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Elasticity effects in electronic structure calculations with periodic boundary conditions

Murray S. Daw

Department of Physics and Astronomy, Clemson University, Clemson, SC 29634, USA

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Abstract

We investigate the effects of elastic interactions between defects in electronic structure calculations with periodic boundary conditions. Our approach, building on the work of Toshio Mura [Proc. Roy. Soc. 280 (1964) 1383], is based on the distortion tensor and the topology of the defects and does not involve evaluating sums of long-range functions. We construct solutions in a straight-forward way that makes them easily applied to electronic structure calculations. The results explain how to interpret volume changes in systems with periodic boundary conditions. We also show that the periodicity may be chosen in such a way as to minimize the elastic effects of the boundary condition.

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The common use of periodic boundary conditions for electronic structure calculations naturally brings up questions about artifacts due to the boundaries [1]. In particular, recent attention has been focused on the nature of the stress-fields produced by a periodic array of defects and how those may affect the calculations.

This is an important issue, for example, in the examination of the effects of stress on dislocation mobility [2]. One would like to know, and be able to control, the complete stress-state of a dislocation to examine how non-glide stress components may affect dislocation motion.

Another simple example nicely illustrates the possibilities. Consider trying to calculate the volume due to a point defect in a material, which one might accomplish by allowing the periodic cell to change volume. It is well known [3] that the volume change is dependent on boundary condition: a point defect in a arbitrarily large but finite medium causes a different change in volume than one in an infinite medium. Keeping that in mind, one might naturally ask whether a calculation with periodic boundary conditions might yield a result appropriate for comparison to experimental conditions or otherwise. Eshelby [4] also showed how the change in volume could be related to the first moment of a force distribution, but that proof relied on boundary conditions appropriate for a finite medium. Is there a corresponding relationship for the periodic case?

Recently several papers [3,5,6] have appeared treating this problem by considering the strain field of a periodic array of defects to be a superposition of the strain fields for those defects isolated in an infinite medium. These superpositions must inevitably deal with issues of conditional convergence. However, the authors of those papers seem unaware of the work in the 60's by Toshio Mura [7]. Mura's approach is very simple and leads immediately to complete solutions; furthermore, his approach also avoids all issues of conditional convergence.

We offer here a representation of Mura's approach. While Mura used an equation of motion approach, our representation is based on a variational form. Although the results are the same, we believe our derivation is a little clearer and more explicit, and the solutions are presented in a simpler form, facilitating the application to electronic structure calculations.

E-mail address: daw@clemson.edu

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To begin, we note that for this class of problems the distortion field (we define distortion as the gradient of the displacement, so $\Delta_{jk} \equiv \partial_j u_k$) is a periodic function of position and so can be expressed in a series of plane waves

$$\underline{\underline{\Delta}}(\underline{r}) = \sum_{\underline{G}} \underline{\underline{\widetilde{\Delta}}}(\underline{G}) \exp(i\underline{G} \cdot \underline{r}) \tag{1}$$

where the $\underline{G}$ are the reciprocal lattice vectors of the periodic array and a tilde over a function refers to its components in reciprocal space. The elastic energy is related to the distortion by

$$W_c = \frac{1}{2} c_{jklm} \int_{\text{cell}} dv \Delta_{jk} \Delta_{lm} = \frac{1}{2} \Omega_c c_{jklm} \sum_G \widetilde{\Delta}_{jk} \widetilde{\Delta}^*_{lm} \tag{2}$$

(repeated indices imply a sum). Our approach is explained almost completely by stating that *at its equilibrium, the distortion minimizes the elastic energy subject to constraints imposed by the defect*. Thus, to form a complete solution, the distortion must match any topological conditions imposed by the defects, and any freedom left in the distortion must minimize the elastic energy in the cell.

In this short paper, we will illustrate the method by solving the two examples mentioned above: the point dilatation and an array of dislocation dipoles.

Consider a point dilatation as an external stress field applied only at the origin, so $\sigma^{\text{ext}}_{jk}(\underline{r}) = M\delta_{jk}\delta(\underline{r})$. The work done by this external stress is

$$W_{\text{ext}} = -\int_{\text{cell}} dv \sigma^{\text{ext}}_{jk}(\underline{r}) \Delta_{kj}(\underline{r}) = -M \sum_G \widetilde{\Delta}_{jj}(G) \tag{3}$$

In the absence of dislocations, the distortion tensor is curl-free, so we have $\underline{G} \times \underline{\underline{\widetilde{\Delta}}} = 0$ which implies that the $G \neq 0$ terms are of the form $\widetilde{\Delta}_{jk} = G_j \tilde{d}_k$. Substituting this into the total energy (including external work) and then minimizing it with respect to each $\tilde{d}(G)$ gives

$$\tilde{d}_m(G) = M(\widetilde{A}^{-1})_{mj} G_j / \Omega_c \tag{4}$$

where $\widetilde{A}_{jm} = c_{jklm} G_k G_l$. For the $G = 0$ term we minimize W_{tot} with respect to $\widetilde{\Delta}_{jk}(0)$ which gives

$$\widetilde{\Delta}_{jk}(0) = M s_{jkll} / \Omega_c \tag{5}$$

with s being the elastic compliance. The volume expansion is then

$$\delta V = \Omega_c \widetilde{\Delta}_{jj}(0) = M s_{jjkk} \tag{6}$$

For an isotropic medium, $\delta V = \frac{3M}{3\lambda + 2\mu}$ which is the (known) result for a *finite* medium [3].

In fact, one can show easily that the $G = 0$ term corresponds in structure to the image term found for a point dilatation in the center of a finite sphere. Thus, the volume expansion for *periodic boundary conditions* is the same as one would have for a *finite medium*, and we have shown that it is appropriate to compare the volume from such calculations with experiment. Using the same approach, one can also demonstrate that the change in volume is still related to the dipole moment of the force distribution f, provided that the force distribution balances to zero net force. Thus the change in volume is

$$\delta V = s_{jjlm} \int_{\text{cell}} dv f_l r_m \tag{7}$$

which is the same as Eshelby's result [4] for a force distribution in a finite medium.

For a more involved case, consider a periodic array of dislocation dipoles, as illustrated in Fig. 1. The distortion field must satisfy the topological condition imposed by the dislocations, which is given by integrating the distortion around a closed path. If the path encloses a dislocation line, then the line integral equals the burger's vector of that dislocation:

$$b_j = \int_{C=\partial S} dl_k \Delta_{kj} = \epsilon_{klm} \int_S da_k \partial_l \Delta_{mj} \tag{8}$$

so the curl of the distortion is the Nye tensor (density of dislocations)

$$\epsilon_{jkl} \partial_k \Delta_{lm} = \alpha_{jm} \tag{9}$$

For a single, straight dislocation passing through the origin along direction $\underline{\xi}$,

$$\alpha(\underline{r})_{jk} = \xi_j b_k \delta(\underline{r}_\perp) \tag{10}$$

where $\underline{r}_\perp$ is the component of $\underline{r}$ perpendicular to $\underline{\xi}$.

Consider a dislocation dipole formed by dislocations of burger's vector $\underline{b}$, line direction $\pm\underline{\xi}$ separated by a dipole vector $\underline{d}$ which is perpendicular to the line direction. We treat the dipole with periodic boundary conditions by setting one periodic direction along $\underline{\xi}$. The other two cell directions (call them $\underline{a}$ and $\underline{b}$) are perpendicular to $\underline{\xi}$ and form a 2D lattice with cell area $\mathscr{A}_c$.

The Fourier transform of the topological condition (Eq. (9)):

$$i\mathscr{A}_c \epsilon_{jkl} G_k \widetilde{\Delta}_{lm} = \xi_j \widetilde{B}_m \tag{11}$$

where

$$\widetilde{B}(G)_j = b_j(\exp(-i\underline{G} \cdot \underline{r}_1) - \exp(-i\underline{G} \cdot \underline{r}_2)) \tag{12}$$

The solution to Eq. (11) for Δ has inhomogeneous and homogeneous parts, the former imposed by the dislocations

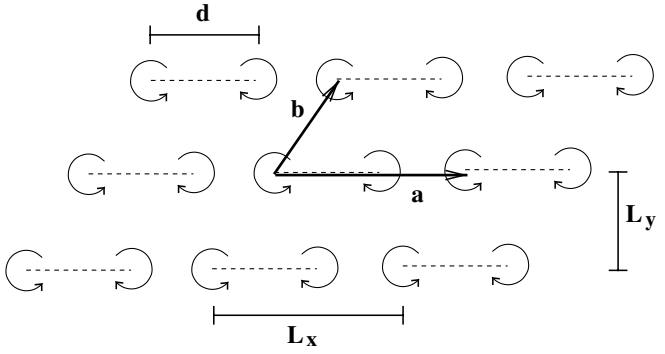

Fig. 1. A periodic array of screw dipoles.

$$\Delta = \Delta^{\text{inh}} + \Delta^{\text{hom}} \tag{13}$$

$$\widetilde{\Delta}^{\text{inh}}_{jk} = \frac{i}{\mathscr{A}_c G^2}(\underline{G} \times \underline{\xi})_j \widetilde{B}_k \tag{14}$$

$$\widetilde{\Delta}^{\text{hom}}_{jk} = G_j \tilde{\chi}_k \tag{15}$$

The homogeneous term is the general solution to $\underline{G} \times \underline{\underline{\widetilde{\Delta}}} = 0$.

The remaining freedom in Δ (that is, χ) is determined by minimizing the energy of the cell (Eq. (2)) with respect to it. Because the different G-components enter the energy separately in the sum, this is easily done

$$\tilde{\chi}_n = -(\widetilde{A}^{-1})_{nj} c_{jklm} G_k \widetilde{\Delta}^{\text{inh}}_{lm} \tag{16}$$

For an isotropic medium, this becomes

$$\underline{\tilde{\chi}}(\underline{G}) = \frac{i}{AG^4}\left((\underline{\xi} \times \underline{G})\underline{G} + \frac{\lambda}{\lambda + 2\mu}\underline{G}(\underline{\xi} \times \underline{G})\right) \cdot \underline{\widetilde{B}} \tag{17}$$

Thus we have constructed the complete solution for a periodic array of dislocation dipoles, except for one detail relating to the singularity at the core. Consider now the distortion field in real-space, obtained by Eq. (1); it is important to consider the convergence of that sum, which appears to be conditional for large G. This difficulty relates back to the properties of a dislocation line in local, linear elasticity, which predicts an (unphysical) singularity at the core of a dislocation. This singularity is caused by the δ-function that appears in Eq. (10), which requires an infinite number of plane waves in its representation. However, it is convenient (and conventional) to tame the singularity by smearing the δ-function [3]. If we smear the core of the dislocation into a Gaussian of spatial width r_s, this carries through in the analysis simply as a multiplicative smearing factor $g(\underline{G}) = \exp[-G^2 r_s^2/4]$. Taking into account such smearing makes the sums absolutely convergent, and allows one to set an upper limit on the size of the G-vectors required in the sums.

We illustrate here the solution for screw dislocations. In the case of screw dislocations, the homogeneous term in Eq. (17) vanishes. To be particular, let us consider the following, suggested by one recent calculation [2] of stress effects on dislocations: $\underline{a} = L_x\hat{x}$, $\underline{b} = sL_x\hat{x} + L_y\hat{y}$, with the screw dipole separated parallel to $\underline{a}$ by a distance d. The single offset parameter s allows one to stack up the dipoles in a variety of ways, so it makes a nice case to consider here. Specifically, we consider $L_y = L_x/2$, and $r_s = L_x/1000$.

In Fig. 2, we show the distortion fields for four periodic cells containing a screw dipole for $d = L_x/2$ for two cases: $s = 0$ and $s = 1/2$. The fields are manifestly periodic and well-behaved. The singularity of the fields is controlled by the smearing of the cores.

In Fig. 3, we show the elastic energy (per unit cell per length) as a function of dipole separation d for two values of cell offset s. Clearly for this geometry the dislocations are in unstable equilibrium for $d = 1/2$. If the dipole is allowed to collapse, the energy vanishes; this is possible because we have smeared the dislocation cores and so the annihilation

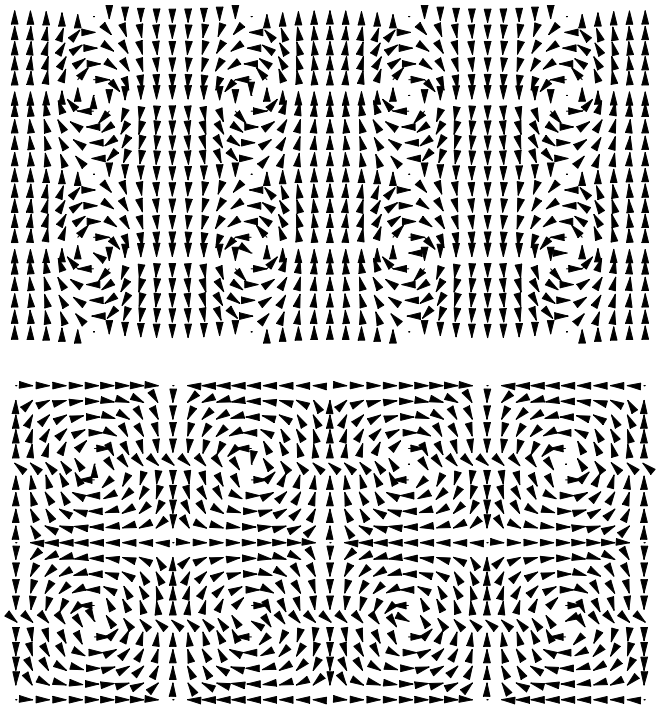

Fig. 2. The distortion field for $s = 0$ (top panel) and $s = 1/2$ (bottom panel) for geometry in Fig. 1. The vector components are $(\Delta_{xz}, \Delta_{yz})$.

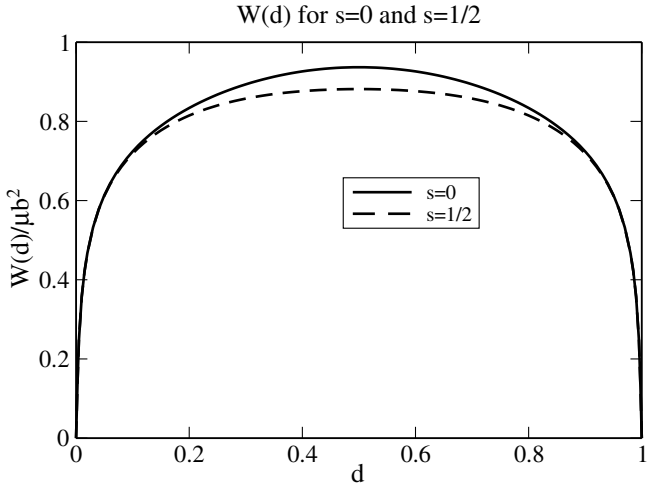

Fig. 3. The cell energy for the geometry of Fig. 1 as a function of dipole separation d/L_x and two values of cell offset s.

of oppositely-signed dislocations can occur without singularity. Likewise, expanding the dipoles beyond the equilibrium causes the members to annihilate with oppositely-signed partners from other periodic cells. One can show numerically that the energy depends logarithmically on r_s.

Now we can examine the issue of the stress on a dislocation caused by all of the dislocations in the periodic array. To do this, we simply subtract the distortion due to a single dislocation, the singularity of which has been softened to

$$\Delta^0_{j3} = \frac{b}{2\pi(x^2+y^2)}(-y\hat{x}+x\hat{y})_j\left[1-\mathrm{e}^{-(x^2+y^2)/r_s^2}\right] \tag{18}$$

The resulting *background* distortion field ($\Delta^b \equiv \Delta - \Delta^0$) vanishes (because of symmetry) at the point where the dislocation resides, but its gradient does not vanish. It is of interest to know how significant this gradient is. To proceed, we define

$$\Delta^{b'}_{jk} = \partial_j \Delta^b_{k3} \tag{19}$$

as a 2×2 matrix, which we can characterize in terms of its two eigenvalues. It is easy to demonstrate that the eigenvalues sum to zero, so in Fig. 4, we show the positive eigenvalue as a function of s. Indeed, as described by Lin and Chrzan [2] the choice of $s = 1/2$ causes the stress and its gradient to vanish.

Finally, we consider how to construct the displacement field, which may be useful in generating starting positions for electronic structure calculations. The displacement is obtained relative to a reference point by performing a line integral

$$u_j(\underline{r}_b) = u_j(\underline{r}_a) + \int_{\text{path } a\to b} dl_k \Delta_{kj} \tag{20}$$

In view of the fact that the curl of Δ is non-zero at a dislocation core (Eq. (9)) it is clear that the displacement field will be dependent on the path chosen. This is equivalent to noting that the precise definition of the displacement field depends on *history*. In other words, it is possible to form the same periodic array of dislocations in many ways. The distortion depends only on the final positions of the dislocations, but the displacement field depends on *how* the dislocations were placed there. By defining a path which does not cross the line between a pair of dislocations, we implicitly place the cut for the displacement field along that line. As shown in Fig. 5, if the first part of the path is parallel to $\underline{b}$ and the second parallel to $\underline{a}$ (and the dipole vector), the path respects the cut between the members of the dipole. The resulting displacement fields are shown in Fig. 6.

It is clear now that the displacement field is *not* periodic, contrary to the statement of some authors [6]. A simple argument demonstrates why the displacement field cannot be periodic. Consider an arbitrary periodic function $f(r)$. If we integrate any derivative of f over a periodic cell, then this must vanish. So, $\int_{\text{cell}} \mathrm{d}v\partial_j f = 0$. If the displacement field $u_k(r)$ were periodic, then $\int_{\text{cell}} \mathrm{d}v\partial_j u_k = 0$ for any k and j, and so the change in cell volume would also vanish because $\delta V = \int_{\text{cell}} \mathrm{d}v\partial_j u_j = 0$. Alternatively, consider that

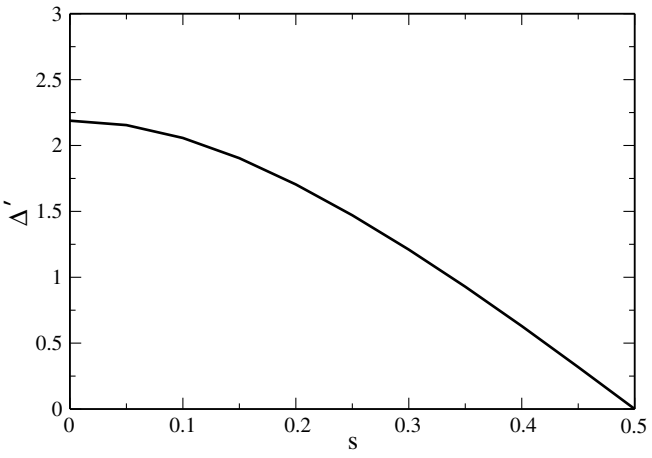

Fig. 4. Gradient of the *background* distortion field as a function of cell offset for the geometry of Fig. 1 and for an isotropic medium.

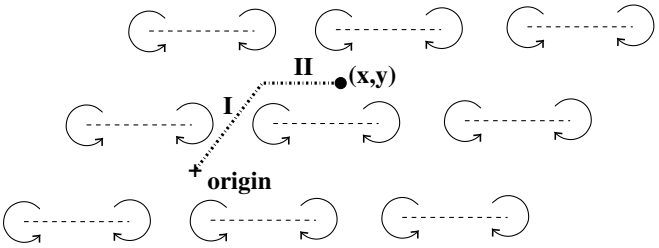

Fig. 5. The displacement field depends on defining a path which does not cross the cut between members of a dipole.

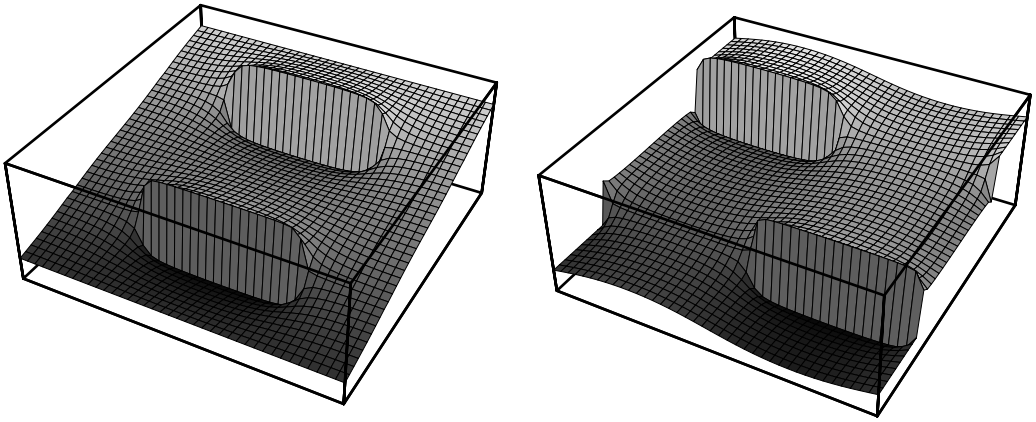

Fig. 6. The displacement fields for a screw dipole in an isotropic medium and with the geometry of Fig. 1. Two values of cell offset are shown: $s = 0$ (left panel) and $s = 1/2$ (right panel).

the overall effect of opening a periodic array of screw dipoles is to produce an overall shear, so the displacement must be cumulative and not periodic, as seen in the Fig. 6.

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