Direct method of calculation of dynamic effective charges: Application to GaAs

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A method is described for the calculation of effective charges and piezoelectric constants in crystals directly from self-consistent electronic calculations. The central equations are based upon moments of the change in electronic charge density $\delta n(\vec{r})$ caused by the displacement of an atom. The long-range Coulomb interactions are taken into account, and it is shown that the moments are rigorously convergent and define longitudinal effective charges and piezoelectric constants. The method is not limited to small displacements and, in fact, uses exactly the same techniques which have been extensively developed for the calculation of surface and interface dipoles. Results are presented for the effective charge in GaAs using the same ionic pseudopotentials and density functional for the electrons that predict accurately the lattice constant and phonon energies. The predicted charge is $e_L^* = 0.16 |e|$ (positive on Ga) compared to the experimental value $e_L^* = e_T^*/\epsilon_0 = \pm 0.20 |e|$.

I. INTRODUCTION

Theoretical progress in calculations of electronic properties of crystals has reached the point where it is feasible to accurately predict, from first principles, the electronic charge density and the total energy of the electron-ion system. The essential ingredient in this development is the density-functional method[1] which gives a rigorous relation of the charge density $n(\vec{r})$ and the total energy. Together with methods which greatly reduce the size of the computations,[2,3] this has made it feasible to calculate accurately many properties of semiconductors,[2-5] such as the equilibrium lattice constants, elastic constants, and phonon energies.[2,5] It has also been extended to more complex lower-symmetry situations[6-8] such as predictions of work functions,[6-8] and relaxations of atomic positions at surfaces[7] and interfaces.[8]

This paper discusses the development and application of a practical method to calculate macroscopic polarizations from the charge density $n(\vec{r})$. The macroscopic polarizations can be directly measured and define, e.g., optic mode dynamic effective charges and piezoelectric constants. It was shown in Ref. 9 (hereafter referred to as I) that these quantities could be related to the change in charge density induced by displacement of individual atoms: the effective charge by the first moment of this induced charge density and the piezoelectric constant by

terms involving the second moment. However, in I no methods for calculation were given and the final results were stated only in terms of the formal long-wavelength limit of finite wave-vector equations. As discussed in I and Refs. 10 and 11, this is nontrivial because of the long-range character of the Coulomb interaction. Here we derive an explicit formulation which is convenient for numerical calculations and which gives a correct, rapidly convergent approximation to the infinite-wavelength limit.

There are four important aspects of the present formulation which determine its usefulness:

(1) It is convenient for numerical calculations. We shall show that properties of the charge density needed for the macroscopic polarizations can be calculated using exactly the same procedure and methods as have already been extensively developed for surfaces and interfaces.[6-8]

(2) The central quantity in the present work is the change in charge density in real space caused by displacement of an atom. We show that one can work with properties of this induced charge density which are localized to a neighborhood of the given atom. The resulting form of the induced charge density is instructive and gives a graphic picture of the nature of the chemical bonding and local polarizability of the electrons.[9,11-13]

(3) Electron-electron interactions are treated self-consistently. This is absolutely essential in any

2081

first-principles calculation of electric fields induced by electronic polarizations because the long-range electron-electron interaction is purely Coulombic and has exactly the same form as the macroscopic fields which we wish to calculate. In the limit of small displacements, the self-consistency is equivalent to carrying out the exact inversion of the dielectric matrix which is necessary for calculation of phonon energies, effective charges, etc.[13]

(4) The present methods are not limited to small displacements of atoms and may be used to calculate moments which are nonlinear in atomic displacements and even in cases of gross changes in chemical bonding. An example is the calculation of interface effective charges in Ref. 8.

Previous work on theoretical understanding of effective charges and piezoelectric constans has been devoted primarily to construction of models for the induced charge density in real space. The model calculations are too numerous to mention completely, but they include shell models[14] and bond-charge models[15] fitted to lattice dynamical data, as well as simplified models of the electronic properties such as semiempirical tight-binding models.[16,17] In each case there is given a specific description of the response of the electronic charge density to displacements of atoms. These models are very useful and, in order to make contact with them, it is particularly advantageous that the charge density plays the essential role in the present general formulation of the interacting electron-ion system. In addition, there have been several calculations[18−20] of effective charges using empirical pseudopotentials. To the knowledge of the present authors, all such calculations have been based upon the assumption that the total self-consistent potential moves rigidly with the displaced ions. This is an approximation used to avoid the full self-consistent calculation, and amounts to neglecting certain off-diagonal elements in the inverse dielectric function matrix.[13] Furthermore, it has been argued[10] that the long-wavelength limit was not taken correctly in Ref. 18.

In Sec. II the general formulation is presented in a way which takes into account the long-range character of the Coulomb fields, and in Sec. III explicit numerical calculations for GaAs are discussed.

II. FORMULATION

Effective charge and piezoelectric coefficients may be defined in an infinite crystal by considering the long-wavelength limit of periodic waves with wave vector $\vec{k}$. The $\vec{k}$ Fourier component of the polariza-

tion is given to linear order by[9,21,22]

$$P_\alpha = V_0^{-1}(Q_{\alpha\beta\gamma}e_{\beta\gamma} + e^*_{\kappa\alpha\beta}u_{\kappa\beta}) + X_{\alpha\beta}E_\beta \quad . \quad (1)$$

Here Greek letters denote Cartesian indices, κ labels the atoms in the unit cell, and it is assumed that repeated indices are summed. The coefficient of $\vec{E}$ is the electronic polarizability $X_{\alpha\beta} = (1/4\pi)(\epsilon_{\alpha\beta} - 1)$. The polarization caused by the atomic displacements $u_{l\kappa\beta} = u_{\kappa\beta}\exp(i\vec{k}\cdot\vec{R}_{l\kappa})$ is divided into a purely acoustic part determined by the strain $e_{\beta\gamma} = \bar{u}_\beta k_\gamma$ where $\bar{u}_\beta$ is the average displacement of a cell and a purely optic part proportional to the displacement of atoms within the unit cell u_κ, where $\sum_\kappa u_\kappa = 0$. Here V_0 is the volume of the unit cell. The coefficient $e^*_{\kappa\alpha\beta}$ is the effective charge defined as the derivative of P_α with respect to $u_{\kappa\beta}$ holding the strain $\vec{e}$ and the field $\vec{E}$ constant. Similarly $Q_{\alpha\beta}$ may be defined as the derivative with respect to $e_{\beta\gamma}$ holding the optic displacement $\vec{u}_\kappa$ and field $\vec{E}$ constant.

It is important to note that Q is not a piezoelectric constant. In general a strain is accompanied by internal optic displacements[9,22,25] which are determined by minimizing the total energy. Here we will consider only Q, which may be termed a "quadrupole coefficient" for reasons described in I and below. The complete expressions for the piezoelectric constant in terms of Q, e^*, and internal strain parameters may be found in Refs. 9 and 22.

The coefficients e^* and Q may be termed "transverse" because in transverse geometries with $\vec{k}\perp\vec{P}$ the macroscopic electric field $\vec{E}$ vanishes. Conversely, in a longitudinal geometry with $\vec{k}\,||\,\vec{P}$, $\vec{E} = -4\pi\vec{P}$ in the absence of external fields, and $\vec{E}$ may be eliminated from Eq. (1) to yield

$$(\vec{P}_L)_\alpha = V_0^{-1}(\epsilon^{-1})_{\alpha\delta}(Q_{\delta\beta\gamma}e_{\beta\gamma} + e^*_{\kappa\delta\beta}u_{\kappa\beta}) \quad . \quad (2)$$

Consequently we may define the longitudinal coefficients

$$(e^*_L)_{\kappa\alpha\beta} = (\epsilon^{-1})_{\alpha\delta}e^*_{\kappa\delta\beta} \quad , \quad\quad\quad (3a)$$

and

$$(Q_L)_{\alpha\beta\gamma} = (\epsilon^{-1})_{\alpha\delta}Q_{\delta\beta\gamma} \quad , \quad\quad\quad 3(b)$$

which are uniquely related to the transverse coefficients through the macroscopic dielectric tensor $\epsilon_{\alpha\beta}$. Note that in a cubic crystal $\epsilon_{\alpha\beta}^{-1} = \delta_{\alpha\beta}(1/\epsilon)$.

In the present work we find that it is most convenient to use the longitudinal geometry to calculate the induced moments using

$$\vec{\nabla}\cdot\vec{P} = i\,\vec{k}\cdot\vec{P} = -\delta\rho \quad ,$$

where $\delta\rho$ is the $\vec{k}$ Fourier component of the total induced charge density (ions plus electrons). In this way we can evaluate the longitudinal coefficients e_L^* and Q_L given by Eqs. (2) and (3). The transverse coefficients e^* and Q may be rigorously derived from e_L^* and Q_L using Eq. (3). The desired expressions in terms of moments of the induced charge density caused by displacement of an individual atom may be derived following exactly the steps in Sec. II of I. It is important to note that in I, only the transverse case $\vec{E} = 0$ was considered, whereas here we shall show that it is more advantageous to consider the longitudinal case with $\vec{E} = -4\pi\vec{P}$. The present analysis will not only eliminate the difficulty discussed in I in the proof of the convergence of the moments, but we shall see that it will provide *rapidly convergent expressions convenient for numerical calculations.* Nevertheless, we can utilize essentially the entire analysis in Sec. II of I which is here reviewed briefly.

Let us define the induced charge density (ionic plus electronic) caused by displacement of the atom at $\vec{R}_{l\kappa}$ in cell l by[26]

$$F_{\kappa\alpha}(\vec{r} - \vec{R}_{l\kappa}) = \frac{\partial \rho(\vec{r})}{\partial R_{l\kappa\alpha}} \ . \tag{4}$$

The total induced charge density $\delta\rho$ is the sum of the contributions caused by the displacement of each atom; therefore the $\vec{k}$ Fourier component of the longitudinal polarization is given by

$$-i\,\vec{k}\cdot\vec{P}_L$$

$$= \frac{1}{V} \sum_{l\alpha} \int d^3r \, \exp(-i\,\vec{k}\cdot\vec{r})F_{\kappa\alpha}(\vec{r} - \vec{R}_{l\kappa})u_{l\kappa\alpha} \ . \tag{5}$$

Here $V^{-1} \int d^3r$ denotes the average over the entire crystal. For a long-wavelength optic mode, with $u_{l\kappa\alpha} = u_{\kappa\alpha}\exp(i\vec{k}\cdot\vec{R}_{l\kappa})$, the integral in (5) is independent of cell l, and to lowest order in $\vec{k}$, may be written

$$\vec{k}\cdot\vec{P}_L = \frac{1}{V_0} \sum_\alpha \int d^3r(\vec{k}\cdot\vec{r})F_{\kappa\alpha}(\vec{r})u_{\kappa\alpha} \ , \tag{6}$$

where V_0 is the volume of a unit cell. From (2), (3), and (6) we find

$$(e_L^*)_{\kappa\alpha\beta} = \int d^3r \, r_\alpha F_{\kappa\beta}(\vec{r}) \ . \tag{7}$$

Following the analysis of I for acoustic modes, the longitudinal elements of the tensor Q are

$$(\vec{k})_\alpha(Q_L)_{\alpha\beta\gamma}(\vec{k})_\gamma = \frac{1}{V_0} \int d^3r(\vec{k}\cdot\vec{r})^2 \sum_\kappa F_{\kappa\beta}(\vec{r}) \ , \tag{8}$$

i.e., a second moment of the function F.

It remains for us to prove that the integrals in Eqs. (7) and (8) are convergent for $r \rightarrow \infty$. Let us define the coordinate r_α in (7) or $\hat{k}\cdot\vec{r}$ in (8) to be z and the integral of $F_{\kappa\beta}(\vec{r})$ over the plane perpendicular to $\hat{z}$ to be $\overline{F}_{\kappa\beta}(z)$, which has dimensions of charge per unit area. At large z the functions F and $\overline{F}$ may be considered in the continuum limit of a dipole at the origin screened by the local macroscopic dielectric tensor $\epsilon_{\alpha\beta}$. The dipole field has the simple property that the integral $\overline{F}(z)$ vanishes for any $z \neq 0$ since it is the average over a plane that does not pass through the dipole. Thus, despite the fact that $F(\vec{r})$ is long ranged, $\overline{F}(z)$ is nonzero only for a small range of z, of the order of atomic dimensions, where the local continuum arguments do not apply.[27] Therefore we have shown that the macroscopic effective charge and piezoelectric tensors can be calculated in terms of well-defined integrals over the function $F_{\kappa\beta}(\vec{r})$, which is the change in charge density caused by displacement of an individual atom.

Finally, we must establish a convenient method for calculation of $\overline{F}_{\kappa\beta}(z)$. Define $P(0)$ to be the plane perpendicular to $\hat{z}$ and passing through atoms of type κ. If z is a high-symmetry direction, the atoms in the plane $P(0)$ form a two-dimensional periodic array which can be labeled by a cell index m. A schematic example is shown in Fig. 1. Now $\overline{F}_{\kappa\beta}(z)$ is the integral of $F_{\kappa\beta}(\vec{r} - \vec{R}_{m\kappa})$ over infinite planes $P(z)$ parallel to $P(0)$, which is independent of the cell index m. Let us define

$$H_{\kappa\beta}(\vec{r}) = \sum_m F_{\kappa\beta}(\vec{r} - \vec{R}_{m\kappa}) \tag{9}$$

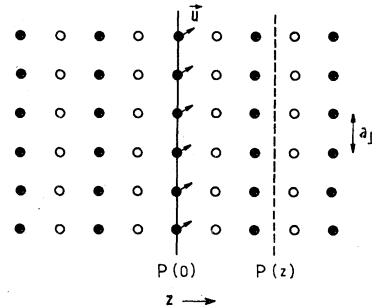which is the two-dimensional periodic function

FIG. 1. Schematic illustration of a crystal with a single plane of atoms displaced by $\vec{u}$. The plane $P(0)$ is defined to pass the undisplaced positions of the lattice plane of atoms, z is the distance normal to the plane, and $P(z)$ is a plane parallel to $P(0)$ separated by z. The distorted crystal now has two-dimensional periodicity with lattice constant $a_\perp$ in the direction perpendicular to $\hat{z}$.

resulting from equal displacement of each atom $m\kappa$ in the plane $P(0)$. The periodic function $H(\vec{r})$ $= H(\vec{r} + \vec{R}_m)$ can be represented by the Fourier components $H(\vec{G},z)$, where $\vec{G}$'s are the reciprocal vectors of the two-dimensional lattice

$$H(\vec{G},z) = \int_{\text{cell}} d^2\vec{r}\, H(\vec{r}) \exp(i\vec{G}\cdot\vec{r}) \ . \tag{10}$$

It is easy to see that $\overline{F}_{\kappa\beta}(z)$ is exactly the same as the zero Fourier component, i.e., the average $H_{\kappa\beta}(\vec{0},z)$. Therefore we have finally

$$(e_L^{*})_{\kappa\beta} = \int dz\, z H_{\kappa\beta}(\vec{0},z) \tag{11a}$$

and

$$\hat{k}_\alpha (Q_L)_{\alpha\beta\gamma} \hat{k}_\gamma = \sum_\kappa \int dz\, z^2 H_{\kappa\beta}(\vec{0},z) \ , \tag{11b}$$

where $H_{\kappa\beta}(\vec{G},z)$ is the $\vec{G}$ Fourier component of the derivative of the charge density with respect to equal displacement of all atoms $m\kappa$ in the plane $P(0)$.

In the present work we shall determine $H(\vec{G},z)$ by numerically calculating the charge density of the crystal with a plane of atoms displaced. The calculations can be done for arbitrary displacements but we shall consider here only small displacements and shall compute numerically the derivative from finite displacements. The problem of calculating the charge distribution of a two-dimensional periodic system is one that has been encountered before in the area of surfaces and interfaces. Extensive techniques have been developed[6-8] to treat such systems and we may carry over these techniques here. The most practical and successful method has been the superlattices method[6-8] which corresponds to forming a lattice of displaced planes with periodicity in the $\hat{z}$ direction large enough so that the potential and charge density have converged to their bulk limits in the regions between the disturbances. In our case this corresponds to a cell similar to that shown in Fig. 2. The calculation of the change in charge density $\Delta\rho(\vec{r})$ and consequently $H_{\kappa\beta}(\vec{G},z)$ is exactly equivalent to the calculation of the self-consistent charge density at an interface or surface.[6,8] Determination of the first moment of $H_{\kappa\beta}(\vec{0},z)$ is exactly equivalent to the calculation of the dipole contribution to work function at a surface or interface.[6-8] Furthermore, the total Hartree potential is calculated as part of the self-consistent electronic calculation. From elementary electrostatics the change in the average potentials from one side of a plane of displaced atoms to the other is given by

$$\Delta V = 4\pi\sigma = (4\pi/A_0)e_L^{*}u \ , \tag{12}$$

where σ is the dipole moment per unit area, A_0 is the area of the plane per atom, and $e_L^{*}u$ is the dipole moment per atom in the linear approximation.

We will not describe further the methods of calculation which can be found elsewhere.[6-8] We will merely note two important aspects: (1) The supercell technique is just a computational tool. Other methods can be used, such as Green's functions[28] and direct integration of the Schrödinger equation in real space.[29] (2) The convergence of the charge density has been examined for many semiconductor interfaces and surfaces, from which it was shown that calculations with feasible superlattices can accurately describe the charge density of an isolated interface or surface, or, in our case, a single plane of displaced atoms.

III. CALCULATION OF e^{*} IN GaAs

We give here calculated results for the charge displacement function $\overline{F}_{\kappa\beta}(z)$ for Ga and As atoms in GaAs for the case of $\hat{z} \parallel [100]$. The case is chosen because our previous work[8,30] has shown that GaAs is very accurately described by the Ga and As ionic pseudopotentials[31] and the local density functional for exchange and correlation $V_{\text{ex}}(\vec{r}) = 0.8 \times \frac{3}{2}[3n(\vec{r})/\pi]^{1/3}$ which is described in Refs. 8 and 30. In particular, the lattice constant, bulk modulus, and transverse optic and zone-boundary phonon frequencies are all predicted with no adju-
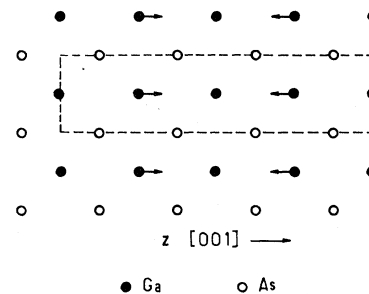

z [001] ⟶

● Ga   ○ As

FIG. 2. Superlattice in GaAs formed by displacing planes of Ga atoms to form a new unit cell as indicated. The atoms are shown projected onto the plane formed by [100] and [001]. The new cell contains four Ga and four As atoms and has its long dimension along the [001] or z direction. The symmetry of the distorted crystal is exactly the same as that of the Ge-GaAs interface superlattice considered in Ref. 8. The charge redistribution which determines the effective charge is therefore calculated in the same manner as for the interface. The analogous case with As atoms displaced gives an independent calculation of the As effective charge.

stable parameters[30]: Each quantity was predicted, except the TA(X) frequency, to within a few percent, and the TA(X) frequency, which is anomalously low and very sensitive to cancellations, was predicted with an error of only -20%. Furthermore, the present calculations bear a remarkable similarity to the interface calculations on Ge-GaAs of Ref. 8. Essentially all the tests for accuracy, convergence, and size of the superlattice are the same as in those calculations. Hence it is natural to use this as a test case for the present calculation of an effective charge from density-functional electronic Hamiltonian. The geometry with $\hat{z}$ parallel to [100] we have chosen has the property that the linear quadrupole coefficient Q or Q_L is zero by symmetry. This is advantageous for accurate calculation of the dipole coefficient e_L^*; however, we cannot compute the quadrupole coefficients from the present results.

To calculate the change in charge density we have used exactly the same supercell periodicity as in our interface calculations on Ge and GaAs,[8] that is, an eight-layer cell (four Ga layers and four As layers) which is 4 times the size of the primitive fcc cell and is illustrated in Fig. 2. In each calculation there are two equivalent layers displaced by exactly equal and opposite amounts. Thus each cell has no dipole by symmetry and there are rigorously no long-range fields. We have carried out two calculations, one with only As atoms displaced and a second with only Ga atoms displaced in the pattern shown in Fig. 2. The magnitude of the displacement was chosen to be $0.01a$ where a is the cube edge $= 5.65$ Å in GaAs. This magnitude of the displacement was found to give linear change in the charge density in the interface calculations[8] and we assume that the same is also true for the present case.

The calculation in the periodic supercell structure was carried out by Fourier analysis. All details are equivalent to the interface calculations.[8] Approximately 570 plane waves were included in the expansion of the wave functions, with 85 treated exactly and the remainder included by second-order Lowdin perturbation theory.[2,8,30] The charge density was evaluated using sets of 1 and 3 special points. Self-consistency was achieved to within 0.6 mRy ($\approx 6\%$) for the worst-behaved Fourier component, the one with the smallest $\vec{G}$ which is the most important in determining the asymptotic behavior of $\rho(\vec{r})$ and $V(\vec{r})$ far from the planes of displaced atoms.

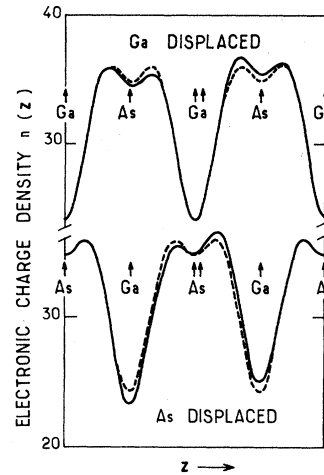The electronic charge density averaged perpendicular to the [100] direction is given in Fig. 3, the top

FIG. 3. The charge density $n(z)$ averaged in the planes perpendicular to the [001] or z direction of the undistorted crystal (dashed line) compared with the charge density $n(z)$ (solid lines) of the crystal with planes of atoms displaced. Only half the unit cell is shown. The other half is exactly symmetric. The upper figure is for Ga atoms displaced by $\vec{u} = +0.01a$ in the [001] direction as indicated in the unit cell shown in Fig. 2. The lower figure is for As atoms displaced. The units are such that the average of $n(z)$ is the number of electrons per cell, which is 32 in the present case. The change in charge density $\Delta n(z)$ is shown more clearly in Fig. 4.

portion for As displacement and the bottom for Ga displacement. For comparison, the dotted line shows the undistorted charge density of the GaAs crystal taken from Ref. 8. The change in charge density is shown on an expanded scale in Fig. 4.
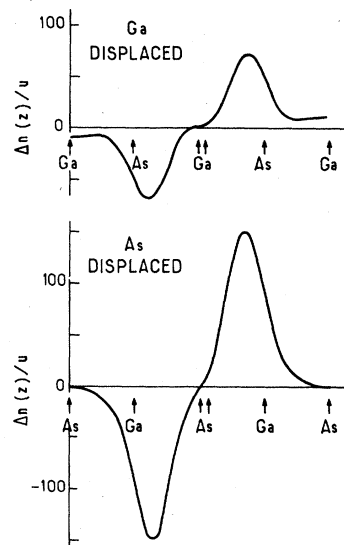

FIG. 4. The change in charge density $\Delta n(z)$ from the undistorted crystal per unit displacement (u/a). See caption to Fig. 3.

Note that in each case the displacement of the positive nuclei is largely offset by the flow of negative electrons. In fact the electrons almost completely screen the nuclei. However, in the case of As we shall see that there is a slight over compensation (i.e., a negative effective charge for the As) and for Ga a slight undercompensation (i.e., a positive effective charge for the Ga). We have computed the effective charge in two ways: First, e_L^* is found from Eq. (12) where ΔV is the difference in the self-consistent Hartree potentials evaluated at the midpoints between the displaced planes, i.e., the positions at the extreme left and right in Figs. 3 and 4. This is evaluated as a matter of course in the process of carrying out the electronic calculations. Second, as a numerical check we have integrated the change in charge density as in Eq. (11) to obtain the moment directly.

In Table I we give the results of both calculations and also the experimental value of the longitudinal effective charge, which is $e_T^*/\epsilon = 2.16/11.0 = 0.20\,|e\,|$. We see that the agreement with experiment is satisfactory, considering that there are no parameters involved and that this is the same potential which can also give so many other electronic and structural properties. We see also that checks of our numerical calculations are very good. The two methods of calculation agree well and the two independent calculations give closely the result $e_{Ga}^* + e_{As}^* = 0$, which is required by translation invariance.[13] The small discrepancies, particularly for Ga displaced, are discussed below.

The figures of the change in charge density also give us other information. First, for displaced As atoms the change in charge density is essentially zero in our supercell far from the displaced atoms. It appears that our cell is large enough and only very small errors result from the fact that we must truncate our integrals rather than integrating from $-\infty$ to $+\infty$ as in Eq. (11a). However, for dis-

placed Ga atoms there is still some overlap. Therefore we expect that the Ga calculation is less accurate and that this is the reason that the charge neutrality condition is not obeyed exactly. This is related to the general conclusion which may be drawn from the figures that the charge displacement is more distributed in the case of Ga than for As.

The displaced charge density in Fig. 3 is clearly spread over neighboring atoms: This is the result of both Coulomb fields and covalent interactions. The general nature of the charge displacement has been examined in Si in previous calculations.[2,12] Our present results are consistent with these except that, of course, here the heteropolar character of the crystal leads to nonzero effective charges. In a bond picture it is clear that this involves transfer of charge from one bond to another and a simple bond polarity model is not sufficient.[16,17] One can see in Fig. 4 that charge is displaced across several layers of atoms, but it is not possible a priori to say whether or not this could be described by a nearest-neighbor tight-binding model in which the charge is transferred sequentially from one bond to a nearest-neighboring bond.

Using the value of $\epsilon_0 = 11$ for the macroscopic dielectric constant, our calculations yield a predicted value of the transverse effective charges of $e^* = -0.154 \times 11 = 1.7\,|e\,|$. This may be compared with the experimental number[21] of 2.16 and with other calculations. From an empirical tight-binding model, Ren and Harrison[16] found $e^* = 1.89$. Empirical pseudopotential methods have been used in Refs. 18−20, to find, respectively, $e^* = 2.39$, 1.95, and 1.95. All these methods have used empirical potentials and have made particular assumption on the change in the potential in the distorted crystal involving unknown approximations.

To the knowledge of the authors, none of the model calculations such as the shell model[14] or bond charge[15] models have been analyzed in a way

TABLE I. Ionic and electronic contributions to the effective charge in GaAs. The total longitudinal charge is compared with experiment taken from Ref. 21 and Eq. (3a). The sign is found to be positive for Ga, an assignment which is not known experimentally.

	ionic	e_L^* electronic	total	e_L^* from self-consistent potential
As	+ 5	− 5.155	− 0.155	− 0.153
Ga	− 3	− 2.852	+ 0.148	+ 0.161
Experiment				±0.197

that can be compared directly. It would be interest-
ing for those who do such calculations to make
comparisons with detailed electronic calculations
such as the present work. It seems feasible to
describe the results given in Fig. 4 by displacements
of shells of charge. For a bond charge model it is
clear that the bond charge must be rather spread
out and that there must be charge transfer between
bonds[15] to describe the true electronic system.

IV. CONCLUSIONS

In summary, we have presented a method for
computation of effective charges and piezoelectric
constants by calculating the change in charge densi-
ty induced by displacement of a plane of atoms.
We showed that all computational considerations
and questions of convergence of the Coulomb sums
are exactly equivalent to calculation of the self-
consistent charge density at an interface between
two semiconductors.[6-8] In particular, calculation of
an effective charge involves the same considerations
and the same numerical steps as does the computa-
tion of the interface dipole potential in the interface

calculation. It is most direct to carry out the calcu-
lation for finite displacements and, from the finite
differences, one can calculate linear and nonlinear
polarizations. We have presented results for the
linear effective charge e^* in GaAs, using the same
pseudopotentials and density functional which we
have shown[8,30] predict accurately the lattice con-
stant, bulk modulus, and phonon frequencies in
GaAs. We found $e^* = 1.7 \,|e\,|$, compared to the
experimental value[21] of 2.16, with a positive effective
charge for Ga. The direct calculation of the change
in charge density, as illustrated in Figs. 3 and 4, has
the advantage that it shows directly the dynamic
charge response that determines the sign and large
magnitude of the effective charges in III$-$V com-
pounds.

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  (Ref. 9) denoted there by lower case f.
[27]Note that in I the corresponding average of f in the ab-
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