k}) & \varepsilon_{yz}(\vec{k}) \\ \varepsilon_{zx}(\vec{k}) & \varepsilon_{zy}(\vec{k}) & \varepsilon_{zz}(\vec{k}) \end{pmatrix}. \quad (4.37)$$

Applying a four-fold rotation about the z -axis, which transforms the vector $\vec{k}$ as $\vec{k} = (k, \theta, \phi) \rightarrow \vec{k}' = (k, \theta, \phi - \pi/2)$, and using Eq. (4.35) to transform the tensor of (4.37), we obtain the following constraint

$$\begin{pmatrix} \varepsilon_{xx}(\vec{k}) & \varepsilon_{xy}(\vec{k}) & \varepsilon_{xz}(\vec{k}) \\ \varepsilon_{yx}(\vec{k}) & \varepsilon_{yy}(\vec{k}) & \varepsilon_{yz}(\vec{k}) \\ \varepsilon_{zx}(\vec{k}) & \varepsilon_{zy}(\vec{k}) & \varepsilon_{zz}(\vec{k}) \end{pmatrix} = \begin{pmatrix} \varepsilon_{yy}(\vec{k}') & -\varepsilon_{yx}(\vec{k}') & \varepsilon_{yz}(\vec{k}') \\ -\varepsilon_{xy}(\vec{k}') & \varepsilon_{xx}(\vec{k}') & -\varepsilon_{xz}(\vec{k}') \\ \varepsilon_{zy}(\vec{k}') & -\varepsilon_{zx}(\vec{k}') & \varepsilon_{zz}(\vec{k}') \end{pmatrix}. \quad (4.38)$$

We are writing a spherical-harmonic expansion for each component and we see that for the zz -component Eq. (4.36) once-again holds. For the xx and yy -components, however, the constraint relation

$$\varepsilon_{xx}(\vec{k}) = \varepsilon_{yy}(\vec{k}'), \quad (4.39)$$

while enforcing consistency doesn't require any of the coefficients in the expansion of $\varepsilon_{xx}(\vec{k})$ to vanish. The result is that for the expansions of $\varepsilon_{xx}(\vec{k})$ and $\varepsilon_{yy}(\vec{k})$ values of

$$m = \{2, 6, 10, \dots\} \quad (4.40)$$

are allowed while they are forbidden for the expansion of $\varepsilon_{zz}(\vec{k})$,

$$C_{\ell,m}^{zz} = 0. \quad (4.41)$$

The relation of Eq. (4.39) also tells us that for m -values given by Eq. (4.40) we have the following relation

$$C_{\ell,m}^{xx} = -C_{\ell,m}^{yy} \quad (4.42)$$

between the expansion coefficients for $\varepsilon_{xx}(\vec{k})$, $(C_{\ell,m}^{xx})$, and for $\varepsilon_{yy}(\vec{k})$, $(C_{\ell,m}^{yy})$. The relations of Eqs. (4.41) and (4.42) are consistent with the fact that the expansion of the trace $\varepsilon_{xx}(\vec{k}) + \varepsilon_{yy}(\vec{k}) + \varepsilon_{zz}(\vec{k})$ cannot contain terms with m -values given by Eq. (4.40).

Restrictions on the allowed values of ℓ can be obtained by performing point-group operations which map the $\hat{z}$ -axis into some other axis such as $\hat{x}$ or $\hat{y}$. Of course such a rotation only applies to the unstrained or hydrostatic strain. Such a rotation, say by $\pi/3$ about the $[111]$ axis, eliminates values of $\ell = 2, 6, 10, \dots$ for scalar functions in full symmetry, while for tensor functions, again these ℓ -values are allowed but now there are certain restrictions. To obtain the relations on ℓ one could use the addition theorem for spherical-harmonics.

To get a feeling for where all of these variations come from let us consider, once again, the integrand associated with the unstrained dielectric function. There are two contributions to the variations in the integrand coming from 1) the matrix-elements in the numerator and 2) the energy gaps in the denominator. Consider the numerators first. For the $\varepsilon_{xx}(\vec{k})$, $\varepsilon_{yy}(\vec{k})$ and $\varepsilon_{zz}(\vec{k})$ components, the numerators transform in the same way as the functions x^2/r^2 , y^2/r^2 and z^2/r^2 , respectively. These functions are written in terms of spherical-harmonics as

$$\frac{x^2}{r^2} = \frac{1}{3} + \frac{1}{2}\sqrt{\frac{4\pi}{5}} \left(\frac{\sqrt{8/3}[Y_{2,2} + Y_{2,-2}]}{2} - \frac{\sqrt{4}Y_{2,0}}{3} \right), \quad (4.43)$$

$$\frac{y^2}{r^2} = \frac{1}{3} - \frac{1}{2}\sqrt{\frac{4\pi}{5}} \left(\frac{\sqrt{8/3}[Y_{2,2} + Y_{2,-2}]}{2} + \frac{\sqrt{4}Y_{2,0}}{3} \right), \quad (4.44)$$

and

$$\frac{z^2}{r^2} = \frac{1}{3} + \frac{1}{3}\sqrt{\frac{4\pi}{5}}\sqrt{4}Y_{2,0}. \quad (4.45)$$

These equations represent most of the essential notions which have been introduced regarding the transformation properties of scalar and tensor functions as applied to the dielectric function. In particular Eqs. (4.43), (4.44) and (4.45) imply (1) the trace is a scalar function (equal to unity in this case), (2) $m = 0$ coefficients:

$$C_{0,0}^{xx} = C_{0,0}^{yy} = C_{0,0}^{zz}, \quad (4.46)$$

$$C_{2,0}^{xx} = C_{2,0}^{yy} = -2C_{2,0}^{zz}, \quad (4.47)$$

and (3) $m = 2$ coefficients:

$$C_{2,2}^{xx} = -C_{2,2}^{yy}, C_{\ell,m}^{zz} = 0. \quad (4.48)$$

The last of these is simply a specific case of Eqs. (4.41) and (4.42). This completes the symmetry analysis of the numerator.

The denominator is a scalar function which must have cubic symmetry (in the unstrained or hydrostatically-strained crystal). As such, the band-gaps, as functions of $\vec{k}$ are expanded in cubic-harmonics. In other words the values of ℓ and m , of the spherical-harmonic expansion for the band gaps, are constrained as: $\ell, m = \{0, 4, 8, 12, \dots\}$. For small k the denominator is spherically symmetric and the dominant oscillations in the integrand come from the numerators. For larger k , the $\ell, m \neq 0$ harmonics in the expansions of the band-gaps become more and more important. Expanding the denominators for small k (see appendix A on $k \cdot p$ theory), leads to products of spherical-harmonics coming from the numerator and denominator. The products of spherical-harmonics can again be written as sums over spherical-harmonics.

The picture that emerges is one in which the integrand of the unstrained dielectric tensor, for a given radius in k , can be written as an expansion in spherical-harmonics with an infinite number of terms, which for small k falls off rather quickly as we go to higher values of ℓ . This last restriction arises from the very general constraints of single-valuedness and continuity of the integrand. Single-valuedness implies that all spherical-harmonic expansion coefficients $C_{\ell,m}(k)$ except for the constant term $C_{0,0}(k)$ must vanish in the limit $k \rightarrow 0$, and continuity implies that for small k , the coefficients with higher and higher values of ℓ and m must be smaller and smaller since they come from higher and higher powers of k of the small- k expansion of the energy denominators.

Thus, we have been able to explain the qualitative features of the integrand associated with the unstrained dielectric function, including the presence of various spherical-harmonic coefficients and relations among them, based on the very general grounds of imposing point-group symmetry, continuity and single-valuedness. Actually, we have only stated which coefficients are not ruled out by symmetry and among these that various relations hold. Up to this point we have not said anything that would rule out the possibility that all coefficients are simply zero. In particular, the question of why the Γ -point region is so important has not been addressed. For such information we must appeal to the dynamics. In appendix A, second-order $k \cdot p$ perturbation theory is used to derive expression for the $C_{\ell,m}$'s up through $\ell = 6$. Each coefficient is written as an expansion through second order in k . What we find is that strain-induced changes to the band gaps and matrix elements are largest where the band gaps are smallest. This is a natural outgrowth of the fact that we are doing perturbation theory — a situation in which energy

denominators in expressions representing perturbed quantities are common. For the particular case of GaAs, the energy gaps are smallest at the Γ -point leading to the largest changes in band gaps and matrix elements, and in turn, the largest strain-induced changes to the integrand associated with the dielectric function.

For the crystal under strain, the above qualitative analysis carries over (with appropriate care taken of broken symmetries) and what we see is that each of the spherical-harmonic coefficients in the unstrained crystal is changed by a small amount due to the strain. Contributions to the photoelastic tensor in the region of k -space described by the spherical-harmonic expansions are obtained by taking appropriate differences of the $C'_{\ell,0}(k)$ coefficients. For example, the k -space integrand corresponding to the $p_{11} - p_{12}$ component of the photoelastic tensor is proportional to $C'^{zz}_{0,0}(k) - C'^{xx}_{0,0}(k)$.

Since we are interested in changes in the $C'_{\ell,0}(k)$'s which are much smaller than the values of $C'_{\ell,0}(k)$'s themselves, we must be able to attain very high accuracy in the description of the $C'_{\ell,0}(k)$'s. In other words, the errors in $C'_{\ell,0}(k)$ must be *much* smaller than the strain-induced changes. The convergence of the $C'_{\ell,0}(k)$'s is determined in terms of the coefficients with higher values of ℓ and m . In short, if the magnitude of the coefficient with highest value of $\ell = \ell^* \equiv \ell_{max}$ and $m = m^* \equiv m_{max}$ is much smaller than the one with the lowest lowest ($\ell = 0, m = 0$), then the value of $C'_{0,0}(k)$ is said to be converged on the assumption that we have correctly integrated all of the components present and have thus eliminated any aliasing error in $C'_{0,0}(k)$. For the example of the $p_{11} - p_{12}$ component of the photoelastic tensor, this convergence criterion is written as

$$\frac{|C'^{zz}_{\ell^*,m^*}(k) - C'^{xx}_{\ell^*,m^*}(k)|}{|C'^{zz}_{0,0}(k) - C'^{xx}_{0,0}(k)|} < 0.1. \quad (4.49)$$

This is a very stringent convergence criterion as can be appreciated by considering the fact that in the unstrained crystal both numerator and denominator vanish. The maximum values of ℓ and m , mentioned above, are related to the number of points used to represent the expansions on a spherical shell at a given radius k . The details will be presented shortly but for now all one needs to know is the rather intuitive fact that the more points we have on a sphere, the more spherical-harmonics we can integrate.

4.9 Estimates of the Γ -point contribution

The methods just described for characterizing the Brillouin-zone integrands in terms of plane-wave and spherical-harmonic expansions are fairly costly computationally and crude estimates were needed to decide whether or not the more expensive methods were really needed. Considering all of the oscillations in the integrand it is quite conceivable that there might not be *any* net contribution to the integrals after all cancellations have been handled. As we will see, this is actually not the case and substantial contributions remain.

Several methods were used to obtain crude (and inexpensive) estimates of the Γ -point corrections. Some of these were 1) one-point estimate based on using the value of the integrand at Γ , 2) refinement of the cubic mesh near Γ , 3) mapping the integrand point-by-point along radial directions and numerical integration and 4) Gaussian integration mesh in Γ -point region, in combination with uniform mesh over the rest of the zone, 5) non-uniform k -point meshes with higher density near Γ obtained through non-linear change of variables.

All of the methods mentioned above led to the conclusion that the Γ -point region really *does* make substantial contributions to the integral and that a careful (albeit expensive) treatment of the Γ -region is warranted. Methods 1 – 5, which will now be briefly discussed, are presented in the order of simplest (1) to most sophisticated (5).

1) The simplest possible estimate of the Γ -point contribution is obtained by multiplying the value of the integrand at Γ by the “volume” of the Γ -point region. This volume was taken to be the volume-per-point in a uniform k -point mesh.

Consider a standard uniform grid of points which yields 60-points in the irreducible zone for the unstrained crystal. For this k -point set there are 2048 points in the first zone giving for the volume per-point $4/2048 = 1/512$ in units of $(2\pi/a)^3$. Using the 60 k -point mesh gave for the unstrained dielectric function a value around 10 or 11 while, in the same units the integrand at the Γ -point was on the order of 1000. Thus this simple estimate indicates that the integrand may be large enough in the Γ region to make corrections of the order of several percent to the unstrained dielectric function. After the fact, we will see that this is actually not a bad estimate as the accurate corrections are around 1%. The one-point estimate for the strain-splitting was found to be roughly three times that value obtained using the 60-points alone. When things are done correctly we will see that the corrections actually are smaller although still significant: as large as 50% of the value with the 60-points alone. These one-point estimates will in all cases be *overestimates* — a fact which results because we are giving $k = 0$ too much weight by not including the volume factor of k^2 . Since we know that the integrand has its largest magnitude at $k = 0$, the one-points provide us with a necessary but *not* sufficient condition for having substantial Γ -point corrections. At this point, one wants to somehow estimate the effect of cancellations in the small- k region.

2) The idea behind refining the cubic mesh near $k = 0$ is to simply get a lot of points in the volume where cancellation has a chance of making a difference. What is done is we, once again, start with a the cubic grid of points corresponding to 60-points in the irreducible zone and replace the 8-points nearest to $k = 0$ with a mesh that has cubic symmetry but contains cubic-shells of points with greater and greater density as we approach $k = 0$. The weights are chosen so that the volume

has the same weight as that initially occupied by the original 8-closest points. To make this clearer, consider the procedure in one dimension. The nearest point is given by $1/12$ in units of $(2\pi/a)$, and has the non-normalized weight 1. The first step is to replace the point $1/12$ by the points $1/24$ and $3/24$ and give each a weight of $1/2$. Then the nearest point $1/24$ would be further subdivided to be replaced by $1/48$ and $3/48$. The point $1/48$ would then be replaced by $1/96$ and $3/96$. The procedure was stopped at this point because the range over which substantial radial variation, defined by the range over which we see the largest band-gap variation has been covered. The results using this mesh for the unstrained dielectric function and the strain-induced changes were consistent with the one-point estimates, in other words substantial corrections were found to the results obtained with the standard 60-points. Obviously these results, obtained using the refined-cubic mesh, can give only a qualitative feeling for the Γ -point corrections (the sign, the rough order of magnitude) since we have not tried to construct the mesh to satisfy any theorems of numerical integration and as such we have no systematics. To construct a mesh in such a way would have required more detailed knowledge as to the mathematical form of the integrand. To this end the small- k behavior was mapped-out point by point.

3) It was found that as we move out from the $k = 0$ point along a given radial direction, the integrand could be fairly-well represented by a Gaussian. To get better estimates of the magnitude of the Γ -point corrections, the integrand, as sampled point-by-point along several radial directions, was fit to an exponential and the analytic forms were then integrated. The form

$$f(k) = a + be^{-\alpha k^2}, \quad (4.50)$$

was used to fit the integrands associated with the unstrained dielectric function $\varepsilon(k)$ and the $p_{11} - p_{12}$ component of the photoelastic tensor along the high-symmetry directions from Γ to X and from Γ to L in the Brillouin-zone. In particular the integrand associated with the $p_{11} - p_{12}$ component of the photoelastic tensor is given by

$$\frac{(\varepsilon_{xx}(\vec{k}) - \varepsilon_{zz}(\vec{k}))}{\varepsilon_o^2(\delta a/a)}. \quad (4.51)$$

The analytical integrations of the fits give 0.12 as the correction to the dielectric function 10.94, and -0.0134 as the correction to the photoelastic tensor 0.045. These represent roughly, a 1.0% correction to the dielectric function and a -30% correction to the photoelastic tensor. This correction to the photoelastic tensor is of the same order of magnitude as the discrepancy between theory (with 60-points in the irreducible zone) and experiment, but unfortunately is of the opposite sign. We are considering here only the static value of the photoelastic tensor and what we see is that the Γ -point corrections push us away from the data. If, however, we consider the whole frequency range below the fundamental gap, what we see is that the Γ -point corrections greatly improve the dispersion of all of the photoelastic tensor components. To summarize the results of the point-by-point mappings, we see, once-again, the same qualitative picture that we obtained using the previously mentioned simple methods, namely, small corrections to the unstrained dielectric function and rather substantial corrections (on the order of 50%) for the photoelastic tensor. At this point we could start to use our knowledge of the functional form of the integrand to construct better integration meshes.

4) As mentioned previously, if we know something about the functional form of the integrand then we have a much better chance of constructing an effective

integration mesh. The method to be described here, was to use two meshes, one for the Γ -region and one for the rest of the zone. Using the information gained from the point-by-point plots and Gaussian fits of the integrand along various radials, a mesh was constructed which was highly accurate for integrating a class of functions that had roughly the shape and extent as the ones used to fit the point-by-point plots. This Gaussian mesh spanned roughly 1 – 2% of the Brillouin-zone volume, that is, the region dictated by the point-by-point plots. For the rest of the zone, a uniform k -point mesh was used to integrate the region where the integrand was believed to be fairly smoothly varying. The Fourier-interpolating function $\hat{f}(\vec{k})$, introduced in section 4.4, was used to correct for double counting, by subtracting the result obtained by integrating the function $\hat{f}(\vec{k})$ on the Gaussian mesh from the integral of the directly sampled integrand $f(\vec{k})$ on the Gaussian mesh. The present method, which gives highly-accurate results for integrating (not necessarily spherically symmetric) Gaussian functions of $\vec{k}$, gave the following results: a 0.084 (0.76%) correction to the dielectric function, and a correction of -0.023 (-55.0%) correction to the $p_{11} - p_{12}$ component of the photoelastic tensor.

We see that the same qualitative results are obtained with this method as with the simpler methods. Despite the pleasing results obtained so far, we still cannot say anything about how well angular oscillations are being integrated. For that matter, the present method does not provide for a systematic convergence criterion. What it does provide, however, is strong evidence that the $\vec{k} = 0$ neighborhood is extremely important and should be treated in a systematic way using the methods to be presented shortly. What we still don't have yet, with the present method, is a clear understanding of the structure of the radial function which is

obtained by correctly averaging over all angular variations. To get some indication for the importance of the angular variations, we compare the results obtained using the present method with those obtained using another method, which is equally well-suited to integrating Gaussian but results from a completely different way of placing the points. If similar quantitative results are found in both cases then we can say that our Gaussian-picture of the small- k behavior is correct and we have correctly solved the problem. As we will see, the quantitative results are quite different despite the fact that the qualitative picture is still supported. What we take away from this is that the angular variations are very important, and a consistent treatment of them is essential to obtaining a well-converged final result.

5) A method was found to take a uniform set of k -points and smoothly “warp” the mesh in such a way so as to move the points to closer to $\vec{k} = 0$ and still retain the nice convergence properties (Euler-Maclaurin theorem⁵) of the uniform k -point set. The idea was to construct an integration mesh with as few points as possible that would accurately integrate a function which was rather smoothly varying throughout the zone but contained a sharply-peaked feature centered around $\vec{k} = 0$. The technique uses the fact that a uniform set of integration points does the best job at integrating a set of plane waves. This fact is a result of the Euler-Maclaurin (E-M) theorem of numerical integration.

We found it possible to use a non-linear change of variables to turn the uniform k -point set into a non-uniform set while maintaining the systematic convergence properties of the uniform set which are implied by the E-M theorem. In the same way that a set of N uniformly distributed k -points exactly integrates N plane waves, the non-uniform k -point set discussed here, exactly integrates N basis functions

which are better suited to describing the integrand with the localized feature near $\vec{k} = 0$. These basis functions, of course, are simply plane waves whose arguments have been scaled to yield higher resolution near $\vec{k} = 0$.

These non-uniform k -point sets were tested and found to give extremely accurate results for the integrals of Gaussian functions of $\vec{k}$, using a small number of points. The Gaussian test functions were chosen to have roughly the extent indicated by the point-by-point plots of our k -space integrands and the number of points used, corresponded to a 28-point (in the irreducible zone) uniform set. To the extent that our Gaussian (spherically symmetric) test-functions gave good representations of the integrands in question, we would expect good agreement between results obtained with the non-uniform k -point sets and the two-mesh scheme discussed previously. Although the qualitative trends were supported, the quantitative results were not in satisfactory agreement between the two methods, indicating that the results were sensitive to the placement of the points. The conclusion is that the assumption of Gaussian-like integrands was not valid, and that the angular variations were much more important than initially suspected. As we will see, the integration approaches mentioned above simply do not have fine-enough resolution to correctly integrate all of the angular variations in the small- k region. In summary, the results of all of the investigations using the simple methods 1 – 5, lead to the conclusion that a highly-accurate treatment of the Γ -point region is essential to the correct qualitative as well as quantitative description of the phenomena of the photoelastic effect. These observations are consistent with earlier theoretical work on this subject in which it was realized that certain points in the Brillouin zone, called critical points, dominate the description of the photoelastic effect. In

particular, the Γ -point is known to be a critical point and plays a large role for frequencies below the fundamental band gap.

4.10 integration methods: spherical harmonics and plane waves

The integration method which solves the numerical problem presented by the calculation of the photoelastic tensor in GaAs uses a spherical-harmonic description of the integrand near $\vec{k} = 0$ and a plane-wave description throughout the rest of the zone.

The method works as a results of the the following two observations: 1) the region near $\vec{k} = 0$ which requires a very dense sampling mesh represents a very small fraction of the total volume of the Brillouin-zone. In this region the radial function, which is the angular average of the integrand at a given radius k , is sufficiently smoothly-varying with k to permit an accurate description with a reasonable number of mesh points. In this context a reasonable number is a number on the order of 1000 in the irreducible zone (for the Γ -point region). Keep in mind that this number is already 1 – 2 orders of magnitude larger than the *total* number of points needed for most electronic-structure calculations. The second observation is 2) outside the Γ -point region, the characteristic wavelength of the oscillations is long enough to permit an adequate description using a uniform mesh. Once again it must be emphasized that an adequate uniform mesh is only obtained once we include roughly 3000 points in the irreducible zone. It can't be over-emphasized that all of this effort is required because we are trying to demonstrate convergence of an integral over a highly oscillatory function which results from subtracting two integrals which are very nearly the same, and that this problem is to be contrasted with the calculation of the unstrained dielectric function, a problem in which accurate results are obtained with far fewer integration points. The unstrained problem

is simpler also because of the fact that the relevant integrals involve functions that have only one sign whereas in the case of the photoelastic effect the integrands oscillate between positive and negative values.

The integration method proceeds as follows. 1) The radial function is converged in the Γ -point region by obtaining accurate values of $C'_{0,0}(k)$ from spherical-harmonic expansions of the integrand at a number of radii k_σ . The $C'_{0,0}(k_\sigma)$ at each radius k_σ , is said to be converged if the spherical-harmonic expansion is converged according to the criterion of section 4.8.

2) The whole zone is sampled by a uniform grid of k -points, of sufficient density, and from this grid, an approximate radial function is constructed using Fourier interpolation (see section 4.4) from the uniform grid to the spherical-harmonic meshes.

3) A maximum radius k^* , which defines the extent of the Γ -point region, is defined as the radius beyond which the (directly-sampled) radial function and the approximate (interpolated) radial function are in sufficiently-close agreement. The fact that such a radius k^* exists is a blessing due to the fact that as one goes to larger and larger k , the characteristic wavelength of the oscillations becomes longer and longer. By definition, outside of k^* the uniform mesh gives an accurate representation and inside of k^* the spherical-harmonic description is appropriate.

In order to obtain a practical integration method, there must be some range of k over which both the uniform-grid description and the spherical-mesh description are adequate. 4) A "matching region" $k' < k < k''$, in which the aforementioned agreement between the two descriptions exists, is obtained as a trade-off between increasing the density of the uniform-grid (smaller k^*) and increasing the number of spherical-mesh shells (larger k^*).

5) The “masking-function” $\xi(k)$ is a function which goes smoothly from 0 to 1 over the “matching-region” and acts to mask-out the Γ -point region of the uniform grid and the function $(1 - \xi(k))$ provides a smooth cutoff of the radial-function on the spherical-mesh.

6) The integral is represented as the sum of two contributions, one from the Γ -point region represented on spherical shells of mesh-points, and one from the uniform-mesh. A clean separation between the contributions coming from the two meshes is obtained by writing the integral in the following way

$$\int d^3k P(\vec{k}) = \int d^3k P(\vec{k})\xi(k) + \int d^3k P(\vec{k})(1 - \xi(k)), \quad (4.52)$$

where we have added and subtracted the integral involving the function $\xi(k)$. $P(\vec{k})$ represents any integrand that we wish to describe using the two-mesh scheme. The first integral on the right is evaluated on the uniform mesh and the second is evaluated on the spherical-shell mesh.

7) A test as to whether or not the matching region is smooth enough and wide enough is obtained by comparing the Fourier transforms of the masked and unmasked integrands. The masking function is considered to be suitable as long as the high-frequency Fourier components are unchanged or reduced in magnitude upon masking.

4.11 The radial function

The radial function is defined by writing the three-dimensional k -space integral over a spherical-region as a one-dimensional integral from $k = 0$ to the maximum

k_{max} , which defines the spherical region. Consider the integral I , over a spherical region in k -space, of some function $f(\vec{k})$

$$I = \frac{1}{V_k} \int d^3k f(\vec{k}) = \frac{1}{V_k} \int_0^{k^*} dk k^2 \int d\Omega f(\vec{k}). \quad (4.53)$$

Expand the integrand in spherical-harmonics as

$$f(\vec{k}) = \sum_{\ell,m} C_{\ell,m}(k) Y_{\ell,m}(\theta, \phi), \quad (4.54)$$

where the expansion has the form discussed previously: real coefficients, real part of the spherical-harmonic and restrictions on the sums. Inserting Eq. (4.54) into Eq. (4.53),

$$\begin{aligned} I &= \frac{1}{V_k} \int_0^{k^*} dk k^2 \int d\Omega \sum_{\ell,m} C_{\ell,m}(k) Y_{\ell,m}(\theta, \phi) \\ &= \frac{\sqrt{4\pi}}{V_k} \int_0^{k^*} dk k^2 C_{0,0}(k) \\ &= \int_0^{k^*} \rho(k) dk, \end{aligned} \quad (4.55)$$

we see that the $C_{0,0}(k)$ term is projected from the expansion and, as such, is the only piece which contributes to the integral. In Eq. (4.55) we have defined the radial function as

$$\rho(k) = \frac{\sqrt{4\pi} k^2 C_{0,0}(k)}{V_{BZ}}. \quad (4.56)$$

In practice, the expansion of Eq. (4.54) is represented by determining the coefficients $C_{\ell,m}(k)$, up to some cutoff in the angular variables $\ell \leq \ell^*, m \leq m^*$, on a collection of radii $\{k_\sigma\}$, spanning the Γ -point region.

The expansion is said to be converged, at a given radius k_σ , once enough terms have been kept to correctly represent the dominant oscillations in the integrand,

as determined by examining the magnitudes of the various coefficients $C_{\ell,m}(k_\sigma)$. Since the magnitudes of these coefficients fall off with increasing ℓ , convergence is attained when the coefficients with the highest values of ℓ , and m are much smaller than $C_{0,0}(k)$,

$$\frac{|C_{\ell^*,m^*}|}{|C_{0,0}(k)|} \ll 1, \quad (4.57)$$

as was discussed previously. Once the expansion is converged in the angular variables $\{\ell, m\}$, then $C_{0,0}(k_\sigma)$ will have the correct value and the radial function $\rho(k_\sigma)$, will be converged. The radial function over range $0 < k < k^*$ is represented by a curve passing through all of the points $\rho(k_\sigma)$, assuming that enough radii $\{k_\sigma\}$ have been included to obtain a smooth fit. The integral I , is then obtained by numerically integrating the radial function.

For each radius k_σ , the integrand is evaluated on a collection of points $k_{\sigma i}$ distributed on the surface of a sphere of radius k_σ . For each point $k_{\sigma i}$ there is a corresponding weight w_i . The points and weights are chosen in such a way as to *exactly* enforce the orthonormality constraint of the spherical-harmonics

$$\sum_i w_i Y_{\ell',m'}^*(\theta_i, \phi_i) Y_{\ell,m}(\theta_i, \phi_i) = \delta_{\ell',\ell} \delta_{m',m}, \quad (4.58)$$

for $\{\ell', \ell\} \leq \ell^*$ and $\{m', m\} \leq m^*$.

The points are chosen as follows. The spherical-harmonics are polynomials of degree 2ℓ in the variable $x = \cos(\theta)$, multiplied by the factor $\cos(m\phi)$. The coordinates ϕ_i are chosen as

$$\phi_i = \frac{2\pi i}{M}, \quad (4.59)$$

for $i = \{0, 1, \dots, M-1\}$. All factors $\cos(m\phi)$ with $m < M$, will be correctly integrated if sampled with the points indicated by Eq. (4.59). The coordinates θ_i

are chosen as

$$\theta_i = \cos^{-1}(x_i), \quad (4.60)$$

where the x_i are zero's of the Legendre Polynomials. This particular choice is based on the Gaussian integration rule for polynomials

$$\int_{-1}^1 dx h(x) = \sum_i w_i h(x_i), \quad (4.61)$$

where the points x_i and weights w_i are tabulated⁶. The number of points x_i used in the above rule determines the accuracy of the method. Any polynomial of degree $< L$ can be exactly integrated by the L -th order rule (i.e., Eq. (4.61) with L points x_i).

If we wish to satisfy Eq. (4.58) we must consider the product of two spherical-harmonics which is a polynomial of degree $\ell' + \ell$ in $x = \cos(\theta)$, multiplied by the product $\cos(m\phi)\cos(m'\phi)$. Since $\ell' + \ell \leq 2\ell^*$ and $m' + m \leq 2m^*$, we need an integration rule of order

$$L > 2\ell^*, \quad (4.62)$$

in $\cos(\theta)$ and

$$M > 2m^*, \quad (4.63)$$

in ϕ . The reason we must choose an L greater than twice the largest $\ell = \ell^*$, is due to the fact that a Legendre polynomial of degree L will not be correctly normalized using the L -th order rule. This results because a Legendre polynomial of degree L , (e.g. the product of two Legendre polynomials of degree $\ell^* = L/2$) will be sampled at all of its zeros x_i when the L -th order rule is used, and the resulting normalization integral vanishes rather than correctly giving unity.

The mesh used to represent the spherical-harmonic expansions is constructed as the set of all points on a sphere of radius k_σ with angular coordinates $\{\theta, \phi\}$, where the θ coordinate is chosen from the set defined by Eq. (4.60) and the ϕ coordinates are chosen from the set defined by Eq. (4.59). In terms of Cartesian coordinates we have

$$\begin{aligned}\vec{k}_{\sigma ix} &= k_\sigma \sin(\theta_i) \cos(\phi_i) \\ \vec{k}_{\sigma iy} &= k_\sigma \sin(\theta_i) \sin(\phi_i) \\ \vec{k}_{\sigma iz} &= k_\sigma \cos(\theta_i),\end{aligned}\tag{4.64}$$

where the index i enumerates all of the pairs of angular coordinates $\{\theta, \phi\}$, formed in the manner described above.

The calculations are simplified by determining $f(\vec{k})$ explicitly only on the much-smaller set of points in the irreducible Brillouin zone and using point-group symmetry operators to reconstruct the integrand over the full sphere-mesh before doing the projections. As an example, consider the spherical-mesh needed to represent the expansion of Eq. (4.54) with $\ell \leq \ell^* = 15$ and $m \leq m^* = 15$ for the crystal in the presence of a uniaxial strain along the $[001]$ direction. Equations (4.62) and (4.63) imply that we must choose the order of the integration rule (L and M) to be larger than $L = 30$ and $M = 30$. The integration rule for $L = 32$ is tabulated⁶ so we let $L = M = 32$. In the full zone, the resulting spherical mesh contains 1024 points. There are 16 point-group operations used to create the irreducible zone from the full zone. These operations consist of the 8 symmetry elements of the crystal of tetragonal symmetry plus 8 more which are obtained by including inversion $\vec{k} \rightarrow -\vec{k}$, which is permitted in k -space due to time-reversal invariance. A simple estimate of the number of points in the resulting irreducible

Brillouin zone is obtained by dividing the number of points in the full zone by the number of symmetry operations $1024/16 = 64$. Actually this estimate is somewhat low considering that we have underestimated the contributions due to boundary points. The irreducible zone contains, in fact, 80 points. Keep in mind that this is only for the radius k_σ . We will see that 11 such radii will be needed to completely represent the Γ -region for the case of the crystal under [001] strain. This represents a total of 880 points in the irreducible zone (the number which is relevant to the expense of the calculation) and 11,264 points in the full zone *just for the Γ -point region which occupies less than 2% of the full-zone volume*.

In summary, the function $f(\vec{k})$ is calculated on the sphere-points of radius k_σ , in the irreducible zone

$$f^{IBZ}(\vec{k}) \Big|_{|\vec{k}|=k_\sigma} = \{f(\vec{k}_{\sigma j}), \text{ for } \vec{k}_{\sigma j} \in IBZ\}. \quad (4.65)$$

From this, the full-zone representation is generated using the symmetry operators S according to

$$f^{BZ}(\vec{k}) = \sum_S S[f^{IBZ}(\vec{k})], \quad (4.66)$$

and the expansion coefficients $C_{\ell,m}(k_\sigma)$ (with $\ell \leq \ell^*$ and $m \leq m^*$) are projected as

$$C_{\ell,m}(k_\sigma) = \sum_i w_i Y_{\ell,m}^*(\theta_i, \phi_i) f^{BZ}(\vec{k}_{\sigma i}), \quad (4.67)$$

for $\vec{k}_{\sigma i}$ on the sphere in the full zone. The symmetry operations of Eq. (4.66) depend on whether we are considering a scalar or tensor function and were discussed in a previous section.

4.12 The uniform grids

The Brillouin zone, which is a polyhedron, centered around the point $\vec{k} = 0$ and inscribed in a cube of edge $4\pi/a$, is spanned by a uniform mesh by constructing a simple-cubic grid of points in the aforementioned cube and excluding points which lie outside the first zone. The cube of edge $4\pi/a$ actually constitutes the first and second zones. If we align the cube-edges along the coordinate axes, then the uniform grid is defined as the set of points

$$\{\vec{k}\} = (k_n, k_p, k_q), \quad (4.68)$$

where each index n , p and q takes on all allowed values from 1 to N_σ , where N_σ (for $\sigma = x, y, z$) is the total number of points in dimension σ . Since we are laying down a cubic grid we let $N_x = N_y = N_z$. The coordinate k_i is defined to exclude the point $\vec{k} = 0$ as

$$k_i = \frac{2\pi}{a} \frac{(2i - 1 - 2N_{dcn})}{2N_{dcn}} \quad (4.69)$$

for $i = \{1, 2, 3, \dots, 2N_{dcn}\}$. In the previous equation we have introduced the variable N_{dcn} which is the linear density of points per $2\pi/a$. In terms of N_{dcn} the total number of points in a given dimension is

$$N_x = N_y = N_z = 2N_{dcn}. \quad (4.70)$$

The region of the first Brillouin zone is obtained from the cube of edge $4\pi/a$ by “cutting off” the cube corners with the eight planes equivalent to $(\pi/a)[1, 1, 1]$. The points in the first Brillouin zone are obtained by excluding from the set defined by Eqs. (4.68) and (4.69) the points which lie outside of the first zone. As discussed in a previous section, the k -point sets constructed in the way discussed above, are

equivalent to the sets generated using the method of Monkhorst and Pack⁴ for the case of full cubic symmetry and for lower symmetries are to be preferred to the sets of Monkhorst and Pack. The k -point sets for the full symmetry case are also equivalent to those obtained using the methods of Cohen and Chadi⁷.

Consider the specific example of 10 “special points.” Let the linear density of k -points be given by $N_{den} = 4$. This produces a total of 512 points in the set defined by Eqs. (4.68) and (4.69). Thus there are 512 points in the first two zones. Excluding the points which are in the second zone gives a total of 256 points in the full zone. The irreducible Brillouin zone is constructed using the point-group symmetry operators in the same way as was done in the discussion of the sphere-points. There are 48, 16 and 12 point-group operations, for full symmetry, [001] symmetry and [111] symmetry, respectively. Thus we arrive at 10, 20, and 30 points in the irreducible zones associated with the three symmetries respectively. The following table gives the numbers of points for $N_{den} = 4, 6, 8, 10$ and 20. The value of $N_{den} = 20$ was the linear density that was ultimately needed to get a good overlap between the uniform-mesh and sphere-mesh descriptions.

TABLE 4.1: Numbers of points in the full zone (BZ) and irreducible zones (IBZ) of different symmetries for uniform-grid sets of various linear densities (N_{den}).

N_{den}	N^{BZ}	N_{cubic}^{IBZ}	$N_{[001]}^{IBZ}$	$N_{[111]}^{IBZ}$
4	256	10	20	30
6	864	28	63	91
8	2,048	60	144	204
10	4,000	110	275	385
22	42,592	1012	2783	3795

In order to calculate Fourier transforms and to perform Fourier interpolations, the integrand on the set of points making up the first and second zones is needed (i.e. the points defined by Eqs. (4.68) and (4.69)). These are obtained from the calculation of the integrand on the points in the irreducible zone as follows. Symmetry operations are used to construct the integrand throughout the full first zone from the calculated values on the points in the irreducible zone. The integrand on the points in the second zone is then determined using the periodicity of k -space to translate, with reciprocal lattice vectors, the values in the first zone. We emphasize that the most computationally demanding step is the calculation of the integrand on the points in the irreducible zone, and the use of symmetry to limit our calculation to *only* the points in the irreducible zones greatly reduces the required computational effort.

At this step, Fourier transforms of the k -space integrand are calculated and Fourier interpolations are performed to construct an approximate radial function.

The Fourier interpolation procedure takes, as input, the integrand on the uniform point-set in the first and second zones and produces an approximate representation of the integrand on all of the spherical-mesh points that were used to represent the spherical-harmonic expansion of the integrand in the Γ -point region. From the approximate representation of the integrand on the sphere-meshes, an approximate radial function $\tilde{\rho}(k)$ is constructed by projecting the coefficients $\tilde{C}_{\ell,m}(k)$ in the same way as was done to construct the “true” radial function $\rho(k)$ from the directly-sampled integrand. In general, the approximate integrand in the Γ -region, obtained by interpolating, is smoother than the directly-sampled integrand, that is, the coefficients $\tilde{C}_{\ell,m}(k)$ die off more quickly with increasing ℓ and m than the $C_{\ell,m}(k)$. As a result, if the expansion of the “true” integrand is well converged, then the expansion of the approximate integral will also be well converged on the same spherical mesh.

4.13 The approximate radial function

The approximate radial function, through comparison with the “true” radial function, allows us to characterize the interplay between the description of the integrand on the sphere-meshes as compared to that on the uniform meshes. In so doing, we will be able to 1) determine the extent of the Γ -region, that is determine k^* , and 2) define a suitable “matching region” by sufficiently increasing the density of the uniform mesh until a suitable overlap occurs which is close enough to the $\vec{k} = 0$ point.

There is a trade-off, in computational expense, between going far-enough out in k with the spherical-meshes and having a high-enough density in the uniform mesh. The reason for the trade-off is as follows.

For a given value of $k = k_\sigma$, one needs a certain number of points on the sphere to converge the angular expansion of the integrand. As we go to larger and larger k the number of points needed on the sphere increases, implying that to minimize costs we wish to have the smallest Γ -point region possible.

The fact that as we go to larger k we need more terms in the angular expansion can be understood from a simple model where we assume the integrand to be described by one term in a plane wave expansion

$$f(\vec{k}) = e^{i\vec{k}\cdot\vec{R}}, \quad (4.71)$$

for some real-space vector $\vec{R}$. Expanding the plane wave in spherical harmonics, we see that the expansion coefficient of order ℓ is proportional to k^ℓ and as such grows with k . We know from the behavior of the integrand on the uniform meshes that the oscillations don't die out as we increase k , but rather, tend to some long-wave (but not infinite wavelength) limit. These observations, coupled with experience with the spherical-harmonic expansions, support the conclusion that the expansion-coefficients $C_{\ell,m}(k)$ grow with increasing k .

Decreasing the size of the Γ -region implies the use of more points in the uniform grid as can be seen from the fact that if the uniform grid were sufficiently-dense then the spherical meshes would not be needed at all. In addition to being computationally intractable, however, such a solution would greatly oversample the rest of the zone and, as such, would be highly inefficient.

Since the radial function is not a single-signed quantity we expect considerable cancellation in the integral of the radial function, which itself is obtained after all of the angular cancellation has been done. For this reason we demand a strong convergence criterion to apply to the region of overlap between the radial function and the approximate radial function. In other words, in circumstances where we say the approximate radial function gives a good representation to the “true” radial function, we mean that we are neglecting differences that are small compared with the overall average of the radial function. This is a much stronger criterion than just requiring, say, agreement to within some small percent of the radial function at any given k since the overall average (the integral) is generally smaller in magnitude than the radial function itself. To make the comparison, we define a “figure of merit” function $F(k)$, as

$$F(k) = \frac{\tilde{\rho}(k) - \rho(k)}{\int_{\text{zone}} \rho(k) dk}, \quad (4.72)$$

where the denominator signifies the zone average, or in other words, the integral we are trying to evaluate. The denominator, as written, doesn’t imply that we really perform the integral over the whole zone — a procedure which would make no sense considering that the BZ is no a sphere — but is merely suggestive. The numerical value of the denominator is not known *a priori* from the calculation since it is precisely the value we are trying to calculate. For this reason, we simply take the experimental value corresponding to the quantity we are trying to calculate (i.e. the appropriate photoelastic tensor component).

By construction, the figure-of-merit function goes to zero wherever the uniform mesh is correctly describing the integrand. We wish an overall accuracy of the Brillouin zone integrals to within a few percent. This implies that we should define

the maximum radius of the Γ -point k^* as the radius beyond which the figure-of-merit function $F(k)$ is smaller in magnitude than roughly 0.02 or 0.03.

4.14 The masking function

The masking function $\xi(k)$ was introduced in Eq. (4.52) in order to provide a clean separation between the contributions to the integral coming from the sphere-meshes and the uniform meshes. The requirement on $\xi(k)$ is that it must go smoothly from 0 to 1 over some interval $k' < k < k''$ that we have called the matching region. The width of the matching region is related to the density of the uniform mesh, in that it must be larger than the point-spacing. If this requirement is not met then it is as if we are integrating a step-function on the uniform mesh, and ringing in the Fourier transforms would be introduced.

The function $\xi(k)$, in the matching region $k' < k < k''$, was chosen to have the form⁸

$$\xi(k) = \frac{1}{2} \left(1 + \tanh \left[\frac{bx}{1-x^2} \right] \right), \quad (4.73)$$

where the dimensionless variable x goes from -1 to 1 in the matching region as

$$x = -1 + \frac{2(k - k')}{(k'' - k')}. \quad (4.74)$$

Outside of the matching region, the masking function is defined as

$$\begin{aligned} \xi(k) &= 0 \text{ for } k < k'; \\ &= 1 \text{ for } k > k''. \end{aligned} \quad (4.75)$$

There are no discontinuities in the masking function because all derivatives of $\xi(k)$ vanish at the end points k' and k'' . The slope of the masking function at the

midpoint of the matching region is related to the parameter b , in Eq. (4.73), as

$$\left. \frac{d}{dk} \xi(k) \right|_{k=\frac{k'+k''}{2}} = \frac{b}{(k'' - k')}. \quad (4.76)$$

The following parameters were used in the definition of the masking function:

$$\begin{aligned} b &= 2; \\ k' &= 0.125; \\ k'' &= 0.375, \end{aligned} \quad (4.77)$$

where the k 's are in units of $(2\pi/a)$. The results are relatively insensitive to the value of the slope parameter b . As b was varied from 0.05 (relatively flat at the midpoint) to 20.0 (steep at the midpoint) the value of the $C'_{\vec{R}=0}$ Fourier coefficient varied by less than 4%.

Some characteristic values of $\xi(k)$, using the parameters of Eq. (4.77), are listed in the following table.

TABLE 4.2: Characteristic values of the masking function $\xi(k)$.

k	$\xi(k)$
0.15	0.0001
0.2	0.1296
0.25	0.5
0.3	0.8704
0.35	0.9999

Equation (4.52) and Table 4.2 demonstrate that at $k = 0.2$ the uniform mesh makes a 12.96% contribution and the sphere mesh makes an 87.04% contribution to the integral while at $k = 0.3$ the roles are reversed. For k -values below 0.2 contributions to the integral come almost entirely from the sphere-meshes (the uniform mesh is masked out) and for k greater than 0.3 the sphere-meshes play almost no role. For this reason, sphere meshes were only needed up to $k = 0.35$.

The parameters of Eq. (4.77) were chosen because the figure-of-merit function demonstrated that the best agreement between the radial function $\rho(k)$ and the approximate radial function $\hat{\rho}(k)$ lies in the range between 0.2 and 0.3. By good agreement we mean that at the smaller k , the spherical mesh is nearly exact and the uniform mesh is making roughly an error of $F(0.2) = 0.1$. If this contribution were not masked we might expect errors in the integral with magnitudes up to 10%. Obviously this estimate is based on a worst-case scenario in which 10% errors of the same sign are made everywhere. As we see from the table, however, the uniform-grid contribution is suppressed by a factor of 0.1296 so we expect the net error to much less -- roughly a few percent at the most.

At $k = 0.3$ we see the uniform mesh doing extremely well as indicated by the small value of the figure-of-merit function $F(0.3) = 0.03$. At this larger value of k the sphere-mesh contribution will be suppressed by the factor of 0.1296. Because of this suppression we can afford to use fewer points on the sphere than would be needed to completely converge the radial function. In particular, at $k = 0.3$ we need 624 points on the sphere in the irreducible zone to converge the result. This corresponds to keeping terms up to $\ell = 46$ in the spherical-harmonic expansion. This, incidentally, is the number of points used to determine the figure-of-merit function

at $k = 0.3$. If, however, we use only 80 points on the sphere in the irreducible zone, corresponding to keeping only up to $\ell = 14$ in the angular expansion, then the sphere mesh description makes an error of about 12% of the zone average. Once again, the masking brings this down by roughly an order of magnitude. For smaller k the use of 80 points per k becomes better. For this reason, 80 points per radius were chosen to span the range from $k = 0$ to $k = 0.35$. The exact placement of these radii will be discussed shortly.

We define the maximum extent of the Γ -region $k^\star$, in terms of the volume which is represented by the sphere meshes. It is found that the total weight given to the Γ -region (i.e., the sum of the weights of all the sphere-mesh points) is given by

$$\sum_i w_i^\Gamma = 0.01757, \quad (4.78)$$

which corresponds to 1.76% of the zone volume. The sum of the weights in Eq. (4.78) gives the ratio of the Γ -region volume to the total volume of the Brillouin zone as

$$\sum_i w_i^\Gamma = \frac{V_\Gamma}{V_{BZ}} = \frac{4\pi(k^\star)^3}{3V_{BZ}}. \quad (4.79)$$

Using Eqs. (4.78), (4.79) and $V_{BZ} = 4$ (volume of Brillouin zone in units of $(2\pi/a)^3$) we obtain for the radius $k^\star$ of the Γ -region

$$k^\star = 0.256, \quad (4.80)$$

which is just slightly larger than the midpoint of the masking region defined by Eq. (4.77).

4.15 Placement of spheres and assignment of weights

The radii that were used to represent the radial function in the Γ -point region were chosen as

$$\{k_\sigma\} = \{0.0, 0.01, 0.01585, 0.02512, 0.03981, 0.0631, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35\}. \quad (4.81)$$

In these units ($2\pi/a$) the point X is given by $(1, 0, 0)$, and the L -point by $(1/2)(1, 1, 1)$. One might wonder why the $k = 0$ point has been included considering the fact that the value of the radial function vanishes at this point. The reason is because although the radial function and its first derivative vanish with k , the second derivative, which is related to the value of $C'_{\ell,m}(0)$ at $k = 0$, does not and, as we see shortly, will be used in the integration rule which applies to the section from $k = 0$ to $k = 0.01$.

The values k_1 through k_6 were chosen, somewhat arbitrarily, to place 6 radii from 0.01 to 0.1 on a logarithmic mesh defined by the rule

$$k_i = k_1 e^{d(i-1)} \text{ for } i = 1, 2, 3, 4, 5, 6. \quad (4.82)$$

The reason for this choice is that the radial function has its greatest variation in the interval between 0.01 and 0.1. From k_6 through k_{11} a linear mesh is used. With the log mesh, the points are equally spaced in the variable $y = \ln k$ with spacing:

$$\Delta(\ln k) = d = 0.46052. \quad (4.83)$$

Simple one-dimensional integration rules which assume equally-spaced sampling points (Simpson's rules) were applied to perform the integral of the radial function.

From k_1 to k_6 one makes a change of variables and writes the integral in terms of $y = \ln k$

$$\int_{k_1}^{k_6} \rho(k) dk = \int_{y_1}^{y_6} e^y \rho(e^y) dy \equiv \int_{y_1}^{y_6} g(y) dy \quad (4.84)$$

where we have made the definition

$$g(y) \equiv e^y \rho(e^y) = k \rho(k). \quad (4.85)$$

Simpson's rules are then applied to the function $g(y)$ sampled at equally-spaced values of y with spacing $\Delta y = d = 0.46052$. From k_6 to k_{11} Simpson's rules are applied directly to the masked radial function $\rho(k)(1 - \xi(k))$ which is sampled at the equally spaced points k_6 through k_{11} with spacing $\Delta k = 0.05$. Note that in Eq. (4.84) we are also sampling the *masked* radial function (i.e. make the replacement $\rho(k) \rightarrow \rho(k)(1 - \xi(k))$ in the first line of Eq. (4.84)) but as we have seen earlier, in the range of k from k_1 to k_6 the approximation $(1 - \xi(k)) \approx 1$ is extremely good.

The following closed-interval, one-dimensional integration rule⁶

$$I_6(f_1, f_2, f_3, f_4, f_5, f_6, h) = \frac{5h}{288} \left(19f_1 + 75f_2 + 50f_3 + 50f_4 + 75f_5 + 19f_6 \right), \quad (4.86)$$

was used to integrate $g(y)$ from y_1 to y_6 with spacing $h = \Delta y = c = 0.46052$ and to integrate $\rho(k)(1 - \xi(k))$ from k_6 to k_{11} with spacing $h = 0.05$. The results were checked through comparison with analytical integrations of fitting-functions. It was possible to fit the radial function piecewise with low-order polynomial expansions. Excellent agreement was found between the Simpson's-rule results and the analytical integration of the fitting functions, which should come as no surprise since the Simpson's-rules are generated on the assumption of polynomial-like integrands. The primary reason for constructing the analytic fits was to verify visually that the use of Simpson's rules was appropriate.

Consider the integration of the radial function from $k = 0$ to $k = 0.01$. To develop an integration rule for this segment, we write the radial function $\rho(k)$ as an expansion in powers of k . Let us evaluate the first term in the series using Eq. (4.56). Since we know $C_{0,0}(k = 0)$ is a constant, the leading term in the expansion of Eq. (4.56) must be second order in k . For this reason, the coefficient of the k^2 term is given by

$$\lim_{k \rightarrow 0} \left(\frac{\rho(k)}{k^2} \right) = \frac{\sqrt{4\pi}}{4} C_{0,0}(k = 0),$$

where we have used $V_{BZ} = 4$ (total BZ volume in units of $(2\pi/a)^3$). Using

$$C_{0,0}(k = 0) = \sqrt{4\pi} f(k = 0), \quad (4.87)$$

we write

$$\lim_{k \rightarrow 0} \rho(k) = \pi k^2 f(0), \quad (4.88)$$

to lowest order in k .

We now complete the integration rule by adding another term to the expansion of $\rho(k)$. We simply want a smooth polynomial fit to the radial function from $k = 0$ to $k = 0.01$ that has the correct behavior at $k = 0$. The first term in the series, which is given by Eq. (4.88), ensures the correct $k \rightarrow 0$ behavior. A cubic term is chosen as the next term in the series for two reasons 1) it is not forbidden and 2) it allows for a smooth polynomial fit of the radial function from $k = 0$ to $k = 0.01$. With the above considerations, we now write the expansion of $\rho(k)$ as

$$\rho(k) = \pi f(0)k^2 + \eta_3 k^3. \quad (4.89)$$

The coefficient of the k^3 term is determined by evaluating the series of Eq. (4.89) at the point $k = k_1$ leading to

$$\eta_3 = \frac{\rho(k_1) - \pi f(0)(k_1^2)}{k_1^3}. \quad (4.90)$$

The integration rule, that is, the set of points and weights, for the integral from $k = 0$ to $k = k_1 = 0.01$, is now obtained by analytically integrating the series of Eq. (4.89) using the expansion coefficient of Eq. (4.90) to obtain

$$\int_0^{k_1} \rho(k) dk = \frac{\pi k_1^3 f(0)}{12} + \frac{k_1}{4} \rho(k_1). \quad (4.91)$$

The first term in Eq. (4.91) gives the weight for the Γ -point and the second term shows how the weights on the sphere of radius $k = k_1$ will be modified. Recall that the factor $\rho(k_1)$ is determined in terms of the angular integral at $k = k_1$ which is evaluated as a weighted sum over the points on the sphere at k_1 . The second term in Eq. (4.91) arises because it is the end points of the integral from $k = 0$ to $k = 0.01$. There will be a further modification to the weights for the points on the sphere at radius $k = 0.01$ coming from the integral over the log-mesh region from $k = 0.01$ to $k = 0.1$. The integral over the log-mesh region will now be discussed.

On the log-mesh, we are integrating the function $\rho(k)(1 - \xi(k))$, which must be replaced by the function

$$g(k) \equiv k\rho(k)(1 - \xi(k)), \quad (4.92)$$

in order to apply Simpson's rule on the evenly spaced points $\ln(k)$, with spacing given by Eq. (4.83).

4.16 Uniform-grid weights

The uniform grid, whose construction has been previously discussed, is uniformly weighted. Each point in full zone gets weight $1/N$ where N is the total number of points in the full zone. A given point in the irreducible zone k_i gets weight p_i/N where p_i is the number of points equivalent to the point k_i including

itself. For example, if $k = 0$ were included in the uniform grid (which it is *not*) it would have weight 1, while the X -point $k = (1, 0, 0)$ (which incidentally is also *not* included) would get weight 6, and the point $L = (1/2)(1, 1, 1)$ would get weight 8.

The net result is that the sum of the weights of the points in the irreducible zone is equal to the number of symmetry operators present in the point-group that is used to define the irreducible zone. When constructing the integral over the full zone from the integral over the irreducible zone the following rule is obeyed:

$$\begin{aligned}
 \frac{1}{V_{BZ}} \int_{BZ} d^3k f(\vec{k}) &= \frac{1}{N} \sum_i f(\vec{k}_i^{BZ}) \\
 &= \frac{1}{V_{IBZ}} \sum_S S \left[\int_{IBZ} d^3k f(\vec{k}) \right] \\
 &= \frac{1}{N_{sym}} \sum_S S \left[\sum_j \frac{p_j}{N} f(\vec{k}_j^{IBZ}) \right], \tag{4.93}
 \end{aligned}$$

where N_{sym} is the number of symmetry operators, and the detailed action of the symmetry operator S depends on whether the function $f(k)$ is a scalar or tensor function of $\vec{k}$ as was discussed in section 4.8.

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CHAPTER V

Results and Discussion

Here we present the results of our *ab initio* calculations in comparison with experimental measurements. The results of detailed convergence studies are also presented and numerical characterization of the Brillouin zone (BZ) integrands – in the form of spherical-harmonic expansions near $k = 0$ – are compared with results predicted by the analytical $(\vec{k} \cdot \vec{p})$ treatment of appendices A and B. With regard to the $\vec{k} \cdot \vec{p}$ treatment, we find strong numerical evidence suggesting that the small gap approximation – in which only one conduction band is retained – is an extremely accurate approximation when dealing with the Γ -point region. We also find that the correct numerical treatment of the $k = 0$ region of the BZ is of crucial importance in obtaining the correct frequency dispersion of the photoelastic tensor as well as substantial corrections to the static components in some cases.

5.1 Results of *ab initio* calculations

Results for the frequency-dependent, unstrained, dielectric function are presented in Figs. 5.1 – 5.3 in comparison with experimental measurements, and for the frequency-dependent photoelastic tensor, the three independent components, $-(p_{11} + 2p_{12})$, $-(p_{11} - p_{12})$ and $-p_{44}$, which correspond to hydrostatic strain, tetragonal [001] shear strain, and trigonal [111] shear strain, respectively, are pre-

sented in Figs. 5.4 – 5.8. Figures 5.7 and 5.8 include available experimental measurements for the $-(p_{11} - p_{12})$ and $-p_{44}$ components.

With regard to these results there are three notable effects to which we turn our attention: 1) k -point convergence, 2) local-field effects, and 3) the effect of the scissors operator.

5.2 The unstrained dielectric function

In contrast to the photoelastic tensor, the unstrained dielectric function is well converged using relatively few points (60 points) in the irreducible zone. Figure 5.1 compares results obtained using the conventional 60 k -point mesh with those obtained using our new two-mesh technique which was developed in order to obtain converged results for the photoelastic tensor (see chapter 4). The numerical difficulties presented by the photoelastic tensor, which arise out of the need to converge a small difference of two large quantities (two components of the *strained* dielectric tensor), are not encountered in the calculation of the unstrained dielectric function. In Fig. 5.1 the results labelled “converged” (three points at $\omega = 0.0$ eV, 0.75 eV, and 1.25 eV), which were produced using the two-mesh technique, are extremely close to the 60-point results. The largest correction is slightly less than 4% at $\omega = 1.25$ eV and for the static value is just under 1%.

These corrections to the unstrained dielectric function, which result from improved sampling of the Γ -point region, although small, are significant, leading to a slightly improved description of the dispersion. Because these corrections are so small, however, we neglect them for the case of the unstrained dielectric function

and conclude that the 60 k -point mesh adequately converges the result. For the photoelastic tensor, on the other hand, the accurate sampling of the Γ -point is crucial to obtaining the correct dispersion as can be seen in Figs. 5.4 – 5.8. The issue of k -point convergence with regard to the photoelastic tensor will be taken up shortly.

Figure 5.2 shows the effects of local-field corrections on the unstrained dielectric function. The net effect is a nearly-constant reduction in the magnitude of the dielectric function. Actually the local field correction is slightly frequency-dependent, shifting the static value by -0.54 and the $\omega = 1.25$ eV value by -0.57 . Both curves are produced with the scissors shift given by $\Delta = 0.8$ eV which is the value suggested by GW calculations^{1,2,3,4} to correct the $k = 0$ bandgap. This local-field correction, as we will see, is also strain-dependent. There are significant local-field corrections to the photoelastic tensor implying that under strain, the various components of the dielectric tensor are have slightly different local-field corrections.

The effect of the scissors operator on the unstrained dielectric function is shown in Fig. 5.3. Local-field effects were included in this calculation. We see a dramatic improvement of the results in comparison with experiment with the use of the scissors shift $\Delta = 0.8$ eV. With no scissors shift (LDA result) the static value of the is overestimated by roughly 20%, and the dispersion is qualitatively incorrect increasing too quickly with frequency. With the $\Delta = 0.8$ eV shift we find excellent agreement with the experiment, with regard the magnitude of the static value as well as the dispersion. It must be emphasized that is good agreement was *not* achieved by adjusting Δ so as to fit the experimental results, nor was Δ adjusted

to fit our *ab initio* band gap to the experimental gap, rather $\Delta = 0.8$ eV was taken from the results of a *GW* calculation^{1,2,3,4}.

This completes the discussion of the our calculated results for the unstrained dielectric function. We now turn to the issue of strain effects, that is, the photoelastic tensor.

5.3 The photoelastic tensor: *k*-point convergence

Of the three effects mentioned in section 5.1 and discussed in section 5.2 in the context of the unstrained dielectric function – *k*-point convergence, local-fields and scissors operator effects – the most dramatic effect regarding the photoelastic tensor, is that of *k*-point convergence. The qualitative as well as quantitative description of the frequency dispersion is not correctly given by the underconverged results, as is illustrated in Figs. 5.4, 5.5 and 5.6. The discrepancy becomes more pronounced as the band gap is approached. For example, near the bandgap, the $-(p_{11} - p_{12})$ and $-p_{44}$ components, *don't even have the correct sign* when underconverged!

The particular *k*-point density used in producing the underconverged results (60 *k*-points in irreducible zone with full cubic symmetry) was chosen for comparison because it is the density which was sufficient to converge the unstrained dielectric function to within 1% at $\omega = 0.0$ eV and 4% at $\omega = 1.25$ eV.

The static ($\omega = 0$) values are largely unaffected – with the exception of the $-(p_{11} - p_{12})$ component which is altered by roughly 50% – while the frequency-dependent values are increasingly affected as the band gap is approached.

The dramatic discrepancies in the frequency-dispersion between the converged and underconverged results is seen to be due to the sampling of the Γ -point. The argument is as follows.

The frequency-dependent energy denominators which enter the Brillouin zone integrands associated with the unstrained dielectric function as well as the photoelastic tensor are of the form

$$[(E_{mc}(\vec{k}) - E_v(\vec{k}))][\omega - (E_{mc}(\vec{k}) - E_v(\vec{k}) + \Delta)][\omega + (E_{mc}(\vec{k}) - E_v(\vec{k}))], \quad (5.1)$$

where $E_{mc}(\vec{k})$ is the m 'th conduction band at point $\vec{k}$. As the photon frequency approaches the smallest direct gap, which occurs at $k = 0$ in GaAs (i.e., smallest gap = $E_c - E_v + \Delta$, with E_c = the lowest conduction band), the energy denominators vanish and the integrand becomes singular. It is this singular behavior in the BZ integrands which leads to the dispersion of the photoelastic tensor and the unstrained dielectric tensor. This is reason why the Γ -point becomes more important as the band gap is approached.

Since the same singularity occurs in the unstrained dielectric tensor as well as the photoelastic tensor we must answer the question: "Why is it so much more difficult to converge the photoelastic tensor than it is to converge the unstrained dielectric function?" The answer is related to the fact that in computing the photoelastic tensor we must subtract two integrals - components of the *strained* dielectric tensor - whose integrands are nearly the same throughout the zone yet have large differences in a very small volume of the zone near the Γ -point.

The integrand associated with the unstrained dielectric function is peaked near Γ being roughly an order of magnitude larger than the integrand throughout the

rest of the zone. The contribution to the integral due to the Γ -point region is highly suppressed because of the very small integration volume over which the integrand is peaked, resulting in a correction of the order of 1% to the dielectric function.

In the case of the photoelastic tensor, however, the relevant integrand is sharply peaked and *much* (three to four orders of magnitude) larger near $k = 0$ than throughout the rest of the zone. Even with this large value of the integrand near $k = 0$ the corrections to the static values are relatively small due to the suppression of the peak by the small integration volume. As the band gap is approached, however, the integrand becomes singular and the precise details of the Γ -point sampling become crucial to the correct description of the dispersion.

It is nearly impossible from looking at Fig. 5.6 to discern any noticeable correction to the static value of the $-p_{44}$ component of the photoelastic tensor but moving to higher frequencies reveals a dramatic discrepancy. Figures 5.7 and 5.8 show that the improved description of the dispersion is required to obtain qualitative agreement with the experiments.

Convergence of the results presented in Figs. 5.4 - 5.8 is obtained using the two-mesh method described in chapter 4 wherein the Γ -point region is spanned by spherical-meshes of points and the rest of the integrand is spanned by a uniform mesh. It must be emphasized that this so-called Γ -point region is extremely small - roughly 2% of the BZ - and is almost completely missed by the uniform grids used to produce the "underconverged" results presented above. To be more specific, the point nearest to $k = 0$ in the 60 k -point mesh has magnitude $0.11(2\pi/a)$, whereas the peak in the integrand has slightly less extent, meaning that in going from $k = 0$

to $k = 0.11(2\pi/a)$ the peak has decreased from its maximum value by more than 95%.

Table 5.1 shows the slow-convergence behavior of the $-(p_{11} - p_{12})$ component of the photoelastic tensor. The first two rows of Table 5.1 support the notion the peak near $k = 0$ is largely unsampled when the uniform grids corresponding to 60 and 110 k -points in the irreducible zone of cubic symmetry (144 and 275 points in tetragonal symmetry appropriate to $[001]$ strain) are used. Changing from the 60-point density to the 110-point density brings only a change of less than 1% to the static value which is less than an order of magnitude of the correction which ultimately results upon reaching convergence. Only if we look at the $\omega = 1.25$ value

a situation in which the integrand near Γ is *much* larger than in the $\omega = 0$ case do we notice any appreciable change that might lead to the conclusion that we have a convergence problem. The change for $\omega = 1.25$ upon going from the 60-point to the 110-point densities is still less than an order of magnitude of that which results upon reaching convergence which, once again, supports our assumption of a sharply-peaked feature near $k = 0$ which is almost entirely unsampled by the 60-point mesh. Even for the case of 2783 points in the irreducible zone – the mesh which was sufficiently dense to be used in the two-mesh scheme to produce the converged result – substantial contributions are still missing: 10% errors for the static value and roughly 70% errors to the $\omega = 1.25$ value.

Actually the peak value of the integrand at $k = 0$ is not of primary importance in determining contributions to the integrand since it is completely suppressed by the vanishing integration volume as $k \rightarrow 0$. The more relevant quantity is the radial function which takes into account the k^2 suppression of the $k \rightarrow 0$ integrand.

The radial function for the integrand associated with the long-wave, static, $-(p_{11} - p_{12})$ component of the photoelastic tensor is shown in Fig. 5.9 along with two approximate radial functions. As was discussed in chapter 4, an approximate radial function is obtained by Fourier interpolation from the uniform grid to the spherical meshes which were used to project the exact radial function. Regions of k -space in which there is good agreement between the approximate and exact radial functions are said to be adequately represented by the uniform mesh. For small k we see large discrepancies between the approximate and exact radial functions. This region is represented by the spherical meshes which are known to represent the radial function to a very high accuracy as determined by examining the fall-off of the spherical-harmonic expansion coefficients with increasing ℓ (see chapter 4). A transition region in which both the spherical-mesh and the uniform-mesh descriptions are appropriate is called a “matching region”. In the matching region the one description (sphere-meshes for small- k) is turned off while the other (uniform mesh for large- k) is turned on with increasing k from the lower k_0 to the upper k_1 limit of the matching region.

One can see from Fig. 5.9 that for the lower density uniform grid (containing 468 points in the irreducible zone) the matching region doesn’t begin until $k_0 = 0.35$ while for the higher density uniform mesh (2783 points) the matching region begins at $k = 0.2$. While the use of the 468-point mesh represents fewer points coming from the uniform grid, the total number of points needed, including all sphere meshes, would be much larger than if the 2783-point uniform mesh were used, owing to the fact that as we go farther out in k not only do we need more spheres of points but on each sphere we need more points to accurately converge the radial function.

The two-mesh scheme which was adopted used the 2783-point uniform mesh and 11 sphere meshes each containing 80 points in the irreducible zone (allowing for the exact integration of spherical-harmonics up to $\ell = 15$). In effect, the difference between the converged results and those obtained using the 2783 uniform points (the last two rows of Table 5.1) is the difference between using the exact radial function of Fig. 5.9 and using the approximate one corresponding to 2783. A similar statement, of course, applies to the difference between the 468 k -point result and the converged result of Table 5.1. Since the frequency dependence of the long-wave dielectric function and the photoelastic tensor only enters the energy denominators, we can be confident that since the two-mesh scheme correctly integrates the static integrals the frequency-dependent integrals will also be properly converged.

This completes the discussion of the k -point convergence of the frequency-dependent dielectric and photoelastic tensors. The evidence which assures us that we are, in fact, converged — details of the spherical-harmonic expansion coefficients will be examined shortly as well as convergence studies relating to the energy cutoff used in our plane wave expansions, and to the number of bands kept in our spectral sums over conduction bands. For now, we briefly turn our attention to local-field effects and the effect of the scissors operator.

5.4 The photoelastic tensor: local-field effects

Corrections to the three components of the photoelastic tensor due to local-field effects are illustrated in Figs. 5.4 – 5.6. We see that the effect of local-fields is to make the photoelastic tensor components slightly more dispersive. For the $-(p_{11} + 2p_{12})$ component, which has same-signed values for all frequencies, local-

fields induce a frequency-dependent increase of the magnitude of $-(p_{11} + 2p_{12})$ with larger increases for higher frequencies. This implies that for a given frequency of light, the strain-induced change in the dielectric function is larger if local field effects are included than if they are omitted.

For the $-(p_{11} - p_{12})$ and $-p_{44}$ components the situation is slightly different since for these components there exists what is called an isotropic point, i.e., a frequency for which there is no strain-splitting. The frequency of the isotropic point is the frequency at which a given photoelastic tensor component vanishes. From Figs. 5.5 and 5.6 one can see that the underconverged results do not have isotropic points.

The effect of local-fields on the converged $-(p_{11} - p_{12})$ and $-p_{44}$ components is to decrease their values, decreasing the magnitude of the positive components and increasing the magnitude of the negative components. Physically this implies that for frequencies below the isotropic point (with no local-fields) the splitting of the dielectric function is decreased while for frequencies above the isotropic point (with no local-fields) the splitting of the dielectric function is increased. In addition, one can see that the frequency of the isotropic point is decreased upon the inclusion of local-fields. The local field-effect is frequency-dependent as it was for the $-(p_{11} + 2p_{12})$ component, with larger shifts at higher frequencies, thus enhancing the frequency dispersion.

5.5 The photoelastic tensor: effects of the self-energy correction

The effect of the scissors operator is to modify one of the three products in the energy denominators which appear in the integrands associated with the dielectric

function and the photoelastic tensor (see Eq. (5.1)), thus changing the position of the singularity. In Figs. 5.7 and 5.8 results are presented for the $-(p_{11} - p_{12})$ and $-p_{44}$ components which were calculated using two different values of Δ . The value $\Delta = 0.8$ eV was predicted by GW calculations^{1,2,3,4} as the correction needed to reproduce the true quasiparticle band gap, and $\Delta = 0.937$ eV was chosen to correct the LDA band-gap at $k = 0$ found in our calculations and align it with the experimental gap. While $\Delta = 0.8$ eV was seen to produce excellent results for the unstrained dielectric function (see Figs. 5.1, 5.2 and 5.3) it leads to results which are slightly too dispersive for the photoelastic tensor, as we see from Figs. 5.7 and 5.8. The larger Δ in Figs. 5.7 and 5.8 is seen to make the photoelastic tensor less dispersive and brings it into better qualitative agreement with the experiments. The LDA results, in contrast are much worse. For example, the effect of setting $\Delta \rightarrow 0$ on the 60 k -point result (of Fig. 5.5) is that the long-wave, static, $-(p_{11} - p_{12})$ component is changed as $0.056 \rightarrow 0.029$ and $0.045 \rightarrow 0.018$ with local-fields. The corresponding numbers at $\omega = 1.25$ eV are $0.021 \rightarrow -0.012$ and $0.0059 \rightarrow -0.026$ respectively.

The effect of the scissors operator can be summarized as follows: the smaller the Δ the more dispersion and the smaller the static value – a result which follows from the analytic structure of the integrand: singular behavior at $k = 0$ for $\omega \rightarrow E_{gap}$. This concludes the discussion of the effects of the scissors operator.

5.6 Spherical-harmonics: the photoelastic tensor

Selected spherical-harmonic expansion coefficients from $\ell = 0$ to $\ell = 8$ for the integrand associated with the $-(p_{11} - p_{12})$ component of the photoelastic tensor are presented in Figs. 5.10 and 5.11. Note that for all but the smallest values of k , the magnitude of the $C_{00}(k)$ coefficient, which is the only one which makes a contribution to the integral, is several orders of magnitude smaller than the higher harmonics.

The $C_{00}(k)$ coefficient, which gives rise to the radial function of Fig. 5.9, was converged at each radius in k by examining the fall-off of the spherical-harmonic expansion with increasing ℓ (not shown). For some of the larger radii, $k = 0.35$ and $k = 0.45$ for instance, it was necessary to go to $\ell = 46$ in order to determine the converged value of C_{00} . Once every value of the radial function, which, up to a constant, is C_{00} multiplied by k^2 , was converged, it was determined that a spherical mesh which could exactly integrate spherical harmonics up to $\ell = 15$ (80 points in the irreducible zone at each k) was sufficient to converge the radial function to within a few percent of its *average*. Since the radial function is a signed quantity, the average value can be much smaller in magnitude at some points, than the radial function itself. For this reason, requiring the radial function to be converged to within a few percent of its average is a far more stringent criterion than simply forcing it to be converged to within a few percent point by point.

The 80-point meshes, mentioned in the previous paragraph, were used to produce the numerical projections of Figs. 5.10 and 5.11. These 80 point meshes,

incidentally, were also used in the two-mesh scheme used to produce the converged results of Figs. 5.1 – 5.9.

As will be discussed shortly, the oscillations in the photoelastic integrand are a natural consequence of the oscillations which occur in the integrand for the unstrained dielectric function. It is demonstrated in appendix A, using second-order $\vec{k} \cdot \vec{p}$ theory, that the spherical-harmonic coefficients of the unstrained dielectric function for $\ell = 0$ through $\ell = 6$ can be derived analytically. To determine harmonics with $\ell \geq 8$ it is necessary to go to third and higher order in the $\vec{k} \cdot \vec{p}$ interaction. The coefficient C_{80} in Fig. 5.11 thus gives us some indication as to how rapidly terms of order k^3 and higher, in the $\vec{k} \cdot \vec{p}$ expansion, become important with increasing k .

5.7 Spherical-harmonics: the dielectric function

The small- k oscillations in the integrand for the photoelastic tensor are a consequence of corresponding oscillations in the integrand for the unstrained dielectric function. The oscillations for the unstrained integrand arise from two sources – the matrix elements which generate $\ell = 0, 2$ harmonics, and the energy denominators which generate oscillations which are compatible with cubic symmetry i.e. $\ell = 0, 4$, etc.

The expansion coefficients for the three diagonal components of the integrand for the unstrained dielectric function at $k = 0.01(2\pi/a)$ are presented in Table 5.2. One can see that for any given component, the C_{00} coefficient is much larger than the higher components. This explains why the existence of the higher harmonics presents no problem for the convergence of the unstrained dielectric function.

When we compute the components of the photoelastic tensor, however, we must take finite differences of various components of the dielectric function under strain. For example, the $(p_{11} - p_{12})$ component is proportional to the difference $\varepsilon_{xx} - \varepsilon_{zz}$. It is instructive to consider such a difference of the components of the unstrained dielectric tensor.

Table 5.3 presents the spherical-harmonic coefficients of the differences $\varepsilon_{xx} - \varepsilon_{zz}$, $\varepsilon_{yy} - \varepsilon_{zz}$, and $\varepsilon_{xx} - \varepsilon_{yy}$ of the unstrained dielectric function. If we were dealing with scalar quantities, we would expect to find vanishing entries for each component in Table 5.3. Due to the tensor character of these differences, however, we see that some of the higher harmonics are still quite large. The C_{00} coefficient is, of course, zero for each of the differences which must from the fact that the unstrained dielectric function is isotropic due to cubic symmetry.

Under strain, each of the coefficients of Table 5.3 are modified, (see Table 5.4) with the C_{00} of the unstrained dielectric function taking on non-zero values leading to non-vanishing photoelastic components. The second column of Table 5.4 is the strained-analog of the first column of Table 5.3 in the presence of a volume conserving tetragonal strain of magnitude $\delta z/z = -0.0004$ where z is any length measured along the $[001]$ direction. We see, in particular that the C_{20} , C_{40} , C_{44} and C_{60} coefficients are still of the same sign and order of magnitude. In fact, the coefficient which changes by the largest magnitude is the C_{00} .

We have thus explained the small- k oscillations of the photoelastic integrand by correspondence with oscillations in the unstrained integrand. The origin of these oscillations, which is treated in detail in appendix A, will be discussed shortly. We now turn briefly to the issue of the convergence of the oscillations themselves with

two important parameters of the *ab initio* calculation: the energy cutoff's for the plane wave expansion and for the spectral sums over conduction bands.

5.8 Spherical-harmonics: convergence with energy cutoff

The oscillations in the photoelastic integrand are converged with a 10 Hartree cutoff for the plane wave expansion of the wavefunctions (see Table 5.4). Going to 12 Hartree brings only a 1% change in the C_{00} coefficient. The higher harmonics are also virtually unchanged upon going to 12 Hartree. At 9 Hartree, however, we make errors of the order of 10% in the C_{00} coefficient. At this lower cutoff we also see a qualitatively as well as quantitatively incorrect behavior of the higher harmonics. A 10 Hartree cutoff was thus adopted and was used to produce all other results presented. Evidently the slow convergence of the oscillations is associated with the need to fully converge the valence-band wavefunctions which are known to be tight-binding-like p -functions (see appendix A). It is reasonable to expect that a large number of planewaves are required to converge such localized wave functions.

Another energy cutoff to be considered is the cutoff on the spectral sum over conduction bands “ecutsp”. Table 5.5 presents the convergence characteristics of the C_{00} coefficient of the photoelastic integrand at $k = 0.01(2\pi/a)$ with the number of bands retained in the spectral sum. We find the surprising behavior that the C_{00} coefficient is converged to within 0.1% by just retaining the *first conduction band*! This gives strong support for the validity of the “small-gap” approximation (in which only one conduction band is retained) used in the $\vec{k} \cdot \vec{p}$ treatment of the small- k integrand (see appendix A). In practice, to ensure convergence throughout

the BZ we used $\text{ecutsp} = 1.65$ which corresponds to retaining roughly 50 bands near Γ and slightly less throughout the zone.

5.9 The unstrained integrand: analytical results

The wavefunctions and energies for the three highest valence bands and the first conduction band near $k = 0$ are for an unstrained zinc-blend insulator derived in appendix A using second-order $\vec{k} \cdot \vec{p}$ perturbation theory. From these, expressions for the integrand of the unstrained dielectric function are expressed as power series expansions in k up to and including terms of order k^2 .

The angular dependence of the squared matrix elements has a simple form which is proportional to k_j^2/k^2 (up to an additive constant), where $j = \{x, y, z\}$ depending on whether we are considering the $\{xx\}$, $\{yy\}$ or $\{zz\}$ component of the dielectric tensor, and the angular dependence of the energy levels is of the form $(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^4$.

The expansion of the integrand in k is cast in the form of an expansion in spherical-harmonics with k -dependent expansion coefficients $C_{\ell,m}(k)$ which are expressed as power series to second order in k . This is done by expressing the quantities k_x^2/k^2 , k_y^2/k^2 and k_z^2/k^2 in terms of spherical-harmonics as is done in Eqs. A73 – A75. The angular dependence of the energy levels is then expressed in terms of products of spherical-harmonics which can further be decomposed in terms of spherical-harmonics.

Matrix elements give rise to harmonics with $\ell = \{0, 2\}$ and the energy denominators have $\ell = \{0, 4\}$ character. When the energy denominators are expanded to

order k we obtain products of $\ell = \{0, 2\}$ harmonics (from the numerator) multiplied by $\ell = \{0, 4\}$ harmonics (from the denominator). These products are decomposed in terms of $\ell = \{0, 2, 4, 6\}$ harmonics. In this way, we obtain analytic expressions for the expansion coefficients $C_{\ell,m}$ for $\ell = \{0, 2, 4, 6\}$.

Table A9 lists the analytical forms for the $C_{\ell,m}$'s for $\ell = \{0, 2, 4, 6\}$ which are written in terms of various undetermined constants representing matrix elements and energy gaps at $k = 0$. We see by inspection of Table A9 that all coefficients with $\ell \neq 0$ should be smaller than C_{00} , since they vanish as k^2 with $k \rightarrow 0$, which is a consequence of the fact that the integrand is single-valued. The analytical forms of Table A9 should be compared with the numerical results for the $\{xx\}$ component of the unstrained integrand (column 1 of Table 5.2).

All of the coefficients for $\ell = 4$, and $\ell = 6$ have the same dependence on the undetermined constants and on k (i.e., k^2), allowing comparisons to be made in terms of ratios of the various coefficients. Table 5.6 compares ratios of the coefficients obtained analytically with the ones obtained by numerical projection (column 1, Table 5.2). We find that all of the ratios are in agreement to within less than an order of magnitude. The ratios of the coefficients with $\ell = 6$ are in especially good agreement. It is reasonable to expect that discrepancies are due to higher-order terms in the $\vec{k} \cdot \vec{p}$ expansion. From the results of Table 5.6 we conclude that the $\vec{k} \cdot \vec{p}$ treatment gives an adequate description of the essential qualitative features of the small- k integrand for the unstrained dielectric function.

The coefficients of Table A9 were derived with the neglect of the spin-orbit interaction. At present our *ab initio* calculations do not include spin-orbit so the comparisons made in Table 5.6 are appropriate. Appendix A discusses the situation

in which spin-orbit is included and expressions for the wavefunctions, energies and matrix elements are derived to second order in k . The derivation of spherical-harmonic expansion coefficients in the presence of spin-orbit is straightforward but somewhat cumbersome leading to expressions which are not very enlightening due to the complicated nature of the wave function expansion coefficients. For this reason, we forego their presentation and concentrate on the angular dependence in the $k \rightarrow 0$ limit.

The qualitative differences which arise in the integrand upon inclusion of spin-orbit are summarized in Table A10. In particular, one transition which was forbidden at $k \rightarrow 0$ becomes allowed. In addition, the angular dependence of the three $k \neq 0$ matrix elements is altered and their associated energy denominators are shifted. In the presence of spin-orbit one valence band is shifted by $-2\Delta_{so}/3$ (the split-off band) and the other two are shifted by $+\Delta_{so}/3$.

To second-order in k , we see that with the inclusion of spin-orbit the sources of oscillations in the integrand are qualitatively the same as without spin-orbit: the matrix elements bring oscillations of the form k_j^2/k^2 ($j = \{x, y, z\}$) and the energy denominators oscillate as k_x^2/k^2 , k_y^2/k^2 and k_z^2/k^2 . Qualitatively we can say that up to k^2 there will exist spherical-harmonic expansion with $\ell = \{0, 2, 4, 6\}$ and that all coefficients with $\ell \neq 0$ will vanish as k^2 while C_{00} goes to a constant as $k \rightarrow 0$. We cannot say much about their relative magnitudes but it is reasonable to expect that they will decrease with ℓ as they did in the absence of spin-orbit.

The effect which the inclusion of spin-orbit has on the $k = 0$ integrand associated with the dielectric function has also been estimated with the result that the magnitude of the integrand should decrease by roughly 24%.

5.10 Strain-effects: analytical results

The effects of strain on the $k = 0$ integrand with and without spin-orbit are discussed in detail in appendix B. With the neglect of spin-orbit, strain-induced changes at $k = 0$ can be expressed in a particularly simple form. These expressions are given by Eqs. B38 – B42 and B49. From these forms we see that the dominant contribution to the strain-splitting is due to band-shifts of the energy denominators, which make contributions that are roughly a factor of 3.5 larger in magnitude than those of the matrix element shifts.

The shifts of the energy-levels are expressed in terms of the so-called “deformation-potential” parameters a , b and c , which characterize the shifts of the band gap under hydrostatic, tetragonal ($[001]$) and trigonal ($[111]$) strains respectively.

When spin-orbit is included (Eqs. B65 and B66) the matrix elements shift under strain in a qualitatively different way, due to strain-induced mixing of the zero-strain states, resulting in much larger matrix-element shifts. In particular, changes in the matrix-element which result from strain-induced mixing of the states are larger by roughly a factor of 4.4 than those which occurred in the absence of spin-orbit. The wave functions which diagonalize the Hamiltonian in the presence of both strain and spin-orbit are linear combinations of the states which diagonalize the spin-orbit Hamiltonian. The strain-dependent wave function expansion coefficients are proportional to the deformation potentials. Table B1 contrasts the strain-split matrix elements with and without spin-orbit for strains parallel and perpendicular to the polarization direction of the electric field.

The effect which spin-orbit has on the $k = 0$ integrand associated with the photoelastic tensor also has been estimated (see appendix B). The result is that the magnitude of the $k = 0$ integrand is expected to be reduced by 41% as compared with the corresponding value in the absence of spin-orbit.

Fig. 5.1 Results for the frequency-dependent, unstrained dielectric function with local-field effects, demonstrating k -point convergence with 60 k -points, compared with experimental measurements. The results designated as “converged” are produced using the two-mesh integration approach which was required in order to converge the photoelastic tensor. A slight improvement in frequency dispersion is obtained with the two-mesh technique, representing roughly a 4% increase in the dielectric function at $\omega = 1.25$, while the static value changes by less than 1%. We conclude that the unstrained dielectric function is well converged with the 60 k -point mesh. The scissors shift is $\Delta = 0.8$ eV. The experimental results were taken from Ref. 5.

Fig. 5.2: Results for the frequency-dependent, unstrained dielectric function with and without local-field effects. The effect of local fields is to decrease the dielectric function by an amount that is very weakly dependent on frequency: the static value is shifted by -0.54 and the $\omega = 1.25$ value by -0.57 . The self-energy correction is $\Delta = 0.8$ eV. The experimental results were taken from Ref. 5.

Fig. 5.3: The effect of the scissors operator on the unstrained, frequency-dependent dielectric tensor (local-fields are included). Results obtained with no scissors shift, $\Delta = 0$ (i.e., LDA), are compared with those obtained with $\Delta = 0.8$ eV and with experimental measurements. Note that $\Delta = 0.8$ eV was *not* chosen to fit the experimental dielectric function, nor was it chosen to fit the bandgap in our calculations to the experimental gap but rather, it is the value suggested by *GW* calculations.^{1,2,3,4} The experimental results were taken from Ref. 5.

Fig. 5.4: Converged results for the frequency-dependent $p_{11} + 2p_{12}$ component of the photoelastic tensor (corresponding to hydrostatic strain) with and without local-field effects, compared with underconverged (60 k -point density) results. The 60 k -point density – 60 k -points in the irreducible zone with full cubic symmetry – which is used for comparison is the density which was required in order to converge the unstrained dielectric function to within 1%. The scissors shift is $\Delta = 0.8$ eV.

Fig. 5.5: Converged results for the frequency-dependent $-(p_{11} - p_{12})$ component of the photoelastic tensor (corresponding to $[001]$ shear strain) with and without local-field effects, compared with underconverged (60 k -point density) results. The 60 k -point density = 60 k -points in the irreducible zone with full cubic symmetry which is used for comparison is the density which was required in order to converge the unstrained dielectric function to within 1%. The scissors shift is $\Delta = 0.8$ eV.

Fig. 5.6: Converged results for the frequency-dependent $-p_{44}$ component of the photoelastic tensor (corresponding to $[111]$ shear strain) with and without local-field effects, compared with underconverged (60 k -point density) results. The 60 k -point density – 60 k -points in the irreducible zone with full cubic symmetry – which is used for comparison is the density which was required in order to converge the unstrained dielectric function to within 1%. The scissors shift is $\Delta = 0.8$ eV.

Fig. 5.7: Converged results for the long-wave, frequency-dependent $-(p_{11} - p_{12})$ component of the photoelastic tensor demonstrating the effect of the scissors operator with $\Delta = 0.8$ eV (*GW* result^{1,2,3,4}) and $\Delta = 0.937$ eV (aligns the band gap), compared with four sets of experimental results. The experimental references are as follows: HC = Ref. 5, GPPY = Ref. 6, NM = Ref. 7, and FH = Ref. 8.

Fig. 5.8: Converged results for the long-wave, frequency-dependent $-p_{44}$ component of the photoelastic tensor (corresponding to $[111]$ shear strain) demonstrating the effect of the scissors operator with $\Delta = 0.8$ eV (*GW* result^{1,2,3,4}) and $\Delta = 0.937$ eV (aligns the band gap), compared with four sets of experimental results. The experimental references are as follows: HC = Ref. 5, GPPY = Ref. 6, and NM = Ref. 7.

TABLE 5.1: Convergence study of the $p_{1111} - p_{1112}$ component of the photoelastic tensor showing very slow convergence using conventional special k -point methods, especially poor is the value for $\omega = 1.25$ eV. The number of k -points are those in the *irreducible* zone. The entry designated as “converged” was obtained using our new approach utilizing spherical meshes near $k = 0$ in combination with a dense (2783 points) uniform mesh. The resolution of the $k = 0$ region is extremely important for the correct description of the dispersion, as is evident from the convergence characteristics of the high-frequency value which changes sign upon convergence.

Number of k -points in irreducible zone	$\omega = 0$	$\omega = 1.25$ eV
144	+0.05713	+0.02300
275	+0.05752	+0.01746
468	+0.05166	+0.00006
735	+0.05148	−0.00449
2783	+0.04237	−0.05866
Converged	+0.03820	−0.17990

Fig. 5.9: Converged radial function for the integrand associated with the static, long-wave $-(p_{11} - p_{12})$ component of the photoelastic tensor compared with two approximate radial functions. For a given approximate radial function, the number given in the legend is the number of points in the irreducible Brillouin zone of the uniform mesh which was used to construct the approximate radial function. Note that for the higher density uniform grid (2783 points in the irreducible zone) a matching region between the exact and approximate radial function exists starting at $k = 0.2$ (units of $2\pi/a$) whereas for the lower density uniform grid (468 points in the irreducible zone) the matching region is farther out in k , starting at $k = 0.35$. The scissors shift is $\Delta = 0.8$ eV.

Fig. 5.10: Spherical-harmonic expansion coefficients ($C_{\ell,m}$) for the integrand associated with the long-wave, static $-(p_{11} - p_{12})$ component of the photoelastic tensor for $\ell = 0$ to $\ell = 4$ as functions of k . Some coefficients have been omitted (e.g., $C_{2,2}$ and $C_{4,2}$) for clarity of presentation - all $C_{\ell,m}$'s with the same ℓ have similar behavior. Note that the only term which contributes to the integral, $C_{0,0}$ (the signal), is at least an order of magnitude smaller than the higher harmonics (the noise) at all but the smallest (not shown) values of k . The scissors shift is $\Delta = 0.8$ eV

Fig. 5.11: Spherical-harmonic expansion coefficients ($C_{\ell,m}$) for the integrand associated with the long-wave, static $-(p_{11} - p_{12})$ component of the photoelastic tensor for $\ell = \{0, 6, 8\}$ as functions of k . Some coefficients have been omitted (e.g., $C_{6,2}$, $C_{8,2}$, $C_{8,4}$ and $C_{8,8}$) for clarity of presentation – all $C_{\ell,m}$'s with the same ℓ have similar behavior. Note the behavior of the $C_{8,0}$ coefficient which grows rapidly with increasing k . The magnitude of this coefficient – the first coefficient which cannot be determined with second order $\vec{k} \cdot \vec{p}$ theory – indicates, for a given k , the importance of third and higher-order effects in the $\vec{k} \cdot \vec{p}$ expansions. The scissors shift is $\Delta = 0.8$ eV

TABLE 5.2: Spherical-harmonic expansion coefficients for the $\{xx\}$, $\{yy\}$ and $\{zz\}$ components of the integrand associated with the unstrained, static, long-wave dielectric function at $k = 0.01(2\pi/a)$ (a is the experimental lattice $a = 10.6807\text{a.u.}$) numerically projected from results of *ab initio* calculations (scissors shift $\Delta = 0.8$ eV). The last column gives the expansion coefficients for the trace of the integrand to illustrate that the trace indeed obeys cubic symmetry.

Coefficient	xx	yy	zz	$(xx + yy + zz)/3$
C_{00}	+213939.3	+213939.3	+213939.3	+213939.3
C_{20}	+5036.9	+5036.9	-10073.8	0.0
C_{22}	-6169.0	+6169.0	0.0	0.0
C_{40}	-58.1	-58.1	-122.2	-238.4
C_{42}	+40.6	-40.6	0.0	0.0
C_{44}	-65.4	-65.4	-11.7	-142.5
C_{60}	-1.4	-1.4	+2.6	-0.6
C_{62}	+1.0	-1.0	0.0	0.0
C_{64}	-0.3	-0.3	+0.8	+0.2
C_{66}	+1.4	-1.4	0.0	0.0

TABLE 5.3: Spherical-harmonic expansion coefficients for various differences ($\{xx\} - \{zz\}$, $\{xx\} - \{yy\}$ and $\{yy\} - \{zz\}$) of the components of the integrand associated with the unstrained, static, long-wave dielectric function at $k = 0.01(2\pi/a)$ (a is the experimental lattice $a = 10.6807\text{\AA}$) numerically projected from the results of *ab initio* calculations (scissors shift $\Delta = 0.8\text{ eV}$). The first column represents the quantity which is relevant for the eigenvalue of the photoelastic tensor corresponding to $[001]$ strain. Under a $[001]$ strain, the C'_{00} coefficient becomes non-zero (the signal) yet remains at least an order of magnitude smaller than some of the higher- ℓ coefficients (the noise).

Coefficient	$xx - zz$	$yy - zz$	$xx - yy$
C'_{00}	0.0	0.0	0.0
C'_{20}	+15110.8	+15110.8	0.0
C'_{22}	-6169.0	+6169.0	-12337.9
C'_{40}	+64.1	+64.1	0.0
C'_{42}	+40.6	-40.6	+81.1
C'_{44}	-53.7	-53.7	0.0
C'_{60}	-3.9	-3.9	0.0
C'_{62}	+1.0	-1.0	+1.9
C'_{64}	-1.0	-1.0	0.0
C'_{66}	+1.4	-1.4	+2.8

TABLE 5.4: Selected spherical-harmonic expansion coefficients at $k = 0.01(2\pi/a)$ for the integrand associated with the $p_{1111} - p_{1112}$ component of the long-wave static photoelastic tensor (analog of first column of Table 5.3 under $[001]$ strain) and their sensitivity to the energy cutoff. These results demonstrate that we make less than 1% error when using 10 Hartree cutoff instead of 12 Hartree whereas if we were to use a 9 Hartree cutoff we would be making error of the order of 10%. For larger k the convergence with energy cutoff is much better, for example at $k = 0.45(2\pi/a)$ the errors incurred using 9 Hartree are of the order of 2%. For these reasons, a 10 Hartree cutoff was judged to give sufficiently accurate results and was therefore used to produce all other results reported.

Coefficient	9H	10H	12H
C'_{00}	-2211.3	-2007.6	-2023.7
C'_{20}	+15397.5	+15200.1	+15173.2
C'_{40}	-39.8	+57.6	+57.0
C'_{44}	+99.8	-53.1	-52.7
C'_{60}	-170.7	-4.0	-3.9
C'_{64}	+79.7	-1.0	-1.0
C'_{80}	+30.1	-1.3×10^{-2}	-1.4×10^{-2}
C'_{84}	-21.7	$+2.8 \times 10^{-2}$	$+1.7 \times 10^{-3}$
C'_{88}	+11.7	$+1.2 \times 10^{-2}$	$+1.5 \times 10^{-3}$

TABLE 5.5: Convergence with the number of conduction bands (N_c) of the C'_{00} spherical-harmonic expansion coefficient at $k = 0.01(2\pi/a)$ for the integrand associated with the $p_{1111} - p_{1112}$ component of the long-wave, static, photoelastic tensor (analog of first column of Table 5.3 under [001] strain). The number of conduction bands is determined by the variable “ecutsp” which is the energy-cutoff for the spectral sum over conduction bands. These results demonstrate that we make less than 0.1% error in the description of the small- k integrand when we retain only the *first* conduction band. To ensure proper convergence throughout the zone we used $\text{ecutsp} = 1.65$ Hartree which corresponds to roughly 50 bands near $k = 0.01(2\pi/a)$ and slightly fewer throughout the zone. We see that the “small-gap” approximation, invoked in the $\vec{k} \cdot \vec{p}$ treatment of the small- k integrands (Appendices A and B) — in which only one conduction band is retained — is an extremely accurate approximation for the present purposes.

ecutsp	N_c	C'_{00}
0.125	1	−2009.62
0.25	4	−2007.66
0.5	10	−2007.57
∞	100	−2007.57

TABLE 5.6: Comparison of analytical (second-order $\vec{k} \cdot \vec{p}$ theory: Table A4 and *ab initio* (Table 5.2) results for the spherical-harmonic coefficients of the integrand associated with the $\{xx\}$ component of the unstrained long-wave static dielectric function at $k = 0.01(2\pi/a)$. Comparisons are presented as ratios of the various coefficients. All ratios are of the same order of magnitude indicating that the analytical treatment gives an accurate description of the qualitative features of the small- k integrand. The ratios for the $\ell = 6$ coefficients are in excellent agreement indicating that terms of order k^3 and higher are small for these coefficients. The discrepancies for the lower- ℓ coefficients indicate that terms of order k^3 and possibly higher are not negligible.

	$\vec{k} \cdot \vec{p}$ (analytical)	<i>ab initio</i>
$ C'_{40}/C'_{42} $	7.50	1.43
$ C'_{40}/C'_{44} $	1.43	0.89
$ C'_{44}/C'_{42} $	5.23	1.60
$ C'_{60}/C'_{40} $	0.10	0.02
$ C'_{60}/C'_{62} $	1.42	1.42
$ C'_{60}/C'_{64} $	3.79	5.28
$ C'_{60}/C'_{66} $	0.93	0.96
$ C'_{62}/C'_{64} $	2.70	3.73
$ C'_{62}/C'_{66} $	0.66	0.67
$ C'_{64}/C'_{66} $	0.24	0.18

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CHAPTER VI

Conclusions

We performed a stringent test of the applicability of our *ab initio* methods afforded by the calculation of the optical property known as the photoelastic effect in GaAs. We observed discrepancies between calculated results and experimental measurements, with regard to the frequency-dispersion of the photoelastic tensor, leading to the discovery of deficiencies in our previous methods with regard to Brillouin zone sampling techniques. A novel integration method has been developed which as led to greatly improved results for the calculation of the photoelastic tensor.

In particular it is found that the details of the sampling of a tiny region of the Brillouin zone (less than 2% of the zone volume) are crucial to obtaining a correct description of the frequency-dispersion of the photoelastic tensor. A 60 *k*-point mesh which is adequate for the purpose of obtaining highly converged results for the unstrained dielectric function, which agree with experiments to within a few percent for the entire frequency range below the direct band gap, is woefully inadequate for a calculation of the photoelastic tensor. While the static value of the photoelastic tensor obtained with the 60 *k*-point mesh is within 10% of the experimental result, the dispersion is not even *qualitatively* correct having same-signed values and relatively flat dispersion throughout the frequency range of interest. The experimental

results, on the other hand, change sign part way through the frequency range below the band gap and diverge as the band gap is approached.

The problem with the dispersion is related to inadequate sampling of the $k = 0$ region of the BZ. The band gap at $k = 0$ is small but increases quite rapidly with k . Effectively the smallest band gap sampled by the 60 k -point is much larger than the true gap, and for this reason, the photoelastic tensor calculated with the 60-point mesh corresponds to a material similar to GaAs but with a much larger gap. It is not surprising therefore that the calculated photoelastic tensor shows little resemblance to that of GaAs.

The dispersion of the photoelastic tensor due to the Γ -point can be modeled by a single, simple-harmonic oscillator forced at a driving frequency below its resonance. This follows on very general grounds from the fact that the dielectric function can also be modeled in this way as a result of causality based on the fact that the imaginary part of the dielectric function has an absorption resonance at the fundamental band gap (Kramers-Krönig). In this way, we can understand the rather flat dispersion characteristics of the photoelastic tensor which was calculated with the 60 point mesh, as that of an oscillator with a much higher resonant frequency.

The single-oscillator interpretation of the dispersion is born out by the studies of the effects of the scissors operator which showed that with smaller scissors shifts (smaller gap) more dispersion resulted.

The sampling problem due to the small gap at $k = 0$ is further complicated by small wavelength oscillations in the integrand leading to extensive cancellation. In addition these oscillations have vary large amplitude yet average to a small quantity. The easy solution to the sampling problem would seem to be to simply

increase the density of the sampling mesh until convergence was reached and be done with it. Unfortunately this would be computationally infeasible due to the fact that the integrand for the dielectric function must be evaluated at every k -point and this evaluation is extremely expensive, especially with the inclusion of local-field corrections, given the present algorithms. Luckily, however, the volume of the zone over which the difficulty occurs is very small and it was possible to devise a two-mesh scheme to accurately integrate these sharply-peaked highly oscillatory integrands.

A detailed discussion of our integration method was presented along the resulting converged results. As expected we find dramatic improvement in the calculated photoelastic tensor in comparison with experiment. The origin of the oscillations in the integrand near $k = 0$ has been identified as resulting from the structure of the energy bands and wavefunctions near $k = 0$ as determined from second-order $\vec{k} \cdot \vec{p}$ theory. When characterized in terms of spherical-harmonic expansions, the matrix elements give rise to harmonics of $\ell = \{0, 2\}$ character and the energy denominators to harmonics of $\ell = \{0, 4\}$ character. The oscillations in the integrands for harmonics of $\ell = \{0, 2, 4, 6\}$ are explained using second order $\vec{k} \cdot \vec{p}$ theory as arising from products of the $\ell = \{0, 2\}$ harmonics from the numerator with the $\ell = \{0, 4\}$ harmonics of the energy denominators. Analytic expressions for the $\ell = \{0, 2, 4, 6\}$ spherical harmonics for the unstrained integrand compare favorably with numerical projections.

In addition to studying the analytic structure of the small- k integrand in the absence of spin-orbit, we have also demonstrated that the $k = 0$ splitting is dominated by the strain-induced changes in the band gaps which dominate matrix-

element changes by an order of magnitude. Estimates of the tetragonal-strain deformation-potential constant b have also been made using the calculated $k = 0$ splitting of the dielectric-function integrand in comparison with analytic expressions. The value so obtained agrees well with an experimental measurement and is also in close agreement with the b obtained directly from observations of our strain-shifted energy bands.

The addition of spin-orbit (which is known to be an important effect in GaAs) would change the situation by increasing the magnitude of the matrix element shifts relative to the energy-band shifts. The matrix element shifts would then be of the same order of magnitude as the energy band shifts but would be of opposite sign, and would then tend to decrease the strength of the $k = 0$ point. Since the converged calculations for the static $-(p_{11} - p_{12})$ (a positive quantity) component are smaller than the experimental value, it is quite possible that the weakening of the $k = 0$ effect (which contributes with a negative sign), upon inclusion of spin-orbit could improve agreement with the experiments.

Appendix A: Small- k behavior of k -space integrands

The purpose of this appendix is to investigate the behavior of the k -space integrand associated with the unstrained, long-wavelength, static dielectric function near the Γ -point ($k = 0$) in a zinc-blende semiconductor with a direct bandgap (i.e., GaAs), by obtaining the energies and eigenstates for small k using $\vec{k} \cdot \vec{p}$ theory.

In particular we wish to understand the oscillations in the k -dependent integrand associated with the *unstrained* dielectric function. These oscillations are characterized by writing the integrand at a given magnitude of k as an expansion in spherical-harmonics. The dependence on the radial variable k is included by allowing the expansion coefficients to be k -dependent.

Analytic expressions for the spherical-harmonic expansion coefficients $C_{\ell,m}(k)$ for $\ell = 0$ through $\ell = 6$ are presented. Each expansion coefficient is written as a power series in k to order k^2 . The analytical expressions for the $C_{\ell,m}(k)$'s compare favorably with the corresponding expansion coefficients obtained by numerical projection using our *ab initio* integrands. More specifically features which are observed in the numerical coefficients, such as the rapid fall-off of the expansion coefficients with increasing ℓ , and the fact that for a given ℓ all m -components are of the same order of magnitude, are reproduced by the analytical expressions.

The plan of this appendix is as follows: 1) the $\vec{k} \cdot \vec{p}$ Hamiltonian and its use in conjunction with perturbation theory to obtain eigenvalues and eigenstates is discussed; 2) the eigenfunctions and eigenvalues for small k with and without the

inclusion of the spin-orbit interaction are constructed as series expansions including terms up to second-order in k ; 3) the integrand associated with the long-wavelength, static, unstrained dielectric function in the absence of spin-orbit is constructed and analytic expressions for the spherical-harmonic expansion coefficients for $\ell = 0$ to $\ell = 6$ are obtained; 4) the unstrained dielectric function including spin-orbit interaction is then considered; 5) lastly strain-induced changes to the k -space integrands are considered.

$\vec{k} \cdot \vec{p}$ theory

The so-called $k \cdot p$ theory allows one to obtain the energies and eigenfunctions in the neighborhood of a given point in k -space k_0 , by using perturbation theory in the basis states corresponding to the point k_0 . The presentation of $\vec{k} \cdot \vec{p}$ theory closely follows that given by Kane,¹ whose notation will be adopted throughout.

The Hamiltonian for an electron in a periodic potential is given by

$$H\psi = \left\{ \frac{p^2}{2m} + V(\vec{r}) \right\} \psi = E\psi, \quad (\text{A1})$$

where the periodicity is that of the crystal lattice and is expressed as $V(\vec{r} + \vec{R}) = V(\vec{r})$, where $\vec{R}$ is a crystal lattice vector.

Bloch's theorem states that the eigenfunctions must be of the following form

$$\psi = e^{i\vec{k} \cdot \vec{r}} u_{n\vec{k}}(\vec{r}), \quad (\text{A2})$$

where $u_{n\vec{k}}(\vec{r})$ has the same periodicity as the potential and the $\vec{k}$ which appears in Eq. (A2) is restricted to take on N discrete values (N is the number of atoms in

the crystal) in the first Brillouin zone. Substituting Eq. (A2) into Eq. (A1) yields the following equation for the periodic part of the wave function

$$\left\{ \frac{p^2}{2m} + \frac{h}{m} \vec{k} \cdot \vec{p} + \frac{h^2}{2m} k^2 + V(\vec{r}) \right\} u_{n\vec{k}}(\vec{r}) = E_n(\vec{k}) u_{n\vec{k}}(\vec{r}). \quad (\text{A3})$$

The $\vec{k} \cdot \vec{p}$ procedure is to use Eq. (A3) to obtain wavefunctions and eigenvalues by treating the second and third terms as perturbations. Because of completeness, the wave function at any point $\vec{k}$ can be expanded in terms of wavefunctions at any other point $\vec{k}_o$:

$$u_{n\vec{k}}(\vec{r}) = \sum_{n'} c_{nn'}(\vec{k} - \vec{k}_o) u_{n'\vec{k}_o}(\vec{r}). \quad (\text{A4})$$

Defining

$$H_{k_o} \equiv \frac{p^2}{2m} + \frac{h}{m} \vec{k}_o \cdot \vec{p} + \frac{h^2}{2m} k_o^2 + V(\vec{r}), \quad (\text{A5})$$

implies

$$H_{k_o} u_{n\vec{k}_o}(\vec{r}) = E_n(\vec{k}_o) u_{n\vec{k}_o}(\vec{r}), \quad (\text{A6})$$

and

$$\left\{ H_{k_o} + \frac{h}{m} (\vec{k} - \vec{k}_o) \cdot \vec{p} + \frac{h^2}{2m} (k^2 - k_o^2) \right\} u_{n\vec{k}}(\vec{r}) = E_n(\vec{k}) u_{n\vec{k}}(\vec{r}). \quad (\text{A7})$$

Now substitute Eq. (A4) into Eq. (A7), multiply both sides of Eq. (A7) by $u_{n\vec{k}_o}(\vec{r})$ and integrate over the normalization volume (i.e., the unit cell). Doing this gives the following eigenvalue problem:

$$\sum_{n'} \left[\left\{ E_n(\vec{k}_o) + \frac{h^2}{2m} (k^2 - k_o^2) \right\} \delta_{nn'} + \frac{h}{m} (\vec{k} - \vec{k}_o) \cdot \vec{p}_{nn'} \right] c_{nn'} = E_n(\vec{k}) c_{nn}, \quad (\text{A8})$$

with

$$\vec{p}_{nn'} = \int_{\Omega} u_{n\vec{k}_o}^*(\vec{r}) \vec{p} u_{n'\vec{k}_o}(\vec{r}) d\vec{r}, \quad (\text{A9})$$

where $\Omega \equiv$ unit cell volume.

Equation (A8) is exact for all $\vec{k}$ and $\vec{k}_o$ and is the starting point for the $\vec{k} \cdot \vec{p}$ method. In $\vec{k} \cdot \vec{p}$ theory the term $\frac{\hbar}{m}(\vec{k} - \vec{k}_o) \cdot \vec{p}_{nm}$ is treated as a perturbation to obtain energies $E_n(\vec{k})$ and eigenstates $u_{n\vec{k}}(\vec{r})$ at points $\vec{k}$ near some $\vec{k}_o$ which is usually chosen to be a point of high symmetry or an extremum of the energy or both (as in the case of the Γ -point in IV and III-V semiconductors).

Perturbation Theory

Kane's¹ approach employs a perturbation theory which was introduced by Löwdin.² In Löwdin's theory, states are grouped into two sets, say A & B. By construction, states in A may interact strongly with one another but must interact only weakly with states in B. The influence of states in B on those in A is included iteratively (as is done in ordinary perturbation theory) leaving a renormalized matrix for the states in A which is then diagonalized. Löwdin's expression for the "renormalized" matrix is^{1,2}:

$$h'_{ij} = h_{ij} + \sum_{\beta} \frac{h_{i\beta} h_{\beta j}}{E_i - h_{\beta\beta}} \quad \{i, j\} \subset A, \quad \beta \subset B, \quad (\text{A10})$$

where the interactions between states in A and B have been removed in lowest order. The eigenvalue E_i is determined by

$$\sum_j^A (h'_{ij} - E_i \delta_{ij}) c_{ij} = 0, \quad \{i, j\} \subset A. \quad (\text{A11})$$

The perturbed states ψ_i^l are given in terms of the unperturbed ones ψ_j by

$$\psi_i^l = \sum_j^{A,B} c_{ij} \psi_j, \quad (\text{A12})$$

where c_{ij} for $\{i, j\} \subset A$ are the eigenvectors of Eq. (A11). When i is in A but j is in B the coefficients are given by

$$c_{ij} = \sum_k^A \frac{h_{jk}}{E_i - h_{jj}} c_{ki}, \quad j \subset B, \quad \{i, k\} \subset A. \quad (\text{A13})$$

where once again the c_{ki} 's on the right of Eq. (A13) are obtained as the eigenvectors of Eq. (A11). This method will be rapidly convergent as long as the condition

$$|h_{ij}| \ll |e_i - e_j|; \quad i \text{ in } A, \quad j \text{ in } B, \quad (\text{A14})$$

can be satisfied ($e_i - e_j$ is the energy spacing of the interacting levels). The set A is chosen in such a way as to satisfy Eq. (A14).

The Γ point in diamond and zinc-blende structures

For a zinc-blende structure such as GaAs, the highest valence band has its maximum at $\vec{k} = 0$. The wavefunctions are bonding p -like functions and have symmetry Γ_{15} for zinc-blende and Γ_{25}^+ in diamond. The group theoretical notation (Γ_{15} , etc.) will be explained shortly. The lowest conduction band has its minimum at Γ and the wavefunctions are anti-bonding s -like functions with Γ_1 symmetry.

The Hamiltonian, Eq. (A1), is invariant under operations of the crystal point group—a fact which leads to the conclusion that each energy eigenfunction must also be a basis function for one of the representations of the point group. This result, which follows from group theory (see, for example, Ref. [3], chap. 4), will not be proven here. The symmetry of a given state is partially dictated by the k -vector of the block state (see Eq. (A2)), in that only symmetry operations which leave $\vec{k}$ invariant constitute the “group-of-the-wave-vector” $\vec{k}$. For example, the

vector $\vec{k} = 0$ is invariant under all operations of the cubic group (in an unstrained cubic crystal), and therefore each state at $k = 0$ must transform as one of the basis functions for a representation of the *full* cubic group. States whose k -vector have lower symmetry (e.g. $\vec{k}$ along the X direction) must transform as basis functions for representations of some *subgroup* of the cubic group. For example, if we consider $\vec{k}$ to lie along the X direction then the three-fold rotations of the cubic group must be excluded. In this case the symmetry group is that of a square, which has five representations as opposed to the ten representations of the full cubic group.

In the present work we will be concerned with the wavefunctions corresponding to the Γ -point ($k = 0$). Any polynomial which has the appropriate transformation properties under the operations of the cubic group can serve as a basis function for one of the representations for the group. Basis functions for the cubic group and various subgroups have been worked out.^{4,5,6} Table A1 presents basis functions for the representations of the cubic group. There are several notation systems currently in use for the various representations of the cubic group. The system adopted here is that due to Bouckaert, Smoluchowski and Wigner.⁶ Much of the information to be learned from $\vec{k} \cdot \vec{p}$ theory is based on the transformation properties of the states at $k = 0$. For the purposes of determining various symmetry related properties such as selection rules we need work only with the polynomials given in Table A1.

TABLE A1. Basis functions for the representations of the cubic point group.

	Parity	Dimension	Basis
Γ_1	+	1	1
$\Gamma_{1'}$	-	1	$xyz(x^4(y^2 - z^2) + y^4(z^2 - x^2) + z^4(x^2 - y^2))$
Γ_2	+	1	$x^4(y^2 - z^2) + y^4(z^2 - x^2) + z^4(x^2 - y^2)$
$\Gamma_{2'}$	-	1	xyz
Γ_{12}	+	2	$2z^2 - x^2 - y^2; \sqrt{3}(x^2 - y^2)$
$\Gamma_{12'}$	-	2	$xyz(2z^2 - x^2 - y^2); \sqrt{3}xyz(x^2 - y^2)$
$\Gamma_{15'}$	+	3	$yz(y^2 - z^2); zx(z^2 - x^2); xy(x^2 - y^2)$
Γ_{15}	-	3	$x; y; z$
$\Gamma_{25'}$	+	3	$yz; zx; xy$
Γ_{25}	-	3	$x(y^2 - z^2); y(z^2 - x^2); z(x^2 - y^2)$

To gain some insight into the various representations and their relationship to the eigenstates of the system, it is instructive to work out the eigenstates at $k = 0$ in two limiting cases: 1) the empty lattice (i.e., plane wave basis with zero potential) and 2) the tight-binding limit. The first case is thoroughly discussed by Kittel¹ and will not be reproduced.

In the tight-binding limit,¹ the wavefunctions at $k = 0$ in a zinc-blende or diamond structure can be viewed as linear combinations of atomic orbitals (s , p , d , etc.). The diamond and zinc-blende structures are comprised of two interpenetrating face-centered-cubic sublattices displaced from one another by the basis vector $(a/4)(1, 1, 1)$ where a is the lattice constant. A tight-binding function is formed by

constructing a linear combination of an atomic function (say an s state) centered around an atom of one sublattice and a similar function centered on the atom of the other sublattice which is displaced from the first by $(a/4)(1, 1, 1)$. In this way “molecular” wave functions are formed between each atom and its nearest neighbor. In the superposition, if the atomic functions on neighboring atoms have the same sign (positive parity under inversion) then a surplus of charge between the two is indicated and the wave function is called a “bonding” function. In the same way if the two have opposite signs (negative parity) then the wave function is called an “anti-bonding” function. The tight-binding wave functions can be decomposed into the various representations of the cubic group and are listed in Table A2.

TABLE A2. Decomposition of tight-binding wavefunctions into representations of the cubic point group. The cubic representations can be taken to be the polynomials of Table A1. The $\pm$ designation for the representations on the right-hand side of the semicolon, which correspond to the diamond structure, indicates the inversion parity of the representation. The $\pm$ designation is not indicated for the representations on the left-hand side of the semicolon as these refer to the zinc-blende structure for which the parity operator is absent from the corresponding point-group. This table was taken from Ref. 1

s^+	$\rightarrow$	$\Gamma_1; \Gamma_1^+$
s^-	$\rightarrow$	$\Gamma_1; \Gamma_{2'}^-$
p^+	$\rightarrow$	$\Gamma_{15}; \Gamma_{25'}^+$
p^-	$\rightarrow$	$\Gamma_{15}; \Gamma_{15}^-$
d^+	$\rightarrow$	$\Gamma_{12}, \Gamma_{15}; \Gamma_{12}^+, \Gamma_{25'}^+$
d^-	$\rightarrow$	$\Gamma_{12}, \Gamma_{15}; \Gamma_{12'}^-, \Gamma_{15}^-$
f^+	$\rightarrow$	$\Gamma_1, \Gamma_{15}, \Gamma_{25}; \Gamma_1^+, \Gamma_{15'}^+, \Gamma_{25'}^+$
f^-	$\rightarrow$	$\Gamma_1, \Gamma_{15}, \Gamma_{25}; \Gamma_{2'}^-, \Gamma_{15}^-, \Gamma_{25}^-$

In Table A3 the symmetries to the left of the semicolon correspond to zinc-blende and those on the right to diamond. The $\pm$ signs give the parity under the inversion operator for diamond (see Table A1). The same symmetry is obtained with either sign in zinc-blende since the inversion operation is absent from the point group of the zinc-blende structure.

We now return to the task of determining the energies and eigenstates near the $k = 0$ point. As was mentioned at the beginning of this section, at $k = 0$ the highest valence band has its maximum, and the lowest conduction band has its minimum. The valence band wavefunctions have symmetry Γ_{15} for zinc-blende and Γ_{25}^+ in diamond, and the conduction band has Γ_1 symmetry. These four states (three valence and one conduction) are fairly closely-spaced in energy (in small gap materials such as GaAs) and therefore interact strongly with each other. The interaction between this group of states and all others is much weaker¹ and for this reason we choose Löwdin's class A to consist of the three highest valence states and the one lowest conduction state. The basis functions for class A will be taken to be the set $\{s, x, y, z\}$ (see Table A1 and the paragraph preceding it).

The “renormalized” matrix for the states in class A, as obtained from Eq. (A10) (excluding spin-orbit) is written:

$$H_{int} = \begin{pmatrix} \begin{pmatrix} A' + E_c \\ +\frac{\hbar^2}{2m}k^2 \end{pmatrix} & \begin{pmatrix} Bk_y k_z \\ +iPk_x \end{pmatrix} & \begin{pmatrix} Bk_x k_z \\ +iPk_y \end{pmatrix} & \begin{pmatrix} Bk_x k_y \\ +iPk_z \end{pmatrix} \\ \begin{pmatrix} Bk_y k_z \\ -iPk_x \end{pmatrix} & \begin{pmatrix} L'k_x^2 + M(k_y^2 + k_z^2) \\ +E_v + \frac{\hbar^2}{2m}k^2 \end{pmatrix} & N'k_x k_y & N'k_x k_z \\ \begin{pmatrix} Bk_x k_z \\ -iPk_y \end{pmatrix} & N'k_x k_y & \begin{pmatrix} L'k_y^2 + M(k_x^2 + k_z^2) \\ +E_v + \frac{\hbar^2}{2m}k^2 \end{pmatrix} & N'k_y k_z \\ \begin{pmatrix} Bk_x k_y \\ -iPk_z \end{pmatrix} & N'k_x k_z & N'k_y k_z & \begin{pmatrix} L'k_z^2 + M(k_x^2 + k_y^2) \\ +E_v + \frac{\hbar^2}{2m}k^2 \end{pmatrix} \end{pmatrix}. \quad (\text{A15})$$

where

$$P = -i\frac{\hbar}{m}\langle s|p_x|x\rangle, \quad (\text{A16})$$

$$L' \equiv F' + 2G, \quad (\text{A17})$$

$$M \equiv H_1 + H_2, \quad (\text{A18})$$

$$N' \equiv F' - G + H_1 - H_2, \quad (\text{A19})$$

$$F' \equiv \frac{\hbar^2}{m^2} \sum_j^{\Gamma_1; \Gamma_{2'}^-} \frac{|\langle x | p_x | u_j \rangle|^2}{(E_v - E_j)}, \quad (\text{A20})$$

$$G \equiv \frac{1}{2} \frac{\hbar^2}{m^2} \sum_j^{\Gamma_{12}; \Gamma_{12'}^-} \frac{|\langle x | p_x | u_j \rangle|^2}{(E_v - E_j)}, \quad (\text{A21})$$

$$H_1 \equiv \frac{\hbar^2}{m^2} \sum_j^{\Gamma_{15}; \Gamma_{15}^-} \frac{|\langle x | p_y | u_j \rangle|^2}{(E_v - E_j)}, \quad (\text{A22})$$

$$H_2 \equiv \frac{\hbar^2}{m^2} \sum_j^{\Gamma_{25}; \Gamma_{25}^-} \frac{|\langle x | p_y | u_j \rangle|^2}{(E_v - E_j)}, \quad (\text{A23})$$

$$A' \equiv \frac{\hbar^2}{m^2} \sum_j^{\Gamma_{15}; \Gamma_{25'}^+} \frac{|\langle s | p_x | u_j \rangle|^2}{(E_v - E_j)}, \quad (\text{A24})$$

$$B \equiv 2 \frac{\hbar^2}{m^2} \sum_j^{\Gamma_{15}} \frac{\langle s | p_x | u_j \rangle \langle u_j | p_y | z \rangle}{[\{(E_c + E_v)/2\} - E_j]}, \quad (\text{A25})$$

$B = 0$; in diamond structure.

In the above equations, the sums are over states of the indicated symmetry Γ_j , with the Γ_j to the left of the semicolon corresponding to zinc-blende and to the right to diamond structures. The primes on the summations in Eqs. (A20), (A24), and (A25) indicate that the states in the subspace “A” should be excluded. All u_j are real due to time reversal symmetry at $\vec{k} = 0$, and P as written is real.

If we had not included the lowest conduction state in the A subspace but rather treated the “P” interaction by perturbation theory,⁷ then the constants A , F , L and N would enter the theory in place of the constants A' , F' , L' and N' of Eqs. (A24), (A20), (A17) and (A19). The relationship between the primed and unprimed

constants is

$$\begin{aligned}
 A &= A' + P^2/(E_c - E_v), \\
 F &= F' + P^2/(E_c - E_v), \\
 L &= F + 2G, \\
 N &= F - G + H_1 - H_2.
 \end{aligned}
 \tag{A26}$$

The primary reason for writing down the relationship of Eq. (A26) is to explain the appearance, in some formulae to follow, of both primed and unprimed constants. The unprimed constants arise in the combination $L' - N' = L - N$.

The dominant interaction in the $\vec{k} \cdot \vec{p}$ Hamiltonian of Eq. (A15) is the coupling represented by the matrix element P in Eq. (A16). Based on this information, Kane's¹ approach is as follows. 1) First neglect all $\vec{k} \cdot \vec{p}$ Hamiltonian matrix elements except those which involve P ; 2) diagonalize the Hamiltonian, and 3) include the neglected interactions using first-order perturbation theory. Spin-orbit interactions within subspace "A" will also be included, but will be neglected between subspace "A" and "B". These "renormalized" spin-orbit interactions are negligibly small they are of the order Δ'_0/E_g , where the Δ'_0 is the splitting of the next conduction band and E_g is the energy separation between the second conduction band and the level to be "renormalized".

The dominant $\vec{k} \cdot \vec{p}$ terms

The approximation whereby all $\vec{k} \cdot \vec{p}$ interactions except P are neglected to lowest order is called the "small-gap" or "three-band" approximation and is a good

approximation for materials with small direct band-gaps such as GaAs. For a general valence state:

$$\psi_v = \alpha_x x + \alpha_y y + \alpha_z z$$

the P interaction with an s state is given as:

$$\langle s | \frac{\hbar}{m} \vec{k} \cdot \vec{p} | \psi_v \rangle = iP \vec{\alpha} \cdot \vec{k}. \quad (\text{A27})$$

Equation (A27) demonstrates that the $\vec{k} \cdot \vec{p}$ interaction polarizes the valence state along $\vec{k}$. For this reason, $\vec{k}$ determines the orbital wavefunctions and can be chosen as the spin-quantization axis (due to isotropy of the spin-orbit interaction). The Hamiltonian of Eq. (A15) is simplified when we transform into a coordinate system which we call the primed frame in which the z -axis (call it z') coincides with the direction of $\vec{k}$. This primed system is the one in which we will work to find the eigenvalues and eigenstates. Once the eigenfunctions have been determined in the primed frame, a transformation back to the unprimed frame reveals their angular dependence—a dependence which is the dominant source of the oscillations in the integrand associated with the dielectric function through its dependence on the optical matrix elements.

In the primed coordinate system, with basis functions $\{s, x', y', z'\}$, the P interaction depends only on the magnitude k of $\vec{k}$, and the only non-diagonal matrix of Eq. (A15) is

$$\langle s | \frac{\hbar}{m} \vec{k} \cdot \vec{p} | z' \rangle = iPk. \quad (\text{A28})$$

The transformed Hamiltonian is given as:

$$H'_{int} = S^\dagger H_{int} S \quad (\text{A29})$$

where,

$$S = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \theta \cos \phi & -\sin \phi & \sin \theta \cos \phi \\ 0 & \cos \theta \sin \phi & \cos \phi & \sin \theta \sin \phi \\ 0 & -\sin \theta & 0 & \cos \theta \end{pmatrix}. \quad (\text{A30})$$

The coordinates $\{\theta, \phi\}$ are the angular coordinates of the vector $\vec{k}$. With the neglect of all $\vec{k} \cdot \vec{p}$ interactions except those involving P (step 1), the transformation of Eq. (A29) is trivial. The primary reason for writing it down is that it indicates how to obtain the previously neglected higher order $\vec{k} \cdot \vec{p}$ interactions in the primed frame, which will be reintroduced using first-order perturbation theory (step 3). Expressions for these neglected interactions in the primed frame, which influence the results using first-order perturbation theory (i.e. they are neglected to zeroth order but enter at first order), will not be reproduced here since they are somewhat cumbersome and their inclusion is not essential to the discussion.

Spin-orbit interactions

Spin-orbit interactions are taken into account by adding the spin-orbit Hamiltonian:

$$H^{so} = \frac{\hbar}{4m^2c^2} [\nabla \times \vec{p}] \cdot \sigma, \quad (\text{A31})$$

to the Hamiltonian for Bloch electrons (Eq. (A1)). In the $\vec{k} \cdot \vec{p}$ language, Eq. (A31) gives rise to two terms:

$$\begin{aligned} H^{kso} &= H_1^{so} + H_2^{so}, \\ H_1 &\equiv \frac{\hbar}{4m^2c^2} [\nabla V \times \vec{p}] \cdot \sigma, \\ H_2 &\equiv \frac{\hbar}{4m^2c^2} [\nabla V \times \vec{k}] \cdot \sigma, \end{aligned} \quad (\text{A32})$$

which are then added to the $\vec{k} \cdot \vec{p}$ Hamiltonian of Eq. (A1). The dominant spin-orbit contribution in diamond and zinc-blende structures comes from the H_1^{so} term. The term H_2^{so} will be neglected since its maximum value is less than one tenth the spin-orbit splitting (H_1^{so}) in Ga, Ge and As (our interest is in GaAs) calculated using the Hartree wavefunctions of the free atom.¹ The states (at $k = 0$) which diagonalize the H_1^{so} term are listed in Table A3.

TABLE A3. States which diagonalize the spin-orbit Hamiltonian H_1^{so} . The energy E_v refers to the valence band energy in the absence of the spin-orbit interaction.

Eigenstate	Eigenvalue
$\psi_1^{so} = s \uparrow$	E_v
$\psi_2^{so} = s \downarrow$	E_v
$\psi_3^{so} = 3/2, 3/2\rangle = \left(\frac{x' + iy'}{\sqrt{2}}\right) \uparrow$	$E_v + \Delta_{so}$
$\psi_4^{so} = 3/2, 1/2\rangle = -\sqrt{\frac{2}{3}}z' \uparrow + \frac{1}{\sqrt{6}}(x' + iy') \downarrow$	$E_v + \Delta_{so}$
$\psi_5^{so} = 3/2, -1/2\rangle = -\frac{1}{\sqrt{6}}(x' - iy') \uparrow - \sqrt{\frac{2}{3}}z' \downarrow$	$E_v + \Delta_{so}$
$\psi_6^{so} = 3/2, -3/2\rangle = -\frac{1}{\sqrt{2}}(x' - iy') \downarrow$	$E_v + \Delta_{so}$
$\psi_7^{so} = 1/2, 1/2\rangle = \frac{1}{\sqrt{3}}(x' + iy') \downarrow + \frac{1}{\sqrt{3}}z' \uparrow$	$E_v - 2\Delta_{so}/3$
$\psi_8^{so} = 1/2, -1/2\rangle = -\frac{1}{\sqrt{3}}z' \downarrow + \frac{1}{\sqrt{3}}(x' - iy') \uparrow$	$E_v - 2\Delta_{so}/3$

The spin-orbit splitting Δ_{so} is defined as:

$$-3i\langle x_j | (\nabla V \times \vec{p})_{x_k} | x_l \rangle \equiv \epsilon_{jkl} \Delta_{so}, \quad (\text{A33})$$

where $x_j, x_k, x_l \in \{x, y, z\}$ and ϵ_{jkl} is the totally anti-symmetric unit tensor. If we use the above basis functions in the order:

$$\{s \uparrow, s \downarrow, |3/2, 3/2\rangle, |3/2, 1/2\rangle, |3/2, -1/2\rangle, |3/2, -3/2\rangle, |1/2, 1/2\rangle, |1/2, -1/2\rangle\},$$

then the Hamiltonian matrix which includes spin-orbit H_1^{so} interactions plus the lowest-order $\vec{k} \cdot \vec{p}$ interactions (i.e., those proportional to P) is of the form:

$$\begin{pmatrix} E_c & 0 & 0 & -\sqrt{2}\tilde{k} & 0 & 0 & \tilde{k} & 0 \\ 0 & E_c & 0 & 0 & -\sqrt{2}\tilde{k} & 0 & 0 & -\tilde{k} \\ 0 & 0 & E_v + \lambda & 0 & 0 & 0 & 0 & 0 \\ \sqrt{2}\tilde{k} & 0 & 0 & E_v + \lambda & 0 & 0 & 0 & 0 \\ 0 & \sqrt{2}\tilde{k} & 0 & 0 & E_v + \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & E_v + \lambda & 0 & 0 \\ -\tilde{k} & 0 & 0 & 0 & 0 & 0 & E_v - 2\lambda & 0 \\ 0 & \tilde{k} & 0 & 0 & 0 & 0 & 0 & E_v - 2\lambda \end{pmatrix},$$

where for brevity we have defined $\tilde{k} \equiv iPk/\sqrt{3}$ and $\lambda \equiv \Delta_{so}/3$.

By taking appropriate linear combinations of the basis functions of Table A3, the above matrix can be rendered block-diagonal. Let these new basis states be designated $\hat{\psi}_i$ as:

$$\begin{aligned} \hat{\psi}_1 &= is \uparrow, \\ \hat{\psi}_2 &= \frac{-(x' + iy') \downarrow}{\sqrt{2}} = -\frac{(|3/2, 1/2\rangle + \sqrt{2}|1/2, 1/2\rangle)}{\sqrt{3}}, \\ \hat{\psi}_3 &= z' \uparrow = -\frac{(\sqrt{2}|3/2, 1/2\rangle - |1/2, 1/2\rangle)}{\sqrt{3}}, \\ \hat{\psi}_4 &= is \downarrow, \\ \hat{\psi}_5 &= \frac{(x' - iy') \uparrow}{\sqrt{2}} = -\frac{(|3/2, 1/2\rangle - \sqrt{2}|1/2, 1/2\rangle)}{\sqrt{3}}, \\ \hat{\psi}_6 &= z' \downarrow = -\frac{(\sqrt{2}|3/2, 1/2\rangle + |1/2, 1/2\rangle)}{\sqrt{3}}, \\ \hat{\psi}_7 &= \frac{(x' + iy') \uparrow}{\sqrt{2}} = |3/2, 3/2\rangle, \\ \hat{\psi}_8 &= -\frac{(x' - iy') \downarrow}{\sqrt{2}} = |3/2, -3/2\rangle. \end{aligned} \tag{A34}$$

In this basis, the Hamiltonian is block-diagonal with the first six states giving rise to two identical 3×3 blocks, and the last two states (the “heavy mass” states) giving two identical 1×1 blocks. For notational convenience we define

$$E_v' = E_v + \Delta_{so}/3, \quad (\text{A35})$$

for use in what follows. The 3×3 block which needs to be diagonalized is given by:

$$\begin{pmatrix} E_c & 0 & Pk \\ 0 & E_v' - 2\Delta_{so}/3 & \sqrt{2}\Delta_{so}/3 \\ Pk & \sqrt{2}\Delta_{so}/3 & E_v' - \Delta_{so}/3 \end{pmatrix}. \quad (\text{A36})$$

The eigenvalues which obtain are the solutions of the following secular equation:

$$(E' - E_c)(E' - E_v')(E' - E_v' + \Delta_{so}) - P^2 k^2 (E' - E_v' + 2\Delta_{so}/3) = 0. \quad (\text{A37})$$

The three bands which result will be denoted: E_i' for $i = 1, 2, 4$, where the notation $E_1 \equiv$ “split-off”, $E_2 \equiv$ “low-mass”, $E_3 \equiv$ “high-mass”, $E_4 \equiv$ “conduction band”, is used. These solutions, to lowest order in k are given as:

$$E_4'(k) = E_c + \frac{P^2 k^2 (E_c - E_v' + 2\Delta_{so}/3)}{(E_c - E_v')(E_c - E_v' + \Delta_{so})} \quad (\text{A38})$$

$$E_2'(k) = E_v' - \frac{P^2 k^2 (2/3)}{(E_c - E_v')} \quad (\text{A39})$$

$$E_1'(k) = E_v' - \Delta_{so} - \frac{P^2 k^2 (1/3)}{(E_c - E_v' + \Delta_{so})} \quad (\text{A40})$$

The corresponding eigenvectors for $i = 1, 2, 4$ are:

$$\begin{aligned} a_i(k) &= kP(E_i'(k) - E_v' + 2\Delta_{so}/3)/N_1(k), \\ b_i(k) &= (\sqrt{2}\Delta_{so}/3)(E_i'(k) - E_c)/N_1(k), \\ c_i(k) &= (E_i'(k) - E_c)(E_i'(k) - E_v' + 2\Delta_{so}/3)/N_1(k); \end{aligned} \quad (\text{A41})$$

where the normalizing factor $N_1(k)$ is, of course, defined by $N_1^2(k) \equiv a_i^2(k) + b_i^2(k) + c_i^2(k)$. The corresponding states are listed in the following table.

TABLE A4. The eight states which diagonalize Hamiltonian including spin-orbit and lowest-order $\vec{k} \cdot \vec{p}$ interactions. The energies $E_4'(k)$, $E_2'(k)$ and $E_1'(k)$ are given by Eqs. (A38), (A39), and (A40) respectively and $E_3'(k) = E_r'$ is k -independent to this order in perturbation theory. The notation $\psi_i^{(1) \prime}$ for the states is understood as follows: 1) the index i denotes one of the eight states in subspace A, 2) the superscript (1) implies that only lowest order (linear in k) terms in the $\vec{k} \cdot \vec{p}$ have been kept, and 3) the prime indicates that we are in the primed frame.

State	Energy
$\psi_1^{(1) \prime} = a_1(k)(is) \uparrow + b_1(k) \left(\frac{-(x' + iy')l}{\sqrt{2}} \right) + c_1(k)z' \uparrow$	$E_1'(k)$
$\psi_2^{(1) \prime} = a_2(k)(is) \uparrow + b_2(k) \left(\frac{-(x' + iy')l}{\sqrt{2}} \right) + c_2(k)z' \uparrow$	$E_2'(k)$
$\psi_3^{(1) \prime} = a_4(k)(is) \uparrow + b_4(k) \left(\frac{-(x' + iy')l}{\sqrt{2}} \right) + c_4(k)z' \uparrow$	$E_4'(k)$
$\psi_4^{(1) \prime} = a_1(k)(is) \downarrow + b_1(k) \left(\frac{(x' - iy')l}{\sqrt{2}} \right) + c_1(k)z' \downarrow$	$E_1'(k)$
$\psi_5^{(1) \prime} = a_2(k)(is) \downarrow + b_2(k) \left(\frac{(x' - iy')l}{\sqrt{2}} \right) + c_2(k)z' \downarrow$	$E_2'(k)$
$\psi_6^{(1) \prime} = a_4(k)(is) \downarrow + b_4(k) \left(\frac{(x' - iy')l}{\sqrt{2}} \right) + c_4(k)z' \downarrow$	$E_4'(k)$
$\psi_7^{(1) \prime} = \frac{(x' + iy')l}{\sqrt{2}}$	$E_3 = E_r'$
$\psi_8^{(1) \prime} = \frac{-(x' - iy')l}{\sqrt{2}}$	$E_3 = E_r'$

Table A5 lists the expansion coefficients $\{a_i(k), b_i(k), c_i(k)\}$ for $i = 1, 2, 4$, defined by Eq. (A41) and expanded to second-order in k , which correspond to the three eigenvalues $E_1'(k)$, $E_2'(k)$, $E_4'(k)$ of the 3×3 block given of Eq. (A36). Each of these three eigenvalues are doubly degenerate (Kramers degeneracy). We will

see that the eigenvalues $E_i'(k)$ will become spin-orbit split when the previously neglected $\vec{k} \cdot \vec{p}$ terms are reintroduced. The states corresponding to the heavy mass band E_3' (i.e., $\hat{\psi}_7$ and $\hat{\psi}_8$ of Eq. (A34)), were not coupled to each other or any of the other states by the P interaction and are thus k -independent, $E_3'(k) = E_3'$, to lowest order in the $\vec{k} \cdot \vec{p}$ interaction. This is the reason why there are no $a_3(k)$, $b_3(k)$, $c_3(k)$ coefficients in Table A5.

TABLE A5. Expansion coefficients $a_i(k)$, $b_i(k)$ and $c_i(k)$ for the split-off ($i = 1$), low-mass ($i = 2$), and conduction ($i = 4$) states which diagonalize the $\vec{k} \cdot \vec{p}$ Hamiltonian of Eq. (A36) to lowest order in the $\vec{k} \cdot \vec{p}$ interaction. These coefficients are defined by Eq. (A41) and expanded to second order in k . We expand only to second-order in k since we only desire the wave functions and energies to second-order (we are using second-order perturbation theory). The wavefunctions implied by these coefficients are superpositions of the states in the basis of Eq. (A34) taken in the order $\hat{\psi}_1$, $\hat{\psi}_2$ and $\hat{\psi}_3$ for one of the Kramers doublets and $\hat{\psi}_4$, $\hat{\psi}_5$ and $\hat{\psi}_6$ for the other. To this order in perturbation theory (i.e., lowest order) there is no splitting of the doublets. The heavy-mass states ($\hat{\psi}_7$ and $\hat{\psi}_8$ of Eq. (A36)) have the k -independent energy $E'_3(k) = E'_v$ to lowest order in the $\vec{k} \cdot \vec{p}$ interaction.

Expansion coefficient	State
$a_1(k) = \frac{-kP}{\sqrt{3}(E_c - E'_v + \Delta_{so})} \left(1 - \frac{k^2 P^2 (3\Delta_{so} - 4(E_c - E'_v + \Delta_{so}))}{6\Delta_{so}(E_c - E'_v + \Delta_{so})^2} \right)$	split-off
$b_1(k) = -\frac{\sqrt{2}}{\sqrt{3}} \left(1 - \frac{k^2 P^2 (\Delta_{so} + 2(E_c - E'_v + \Delta_{so}))}{6\Delta_{so}(E_c - E'_v + \Delta_{so})^2} \right)$	
$c_1(k) = \frac{1}{\sqrt{3}} \left(1 - \frac{k^2 P^2 (\Delta_{so} - 4(E_c - E'_v + \Delta_{so}))}{6\Delta_{so}(E_c - E'_v + \Delta_{so})^2} \right)$	
$a_2(k) = \frac{2kP}{\sqrt{6}(E_c - E'_v)} \left(1 - \frac{P^2 k^2 (12\Delta_{so} + 4(E_c - E'_v))}{12\Delta_{so}(E_c - E'_v)^2} \right)$	low-mass
$b_2(k) = \frac{1}{\sqrt{3}} \left(-1 + \frac{P^2 k^2 (4\Delta_{so} - 8(E_c - E'_v))}{12(E_c - E'_v)^2 \Delta_{so}} \right)$	
$c_2(k) = \frac{2}{\sqrt{6}} \left(-1 + \frac{P^2 k^2 (4\Delta_{so} + 4(E_c - E'_v))}{12\Delta_{so}(E_c - E'_v)^2} \right)$	
$a_4(k) = 1 - \frac{P^2 k^2 ((E_c - E'_v + 2\Delta_{so}/3)^2 + 2\Delta_{so}^2/9)}{2(E_c - E'_v)^2 (E_c - E'_v + \Delta_{so})^2}$	conduction
$b_4(k) = \frac{(\sqrt{2}\Delta_{so}/3)Pk}{(E_c - E'_v)(E_c - E'_v + \Delta_{so})}$	
$c_4(k) = \frac{(E_c - E'_v + 2\Delta_{so}/3)Pk}{(E_c - E'_v)(E_c - E'_v + \Delta_{so})}$	

First-order perturbation theory

Now that the eigenstates are known, first-order perturbation theory can be applied to include the neglected higher-order $\vec{k} \cdot \vec{p}$ interactions. The simplest case is that of the “heavy-band” states. These states have no interaction with each other or with the first six states that were discussed. Bringing in the previously neglected pieces gives:

$$E_3 = ((H'_{int})_{xx} + (H'_{int})_{yy})/2 \quad (\text{A42})$$

where $(H'_{int})_{xx}$ and $(H'_{int})_{yy}$ are previously neglected contributions to the matrix elements of the $\vec{k} \cdot \vec{p}$ Hamiltonian in the primed frame. Equivalently one could have worked with the unprimed matrix elements of Eq. (A15) after transforming the eigenstates of the lowest order $\vec{k} \cdot \vec{p}$ Hamiltonian back into the unprimed frame using Eq. (A34), Table A5 and Eq. (A30). After some algebra Eq. (A42) yields:

$$E_3 = E'_c + \frac{\hbar^2}{2m_o} k^2 + M k^2 + (L - M - N) \frac{(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)}{k^2} \quad (\text{A43})$$

For the six states which comprise the E_4 , E_2 , and E_1 bands, we have 3 pairs of degenerate states. After the previously neglected $\vec{k} \cdot \vec{p}$ pieces are reintroduced the six states become coupled pairwise – each Kramers doublet will become split. For this reason degenerate perturbation theory must be applied to each of the pairs. Formally we solve for the eigenvalues and eigenvectors of the following 2×2 matrix:

$$\begin{pmatrix} \gamma & \delta \\ \delta^* & \gamma \end{pmatrix}. \quad (\text{A44})$$

The eigenvalues are:

$$\lambda_{\pm} = \gamma \pm \sqrt{\delta \delta^*}, \quad (\text{A45})$$

and the eigenvectors are:

$$\phi^{\pm} = \frac{\sqrt{2}}{2\sqrt{\delta\delta^*}} \left(\pm \sqrt{\delta\delta^*} \right), \quad (\text{A46})$$

where,

$$\begin{aligned} \gamma &\equiv a_j^2(k)(H'_{int})_{ss} + \frac{b_j^2(k)}{2} \left((H'_{int})_{xx} + (H'_{int})_{yy} \right) + c_j^2(k), (H'_{int})_{zz} \\ \delta &\equiv -a_j(k)b_j(k) \frac{\left(i(H'_{int})_{sx} + (H'_{int})_{sy} \right)}{\sqrt{2}}; \quad j = 1, 2, 4. \end{aligned} \quad (\text{A47})$$

Thus for the eigenvalues we have:

$$\begin{aligned} E_j^{\pm} &= E'_j(k) + \frac{\hbar^2}{2m_o} k^2 + a_j^2(k) A' k^2 \\ &\quad + b_j^2(k) \{ M k^2 + (L - M - N)(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^2 \} \\ &\quad + c_j^2(k) \{ L' k^2 - 2(L - M - N)(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^2 \} \\ &\quad \pm \sqrt{2} a_j(k) b_j(k) B \frac{\{ k^2 (k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2) - 9 k_x^2 k_y^2 k_z^2 \}^{1/2}}{k}, \end{aligned} \quad (\text{A48})$$

for $j = 1, 2, 4$. The corresponding states are listed in Table A6.

TABLE A6. The eight states which diagonalize Hamiltonian including spin-orbit interactions and $\vec{k} \cdot \vec{p}$ interactions to second order. The energies $E_3(\vec{k})$, and the set of energies $E_1^\pm(\vec{k})$, $E_2^\pm(k)$ and $E_4^\pm(k)$ are given by Eqs. (A43) and (A48) respectively. The heavy-mass states ($E_3(\vec{k})$) remain degenerate. The notation $\psi_i^{(2) \prime}$ for the states is understood as follows: 1) the index i denotes one of the eight states in subspace A, 2) the superscript (2) implies that interactions to second order (quadratic in k) are included using first-order perturbation theory, and 3) the prime indicates that we are in the primed frame. The states $\psi_i^{(1) \prime}$ are the states which diagonalize the first-order $\vec{k} \cdot \vec{p}$ Hamiltonian and are found in Table A4. The phase factors α and β which appear in the first six states are defined as $\alpha = \delta/\sqrt{2\delta\delta^*}$ and $\beta = 1/\sqrt{2}$ where δ is defined by Eq. (A47).

State	Energy
$\psi_1^{(2) \prime} = \alpha\psi_1^{(1) \prime} - \beta\psi_4^{(1) \prime}$	$E_1^-(\vec{k})$
$\psi_2^{(2) \prime} = \alpha\psi_1^{(1) \prime} + \beta\psi_4^{(1) \prime}$	$E_1^+(\vec{k})$
$\psi_3^{(2) \prime} = \alpha\psi_2^{(1) \prime} - \beta\psi_5^{(1) \prime}$	$E_2^-(\vec{k})$
$\psi_4^{(2) \prime} = \alpha\psi_2^{(1) \prime} + \beta\psi_5^{(1) \prime}$	$E_2^+(\vec{k})$
$\psi_5^{(2) \prime} = \alpha\psi_2^{(1) \prime} - \beta\psi_5^{(1) \prime}$	$E_4^-(\vec{k})$
$\psi_6^{(2) \prime} = \alpha\psi_2^{(1) \prime} + \beta\psi_5^{(1) \prime}$	$E_4^+(\vec{k})$
$\psi_7^{(2) \prime} = \psi_7^{(1) \prime}$	$E_3(\vec{k})$
$\psi_8^{(2) \prime} = \psi_8^{(1) \prime}$	$E_3(\vec{k})$

k -space integrands

Now that the wavefunctions and energies are known, it is a relatively simple matter to construct the k -space integrand associated with the static dielectric function. Momentum matrix elements between valence and conduction states are easily expressed in terms of the constant P . The formulae which result in the *absence* of the spin-orbit interaction are simpler and therefore will be presented first.

Neglecting spin-orbit interaction

The derivation for $\Delta_{so} = 0$ is very similar to the one given above for the case of a non-zero Δ_{so} . The same set of basis functions, Eq. (A34), will be used. The difference in this case is that the states: $\hat{\psi}_2$ and $\hat{\psi}_3$ which used to be coupled through the spin-orbit interaction become decoupled. In other words, let $\Delta_{so} \rightarrow 0$ in the 3×3 block of Eq. (A36) and notice that the state $\hat{\psi}_2$ becomes an eigenstate. There is a similar decoupling of the states: $\hat{\psi}_5$ and $\hat{\psi}_6$ with the result that $\hat{\psi}_5$ becomes an eigenstate. Note that with regard to the solutions of Eq. (A36), the limits $\Delta_{so} \rightarrow 0$ and $k \rightarrow 0$ do not commute. Physically, including the spin-orbit interaction alters the symmetry of the Hamiltonian, and therefore we must take the $\Delta_{so} \rightarrow 0$ limit in Eq. (A36) and proceed from there.

Consider first the states which are connected by the Pk term. These are the states $\hat{\psi}_1$, $\hat{\psi}_3$, $\hat{\psi}_4$, and $\hat{\psi}_6$. The states $\hat{\psi}_1$, and $\hat{\psi}_3$, interact with only each other and give rise to the 2×2 block obtained from Eq. (A36) by striking out the second row and second column. Likewise the states $\hat{\psi}_4$, and $\hat{\psi}_6$, give rise to the same 2×2

block. This block yields the secular equation:

$$(E_c - E'(k))(E'_v - E'(k)) - P^2 k^2 = 0 \quad (\text{A49})$$

The two solutions which obtain are the conduction band and the “split-off” band (i.e., E_4 and E_1). E_1 of course is not “split-off” in this case but rather is simply the $\Delta_{so} \rightarrow 0$ limit of the “split-off” band). Those are:

$$E'_4 = \frac{E_c + E_v}{2} + \left[\left(\frac{E_c - E_v}{2} \right)^2 + k^2 P^2 \right]^{1/2}, \quad (\text{A50})$$

$$E'_1 = \frac{E_c + E_v}{2} - \left[\left(\frac{E_c - E_v}{2} \right)^2 + k^2 P^2 \right]^{1/2}. \quad (\text{A51})$$

the corresponding eigenstates are:

$$\begin{aligned} a_j(k) &= kP/N_2(k), \\ c_j(k) &= (E'(k) - E_c)/N_2(k), \end{aligned} \quad (\text{A52})$$

with $N_2^2(k) = a_j^2(k) + c_j^2(k)$. Expanding to second order in k gives

$$a_1(k) = \frac{kP}{(E_c - E'_v)} \left(1 - \frac{(3/2)k^2 P^2}{(E_c - E'_v)^2} \right) \quad (\text{A53})$$

$$c_1(k) = - \left(1 - \frac{(1/2)k^2 P^2}{(E_c - E'_v)^2} \right) \quad (\text{A54})$$

$$a_4(k) = -c_1(k) \quad (\text{A55})$$

$$c_4(k) = a_1(k) \quad (\text{A56})$$

The higher order $\vec{k} \cdot \vec{p}$ interactions are brought in through first-order perturbation theory in much the same way as before. The analog of Eq. (A44) now has no off-diagonal elements and the energies are given by taking the $b_j(k) \rightarrow 0$ limit of Eq. (A48):

$$\begin{aligned} E_j &= E'_j(k) + \frac{\hbar^2}{2m_o} k^2 + a_j^2(k) A' k^2 \\ &\quad + c_j^2(k) \{ L' k^2 - 2(L - M - N)(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^2 \}, \end{aligned} \quad (\text{A57})$$

for $j = 1, 4$.

Next consider the interactions between $\hat{\psi}_2$, $\hat{\psi}_5$, $\hat{\psi}_7$, and $\hat{\psi}_8$. The states $\hat{\psi}_2$, and $\hat{\psi}_8$, interact with only each other. Likewise states $\hat{\psi}_5$, and $\hat{\psi}_7$, interact with only each other. Taking the states in the order $\{\hat{\psi}_2, \hat{\psi}_8, \hat{\psi}_5, \hat{\psi}_7\}$ gives the following matrix:

$$\begin{pmatrix} \eta & \zeta & 0 & 0 \\ \zeta^* & \eta & 0 & 0 \\ 0 & 0 & \eta & \zeta^* \\ 0 & 0 & \zeta & \eta \end{pmatrix}. \quad (\text{A58})$$

Each 2×2 block can be solved separately. In each case the eigenvalues are:

$$\lambda_{\pm} = \eta \pm \sqrt{\zeta\zeta^*}. \quad (\text{A59})$$

For the upper-left block the eigenstates are:

$$\phi^{\pm} = \frac{\sqrt{2}}{2\sqrt{\zeta\zeta^*}} \left(\pm \sqrt{\zeta\zeta^*} \right), \quad (\text{A60})$$

and for the lower-right block:

$$\phi^{\pm} = \frac{\sqrt{2}}{2\sqrt{\zeta\zeta^*}} \left(\pm \sqrt{\zeta\zeta^*} \right). \quad (\text{A61})$$

Explicit expressions for the energies and eigenstates are obtained with the help of Eqs. (A15) and (A29) as before. The remaining pieces of information are:

$$\begin{aligned} \eta &= \frac{(H'_{int})_{xx} + (H'_{int})_{yy}}{2} \\ &= E_v + \frac{\hbar^2}{2m_o} k^2 + Mk^2 + 2(L - M - N)(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^2, \end{aligned} \quad (\text{A62})$$

and

$$\zeta = \frac{1}{2} \left[(H'_{int})_{xx} - (H'_{int})_{yy} - i \left((H'_{int})_{xy} + (H'_{int})_{yx} \right) \right], \quad (\text{A63})$$

giving

$$\begin{aligned} \sqrt{\zeta\zeta^*} &= \left\{ \frac{\left((H'_{int})_{xx} - (H'_{int})_{yy} \right)^2 + 4 \left((H'_{int})_{xy} \right)^2}{4} \right\}^{1/2} \\ &= \frac{|L - M - N| \left(k_x^4 k_y^4 + k_x^4 k_z^4 + k_y^4 k_z^4 - k^2 k_x^2 k_y^2 k_z^2 \right)^{1/2}}{k^2}. \end{aligned} \quad (\text{A64})$$

Thus the “heavy-mass” and “low-mass” energies are given as:

$$E_3 = \eta + \sqrt{\zeta\zeta^*} \quad (\text{A65})$$

$$E_2 = \eta - \sqrt{\zeta\zeta^*} \quad (\text{A66})$$

The eigenstates (denoted as ψ'_j) are listed in Table A7.

TABLE A7. Eigenstates of the second-order $\vec{k} \cdot \vec{p}$ Hamiltonian in the primed frame (with no spin-orbit). The energies E_1 , E_4 , E_3 and E_2 are given by Eqs. (A57), (A65) and (A66) respectively. The expansion coefficients $a_1(k)$, $c_1(k)$, $a_4(k)$ and $c_4(k)$ in the first four states are given by Eqs. (A53) through (A56), and the coefficients α and β in the last four eigenstates are defined as $\alpha = \zeta/\sqrt{2\zeta\zeta^*}$ and $\beta = 1/\sqrt{2}$ where ζ is given by Eq. (A63).

Eigenstate	Energy
$\psi'_1 = a_1(k)(is \uparrow) + c_1(k)(z' \uparrow)$	E_1
$\psi'_2 = a_1(k)(is \downarrow) + c_1(k)(z' \downarrow)$	E_1
$\psi'_3 = a_4(k)(is \uparrow) + c_4(k)(z' \uparrow)$	E_4
$\psi'_4 = a_4(k)(is \downarrow) + c_4(k)(z' \downarrow)$	E_4
$\psi'_5 = \alpha \left(-\frac{(x'+iy')\downarrow}{\sqrt{2}} \right) - \beta \left(\frac{(x'-iy')\downarrow}{\sqrt{2}} \right)$	E_2
$\psi'_6 = \alpha^* \left(\frac{(x'-iy')\downarrow}{\sqrt{2}} \right) - \beta \left(\frac{(x'+iy')\downarrow}{\sqrt{2}} \right)$	E_2
$\psi'_7 = \alpha \left(-\frac{(x'+iy')\downarrow}{\sqrt{2}} \right) + \beta \left(\frac{(x'-iy')\downarrow}{\sqrt{2}} \right)$	E_3
$\psi'_8 = \alpha^* \left(\frac{(x'-iy')\downarrow}{\sqrt{2}} \right) + \beta \left(\frac{(x'+iy')\downarrow}{\sqrt{2}} \right)$	E_3

The dielectric function without spin-orbit

The following is the band-theoretic expression for the $\{x, x\}$ component of the static long-wave dielectric function in the scissors-operator formalism with no spin-orbit:

$$\epsilon_{xx} - 1 = \int d^3k \sum_m^{val} \sum_n^{cond} \frac{\langle m\vec{k}|p_x|n\vec{k}\rangle \langle n\vec{k}|p_x|m\vec{k}\rangle}{\left(E_m(\vec{k}) - E_n(\vec{k})\right)^2 \left(E_m(\vec{k}) + \Delta - E_n(\vec{k})\right)}. \quad (\text{A67})$$

where Δ is the scissors shift (not to be confused with the spin-orbit splitting Δ_{so} of the previous section). We wish to investigate the behavior of the integrand for small values of k (near the Γ point). We will approximate Equation (A67) by summing only over the eight states of Table A7. Keeping only these states is consistent with Kane's "small-gap" approximation (on which our derivation of the eigenvalues and eigenfunctions has been based), as well as with the observation that our *ab initio* integrands converge very rapidly with the number of conduction bands retained. The integrand of Eq. (A67) becomes:

$$\begin{aligned} \sum_m^{val} \sum_n^{cond} \frac{\langle m\vec{k}|p_x|n\vec{k}\rangle \langle n\vec{k}|p_x|m\vec{k}\rangle}{[E_m(\vec{k}) - E_n(\vec{k})]^2 [E_m(\vec{k}) + \Delta - E_n(\vec{k})]} = \\ \frac{2|\langle \hat{\psi}_3|p_x|\hat{\psi}_1\rangle|^2}{[E_4(\vec{k}) - E_1(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_1(\vec{k})]} + \frac{|\langle \hat{\psi}_3|p_x|\hat{\psi}_6\rangle|^2}{[E_4(\vec{k}) - E_2(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_2(\vec{k})]} \\ + \frac{|\langle \hat{\psi}_4|p_x|\hat{\psi}_5\rangle|^2}{[E_4(\vec{k}) - E_2(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_2(\vec{k})]} + \frac{|\langle \hat{\psi}_3|p_x|\hat{\psi}_8\rangle|^2}{[E_4(\vec{k}) - E_3(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_3(\vec{k})]} \\ + \frac{|\langle \hat{\psi}_4|p_x|\hat{\psi}_7\rangle|^2}{[E_4(\vec{k}) - E_3(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_3(\vec{k})]}. \end{aligned} \quad (\text{A68})$$

The matrix elements are easily evaluated using the coordinate transformation:

$$x' = x \cos \theta \cos \phi + y \cos \theta \sin \phi - z \sin \theta,$$

$$y' = -x \sin \phi + y \cos \phi, \quad (\text{A69})$$

$$z' = x \sin \theta \cos \phi + y \sin \theta \sin \phi + z \cos \theta,$$

and recalling that by symmetry, the only non-vanishing momentum matrix element, P , is given by Eq. (A16). Using these we find:

$$\begin{aligned} \langle s|p_x|x'\rangle &= \frac{imP}{h} \cos \theta \cos \phi, \\ \langle s|p_x|y'\rangle &= -\frac{imP}{h} \sin \phi, \\ \langle s|p_x|z'\rangle &= \frac{imP}{h} \sin \theta \cos \phi. \end{aligned} \quad (\text{A70})$$

All of the matrix elements and their squares, which are needed for the evaluation of Eq. (A68), are presented in Table A8. In Table A8 the squares of the matrix elements have been simplified using the relations $k_x^2/k^2 = \sin \theta \cos \phi$, and $|\alpha|^2 + \beta^2 = 1$.

TABLE A8. Matrix elements (and their squares) needed for the evaluation of Eq. (A68). The squared matrix elements have been simplified using the relations $k_x^2/k^2 = \sin \theta \cos \phi$, and $|\alpha|^2 + \beta^2 = 1$.

$\langle \hat{\psi}_3 p_x \hat{\psi}_1 \rangle = \frac{mP}{h} \sin \theta \cos \phi \left[a_1(k) c_4(k) + a_4(k) c_1(k) \right]$
$ \langle \hat{\psi}_3 p_x \hat{\psi}_1 \rangle ^2 = \left(\frac{mP}{h} \right)^2 \left(\frac{k_x}{k} \right)^2 \left[a_1(k) c_4(k) + a_4(k) c_1(k) \right]^2$
$\langle \hat{\psi}_3 p_x \hat{\psi}_6 \rangle = \frac{a_4(k) m P}{\sqrt{2} h} \left[(\alpha^* - \beta) \cos \theta \cos \phi + i(\alpha^* - \beta) \sin \phi \right]$
$ \langle \hat{\psi}_3 p_x \hat{\psi}_6 \rangle ^2 = \frac{a_4^2(k) m^2 P^2}{2 h^2} \left[(1 - \sin^2 \theta \cos^2 \phi) \right.$
$\quad \left. + 2\beta \text{Re}(\alpha) (\sin^2 \phi - \cos^2 \theta \cos^2 \phi) - 4\beta \text{Im}(\alpha) \cos \theta \sin \phi \cos \phi \right]$
$\langle \hat{\psi}_4 p_x \hat{\psi}_5 \rangle = \frac{-a_4(k) m P}{\sqrt{2} h} \left[(\alpha + \beta) \cos \theta \cos \phi - i(\alpha - \beta) \sin \phi \right]$
$ \langle \hat{\psi}_4 p_x \hat{\psi}_5 \rangle ^2 = \frac{a_4^2(k) m^2 P^2}{2 h^2} \left[(1 - \sin^2 \theta \cos^2 \phi) \right.$
$\quad \left. - 2\beta \text{Re}(\alpha) (\sin^2 \phi - \cos^2 \theta \cos^2 \phi) + 4\beta \text{Im}(\alpha) \cos \theta \sin \phi \cos \phi \right]$
$ \langle \hat{\psi}_3 p_x \hat{\psi}_6 \rangle ^2 + \langle \hat{\psi}_4 p_x \hat{\psi}_5 \rangle ^2 = \frac{a_4^2(k) m^2 P^2}{h^2} \left[(1 - \sin^2 \theta \cos^2 \phi) \right]$
$\quad = \frac{a_4^2(k) m^2 P^2}{h^2} (1 - k_x^2/k^2)$
$ \langle \hat{\psi}_3 p_x \hat{\psi}_8 \rangle ^2 = \langle \hat{\psi}_4 p_x \hat{\psi}_5 \rangle ^2$
$ \langle \hat{\psi}_4 p_x \hat{\psi}_7 \rangle ^2 = \langle \hat{\psi}_3 p_x \hat{\psi}_6 \rangle ^2$

Equation (A68) is now evaluated using Eqs. (A53) through (A56) and the information of Table A8. Using the symbol $I_{xx}(\vec{k})$ to denote the left-hand side of Eq. (A68), we write the integrand for the static long-wave dielectric function (no

spin-orbit) as

$$\begin{aligned}
I_{xx}(\vec{k}) = \frac{m^2 P^2}{h^2} & \left(\frac{2(k_x/k)^2}{[E_4(\vec{k}) - E_1(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_1(\vec{k})]} \left[1 - \frac{4k^2 P^2}{[E_c - E_v]^2} \right] \right. \\
& + \left[1 - (k_x/k)^2 \right] \left[1 - \frac{k^2 P^2}{[E_c - E_v]^2} \right] \left[\frac{1}{[E_4(\vec{k}) - E_2(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_2(\vec{k})]} \right. \\
& \left. \left. + \frac{1}{[E_4(\vec{k}) - E_3(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_3(\vec{k})]} \right] \right), \tag{A71}
\end{aligned}$$

which has the value

$$I_{xx}(0) = \frac{(2m^2 P^2/h^2)}{(E_c - E_v)^2 (E_c + \Delta - E_v)}. \tag{A72}$$

at the Γ -point. Remember that Δ in Eqs. (A71) and (A72) is the scissors-operator shift.

Spherical-harmonic expansion coefficients

It is now possible to write the integrand of Eq. (A71) as an expansion in spherical-harmonics and extract analytic expressions for the expansion coefficients. By going to only second order in k we obtain expressions for $\ell = 0$ through $\ell = 6$, each of which is expressed as a power series in k up to and including terms of order k^2 . To this order, all of the angular variation of the integrand arises from the factors $(k_x/k)^2$ in the numerator (from the matrix elements) and the terms of the form $(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^4$ from the energy denominators. We need not consider the angular dependence arising from the energy term of Eq. (A64), which contributes to the heavy-mass energy, Eq. (A65), and the low-mass energy of, Eq. (A66), because terms involving Eq. (A64) cancel in the expansion of the energy denominators to second order in k .

The quantities $(k_x/k)^2$, $(k_y/k)^2$ and $(k_z/k)^2$ are expressed in spherical-harmonics as

$$\frac{k_x^2}{k^2} = \frac{1}{3} + \frac{1}{2}\sqrt{\frac{4\pi}{5}} \left(\frac{\sqrt{8/3}\text{Re}[Y_{2,2}(\theta, \phi)]}{2} - \frac{\sqrt{4}Y_{2,0}(\theta, \phi)}{3} \right). \quad (\text{A73})$$

$$\frac{k_y^2}{k^2} = \frac{1}{3} - \frac{1}{2}\sqrt{\frac{4\pi}{5}} \left(\frac{\sqrt{8/3}\text{Re}[Y_{2,2}(\theta, \phi)]}{2} + \frac{\sqrt{4}Y_{2,0}(\theta, \phi)}{3} \right), \quad (\text{A74})$$

$$\frac{k_z^2}{k^2} = \frac{1}{3} + \frac{1}{3}\sqrt{\frac{4\pi}{5}} \sqrt{4}Y_{2,0}(\theta, \phi). \quad (\text{A75})$$

The preceding three equations can be used to express the quantity $(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^4$ in terms of spherical-harmonics as

$$(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^4 = \frac{1}{3} - \frac{2\pi}{15}(\text{Re}[Y_{2,2}(\theta, \phi)])^2 - \frac{4\pi}{15}Y_{2,0}^2(\theta, \phi) \quad (\text{A76})$$

The second and third terms of Eq. (A76) can likewise be expanded (with the use of recurrence relations) as

$$\begin{aligned} (\text{Re}[Y_{2,2}(\theta, \phi)])^2 &= \sqrt{\frac{5}{14\pi}}\text{Re}[Y_{4,4}(\theta, \phi)] + \sqrt{\frac{1}{7\pi}}Y_{4,0}(\theta, \phi) \\ &\quad - \frac{2}{7}\sqrt{\frac{5}{\pi}}Y_{2,0}(\theta, \phi) + \sqrt{\frac{1}{\pi}}Y_{0,0}, \end{aligned} \quad (\text{A77})$$

for the second term and

$$Y_{2,0}^2(\theta, \phi) = \frac{3}{7\sqrt{\pi}}Y_{4,0}(\theta, \phi) + \frac{1}{7}\sqrt{\frac{5}{\pi}}Y_{2,0}(\theta, \phi) + \frac{1}{2\sqrt{\pi}}Y_{0,0}, \quad (\text{A78})$$

for the third. The right-hand side of Eq. (A76) now be expressed as

$$(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^4 = -\frac{1}{3}\sqrt{\frac{2\pi}{35}}\text{Re}[Y_{4,4}(\theta, \phi)] - \frac{2\sqrt{\pi}}{15}Y_{4,0}(\theta, \phi) + \frac{2\sqrt{\pi}}{5}Y_{0,0}. \quad (\text{A79})$$

When we expand Eq. (A71) we will also encounter products of the form $(k_x^2/k^2)(k_x^2 k_y^2 + k_x^2 k_z^2 + k_y^2 k_z^2)/k^4$, which are expanded in spherical-harmonics by

multiplying Eqs. (A73) and (A79). In order to write the resulting expression as a spherical-harmonic expansion we must expand the following four products: $\text{Re}[Y_{4,4}(\theta, \phi)]\text{Re}[Y_{2,2}(\theta, \phi)]$, $\text{Re}[Y_{4,4}(\theta, \phi)]Y_{2,0}(\theta, \phi)$, $\text{Re}[Y_{2,2}(\theta, \phi)]Y_{4,0}(\theta, \phi)$ and $Y_{2,0}(\theta, \phi)Y_{4,0}(\theta, \phi)$. These are given as:

$$\begin{aligned} \text{Re}[Y_{4,4}(\theta, \phi)]\text{Re}[Y_{2,2}(\theta, \phi)] &= 3\sqrt{\frac{5}{96\pi}} \left(\sqrt{\frac{120}{143}} \text{Re}[Y_{6,6}(\theta, \phi)] + \frac{2}{11} \sqrt{\frac{2}{39}} \text{Re}[Y_{6,2}(\theta, \phi)] \right. \\ &\quad \left. - \frac{8}{11} \sqrt{\frac{1}{7}} \text{Re}[Y_{4,2}(\theta, \phi)] + \frac{4}{\sqrt{21}} \text{Re}[Y_{2,2}(\theta, \phi)] \right), \quad (\text{A80}) \end{aligned}$$

$$\begin{aligned} \text{Re}[Y_{4,4}(\theta, \phi)]Y_{2,0}(\theta, \phi) &= \frac{1}{4} \sqrt{\frac{5}{\pi}} \left(\frac{3}{\sqrt{11}} \left[\sqrt{\frac{20}{143}} \text{Re}[Y_{6,4}(\theta, \phi)] + \frac{1}{\sqrt{11}} \text{Re}[Y_{4,4}(\theta, \phi)] \right] \right. \\ &\quad \left. - \text{Re}[Y_{4,4}(\theta, \phi)] \right), \quad (\text{A81}) \end{aligned}$$

$$\begin{aligned} \text{Re}[Y_{2,2}(\theta, \phi)]Y_{4,0}(\theta, \phi) &= \sqrt{\frac{15}{31\pi}} \left(\frac{1}{11} \sqrt{\frac{560}{143}} \text{Re}[Y_{6,2}(\theta, \phi)] - \frac{12\sqrt{10}}{77} \text{Re}[Y_{4,2}(\theta, \phi)] \right. \\ &\quad \left. + \frac{2}{7} \sqrt{\frac{2}{15}} \text{Re}[Y_{2,2}(\theta, \phi)] \right), \quad (\text{A82}) \end{aligned}$$

and

$$Y_{2,0}(\theta, \phi)Y_{4,0}(\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{\pi}} \left(\frac{30}{11\sqrt{13}} Y_{6,0}(\theta, \phi) + \frac{40}{77} Y_{4,0}(\theta, \phi) + \frac{12}{7\sqrt{5}} Y_{2,0}(\theta, \phi) \right). \quad (\text{A83})$$

All of the information needed to cast Eq. (A71) in the form of a spherical-harmonic expansion has been set forth. The procedure is to expand the energy denominators to second order in k and decompose each product of angular functions as indicated in the preceding equations of this section. Incidentally, since the energy denominators depend quadratically on k , the indicated expansion of the energy denominators is the lowest order expansion. We assume the following form

$$I_{xx}(\vec{k}) = \sum_{\ell, m} C_{\ell, m}(k) Y_{\ell, m}, \quad (\text{A84})$$

for the spherical-harmonic expansion of ψ in Eq. (A71). By symmetry, all coefficients $C_{\ell,m}$ are real, only even values of $\{\ell, m\}$ are non-zero and coefficients corresponding to negative values of m are identical to those with positive m $C_{\ell,-m} = C_{\ell,m}$. Going to higher order in k (which we will not do) by going to third-order (and higher) in perturbation theory and expanding the energy denominators to higher orders will lead to: 1) terms with higher ℓ in the expansion of Eq. (A84), whose leading k -behavior goes as k^3 (and higher), and 2) contributions of order k^3 (and higher) to the series expansions for the coefficients with $\ell = 0$ to $\ell = 6$. In summary, what we find is that the coefficients to be presented in Table A9 (i.e., with $\ell = 0$ through $\ell = 6$ to second order in k) contain all terms to order k^2 .

TABLE A9. Coefficients of the spherical-harmonic expansion, Eq. (A84), of the small- k integrand associated with the unstrained long-wave static dielectric constant in the scissors-operator formalism neglecting spin-orbit. Each coefficient is given as a series expansion in k up to and including terms of order k^2 . The parameters P , L , L' , M , N , A' , are the $\vec{k} \cdot \vec{p}$ matrix elements given by Eqs. (A16) through (A26). The constants X and Y are given as: $X \equiv 1/[(E_c - E_v')^2(E_c + \Delta - E_v')]$ and $Y \equiv [2/(E_c - E_v') + 1/(E_c + \Delta - E_v')]$.

$$\frac{C_{0,0}(k)}{(m^2/h^2)} = 4\sqrt{\pi}XP^2 \left(1 - \frac{k^2}{3} \left[\frac{4P^2}{(E_c - E_v')^2} + \frac{4P^2}{(E_c - E_v')(E_c + \Delta - E_v')} \right. \right. \\ \left. \left. + Y \left(3A' - 2M - L' - \frac{4(L - N - M)}{5} \right) \right] \right)$$

$$\frac{C_{2,0}(k)}{(m^2/h^2)} = \frac{4\sqrt{\pi}XP^2k^2}{3\sqrt{5}} \left(\frac{5P^2}{(E_c - E_v')^2} + \frac{P^2}{(E_c - E_v')(E_c + \Delta - E_v')} \right. \\ \left. - Y \left(\frac{(L - M - N)}{5} + (L' - M) \right) \right)$$

$$\frac{C_{2,2}(k)}{(m^2/h^2)} = -\frac{2\sqrt{2\pi}XP^2k^2}{\sqrt{3}} \left(\frac{\sqrt{5}P^2}{(E_c - E_v')^2} + \frac{\sqrt{5}P^2}{5(E_c - E_v')(E_c + \Delta - E_v')} \right. \\ \left. - Y \left(\frac{(L - M - N)}{7\sqrt{5}} - (L' - M) \right) \right)$$

$$C_{4,0}(k) = -(m^2/h^2)(128\sqrt{\pi}(L - M - N)XY P^2 k^2)/385$$

$$C_{4,2}(k) = -[385\sqrt{2}/1848\sqrt{5}]C_{4,0}(k)$$

$$C_{4,4}(k) = +[385\sqrt{2}/132\sqrt{35}]C_{4,0}(k)$$

$$C_{6,0}(k) = -[385/1056\sqrt{13}]C_{4,0}(k)$$

$$C_{6,2}(k) = +[385\sqrt{2}/2112\sqrt{1365} + 385\sqrt{7}/1056\sqrt{195}]C_{4,0}(k)$$

$$C_{6,4}(k) = -[385\sqrt{2}/2112\sqrt{91}]C_{4,0}(k)$$

$$C_{6,6}(k) = +[385/64\sqrt{3001}]C_{4,0}(k)$$

This completes the discussion of the unstrained, static dielectric function for small k and in the absence of spin-orbit. The inclusion of spin-orbit will be considered in the next section.

Inclusion of spin-orbit

We wish now to consider the small- k integrand associated with the static dielectric function in the presence of the spin-orbit interaction. Conceptually the procedure to be followed is the same as the one which was used to produce the analytical expressions for the spherical-harmonic expansion coefficients in the absence of the spin-orbit. Matrix elements are computed using the wavefunctions of Table A6 and the energies of Eqs. (A48) and (A43) are used in the denominators of the integrand of Eq. (A67).

To second order in k , the angular dependence will once again arise from either the $(k_x/k)^2$ terms from the matrix elements or the $(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)/k^4$ terms in the energy denominators. The spin-orbit splitting of the conduction, low-mass and split-off bands as well as the corresponding angular dependence (last term of Eq. (A48)) doesn't enter the problem at second-order in k , because the product $a_i(k)b_i(k)$ goes as k for small k (see Table A5) hence the splitting is of order k^3 . This implies that to second order in k , coefficients corresponding to $\ell = 0$ through $\ell = 6$ will result, as was found in the case where spin-orbit was neglected.

The derivation of spherical-harmonic coefficients is hindered by the fact that although the matrix elements have simple angular dependence (depending on k_x^2/k^2) their magnitude is given by a rather complicated radial function of k comprised of

products of the expansion coefficients $a_i(k)$, $b_i(k)$ and $c_i(k)$ of Table A5. For example, the sum of the squared matrix elements associated with transitions between the conduction and split-off levels is given by:

$$\sum_{m=5,6} \sum_{n=1,2} |\langle \psi_m^{(2)'} | p_x | \psi_n^{(2)'} \rangle|^2 = \frac{m^2 P^2}{h^2} \left(2(k_x/k)^2 [a_4(k)c_1(k) + a_1(k)c_4(k)]^2 \right. \\ \left. + (1 - (k_x/k)^2) [a_4(k)b_1(k) - a_1(k)b_4(k)]^2 \right) \quad (\text{A85})$$

While these simple-looking radial functions of k (terms in square brackets above) are easily expressed as power series in k , the coefficients of the k^2 terms are quite cumbersome and their inclusion leads to no new qualitative understanding. For this reason we will forego writing down explicit expressions for the spherical-harmonic coefficients, replace each radial- k function in Eq. (A85) by its $k = 0$ value and focus our attention on the qualitative differences which arise when Eq. (A67) is evaluated with and without spin-orbit.

Upon making the aforementioned replacements, the analog of Eq. (A71) when spin-orbit is included is:

$$I_{xx}(\vec{k}) = \frac{m^2 P^2}{h^2} \left(\frac{2/3}{[E_4(\vec{k}) - E_1(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_1(\vec{k})]} \right. \\ \left. + \left[\frac{(1 + 3(k_x/k)^2)/3}{[E_4(\vec{k}) - E_2(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_2(\vec{k})]} \right. \right. \\ \left. \left. + \frac{(1 - (k_x/k)^2)}{[E_4(\vec{k}) - E_3(\vec{k})]^2 [E_4(\vec{k}) + \Delta - E_3(\vec{k})]} \right] \right), \quad (\text{A86})$$

which has the reassuring feature that it gives the same value at $k = 0$ (see Eq. (A72)) in the limit of vanishing spin-orbit splitting ($\Delta_{so} \rightarrow 0$). The $k = 0$ limit with $\Delta_{so} \neq 0$ is easily obtained from Eq. (A86) by setting $k_x = 0$ and making the replacements:

$$(E_4(\vec{k}) - E_1(\vec{k})) \rightarrow (E_c + (2/3)\Delta_{so} - E_v), \quad (\text{A87})$$

$$(E_4(\vec{k}) - E_2(\vec{k})) \rightarrow (E_c - (1/3)\Delta_{so} - E_v), \quad (\text{A88})$$

$$(E_4(\vec{k}) - E_3(\vec{k})) \rightarrow (E_c - (1/3)\Delta_{so} - E_v). \quad (\text{A89})$$

Thus the analog of Eq. (A72) in the presence of spin-orbit is

$$I_{xx}(0) = \frac{m^2 P^2}{h^2} \left(\frac{2/3}{(E_c + (2/3)\Delta_{so} - E_v)^2 (E_c + (2/3)\Delta_{so} + \Delta - E_v)} + \frac{4/3}{(E_c - (1/3)\Delta_{so} - E_v)^2 (E_c - (1/3)\Delta_{so} + \Delta - E_v)} \right). \quad (\text{A90})$$

For the small- k integrand associated with the unstrained dielectric function, qualitative differences with and without spin-orbit are summarized in Table A10.

By comparing Eqs. (A71) and (A86) we find that there are three qualitative differences that arise when spin-orbit is included concerning: 1) energy denominators, 2) magnitudes of the matrix elements; and 3) their angular dependence. With regard to the energy denominators, the primary difference is that the contribution to Eq. (A86) from the split-off band now has a larger denominator increased by the spin-orbit splitting $(2/3)\Delta_{so}$ and the other two denominators are reduced by $(1/3)\Delta_{so}$ with respect to the valence band of the unstrained crystal. The remaining qualitative difference concerning energy denominators, as was mentioned previously, would only concern us if we were to go to third or higher order in k . Regarding the matrix elements, we see that the inclusion of spin-orbit allows for transitions between the conduction and split-off bands at $k = 0$ which were forbidden in the absence of spin-orbit. The sum of the squared matrix elements associated with these transitions gives $(2m^2 P^2/3h^2)$ at $k = 0$ in the presence of spin-orbit compared to a vanishing sum as $k_x \rightarrow 0$ in its absence. There is also a shift in the relative magnitudes of the matrix elements associated with transitions between the conduction band and the low-mass band as compared to transitions between the conduction and heavy mass band. The sum of the squared matrix elements associated with transitions between the conduction band and the low-mass valence band is reduced

by one third while that for the heavy-mass bands is unchanged upon the inclusion of spin-orbit.

Lastly one notes that upon the inclusion of spin-orbit, the sum of the squared matrix elements associated with split-off transitions goes from having angular dependence of the form $(k_x/k)^2$ (which vanishes for $k_x \rightarrow 0$) to having no angular dependence. Likewise the angular dependence for the low- and heavy-mass bands, which was of the form $(1 - (k_x/k)^2)$ for each band in the absence of spin-orbit, changes to $(1 + 3(k_x/k)^2)$ for the low-mass transitions while remaining $(1 - (k_x/k)^2)$ for the heavy-mass transitions when spin-orbit is included. The qualitative differences just discussed are summarized in Table A10.

Using Eqs. (A72) and (A90), it is possible to estimate the effect of the inclusion of spin-orbit on the integrand associated with the unstrained dielectric function. Recall that the purpose of the scissors shift Δ is to correct for the LDA underestimate of the band gap. Upon the inclusion of spin-orbit, the smallest bandgap decreases by $-(1/3)\Delta_{so}$. For the spin-orbit case we therefore chose a larger scissors shift—larger by the amount $+(1/3)\Delta_{so}$ —so that in both cases, with and without spin-orbit, we have the same smallest bandgap. Our *ab initio* calculations use $\Delta = 0.8$ eV, so to make the estimate for the spin-orbit case we use $\Delta = 0.91$ eV since, for GaAs, $\Delta_{so} = 0.34$ eV. The LDA band gap that was found in our calculations was $E_c - E_v = 0.5$ eV. Using these values in Eqs. (A72) and (A90) shows that upon inclusion of spin-orbit (an maintaining the same smallest bandgap) the magnitude of the integrand at $k = 0$ for the unstrained dielectric function is decreased by 24% over its value with no spin-orbit.

We can make an estimate of the size of the effect on the entire integral, that is, on the dielectric function itself, based on the differences between the “converged” and 60-point results of Fig. 5.1. When we went from the 60-point results to the “converged” results, the static value increased by roughly 1% and the value at $\omega = 1.25$ eV increased by roughly 4%. These corrections due to improved sampling are almost entirely due to the integrand in the Γ -point region and can be used to estimate the $k = 0$ contribution to the entire integral. In particular, we assume that the Γ -point contributes roughly 1% to the static value and 4% to the $\omega = 1.25$ eV value. Thus with the inclusion of spin-orbit we conclude that converged static value would be roughly 0.76% larger than the 60-point value (rather than 1% without spin-orbit) and at $\omega = 1.25$ eV the converged value would be roughly 3.0% (rather than 4.0% without spin-orbit) larger than that obtained using 60-points.

Of course the above estimates are somewhat oversimplified in that they assume that the rest of the integrand (all except the $k = 0$ region) is unchanged when spin-orbit is included. To the extent that this assumption is valid, however, we conclude that the net result of including spin-orbit is that the static value of the dielectric function as well as the dispersion of the unstrained dielectric function would be improved.

TABLE A10. Summary of qualitative differences in the the $\{xx\}$ component of the small- k integrand associated with the static, long-wave, unstrained dielectric function in the scissors operator formalism with (Eq. (A86)) and without (Eq. (A71)) spin-orbit. The magnitude and angular dependence of sum-over-squared-matrix-elements, as well as energy separations are compared. Each sum over squared matrix elements includes four terms corresponding to the four possible transitions between any two levels – the conduction band as well as each the three valence bands are doubly degenerate (Kramers degeneracy). The squared matrix elements are given in units of $m^2 P^2 / \hbar^2$

	$\sum M ^2$	$\sum M ^2$	gap	gap
Transition	with spin-orbit	no spin-orbit	with spin-orbit	no spin-orbit
$E_1 \rightarrow E_4$	2/3	$2(k_x/k)^2$	$E_c + (2/3)\Delta_{so} - E_v$	$E_c - E_v$
$E_2 \rightarrow E_4$	$(1 + 3(k_x/k)^2)/3$	$(1 - (k_x/k)^2)$	$E_c - (1/3)\Delta_{so} - E_v$	$E_c - E_v$
$E_3 \rightarrow E_4$	$(1 - (k_x/k)^2)$	$(1 - (k_x/k)^2)$	$E_c - (1/3)\Delta_{so} - E_v$	$E_c - E_v$

This concludes the discussion of the small- k behavior of the integrand associated with the static, unstrained, long-wave dielectric function in the scissors-operator formalism.

Oscillations in this integrand near $k = 0$ – quantified in terms of spherical-harmonic expansions – which were found in our *ab initio* calculations, have been supported by this analytical treatment in which expressions for the spherical-harmonic expansion coefficients from $\ell = 0$ to $\ell = 6$ have been obtained using $\vec{k} \cdot \vec{p}$ theory. Upon inclusion

of spin-orbit we find the same sources of angular variation in the integrand, that is, the factor $(k_x/k)^2$ from the matrix elements and $(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)/k^4$ from the energy denominators with qualitatively different sources of angular variation appearing only if we go to third and higher order in k . At $k = 0$, with and without spin-orbit, we find qualitatively different contributions coming from the matrix elements and one of the energy denominators (Table A10) but recover the same $k = 0$ value of the integrand as we take the $\Delta_{so} \rightarrow 0$ limit.

We have also estimated that upon including spin-orbit the magnitude of the $k = 0$ integrand decreases in magnitude by roughly 24%. If the $k = 0$ region was the only part of the integrand to be affected by spin-orbit, we would expect roughly a -0.24% correction to the static value of the dielectric function and roughly a -1% correction to the $\omega = 1.25$ eV value. These estimates are made based on the size of the Γ -point contribution to the overall integrand — one percent for the static value and four percent at $\omega = 1.25$ eV — the Γ -contribution is estimated by comparing from the 60-point results to the converged result (see Fig. 5.1).

Spin-orbit has a similar effect on the integrand associated with the photoelastic effect. In appendix B it is shown that the inclusion of spin-orbit reduces the magnitude of the photoelastic integrand at $k = 0$ by 41% which would change the converged result for the static value of $-(p_{11} - p_{12})$ from 0.0382 to 0.049 if the Γ -point were the only part of the integrand to be affected by spin-orbit.

Appendix B: Strain effects

We wish now to consider energy-level shifts and changes in optical matrix elements induced by applied strains. Traditionally, effects due to strain in semiconductors have been incorporated into the context of band theory by writing down a phenomenological strain-Hamiltonian whose empirical parameters – called deformation potentials – are obtained by comparison of theoretical predictions to the results of experiments.^{8–18}

The following Hamiltonian^{8,9,18} is commonly used to describe strain-induced changes in band energies at $k = 0$:

$$\begin{aligned}
 H_\epsilon = & -a(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) - 3b[(L_x^2 - \frac{1}{3}L^2)\epsilon_{xx} + \text{c.p.}] \\
 & - \sqrt{3}d[(L_xL_y + L_yL_x)\epsilon_{xy} + \text{c.p.}]
 \end{aligned} \tag{B1}$$

where ϵ_{ij} denote the components of the strain-tensor, L is the angular-momentum operator, c.p. implies cyclic permutations of the indices x , y , and z and the constants a , b and d are the so-called deformation potentials. The effect of hydrostatic strain is described by the first term while the effects of tetragonal ($\{001\}$) and trigonal ($\{111\}$) strains are described by the second and third terms of Eq. (B1) respectively. In practice, one writes Eq. (B1) in matrix form in the basis of the valence states and the eigenvalues which result represents changes in the *energy gap* between the conduction band and a given valence state.

Once again it must be emphasized that the strain-Hamiltonian of Eq. (B1) is written down purely on the grounds of symmetry arguments based on the fact that we are dealing with a cubic crystal. Formally the linear strain Hamiltonian¹⁴ is written as

$$H_\epsilon = \sum_{ij} \epsilon_{ij} h_{ij}, \quad (\text{B2})$$

where ϵ is the strain tensor and h_{ij} is some hermitian one-electron operator. Equation (B2) is then cast in a form which transforms *irreducibly* under the point-group operations of the crystal

$$H_\epsilon = \sum_{j\alpha} \epsilon_{j\alpha} h_{j\alpha}, \quad (\text{B3})$$

where the indices $\{j\alpha\}$ denote linear combinations which transform as irreducible representations of the point-group (see Table A1). The strain-tensor can be decomposed into the following representations of the cubic group:

$$\epsilon_1 \equiv (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})/\sqrt{3}; \quad \Gamma_1, \quad (\text{B4})$$

$$\epsilon_{3\alpha} \equiv (2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})/\sqrt{6}; \quad \Gamma_{12}, \quad (\text{B5})$$

$$\epsilon_{3\beta} \equiv (\epsilon_{xx} - \epsilon_{yy})/\sqrt{2}; \quad \Gamma_{12}, \quad (\text{B6})$$

$$\epsilon_{5yz} = \epsilon_{5yz}; \quad \Gamma_{25'}, \quad (\text{B7})$$

$$\epsilon_{5xz} = \epsilon_{5xz}; \quad \Gamma_{25'}, \quad (\text{B8})$$

$$\epsilon_{5xy} = \epsilon_{5xy}; \quad \Gamma_{25'}, \quad (\text{B9})$$

where Kane's¹⁴ notation is used on the left hand side of each equation (the α in Eq. (B5) is not to be confused with the α of Eq. (B3)) and the notation of Bouckaert, Smoluchowski and Wigner⁶ (see Table A1) is indicated to the right of the semicolon.

Strain-induced couplings between the various one-electron states arise only when matrix elements of the $h_{j\alpha}$ operator of Eq. (B3) are non-vanishing. The

transformation properties of the one-electron states as well as those for the h_{ja} operator provide sufficient information to work out selection rules for the strain induced couplings. The non-vanishing expectation value of the h_{ja} operator for a given state is the deformation potential (up to a constant). The angular momentum operators appearing in Eq. (B1) were chosen as convenient one-electron operators having the appropriate transformation properties.

We shall now look a bit more deeply into the connection between deformation potentials and matrix elements of one-electron operators. The approach introduced by Pikus and Bir^{9,10,19} is based on the assumption that strain-effects can be treated with perturbation theory and starts from the following first-order $\vec{k} \cdot \vec{p}$ -strain Hamiltonian

$$H\psi = (H_0 + H')\psi = E\psi, \quad (\text{B10})$$

$$H_0 = \frac{p^2}{2m} + V(\vec{r}), \quad (\text{B11})$$

$$H' = \frac{\hbar \vec{k} \cdot \vec{p}}{m} - \frac{\hbar}{m} \sum_{ij} \epsilon_{ij} p_i k_j - \left(\frac{1}{m} \right) \epsilon_{ij} p_i p_j + \epsilon_{ij} V_{ij}, \quad (\text{B12})$$

$$V_{ij} = \frac{\partial}{\partial \epsilon_{ij}} V[(I + \epsilon) \cdot \vec{r}] \Big|_{\epsilon=0}, \quad (\text{B13})$$

where I is the unit tensor and ϵ is the strain tensor. The deformation-potential constants of Eq. (B1) are obtained in terms of matrix elements of the Pikus-Bir $\vec{k} \cdot \vec{p}$ -strain Hamiltonian. In demonstrating this assertion we adopt the notation and follow the argument of Aspnes and Cardona²⁰ defining hydrostatic, tetragonal (along [001]) and trigonal (rhombohedral) strains, respectively, as

$$\epsilon_H = \frac{1}{3} \text{Tr}(\epsilon) = \frac{\sqrt{3}}{3} \epsilon_1 \quad (\text{B14})$$

$$\epsilon_T = \epsilon_{zz} - \frac{1}{3}Tr(\epsilon) = \frac{1}{3}\sqrt{6}\epsilon_{3\alpha} \quad (\text{B15})$$

$$\epsilon_R = \epsilon_{xy} = \epsilon_{5xy} \quad (\text{B16})$$

where ϵ_1 , $\epsilon_{3\alpha}$, and ϵ_{5xy} are the previously defined (Eqs. (B4) through (B9)) irreducible representations into which the strain tensor is decomposed.

Under the influence of hydrostatic strain ϵ_H , with $\vec{k} = k\hat{x}$, the $\vec{k} \cdot \vec{p}$ -strain Hamiltonian of Eq. (B12) becomes

$$H'_H = (\hbar k/m)(1 - \epsilon_H)p_x + H'_{\epsilon_H}, \quad (\text{B17})$$

where

$$H'_{\epsilon_H} = \epsilon_H [-(p^2/m) + (V_{xx} + V_{yy} + V_{zz})]. \quad (\text{B18})$$

The deformation potential a_ν describing the energy shift of the ν th state is defined by

$$3a_\nu\epsilon_H = \langle \Gamma_\nu | H'_{\epsilon_H} | \Gamma_\nu \rangle. \quad (\text{B19})$$

Thus for the conduction and valence bands respectively we have

$$a_1 = \langle \Gamma_1 | H'_{\epsilon_H} | \Gamma_1 \rangle / 3\epsilon_H, \quad (\text{B20})$$

and

$$a_{15} = \langle \Gamma_{15} | H'_{\epsilon_H} | \Gamma_{15} \rangle / 3\epsilon_H, \quad (\text{B21})$$

which implies

$$a = a_1 - a_{15}, \quad (\text{B22})$$

for the value of the Pikus-Bir deformation potential a in the first term of Eq. (B1). Equation (B22) follows from the fact that Eq. (B1) represents energy differences between the conduction and valence bands and the fact that the conduction band

is strain-shifted *only* by a hydrostatic strain — a result which follows from the symmetry of the conduction band wavefunctions.

Equation (B17) also provides us with the information required to determine the strain-induced changes of the optical matrix elements which arise in our theory of the dielectric function. The quantity P was defined in the absence of strain in terms of the matrix element of the $\vec{k} \cdot \vec{p}$ Hamiltonian between the lowest conduction state and one of the highest valence states (see Appendix A) as

$$\langle \Gamma_{15}(x) | \frac{\hbar \vec{k} \cdot \vec{p}}{m} | \Gamma_1(s) \rangle = ik_x P, \quad (\text{B23})$$

with similar definitions for the other two valence states. In order to find the strain-induced changes in P , we take matrix elements of H_H' (Eq. (B17)) — the generalization of the $\vec{k} \cdot \vec{p}$ Hamiltonian in the presence hydrostatic strain — between a conduction and valence state, giving

$$\langle \Gamma_{15}(x) | H_H' | \Gamma_1(s) \rangle = ik_x P(1 - \epsilon_H), \quad (\text{B24})$$

as the strain-analog of Eq. (B23). Equation (B24) implies that under hydrostatic stress, the matrix element P changes according to

$$P^{\epsilon_H} = P(1 - \epsilon_H). \quad (\text{B25})$$

That Eq. (B25) gives the correct strain-induced changes for the *optical* matrix element P is perhaps not immediately obvious since we have only been dealing with the strain- $\vec{k} \cdot \vec{p}$ Hamiltonian and have not considered the optical perturbation $-\epsilon/c\vec{A} \cdot \vec{p}$. Since the optical perturbation enters the theory in the minimal coupling scheme²¹ $\vec{p} \rightarrow \vec{p} - (e/c)\vec{A}$, the vector potential formally plays the same role as the vector $\vec{k}$. If we thus replaced every k_i in Eq. (B12) by $-(e/c)A_i$ we would obtain

the perturbed Hamiltonian for states at $k = 0$ in the presence of both the strain and the optical perturbation, matrix elements of which – the optical matrix elements – would be strain-shifted as given by Eq. (B25).

For the tetragonal ([001]) and trigonal strains, the following relationships

$$b = \frac{1}{3}b_{15}, \quad (\text{B26})$$

and

$$d = d_{15}/2\sqrt{3}, \quad (\text{B27})$$

between the Pikus-Bir deformation potentials b and d , of Eq. (B1) and the matrix elements

$$b_{15} \equiv \langle \Gamma_{15} | H'_{cT} | \Gamma_{15} \rangle / \epsilon_T, \quad (\text{B28})$$

and

$$d_{15} \equiv \langle \Gamma_{15} | H'_{cR} | \Gamma_{15} \rangle / \epsilon_R, \quad (\text{B29})$$

hold. In the above two equations, H'_{cT} and H'_{cR} are the analogs of H'_{cH} (Eq. (B18)) for the cases of tetragonal and trigonal strains, respectively. The operators H'_{cT} and H'_{cR} are easily worked out using Eqs. (B10) – (B16) and are listed in Ref. 20.

In order to find changes in the optical matrix elements induced by tetragonal and trigonal strains we follow a procedure analogous to the one which lead to Eq. (B25). With these strains, however, there will be a preferred direction defined by the strain and, as a result, strain-induced changes in the optical matrix elements will depend on the relative orientation of the strain axis and the direction of polarization of the light field. For tetragonal strain we find

$$P_{\parallel}^{\epsilon_T} = (1 - \epsilon_T)P, \quad (\text{B30})$$

and

$$P_{\perp}^{\epsilon T} = (1 + (1/2)\epsilon_T)P, \quad (\text{B31})$$

where we distinguish between stress parallel ($\parallel$) and perpendicular ($\perp$) to the polarization direction. Similarly for trigonal ($[111]$) strain we obtain

$$P_{\parallel}^{\epsilon R} = (1 - 2\epsilon_R)P, \quad (\text{B32})$$

and

$$P_{\perp}^{\epsilon R} = (1 + \epsilon_R)P, \quad (\text{B33})$$

Strained $k = 0$ integrand (no spin-orbit)

In the absence of spin-orbit, the basis states at $k = 0$ which diagonalize the strain Hamiltonian (Eq. (B1)) for a strain along $[001]$ are given by

$$\begin{aligned} |v_1\rangle &= z \\ |v_2\rangle &= \frac{(x + iy)}{\sqrt{2}} \\ |v_3\rangle &= \frac{-(x - iy)}{\sqrt{2}}, \end{aligned} \quad (\text{B34})$$

and the corresponding eigenvalues

$$\begin{aligned} \Delta(E_c - E_1)_{001} &= -3b\epsilon_T, \\ \Delta(E_c - E_2)_{001} &= +(3/2)b\epsilon_T, \\ \Delta(E_c - E_3)_{001} &= +(3/2)b\epsilon_T, \end{aligned} \quad (\text{B35})$$

represent the strain-induced changes in the band gaps.

For the case of a strain along $[111]$ the basis states have the same form as those of Eq. (B34) upon replacement of the variables $\{x, y, z\}$ by the variables $\{\bar{x}, \bar{y}, \bar{z}\}$ where the new coordinate system is defined in such a way so that the $\bar{z}$ axis lies along the $[111]$ axis as

$$\begin{aligned} \bar{x} &= \frac{1}{\sqrt{2}}(x - y), \\ \bar{y} &= \frac{1}{\sqrt{6}}(x + y - 2z), \\ \bar{z} &= \frac{1}{\sqrt{3}}(x + y + z). \end{aligned} \quad (B36)$$

The energy changes which accompany a strain along $[111]$ are given as

$$\begin{aligned} \Delta(E_c - E_1)_{111} &= -2d\sqrt{3}\epsilon_R, \\ \Delta(E_c - E_2)_{111} &= +\sqrt{3}d\epsilon_R, \\ \Delta(E_c - E_3)_{111} &= +\sqrt{3}d\epsilon_R, \end{aligned} \quad (B37)$$

for a hydrostatic strain ϵ_H the energy change is

$$\Delta(E_c - E_v) = +3a\epsilon_H$$

for each of the three valence bands.

We now have enough information to write down expressions for the strain-induced changes in the $(k = 0)$ integrands $I_{xx}(0)$ and $I_{zz}(0)$ associated with the components of the dielectric function perpendicular and parallel to an applied $[001]$ strain, respectively, in the absence of spin-orbit. For the case of hydrostatic strain, each component $I_{xx}(0)$ and $I_{zz}(0)$ changes in the same way. For the $[111]$ strain, we work in the “barred” system (see Eqs. (B36)) – the system in which the dielectric tensor is diagonal – and consider changes in the components $I_{\bar{x}\bar{x}}(0)$ and $I_{\bar{z}\bar{z}}(0)$

which correspond to light polarized perpendicular and parallel to the [111] strain-axis respectively. In the following we will use the symbol $I(0)$ — with no subscript — to denote one of the components of the unstrained long-wave dielectric function. There is no confusion as to which component $I(0)$ refers since they are all equal in the unstrained dielectric function.

For hydrostatic strain we find

$$\frac{\delta I(0)}{\epsilon_H} = I(0)[-2 - 3aY], \quad (\text{B38})$$

where the first term is due to matrix element changes and the second is due to changes in the band gaps. The quantity Y appearing in Eq. (B38) results from expanding the energy denominators and is defined in Table A9 and a is the Pikus-Bir deformation potential parameter.

For tetragonal strain along [001] (the z direction) we find

$$\frac{\delta I_{xx}(0)}{\epsilon_T} = I(0)(1 - (3b/2)Y), \quad (\text{B39})$$

$$\frac{\delta I_{zz}(0)}{\epsilon_T} = -2 \frac{\delta I_{xx}(0)}{\epsilon_T}. \quad (\text{B40})$$

Lastly we have

$$\frac{\delta I_{xx}(0)}{\epsilon_R} = I(0)(2 - d\sqrt{3}Y). \quad (\text{B41})$$

$$\frac{\delta I_{zz}(0)}{\epsilon_R} = -2 \frac{\delta I_{xx}(0)}{\epsilon_R}. \quad (\text{B42})$$

for the trigonal [111] strain.

Let us consider the case of tetragonal strain and compare the preceding formulae with results of our *ab initio* calculations. To estimate the validity of Eqs. (B39) and (B40) for the splitting of the $k = 0$ integrand we estimate the deformation

potential parameter by comparing Eqs. (B39) and (B40) to *ab initio* results. At $k = 0$, our *ab initio* integrand has the following values

$$\varepsilon_{xx}(0) = 3414.3, \quad (\text{B43})$$

$$\varepsilon_{zz}(0) = 3449.1, \quad (\text{B44})$$

in the presence of a volume-conserving strain of magnitude $\delta z/z = -0.0004$ where z represents any length along the $[001]$ direction. Comparison of Eqs. (B43) and (B44) with Eqs. (B39) and (B40), respectively, yields for the deformation potential the value

$$b_\varepsilon = -1.07 \text{ eV}. \quad (\text{B45})$$

Our *ab initio* value of b as obtained by examining the strain-dependence of the band-gaps (see Fig. 3.1) and is given by

$$b_{gap} = -1.69 \text{ eV}. \quad (\text{B46})$$

Both of these values have the correct sign and are of the same order of magnitude as that which is calculated in Ref. 20 ($b = -2.38 \text{ eV}$) and measured in Ref. 22 ($b = -2.86 \text{ eV}$). The discrepancy between Eqs. (B45) and (B46), however, suggests that the contributions due to the matrix elements are not correctly given by the first terms in Eqs. (B39) and (B40).

Let us take a closer look at the strain-induced changes in the matrix elements given by Eqs. (B30) and (B31). These forms were obtained using symmetry arguments which placed no constraint on the coefficient of the term proportional to the strain. We are thus free to assume that there is some “deformation-potential”, $\tilde{b}$, associated with the matrix element changes. In other words we generalize Eqs.

(B30) and (B31) to be of the form

$$P_{\parallel}^{cT} = (1 - \hat{b}c_T)P, \quad (\text{B47})$$

and

$$P_{\perp}^{cT} = (1 + (1/2)\hat{b}c_T)P, \quad (\text{B48})$$

which imply that Eq. (B39) must be modified to read

$$\frac{\delta I_{xx}(0)}{c_T} = I(0)(\hat{b} - (3b/2)Y), \quad (\text{B49})$$

while Eq. (B40) still holds since its form is determined by group theory. The parameter $\hat{b}$ is obtained by using the *ab initio* data of Eqs. (B43) and (B44) in Eqs. (B49) and (B40), respectively, while fixing $b = b_{gap} = -1.69$ eV (that which is obtained directly from the *ab initio* strain-induced band splittings). The “deformation-potential” associated with the matrix elements is thus found to be

$$\hat{b} = -3.4. \quad (\text{B50})$$

We can estimate the relative magnitude of the contributions due to the energy level shifts as compared to those due to matrix element splittings as follows:

$$|b| = 1.69 \text{ eV}, \quad (\text{B51})$$

$$Y = 4.67(\text{ eV})^{-1}, \quad (\text{B52})$$

$$3bY/2 = -11.8, \quad (\text{B53})$$

where $b = b_{gap}$ (Eq. (B46)) and Y (see Table A9) is evaluated using the LDA bandgap $E_c - E_v = 0.5$ eV and the scissors shift $\Delta = 0.8$ eV. Equation (B53) represents the changes due to the energy-level shifts and is to be compared with Eq. (B50) which gives the changes due to the matrix elements.

We find that changes due to energy-level shifts are of the same sign as those due to the matrix elements but are larger by roughly a factor of 3.5.

Strained $k = 0$ integrand including spin-orbit

In order to include spin-orbit we assume that the spin-orbit splitting is much larger than the strain splitting and work in the basis which diagonalizes the spin-orbit Hamiltonian and treat the strain as a perturbation.¹⁵ These states are

$$\begin{aligned} |v_{3,0}\rangle &= |3/2, 3/2\rangle_{001} = |(1/\sqrt{2})(x + iy) \uparrow \rangle_{001}, \\ |v_{2,0}\rangle &= |3/2, 1/2\rangle_{001} = |(1/\sqrt{6})[2z \uparrow - (x + iy) \downarrow]\rangle_{001}, \\ |v_{1,0}\rangle &= |1/2, 1/2\rangle_{001} = |(1/\sqrt{3})[z \uparrow - (x + iy) \downarrow]\rangle_{001}, \end{aligned} \quad (\text{B54})$$

where we need consider only three states since the three valence bands are each doubly degenerate at $k = 0$ — the strain doesn't lift the degeneracy.

For a uniaxial strain along $[001]$ — that is a strain containing both tetragonal ϵ_T and hydrostatic ϵ_H components — the strain-plus-spin-orbit Hamiltonian takes the following matrix form

$$\begin{pmatrix} \Delta_{so}/3 - \delta E_H - \delta E_{001}/2 & 0 & 0 \\ 0 & \Delta_{so}/3 - \delta E_H + \delta E_{001}/2 & \delta E_{001}/\sqrt{2} \\ 0 & \delta E_{001}/\sqrt{2} & -2\Delta_{so}/3 - \delta E_H \end{pmatrix}, \quad (\text{B55})$$

where $\delta E_{001} = 3b\epsilon_T$, $\delta E_H = 3a\epsilon_H$ and we have adopted the convention that the zero of energy is the unstrained valence band energy in the absence of spin-orbit.

The eigenvalues are given by

$$\begin{aligned}\Delta(E_c - E_3) &= -\Delta_{so}/3 + \delta E_H + \delta E_{001}/2, \\ \Delta(E_c - E_2) &= \Delta_{so}/6 + \delta E_H - \delta E_{001}/4 \\ &\quad - (1/2)[\Delta_{so}^2 + \Delta_{so}\delta E_{001} + (9/4)(\delta E_{001})^2]^{1/2},\end{aligned}\tag{B56}$$

$$\begin{aligned}\Delta(E_c - E_1) &= \Delta_{so}/6 + \delta E_H - \delta E_{001}/4 \\ &\quad + (1/2)[\Delta_{so}^2 + \Delta_{so}\delta E_{001} + (9/4)(\delta E_{001})^2]^{1/2},\end{aligned}\tag{B57}$$

which when expanded to first order in $\delta E_{001}/\Delta_{so}$, become

$$\Delta(E_c - E_3) = -\Delta_{so}/3 + \delta E_H + \delta E_{001}/2,\tag{B58}$$

$$\Delta(E_c - E_2) = -\Delta_{so}/3 + \delta E_H - \delta E_{001}/2,\tag{B59}$$

$$\Delta(E_c - E_1) = +2\Delta_{so}/3 + \delta E_H.\tag{B60}$$

The eigenstates to first order in $\alpha_0 \equiv \delta E_{001}/\Delta_{so}$ are given by

$$\begin{aligned}|v_{3,c}\rangle_{001} &= |3/2, 3/2\rangle, \\ |v_{2,c}\rangle_{001} &= |3/2, 1/2\rangle + (\alpha_0/\sqrt{2})|1/2, 1/2\rangle, \\ |v_{1,c}\rangle_{001} &= |1/2, 1/2\rangle - (\alpha_0/\sqrt{2})|3/2, 1/2\rangle.\end{aligned}\tag{B61}$$

The strain-induced mixing of the unstrained spin-orbit states leads to an additional splitting of the matrix elements which is proportional to α_0 . We will see that this mixing leads to a larger splitting of the matrix elements than was found in the absence of spin-orbit. The following table contrasts the “spin-orbit” vs. “no-spin-orbit” situations regarding strain-induced changes in the matrix elements.

TABLE B1. Strain-induced changes in squared optical matrix elements for tetragonal strain (ϵ_T) parallel and perpendicular to the direction of electric-field polarization contrasted with and without spin-orbit. The squared matrix elements are given in units of $m^2/\hbar^2$. Each squared matrix element listed represents the sum over both states in the doublet and as such is simply twice the value for each state in the doublet. The change due to strain-induced mixing is proportional to $3b\epsilon_T/\Delta_{so}$.

Transition	$2 M ^2$ with spin-orbit	$2 M ^2$ no spin-orbit
$(\perp) E_1 \rightarrow E_4$	$(2/3)P^2(1 + \tilde{b}\epsilon_T + 3b\epsilon_T/\Delta_{so})$	0
$(\perp) E_2 \rightarrow E_4$	$(1/3)P^2(1 + \tilde{b}\epsilon_T - 6b\epsilon_T/\Delta_{so})$	$P^2(1 + \tilde{b}\epsilon_T)$
$(\perp) E_3 \rightarrow E_4$	$P^2(1 + \tilde{b}\epsilon_T)$	$P^2(1 + \tilde{b}\epsilon_T)$
$(\parallel) E_1 \rightarrow E_4$	$(2/3)P^2(1 - 2\tilde{b}\epsilon_T - 6b\epsilon_T/\Delta_{so})$	$2P^2(1 - 2\tilde{b}\epsilon_T)$
$(\parallel) E_2 \rightarrow E_4$	$(4/3)P^2(1 - 2\tilde{b}\epsilon_T + 3b\epsilon_T/\Delta_{so})$	0
$(\parallel) E_3 \rightarrow E_4$	0	0

We see from Table B1 that in the absence of spin-orbit all of the matrix elements for a given direction of polarization are shifted in the same way. Likewise the energy denominators for each polarization are also shifted in the same way. This is what allowed us to write down simple expressions for the strain-induced changes for the integrands of interest (see Eqs. (B38) through (B42)). The situation is somewhat more complicated when spin-orbit is included because, as we see from Table B1., for a given polarization direction (parallel or perpendicular to the strain), several terms appear which shift in different ways with the strain. In other words, we

cannot combine terms to obtain an expression of the form

$$\delta I_{xx} = I(0) \times (\text{function proportional to strain}).$$

The notation is only slightly more complicated by the fact the factor $I(0)$ of Eqs. (B38) – (B42) and (B49) must be generalized to $I_1^\perp(0)$ and $I_2^\perp(0)$ which are defined as

$$I_1^\perp(0) \equiv \frac{m^2 P^2}{h^2} \left(\frac{2/3}{(E_c + (2/3)\Delta_{so} - E_v)^2 (E_c + (2/3)\Delta_{so} + \Delta - E_v)} \right), \quad (\text{B62})$$

and

$$I_2^\perp(0) \equiv \frac{m^2 P^2}{h^2} \left(\frac{1/3}{(E_c - (1/3)\Delta_{so} - E_v)^2 (E_c - (1/3)\Delta_{so} + \Delta - E_v)} \right). \quad (\text{B63})$$

The meaning of the notation of Eqs. (B62) and (B63) is as follows. The subscripts 1 and 2 refer to the transitions $E_1 \rightarrow E_4$ and $E_2 \rightarrow E_4$, respectively, and superscript ($\perp$) implies that the light field is polarized in a direction perpendicular to that of the strain direction. There are three transitions: $E_1 \rightarrow E_4$, $E_2 \rightarrow E_4$, and $E_3 \rightarrow E_4$, and two independent strain directions: ($\perp$) and ($\parallel$), implying six factors $I_1^\perp(0)$, $I_2^\perp(0)$, $I_3^\perp(0)$, $I_1^\parallel(0)$, $I_2^\parallel(0)$ and $I_3^\parallel(0)$. Out of these six, however, only two are independent and are given by Eqs. (B62) and (B63). The rest of the factors are related to these two by the following relations:

$$I_3^\perp(0) = 3I_2^\perp(0) \quad (\text{B64})$$

$$I_1^\parallel(0) = I_1^\perp(0) \quad (\text{B65})$$

$$I_2^\parallel(0) = 4I_2^\perp(0) \quad (\text{B66})$$

$$I_3^\parallel(0) = 0 \quad (\text{B67}).$$

We now have enough information to write expressions for the strain-induced changes in the $k = 0$ integrand associated with the dielectric function in the presence

of the spin-orbit interaction. Let us once again assume the z direction to be the strain direction and the x direction as that perpendicular to the strain, and let the changes in the $k = 0$ integrand be denoted as $\delta I_{zz}(0)$ and $\delta I_{xx}(0)$ respectively. Explicitly we write:

$$\begin{aligned} I_{xx}(0) = & I_1^\perp(0)(1 + \dot{b}\epsilon_T + 3b\epsilon_T/\Delta_{so}) \\ & + I_2^\perp(0)(1 + \dot{b}\epsilon_T - 6b\epsilon_T/\Delta_{so})(1 + 3bY\epsilon_T/2) \\ & + 3I_2^\perp(0)(1 + \dot{b}\epsilon_T)(1 - 3bY\epsilon_T/2), \end{aligned} \quad (\text{B68})$$

$$\begin{aligned} I_{zz}(0) = & I_1^\perp(0)(1 - 2\dot{b}\epsilon_T - 6b\epsilon_T/\Delta_{so}) \\ & + 4I_2^\perp(0)(1 - 2\dot{b}\epsilon_T + 3b\epsilon_T/\Delta_{so})(1 + 3bY\epsilon_T/2), \end{aligned} \quad (\text{B69})$$

which, using Eqs. (B62)–(B67), can be seen to satisfy

$$\frac{\delta I_{xx}(0)}{\epsilon_T} = -2 \frac{\delta I_{zz}(0)}{\epsilon_T}, \quad (\text{B70})$$

as required by symmetry.

In Eqs. (B68) and (B69) the first factor in parenthesis is due to the matrix-element changes and the second is due to energy-band shifts. For $\delta I_{xx}(0)$ there is no energy-band contribution coming from the $E_1 \rightarrow E_4$ transition (i.e., no second factor in parenthesis), and for $\delta I_{zz}(0)$ there is no contribution whatsoever coming from the $E_3 \rightarrow E_4$ transition.

The matrix-element shifts due to strain-induced mixing of the states (which were absent with no spin-orbit) involve the factor $3b/\Delta_{so} = -14.9$, which is roughly a factor of 4.4 larger in magnitude than $\dot{b} = -3.4$. Thus the inclusion of spin-orbit gives rise to an additional source of matrix-element splitting which is substantially larger in magnitude but not always of the same sign as the source of splitting which

arises without spin-orbit (i.e., $\tilde{b}$). For example, the splitting due to strain-induced mixing is of the same sign as that due to $\tilde{b}$ in the first term of Eq. (B68) but is of the opposite sign in the second term. In this second term we also see competition between the splitting due to strain-induced mixing and that which arises due to energy-band changes (i.e., $-6b/\Delta_{so}$ is positive and $3bY/2$ is negative). In the second term of Eq. (B69), however, the situation is reversed and the splitting due to strain-induced mixing enhances that which is due to changes in the energy bands.

We are now in a position to estimate the effect on the $k = 0$ integrand associated with the photoelastic tensor due to the inclusion of spin orbit by keeping only linear-in-strain terms in Eqs. (B68) and (B69). All of the parameters in Eqs. (B68) and (B69) have been fixed previously by comparing with *ab initio* results (no spin-orbit). The parameter Y is slightly different, however, since we use a different value for the scissors operator when we include spin-orbit. As was done in appendix A, in the case of the $k = 0$ integrand associated static dielectric constant, we choose the scissors Δ to be that which is given by *GW* calculations ($\Delta = 0.8$ eV, see sections 2.11 and 2.12 for references) for the case with no spin-orbit. To make the estimates for the case when spin-orbit is included, we adjust the value of Δ as $\Delta \rightarrow \Delta + (1/3)\Delta_{so}$ so as to have the same smallest band gap with and without spin-orbit.

The result we find is that, upon inclusion of spin-orbit, the strength of the $k = 0$ photoelastic integrand is reduced by 41%, which is to be contrasted with the result for the unstrained dielectric function whose $k = 0$ integrand was reduced in strength by 24% upon inclusion of spin-orbit. This result for the photoelastic integrand suggests that the inclusion of spin orbit will improve agreement with experiment.

We make the simplified assumption that only the $k = 0$ integrand is affected by spin-orbit, and take the $k = 0$ contribution to be that change which was observed upon going from the 60-point to the converged result, that is, -0.018 for $\omega = 0$ and -0.2 for $\omega = 1.25$. The inclusion of spin-orbit reduces the magnitude of the $k = 0$ effect by 41% which implies that on going from 60-points to the converged result we obtain a -0.0074 correction at $\omega = 0$ (as opposed to -0.018 without spin-orbit) and a -0.0824 correction at $\omega = 1.25$ eV (as opposed to -0.2 without spin-orbit). We expect, of course, that spin-orbit should make a significant correction to the integrand throughout the zone. This simplified estimate, however, suggests that the agreement with experiment will be improved with the inclusion of spin-orbit as one would hope.

This completes the treatment of the strain-induced effects. We have derived simple expressions (Eqs. (B38)–(B42), (B49), (B68) and (B69)) for the $k = 0$ strain-dependent integrand with and without spin-orbit. We find the simple behavior that under uniaxial strain ($[001]$ or $[111]$), the component corresponding to polarization parallel to the strain axis (δI_{zz}) changes by an amount which is a factor of -2 times the change induced in the components corresponding to polarization perpendicular to the strain-axis (δI_{xx}) (see Eq. (B40). Secondly, in the absence of spin-orbit splitting, changes in the energy bands make contributions which are roughly a factor of 3.5 larger in magnitude than those due to the matrix elements. For the spin-orbit case, on the other hand, an additional source of matrix-element splitting due to strain-induced mixing of the zero-strain states arises and is found to be larger in magnitude by roughly a factor of 4.4 as compared with the matrix-element splitting in the absence of spin-orbit.

The effect which spin-orbit has on the $k = 0$ integrand associated with the photoelastic tensor also has been estimated. The result is that the magnitude of the $k = 0$ integrand is expected to be reduced by 41% as compared with the corresponding value in the absence of spin-orbit.

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