PHYSICAL REVIEW B **66**, 092106 (2002)

Calculation of polarization

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(Received 31 July 2002; published 30 September 2002)

It has been argued that a recent advance in the theory of polarization implies that Clausius-Mossotti type models of polarization, which express polarization in terms of the dipole moments of overlapping atomiclike densities, are fundamentally flawed. Here we show the argument is unjustified.

DOI: 10.1103/PhysRevB.66.092106 PACS number(s): 77.22.Ej, 63.20.Dj, 71.15.Mb

I. INTRODUCTION

The polarization of a crystal is its dipole moment $\mathbf{p}_c$ divided by its volume V_c. This quantity is only defined to within a constant because its value will depend on surface structure. However, a *change* in polarization is given uniquely by $\Delta\mathbf{P}=\Delta\mathbf{p}_c/V_c$ for large crystals.

Martin[1] has shown that one cannot unambiguously compute a change in polarization from changes in charge density that occur within a unit cell volume of the crystal, because the result, in general, will depend on the particular unit cell volume selected. This posed a problem for band-structure methods that went unsolved until King-Smith and Vanderbilt[2,3] cast the change in polarization in terms of a current density, which is ultimately determined by integrations of quantities over the Brillouin zone and a Berry phase.

While this was an important advance for band-structure methods, unfortunately it also has been used (incorrectly) to imply that more direct approaches based on overlapping atomiclike densities are fundamentally flawed.[4,5] Examples of overlapping-atom models vary in their levels of sophistication, from methods that calculate atomiclike densities from a density-functional approach,[6–9] to early models of lattice dynamics[10,11] based on this principle. Following Resta,[4] we call such models Clasius-Mossetti (CM) type models, and use the term "extreme" CM-type models to identify systems whose atomiclike charges are so localized that they are nonoverlapping. On the other hand, Souza *et al.*[5] state that the CM approximation itself implies nonoverlapping charge distributions. We believe the definition of CM-type models offered in Sec. II is probably closer to the original idea leading to the CM equation. According to Scaife[12] the concept of isolated charges was introduced by Faraday to ensure the insulating property of the medium. In other words, the charges in a CM-type model are isolated from each other in the sense that they would be in an insulator—they do not move from site to site.

The argument that CM-type models are fundamentally flawed is simple. It goes as follows: (1) Martin[1] has shown that polarization defined in terms of the charge density in a unit cell is ambiguous. (2) This is true for any model in which the charge density is nonzero everywhere in the unit cell. (In other words, the argument would not apply to extreme CM-type models.) (3) Thus any *realistic* CM-type model is fundamentally flawed.

This argument would be correct if CM-type models determined polarization (as assumed in Martin's paper) by integrating over a unit cell volume. In fact, they do not. Integrations are carried out over all space. We continue the discussion of polarization as described by CM-type models.

II. POLARIZATION FOR CLAUSIUS-MOSSOTTI TYPE MODELS

Here we offer a general definition of CM-type models for which the calculation of polarization is unambiguous. Specifically, CM-type models (1) express the total charge density of a system as a sum over atomiclike densities that are localized in space, and (2) have fixed total charge in each atomiclike density. No assumption is made regarding the amount of overlap between the charge density of a given atomic site and that of its neighbors.

The total electron density is given by

$$n(\mathbf{r})=\sum_{i=1}^{N_c} n_i(\mathbf{r}-\mathbf{R}_i), \tag{1}$$

where $\mathbf{R}_i$ are the positions of the N_c atomic nuclei in the system. At this point our system could be any form of matter, i.e., solid, liquid, or gas. However, since the focus of this discussion is a description for the crystalline forms of matter, we call our system a crystal. The density at each site i can be written in the form

$$n_i(\mathbf{r})=\sum_{l,m} n_{l,m}^{(i)}(r)Y_{l,m}(\hat{\mathbf{r}}). \tag{2}$$

where each n_i is expressed about an origin at $\mathbf{R}_i$ and the radial functions $n_{l,m}^{(i)}(r)$ are assumed to be localized in a space that is small compared to the size of the crystal. We note that this way of expressing the charge density is completely general as long as the spherical harmonic expansion is summed to sufficiently high values of l and m and the radial functions are given sufficient variational freedom.

As the positions of the atomic nuclei are varied, the $n_{l,m}^{(i)}(r)$ functions adjust to minimize the total energy of the crystal. However, this does not change the amount of charge for any of the atoms (or ions). Monopole moments have fixed values, with

$$Q_i = \sqrt{4\pi}\int_0^{\infty} n_{0,0}^{(i)}(r) r^2 dr \tag{3}$$

giving the number of electrons on site i. Having fixed monopole moments is a necessary condition that permits a simple treatment of polarization. Otherwise, ambiguity similar to that pointed out by Martin[1] would be present, because any of the infinitely many equivalent sites could receive the charge transferred from a given ion. Empirical models impose the fixed monopole condition in order to treat insulators properly, while a first-principles approach starting from Eqs. (1) and (2) predicts fixed monopoles for insulators.[9,13,14] We can carry this one step further and say that if such a model were to make the prediction of charge transfer (variable monopoles) for a known insulator, that would imply the breakdown of some approximation of the method.

For simplicity, we assume our crystal has zero net charge: $\Sigma_{i=1}^{N_c}(Z_i - Q_i) = 0$, where Z_i is the charge of the ith nucleus. The total dipole moment of the crystal is, by definition,

$$\mathbf{p}_c = \sum_{i=1}^{N_c} Z_i \mathbf{R}_i \, . - \int_{\infty} \mathbf{r} n(\mathbf{r}) d^3 r, \tag{4}$$

where $\int_{\infty} d^3 r$ implies integration over all space. Substituting Eq. (1) into Eq. (4) we have

$$\mathbf{p}_c = \sum_{i=1}^{N_c} \left\{ Z_i \mathbf{R}_i - \int_{\infty} \mathbf{r} n_i(\mathbf{r} - \mathbf{R}_i) d^3 r \right\}. \tag{5}$$

Changing the variable of integration to $\mathbf{r} - \mathbf{R}_i$ gives

$$\mathbf{p}_c = \sum_{i=1}^{N_c} \left\{ Z_i \mathbf{R}_i - \int_{\infty} (\mathbf{r} + \mathbf{R}_i) n_i(\mathbf{r}) d^3 r \right\}. \tag{6}$$

Upon substituting Eq. (2) into Eq. (6) it is evident, from the orthogonality of the spherical harmonics, that only the monopole term ($l = 0$) contributes to $\int_{\infty} n_i(\mathbf{r}) d^3 r$, and only the dipole terms ($l = 1$) contribute to $\int_{\infty} \mathbf{r} n_i(\mathbf{r}) d^3 r$. Equation (6) becomes

$$\mathbf{p}_c = \sum_{i=1}^{N_c} \{ (Z_i - Q_i) \mathbf{R}_i + \mathbf{p}_i \}, \tag{7}$$

where $Z_i - Q_i$ is the charge of each atom (or ion) and the x, y, and z components of $\mathbf{p}_i$ are, respectively,

$$p_x^{(i)} = \sqrt{\frac{2\pi}{3}} \int_0^{\infty} r^3 [n_{1,-1}^{(i)}(r) - n_{1,1}^{(i)}(r)] dr, \tag{8}$$

$$p_y^{(i)} = -\sqrt{\frac{-2\pi}{3}} \int_0^{\infty} r^3 [n_{1,-1}^{(i)}(r) + n_{1,1}^{(i)}(r)] dr, \tag{9}$$

$$p_z^{(i)} = 2\sqrt{\frac{\pi}{3}} \int_0^{\infty} r^3 n_{1,0}^{(i)}(r) dr. \tag{10}$$

As stated at the beginning, the actual value of the dipole moment, or polarization, of a macroscopic crystal is not well defined. To illustrate, consider a crystal of alternate layers of + and − charges. Transferring one surface layer to the other side of the crystal reverses the polarization. On the other hand, if a macroscopic field is applied to the crystal, then the resultant change in polarization is a well defined bulk property given by

$$\Delta \mathbf{P} = \frac{1}{V_c} \sum_{i=1}^{N_c} \{ (Z_i - Q_i) \Delta \mathbf{R}_i + \Delta \mathbf{p}_i \} \tag{11}$$

where $\Delta \mathbf{R}_i$ and $\Delta \mathbf{p}_i$ are the resultant changes in the positions and dipole moments of the ions. If N_c is large compared to the number of surface ions, then

$$\Delta \mathbf{P} = \frac{1}{V} \sum_{i=1}^{N} \{ (Z_i - Q_i) \Delta \mathbf{R}_i + \Delta \mathbf{p}_i \}, \tag{12}$$

where N is the number of atoms in one structural unit of the crystal and $V = V_c N / N_c$. We avoid using the term "unit cell" because, in a CM-type model, polarization is *not* determined by integrations over any particular cell with volume V. As we have seen, integrations required to define polarization are carried out over all space. Thus, there is nothing fundamentally wrong with the treatment of polarization using CM-type models.

In summary, the advance in band-structure methods for calculating polarization[2–4] says nothing about the validity of formulations based on CM-type models. Assertions to the contrary are evidently motivated by the false assumption that CM-type models attempt to calculate polarization by performing integrations over a single unit cell.

ACKNOWLEDGMENTS

We are grateful for helpful comments from Dr. Dimitri Papaconstantopoulos, Dr. David Singh, and Professor John Hardy. This work was supported by the Office of Naval Research.

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