

Comment on calculations of electric polarization in crystals

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A calculation of lattice dynamical effective charges by Bennett and Maradudin is shown to be based upon an incorrect expression for the electric polarization produced by displacement of the atoms. The basic point is that the polarization of a crystal cannot be derived solely in terms of the charge density in a unit cell in an infinite periodic crystal. The correct polarization is most readily evaluated from well-known finite-wave-vector expressions.

In a recent paper Bennett and Maradudin¹ presented a calculation of the lattice-dynamical effective charges in zinc-blende-structure crystals. Their approach was to calculate, using a pseudopotential technique, the charge density $\rho_0(\mathbf{r})$ in a unit cell with the atoms at their equilibrium sites and a new charge density $\rho(\mathbf{r})$ with the two sublattices displaced a relative distance $\hat{\mathbf{d}}$. They identified the effective charge e^* , i.e., the moment per unit displacement $|\hat{\mathbf{d}}|$, with

$$\lim_{|\hat{\mathbf{d}}| \rightarrow 0} |\hat{\mathbf{d}}|^{-1} \int_{\text{cell}} \hat{\mathbf{d}} \cdot \mathbf{r} [\rho(\mathbf{r}) - \rho_0(\mathbf{r})] d^3r. \quad (1)$$

This approach is very appealing, since the translation symmetry of the crystal is preserved under the displacements, and calculation of both $\rho(\mathbf{r})$ and $\rho_0(\mathbf{r})$ are computationally straightforward. With the advent of new techniques² for efficient computation of $\rho(\mathbf{r})$ using only a few points in the Brillouin zone (BZ), this approach would appear to yield a simple method for computation of any polarization effect, for example, linear and nonlinear dielectric constants, piezoelectric constants, and effective charges.

The purpose of this comment is to point out that integrals of the form (1) are not complete expressions for the polarization. The total polarization is made up not only of the sum of dipole moments of the constituent entities, in this case unit cells, but also contributions that result from transfer of charge between the entities. The latter are not included in (1). In a calculation of the polarization from the electronic states of crystal, the charge-transfer term is always present unless it is excluded by symmetry. We shall see that in nontrivial cases it is impossible to choose a cell *a priori* for which this term vanishes.

The contributions to the macroscopic polarization $\vec{\mathbf{P}}$, in addition to that given in integrals of the form (1), can be derived formally from the basic definition of $\vec{\mathbf{P}}$,

$$\vec{\mathbf{P}} = \Omega^{-1} \int_{\text{cell}} \vec{\mathbf{P}}(\mathbf{r}) d^3r, \quad (2)$$

where $\vec{\mathbf{P}}(\mathbf{r})$ is the polarization as a function of position related to $\rho(\mathbf{r})$ by

$$\vec{\nabla} \cdot \vec{\mathbf{P}}(\mathbf{r}) = -\rho(\mathbf{r}), \quad (3)$$

and where Ω is the cell volume. Integration of Eq. (2) by parts and use of Eq. (3) yields

$$\vec{\mathbf{P}} = \Omega^{-1} \int_{\text{cell}} \mathbf{r} \rho(\mathbf{r}) d^3r + \Omega^{-1} \int_{\text{surface}} \mathbf{r} [\hat{\mathbf{n}} \cdot \vec{\mathbf{P}}(\mathbf{r})] ds, \quad (4)$$

where $\hat{\mathbf{n}}$ is outward surface-normal unit vector. The first term is the one considered by Bennett and Maradudin.¹ The second involves an integral over the surface charge density $\hat{\mathbf{n}} \cdot \vec{\mathbf{P}}(\mathbf{r})$, which is the charge transferred across the cell boundary.³ The role of the surface term is well known in electrostatics.³ It is clear from Eq. (4) that knowledge of the charge density in a unit cell in a periodic crystal is not sufficient to determine the polarization. Precise definitions³ of $\vec{\mathbf{P}}(\mathbf{r})$ needed in Eq. (4) can be given in terms of all the charges in the crystal. For our purposes, however, it is sufficient to note that $\vec{\mathbf{P}}(\mathbf{r})$ is nonzero. We shall only examine the invariance properties of the terms given in Eq. (4). In actual computations a different form for the polarization is more useful.

It is particularly important to note that each of the two terms in the polarization in Eq. (4) depend upon the particular choice of the boundaries of the unit cell. Thus the magnitudes of the two terms are both functions of the choice of the cell, and only their sum is invariant. Moreover, the cell can be chosen to have lower symmetry than the crystal, so that, in general, symmetry requirements are intrinsic only to the total polarization and not to the two individual terms in (4). Thus neither the correct magnitude nor symmetry requirements of $\vec{\mathbf{P}}$ are in general given by either term in (4) separately. For example, even in a diamond-structure crystal in which there can be no effective charge, the first term in Eq. (4) may be nonzero depending upon choice of the cell. The boundaries of the cell chosen by Bennett and Maradudin¹ pass through atoms on only one sublattice

and there appears to be no reason that $\vec{P}(\vec{r})$ should vanish on the surface. Thus their calculation of only the first term in Eq. (4) would be expected to yield a nonzero $e\vec{r}$ even for diamond. To insure that each term is separately zero, one would have to define a cell with boundaries which pass through the centers of inversion at the midpoints between neighboring atoms. In the general case in which $e\vec{r} \neq 0$ by symmetry, there is no center of inversion between atoms, and it is *impossible* to choose a surface *a priori* for which the surface integral vanishes.

A model for the surface term has been discussed by the present author in a comment⁴ concerning the piezoelectric effect. There it was shown that in an ionic-charge-transfer model for zinc-blende crystals, the surface term can be expressed as the moment of the charge accumulation on the "surfaces" of a finite crystal. The division between "bulk" and "surface" terms was shown to be arbitrary, and only with both terms included does one find the correct symmetry of the piezoelectric coefficients. Neglect of the surface term within this model led Woo and Landauer⁵ to predict a piezoelectric effect which violated the requirements of crystal symmetry.

A better approach to the calculation of any of the material relations involving polarizations (dielectric constant, effective charge, piezoelectric constants, etc.) is the method of long waves, i. e.,

the long-wavelength limit of finite-wave-vector ($\vec{q}$) expressions. Then one evaluates $\lim_{q \rightarrow 0} \vec{P}(\vec{q})$ rather than $\vec{P}(\vec{r})$ on some particular surface. This eliminates the need for choosing an arbitrary unit cell. Moreover, in practice, $\vec{P}(\vec{r})$ would be calculated by a transform of $\vec{P}(\vec{q})$ involving all the states $\vec{q}$ in the BZ so that $\vec{P}(\vec{r})$ is much more difficult to calculate than is $\lim_{q \rightarrow 0} \vec{P}(\vec{q})$. The full expressions for the dielectric tensor⁶ and effective charge tensors⁷ in terms of the electronic band states and ion-electron potential are well known. Similar expressions would hold for the piezoelectric constant.⁸

In conclusion, it has been shown that the polarization of a crystal cannot be derived solely from the charge density within a unit cell. The effects of charge transfer between cells must also be included. This latter part of the polarization is omitted in the procedure for calculating effective charges given by Bennett and Maradudin.¹ The necessity of the charge-transfer term is clear, since not only does it affect the magnitude of the calculated polarization, but also it is essential for the final result to be independent of the choice of the cell. In actual calculations of the polarization from electronic states of an infinite periodic crystal, it will always be simpler to eliminate the unwieldy separation of the polarization into the above arbitrary contributions, and instead to utilize the long-wavelength limit of finite-wave-vector expressions.^{6,7}

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