

“Absolute” Deformation Potentials: Formulation and *ab Initio* Calculations for Semiconductors

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The subjects of this paper are the proper inclusion of long-range electrostatic terms in the theory of electronic deformation potentials, a way to include these terms by using supercells in *ab initio* density-functional methods, and calculations for selected semiconductors. We describe the connection with the heterojunction problem, and compare our values with previous model theories and with experiment.

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In 1950, Bardeen and Shockley introduced the concept of a deformation potential to describe the interaction between electrons and acoustic phonons.¹ The strains in the lattice associated with acoustic waves induce shifts in the conduction and valence bands, which affect carrier mobilities and were described in terms of scattering by a deformation potential. By making the explicit assumption that the potential in a region of the crystal is uniquely related to the strain in the same region, they showed that the deformation potentials are straightforward derivatives of the energies with respect to the strains. This formulation has been used widely both in analysis of experiment and in theoretical calculations of the values for deformation potentials.^{2,3}

The subject of the present work is the role of long-range Coulomb fields, which can qualitatively modify the interactions of electrons with acoustic phonons. One well-known example occurs in piezoelectric crystals, where macroscopic electric fields must be treated explicitly.⁴ A signature of the long-range nature of the interaction is that it leads to scattering which is nonanalytic in the wave vector \mathbf{q} of the phonons in the long-wavelength ($|\mathbf{q}| \rightarrow 0$) limit. It is less well known that there are long-range electrostatic contributions to the interactions even in nonpiezoelectric crystals. This has been pointed out by Tolpygo⁵ and by Lawaetz;⁶ however, to our knowledge these effects have never before been calculated in any solid.

It is important to distinguish between terms which refer to *relative* energies of different electronic states, and those that correspond to the “absolute” energy relative to some reference. Because of long-range electrostatic interactions, the energies of the electrons in any given macroscopic region of the crystal depend not only upon the strain in the given region, but also upon other terms which arise from macroscopic electric fields. In the long-wavelength limit the bands are shifted rigidly by the field; thus the macroscopic electric fields affect the absolute energies, but not the relative energies of the electronic bands. The present considerations therefore have no effect upon the definitions of, or calculational procedures for, deformation potentials which describe

relative energies. These include deformation potentials for band gaps, splitting of states under uniaxial strains, etc.^{3,7}

The present work deals with aspects which are crucial for proper consideration of effects which have been attributed to the “absolute” deformation potential. For these terms there are many disagreements and uncertainties in the literature. For example, reported experimental values for the conduction-band deformation potentials in InSb range from 4 to 30 eV.⁸ Previous theoretical work has also shown large variations,⁹⁻¹¹ some of them due to implicit assumptions on the form of the long-range terms. The problem is that the absolute energy in a crystal is ill defined.¹² Because of the long-range Coulomb interactions the energy of any charged particle involves the electrostatic potential which in turn depends on the charge density everywhere, not just in the local region. Thus the absolute energies of electronic states for different strain conditions cannot be directly compared with one another, and it is in principle impossible to define an absolute deformation potential. Nevertheless, for important cases with experimental consequences, one can determine the relevant changes in electronic energies because one can find the electrostatic potential including all nonlocal long-range effects. We shall derive the form for electron-acoustic phonon interactions in the present paper.

Tolpygo⁵ and Lawaetz⁶ showed that the long-range Coulomb terms can be properly described in terms of quadrupole and octupole moments which are generated when an atom is displaced in a crystal. In a crystal with an inhomogeneous strain caused, for example, by an acoustic phonon, the multipole fields can be summed and lead to an inhomogeneous electric field. Since this field can be shown to be proportional to the gradient of the strain, it is allowed by symmetry for all crystal classes. By integrating the electric field and the strain gradient from one region of the crystal to another, one finds a change in electrostatic potential proportional to the change in strain. This term contributes to the change in energy of all electronic states, along with any other short-range contributions to the deformation potential

described by the usual local formulations.¹⁻³ Lawaetz⁶ showed that the effects upon the electronic energies can be described as the sum of an analytic part plus terms which are nonanalytic as a function of \mathbf{q} for $|\mathbf{q}| \rightarrow 0$. The latter terms lead to a different dependence of the energy-strain relationship as a function of direction of propagation of the acoustic phonon $\hat{\mathbf{q}}$ than is predicted by local theory.¹⁻³ The former, analytic, terms may be interpreted as absolute hydrostatic deformation potentials, $a_i = dE_i/d \ln \Omega$, where E_i is the energy of state i and $d \ln \Omega = d\Omega/\Omega$ is the fractional volume change.

In the present work we propose a way to calculate deformation potentials for acoustic phonons including all long-range fields by using an approach which has proven useful in calculations of heterojunctions.^{7,13,14} Heterostructures are characterized by spatial variations in both the chemical composition and the strain. In particular, strained-layer superlattices involve static strains of the same form as the time-dependent strains produced by acoustic phonons. The lineup of conduction and valence bands depends on dipole shifts at the interface, which affect the relative band positions of the two sides of the interface. This involves exactly the same considerations of the electrostatic fields as does the spatially varying potential caused by the spatially varying strain in an acoustic phonon. In this study of deformation potentials we are therefore able to make use of our theoretical developments applied previously to heterostructures. Furthermore, our understanding of both heterostructures and deformation potentials is increased by considering them in a unified way.

Because the absolute energy of the average potential in an infinite crystal is ill defined,¹² the electronic states resulting from two separate calculations, corresponding to different strain conditions, cannot be directly compared with one another. The relation of the energies is well defined only when specific boundary conditions are introduced, which relate the potentials in both regions to a common zero of energy. We have accomplished this by performing calculations in which compressed and expanded regions of the crystal are simultaneously present, in a large supercell. This is similar to our previous heterojunction calculations,¹⁴ in which the supercell contained slabs of the two semiconductors that form the heterostructure. Here we carry out self-consistent calculations for supercells which contain two layers of the same semiconductor in different strain conditions (one layer uniaxially expanded by 1%, the other compressed by 1%). The interfaces are pseudomorphic, i.e., the lattice constant in the directions parallel to the interface is kept equal to the unstrained bulk lattice constant on both sides. We will discuss the effects of uniaxial versus hydrostatic contributions to the deformation potentials later.

It is important to establish that the supercell calculation is relevant to the problem of acoustic-phonon deformation potentials. Consider a longitudinal phonon with

wave vector \mathbf{q} along a high-symmetry direction. Planes of atoms normal to $\hat{\mathbf{q}}$ are displaced rigidly by amounts which vary sinusoidally as a function of position of each plane R_i along the direction parallel to $\hat{\mathbf{q}}$, $u_i = A \times \cos(qR_i)$. The strain is given by $\epsilon_i = (u_{i+1} - u_i)/(R_{i+1} - R_i) \rightarrow -Aq \sin(qR_i) = -|\epsilon| \sin(qR_i)$, and the strain gradient is $\delta\epsilon_i = -|\epsilon|q \cos(qR_i)$. Since we consider only effects linear in $|\epsilon|$, the sinusoidal variation in the strain gradient $\delta\epsilon_i$ can be considered as a superposition of the strain gradients at each plane i . In our approach we calculate the effect of a strain gradient in one plane, i.e., a constant strain for planes $j \leq i$ and a different constant strain for planes $j \geq i+1$. Any longitudinal-acoustic wave with $\hat{\mathbf{q}}$ perpendicular to the planes can be formed as a linear combination of strain gradients at each plane.

It should be emphasized that by making this choice, we are *not* making a strain gradient more abrupt than an acoustic wave. In fact, we are properly treating the variations on an atomic scale that occur in an acoustic phonon. The long-wavelength limit is a superposition of strain gradients $\delta\epsilon_i$ which vary slowly as a function of i . Therefore, the effect of the strain gradient can be used to describe the deformation potential due to any phonon with direction $\hat{\mathbf{q}}$. Each different direction $\hat{\mathbf{q}}$ in principle requires a separate calculation with different orientation of the planes. We will describe results for three such directions.

Our calculations are based on the local-density-functional method,¹⁵ using *ab initio* pseudopotentials.¹⁶ Details of the computations, which are very similar to those performed in our earlier work on heterojunction band offsets, may be found in Ref. 14. Separate bulk calculations on strained materials provide information on the variations of individual band edges with respect to the reference potential when strain is applied. The strain-induced shift in the reference potential itself is given by the self-consistent potential in the supercell, provided the interfaces between differently strained regions are far enough apart. Combining the information, we can derive band-edge deformation potentials for valence and conduction bands.

The most extensive calculations were performed for Si. We examined supercells with eight and twelve atoms, strained along (001), (110), or (111) directions. The energy cutoff was 6 Ry, and three or four special points in the irreducible part of the Brillouin zone were used for reciprocal-space integration. To test convergence, we increased the cutoff up to 11 Ry, and found that the calculated value of the deformation potential at 6 Ry is within 0.2 eV of the converged result. We also increased the number of special points from three to ten and found an effect smaller than 0.2 eV. For the (001) supercell, we changed the number of atoms from eight to twelve, and found a change in the deformation potential of less than 0.2 eV. This shows that our values are converged to this accuracy with respect to the number of atoms in the

supercell, and that the transition in the potential between regions subject to different strains occurs on a length of one or two atomic layers around the interface. For the (111) and (110) orientations, the off-diagonal components of the strain in the supercell give rise to internal displacements of the atoms;¹⁷ we have included these displacements in each of the strained layers using the internal displacement parameter $\zeta=0.53$ that was derived for bulk Si from theoretical calculations that used the same methods as the present study.³ Uncertainties in the value of the ζ , or deviations from the displacement pattern near the interface, have only a small effect on the calculated potential lineup. As a check, setting $\zeta=0$ in a calculation for the (111) orientation produced a change in a_v of ~ 1 eV, bringing it closer to the value for the (001) orientation, where internal displacements are absent.

The bulk calculations for strained materials were performed with a 24-Ry cutoff, and two special points in the irreducible part of the zone. Only hydrostatic components of the strain were applied, and the changes in the band structure were derived from calculations in which the number of reciprocal-space vectors in the plane-wave basis was kept constant. In terms of intrinsic accuracy of the methods, previous comparisons with experiment indicate that the local-density approximation works well for the problem at hand.^{3,7,14} Based on all of our convergence tests, we put a rather conservative numerical error bar of ± 1 eV on our calculated deformation potentials (note that this requires a calculation of the band lineups to an accuracy of better than 0.02 eV, for a 2% strain). This error bar is quite small compared to certain relevant deformation potentials (e.g., those for direct band gaps), and *much* smaller than the range of (theoretical and experimental) values suggested before.

In Table I we give our calculated values for derivatives of the valence- and conduction-band edges $dE_v/d\ln\Omega$ and $dE_c/d\ln\Omega$. These include both analytic terms (which are the same for all orientations and can be identified with the hydrostatic deformation potentials a_v and a_c) and nonanalytic terms (which depend upon orientation).⁶ As a check, Table I also lists values for

the band-gap deformation potential obtained by subtracting the valence-band from the conduction-band values; the results are orientation independent and agree well with experimental values. The orientation listed in the table refers to the *supercell* that was used in the derivation of the potential lineup; all *bulk* calculations were performed for hydrostatic strains only. Effects of uniaxial strains on the band structure, which lead to splitting of degenerate bands, are well known and not addressed here. However, because the potential lineups are determined from supercell calculations for different orientations, the nonanalytic contributions to the deformation potential discussed above lead to different values for (001), (110), and (111). In principle, the nonanalytic terms [corresponding to the “ C_2 term” in Ref. 6, Eqs. (3.17) and (4.4)] can be explicitly extracted. In practice, however, these terms are small in magnitude; Lawaetz⁶ estimated $|C_2| < 1$ eV. An explicit determination is therefore very difficult, due to numerical uncertainties which are especially hard to estimate when comparing calculations for very different geometries like the present supercells. The smallness of the nonanalytic contributions is illustrated by the fact that the deformation potential values for different supercell orientations are very similar (to within the numerical error bar). We therefore do not pursue the determination of the nonanalytic contribution here, and suggest that the present values be interpreted as representative of hydrostatic deformation potentials.

We thus find that, to within the error limits, the hydrostatic component is dominant in the deformation potential, and the dependence on direction \hat{q} is weak. That is, the nonanalytic terms of Lawaetz⁶ are smaller than our error limits. If the nonanalytic terms were negligible, then in fact the deformation potential could be regarded as absolute, i.e., having the same form as in the usual Bardeen-Shockley theory, with only its magnitude affected by considerations of the electrostatic fields. This is exactly parallel to our conclusion for many heterojunction interfaces: Because of orientation independence and transitivity the bands can be considered to be lined up in terms of a locally defined reference energy. Further

TABLE I. Band-edge deformation potentials for various semiconductors, obtained from self-consistent interface calculations. Listed are values of $dE_v/d\ln\Omega$ for the valence band, $dE_c/d\ln\Omega$ for the lowest conduction band, and their difference a . Also given are experimental values for the band-gap deformation potential a . All values are in eV.

	Orientation	$\frac{dE_v}{d\ln\Omega}$	$\frac{dE_c}{d\ln\Omega}$	a	a (expt.)
Si	(001)	1.3	3.1	1.7	1.5 ± 0.3^a
	(110)	0.4	2.1		
	(111)	3.1	4.8		
Ge	(001)	1.8	-1.0	-2.8	-2.0 ± 0.5^b
GaAs	(110)	1.1	-7.3	-8.3	-8.4 ± 0.9^c

^aReference 18.

^bReference 19.

^cReference 20.

studies with smaller uncertainties would be needed to identify the nonanalytic terms of Lawaetz.⁶

Finally, we turn to a comparison of our values with model theories and with experiment. The problem of associating a reference energy with an infinite crystal can also be addressed within a model theory, eliminating the need for self-consistent interface calculations. The "model-solid" theory developed by the present authors is described in detail elsewhere,^{14,21} with examples for many different semiconductors. For the cases listed in Table I, that model theory is within 1 eV of the self-consistent results. A general condition from the values in Ref. 21 is that the valence-band deformation potentials are all small compared to the deformation potentials for the direct gap.

Vergés *et al.*¹¹ used self-consistent linear muffin-tin-orbital (LMTO) calculations for bulk solids to derive deformation potentials. The zero of energy which is implicit in the atomic-sphere approximation was chosen as a reference to compare bulk calculations at different volumes. Their values differ from the present work by more than 7 eV. More recently, it was argued that screening needs to be included in the previous approach,²² and Cardona and Christensen⁹ proposed a model theory to calculate these effects. This substantially improves the agreement with the present work.

Experimental determinations of absolute deformation potentials have been quite controversial. Measurements are indirect, and require a significant amount of analysis, interpretation, and assumptions. A discussion of experimental values and techniques is included in Refs. 9 and 21. Here we only mention some of the more recent and reliable values. From mobility measurements on high-purity GaAs, the value for $|a_c|$ is found to be ~ 7 eV.²³ To our knowledge, this is the only class of measurements in which the quantity of interest can be clearly identified with the deformation potential discussed in this paper. A second class of measurements is based on the use of transition-metal impurity levels as reference levels in band-structure lineups. Nolte *et al.*²⁴ found values of $a_c = -9.3$ eV for GaAs and 2.4 eV for Si. A third class of measurements relies on the effects of heavy doping on the lattice constant. Cargill *et al.*,²⁵ using x-ray scattering and extended x-ray-absorption fine-structure (EXAFS) measurements, separated the "size effect" from the electronic effect, and found $a_c = 3.3 \pm 0.7$ eV for Si. All of these values are in reasonable agreement with the present first-principles calculations.

In conclusion, we have reported the first *ab initio* determination of "absolute" deformation potentials, which takes into account the important long-range electrostatic effects. Our values are in good agreement with recent experiments.

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