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SEMICONDUCTOR DYNAMICS FROM FIRST PRINCIPLES: PHONONS, FORCES,
AND DIELECTRIC PROPERTIES

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Recent applications of 'direct' methods for *ab initio* treatment of dynamical properties of semiconductors are summarized with emphasis upon our own results based on the Local Density Functional. Extending beyond the 'frozen phonon' approach, the applications include treatment of forces (in perfect structures and crystals with substitutional defects) and a 'direct' study of certain dielectric properties.

1. INTRODUCTION

The approach termed 'direct' gave a new impetus to *ab initio* theories of semiconductor dynamics and its present applications extend far beyond the determination of energies of a few isolated phonons, its sole ambition at the origins. In contrast to the classical approach, which considers a phonon as a small perturbation to be handled by dielectric response theory¹, the direct methods view a crystal with periodic distortions as a new crystal structure, to be dealt with as a completely new system, independent of the undistorted one. The direct methods became practicable with development of the Local Density Functional² (LDF) - though the general idea does not depend on this particular method and is not restricted to total energy, either. The direct approach is presently applied along three distinct lines, that derive from the same Hamiltonian: energies, forces and electrostatics.

Difference in *total energies*, evaluated for structures with and without phonon-induced displacements, defines the energy of 'frozen phonon'. Clearly, an extreme accuracy is needed because the small differences are of order 0.01 % of total energy, but using the LDF the errors in calculated vibrational frequencies are typically ~3%. The method of frozen phonons only applies to several high-symmetry modes but, as it does not restrict the amplitude of displacements, it provides a tool for studying anharmonicity. Using this concept, Grüneisen parameters were evaluated and soft-mode phase transitions in GaAs predicted³. Also, we have shown how the phonon displacement patterns can be determined, simultaneously with frequencies, in cases where

the symmetry does not predict them completely⁴.

The frozen phonon approach can be equivalently formulated in terms of *forces*; these can be evaluated by applying the Hellmann-Feynman theorem to self-consistent charge densities used for calculation of total energy. Physically it is irrelevant whether we proceed via forces or via energies because both approaches are based on the same expression for total energy (density functional). Nevertheless, the force approach allows to get out of the frozen phonon framework and leads to a more general treatment of lattice dynamics - which, in a sense, means a return to sources⁵: sets of force constants can be evaluated which determine the entire phonon dispersion along a selected direction of reciprocal space^{6,7}.

Finally, it has not remained unnoticed that the self-consistent charge densities - the starting point of either of the above paths - encompass the complete information about the *electrostatics* of the electron-ion system. The self-consistent solutions can thus be employed to determination of the dielectric response and can supply some macroscopic dielectric properties.

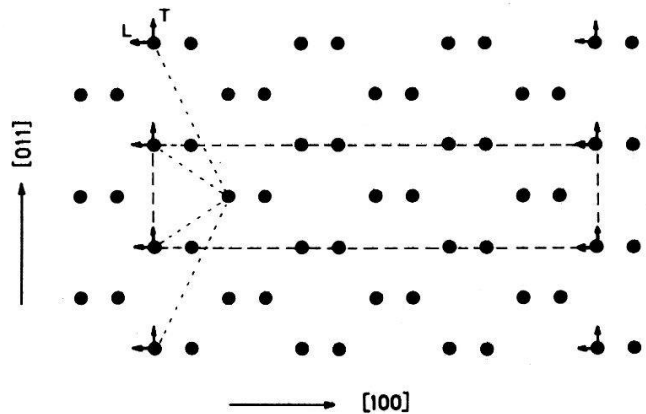
Our work based on the first two concepts was summarized in a recent review⁸; in the present paper, which intends to be a loose continuation of Ref. 8, we report the latest applications of the force approach (Section 2) and elaborate upon the direct treatment of dielectric properties (Section 3).

2. FORCE CONSTANTS

The self-consistent charge densities supply complete information about forces acting on atoms; giving an atom a displacement and finding the forces acting on its neighbors suggests the possibility of determination of force constants.

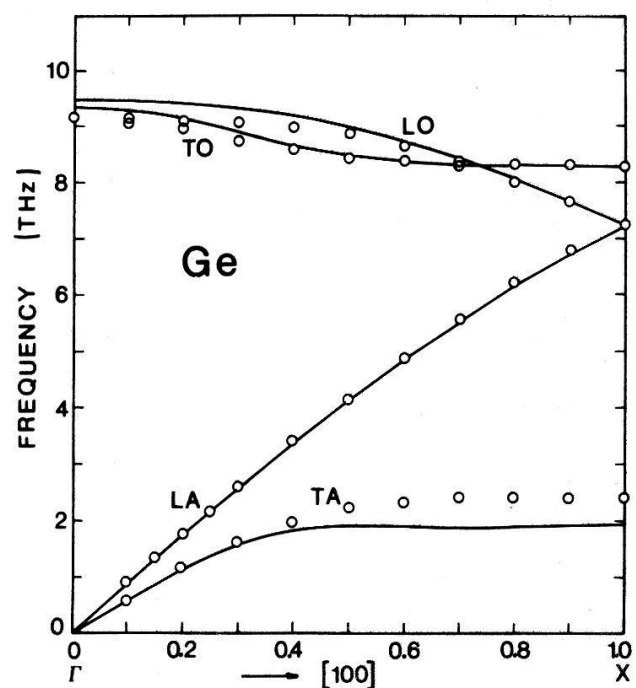
2.1. Perfect Crystals. As most of the self-consistent calculations are performed on supercells of limited dimensions, any given atom will perceive a *sum* of forces coming from *several* displaced equivalent sites (see dotted lines in Fig. 1), so that only the *interplanar* force constants $K(\ell\kappa; \ell'\kappa')$ are determined, rather than the interatomic ones $\Phi_{\alpha\beta}$. The planar force constants K are well defined sums of the interatomic ones, but a conversion of the former into latter is not possible in general, because the slow fall-off of Φ 's makes the numerical problem ill-defined. The set of K 's determines, however, the entire phonon dispersion along a selected direction of reciprocal space^{6,7}: For a phonon propagation along, say $[100]$ direction, all (100) planes

Fig. 1. Periodic supercell used for determination of $[100]$ interplanar force constants in Ge. Entire planes are given longitudinal or transverse displacements and any given atom feels the force produced by displacements of all atoms in the shifted plane (dotted lines).



vibrate as rigid units and their vibrations can be assimilated to oscillations of a linear chain - problem which leads to a 2×2 secular equation, however far the interactions may extend. Fig. 2 shows a result for Ge obtained⁹ on the supercell of Fig. 1. Planar force constants decrease relatively fast with distance, however, all the forces up to the 5th neighbors had to be included in Fig. 2 so as to reproduce the flat TA branches; the remaining discrepancy at TA(X) is believed to be consequent to the choice of Slater's exchange. With the dispersion of eigenfrequencies one also gets the displacements, the dispersion of eigenvectors. In case of polar crystal, such as GaAs, the procedure is somewhat more complicated because the longitudinal displacement pattern generates a macroscopic electric field whose contribution to forces has to be separated; this is explained in Ref. 6 and the field itself is further discussed in Section 3.2. Planar force constants can be related to the *internal strain parameter* ζ and expressions were derived¹⁰ for tetrahedral semiconductors, giving ζ in terms of $K(0,n)$ for $[100]$ and $[111]$ directions. The rarity of present experimental determinations of ζ and the often contradictory results suggest that the *measured* values of ζ be checked against those calculated *ab initio* !

Fig. 2. Phonon dispersion calculated from planar force constants (solid lines), compared with experiment (circles). Transverse forces up to the 5th and longitudinal up to the 4th neighbors are accounted for.¹⁵ (From Ref. 9.)



2.2. Defects. Replacing the atoms of the displaced plane by defects (Fig. 3), one can determine the *variation* $\Delta K(0,n)$ of the planar forces caused by substitutional impurities - simply by repeating calculations of the Section 2.1 twice: with impurities and with the original atoms. The $\Delta K(0,n)$ decrease with distance considerably faster than the $K(0,n)$ themselves and the problem of conversion $\Delta K(\ell\kappa; \ell'\kappa') \rightarrow \Delta\Phi(\ell\kappa; \ell'\kappa')$ is no more ill-defined; even when working in other than planar geometries, it is possible to separate the contributions from individual atoms and evaluate variations of interatomic force constants $\Delta\Phi$.

Although the very short range of $\Delta\Phi$ seems to make the problem easier for defects than for perfect crystals, the essential complication comes from the *lattice relaxation* around the defect. Knowing the amount of relaxation is crucial to understanding any property related to defects and the LDF certainly could be used to finding the new atomic positions, by minimization of total energy; the direct determination would only require working on supercells of considerable size. It was, however, noticed¹¹ that the *effect* of relaxation on $\Delta\Phi$ can be worked out in a simple additional calculation, without even knowing explicitly the exact amount of relaxation.

The neighbors of the impurities shown in Fig. 3 in their unrelaxed positions are, in fact, displaced from their new (relaxed) equilibrium positions; consequently, the force they experience originates 1) from the displaced defects, and 2) from the displacements of the 'probe'-atom itself. As the total force resulting from several displacements is additive in harmonic approximation, the second contribution is readily determined in a separate

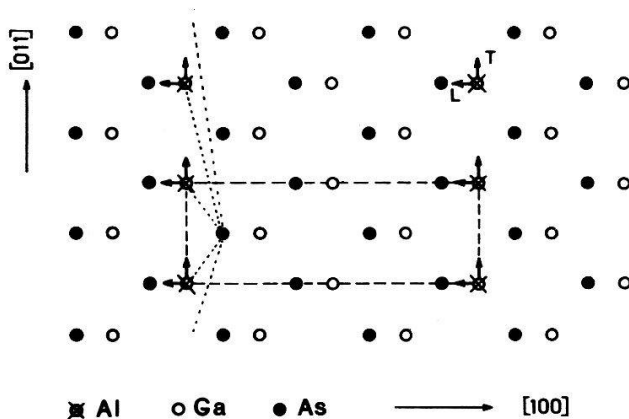


Fig. 3. Supercell used for finding the variation of force constants around a substitutional Al in GaAs. (From Ref. 11.)

self-consistent calculation, on a supercell with defects undisplaced and their neighbors unrelaxed, i.e. situated at the original sites of perfect crystal. The idea is that from forces caused by displacements, or from their variation caused by introduction of impurity, one has to subtract the force due to 'non-relaxation'; no knowledge of the amount of relaxation itself is required. This way of accounting for relaxation

is rigorous - to first order, i.e. as long as the relaxation is small.

The first results given in Ref. 11 for GaAs:Al were obtained in planar geometry of Fig. 3. They confirmed that, indeed, ΔK or $\Delta\Phi$ can be neglected for 3rd neighbors, and determined the variations for first and second neighbors. For the first neighbors, the $\Delta\Phi$ corresponds to strengthening of the bonds; the second neighbor variation is weak but perceptible, and it means strengthening of one component of $\Phi_{\alpha\beta}$, weakening of another. Note that in planar geometry only a part of the information for second neighbors is accessible; in fact, the configuration of Fig. 3 is somewhat artificial and another geometry, more convenient for the defect problem, was suggested in Ref. 11. However, an *estimate* of the amount of relaxation can be given if the planar configuration is used¹¹ - however superfluous its knowledge may be for the present purposes.

3. DIELECTRIC PROPERTIES

Two quantities characterize the ground state in the LDF formalism: total energy E^{tot} and electronic charge density $n(\vec{r})$. Although the description offered by $n(\vec{r})$ is less detailed than the one provided by the many-particle wave function, the LDF assumes that the charge density - and equivalently the potential consistent with it - carries the relevant information about ground state properties. Through Poisson's equation the distribution of charges defines the *electrostatics* of the system, so that with self-consistent solutions of the LDF equations we possess the information about the (local) electric field, including its fast variations from atom to atom. *A fortiori*, we are also in possession of all information about *macroscopic* fields, defined as space averages of the local (microscopic) ones. The self-consistent or Hartree potentials, V^{sc} or $V^{\text{H}} \equiv V^{\text{sc}} - V^{\text{xc}}$ thus enable to 'probe' the response of dielectric to different perturbations.

3.1. Zero macroscopic field. Displacement pattern shown in Fig. 4a was used for calculation of the longitudinal effective charges e_L^* in GaAs^{3,4,12} - which amounts to determination of polarization $\vec{P}(\vec{r})$ produced by displacement of the respective atoms. The effective charges, determining the TO(Γ)-LO(Γ) splitting, are needed because the frozen phonon approach cannot handle the LO(Γ) mode, distinguished from TO(Γ) by presence of the macroscopic (i.e. unperiodic) electric field.

Displacement pattern of Fig. 4a does not produce any field in most of the volume of the supercell - but it shifts the respective levels of

potential in the two halves of it. The situation is schematically illustrated in Fig. 4b which shows the *change* in electrostatic potential when two planes, charged with a density σ are given a small displacement \vec{u} : the two dipole layers created by the displacements will produce a *shift* of the levels by the amount $4\pi\sigma u$.

The *actual* self-consistent potential corresponding to the pattern Fig. 4a is shown in Fig. 4c. The fast oscillations from atom to atom are uninteresting for our purposes, on notices, however, the shift of the average levels in one and another half of the supercell - e.g. by comparing with the undisplaced situation shown by dotted lines. For getting the potential difference $\Delta V = 4\pi\sigma u$, we simply took

$\bar{V}^{sc}(A) - \bar{V}^{sc}(B)$; from here $\sigma = e_L^*/A$ where A is the area per atom. The value we found for GaAs³, $|e_L^*| = 0.158 \pm 0.005 |e|$, positive for Ga, negative for As, is 20 % below the experiment. Note that the sign, although physically commonsense, has never been determined experimentally.

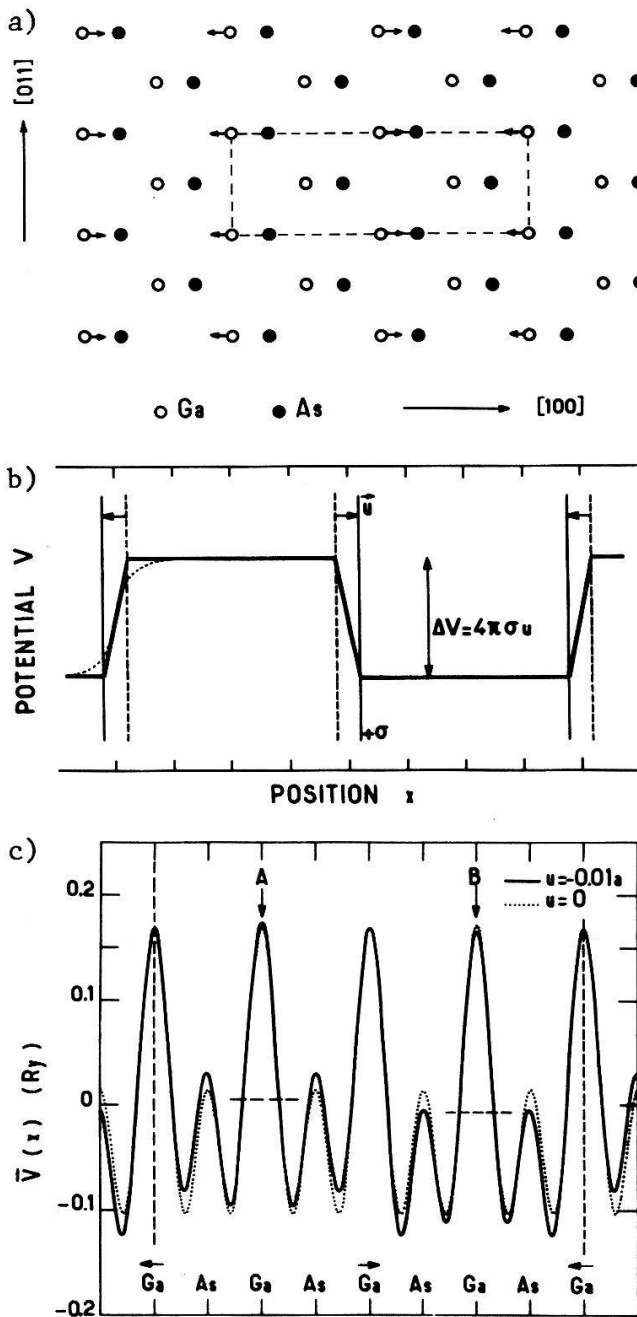


Fig. 4. Evaluation of effective charge $e_L^*(Ga)$. (From Ref. 4.)

a) Two planes of Ga shifted in opposite directions in a quadrupled unit cell of GaAs.

b) Variation of potential caused by displacing charged planes in the pattern (a) - schematic representation. The two dipole layers produce a shift of respective levels of potential^{16,17}.

c) Self-consistent potential obtained for configuration (a) (solid lines), compared with the situation without displacements (dotted lines)¹⁸.

3.2. Nonvanishing macroscopic field. By choosing the displacement pattern differently, one can also find the other effective charge e_T^* - and consequently the dielectric constant of polar crystal, $\epsilon \equiv e_T^*/e_L^*$. The situation described below occurred in a study of vibrations in GaAs⁶; for getting the interplanar forces, one chooses exactly the same pattern as in Ge (Fig. 1); in polar crystal, however, the longitudinal displacement of charged planes produces, in addition to forces, a macroscopic electric field. The resulting electrostatic potential is schematically shown in Fig. 5a. A simple way of arriving at this potential is to represent it as a sum of two contributions (Fig. 5b): potential of a chain of dipole-layers, reminiscent of Fig. 4b, and a depolarizing field, constant over the volume of crystal, which compensates the potential difference at the two ends of the crystal, cancels the surface charges which otherwise would accumulate at both ends, and brings the average electric field in each supercell to zero.

We notice that inside each supercell a net macroscopic field appeared - although the supercell average of this field is zero, as dictated by periodic boundary conditions. Returning to the actual self-consistent potential $\bar{V}^{sc}(x)$, with atom-to-atom oscillations, the slope of the underlying 'saw' can be found as a space average of the $\partial \bar{V}^{sc}/\partial x$ over major part of the supercell volume - we simply took the 'inclination' of the central part of the plot $\bar{V}^{sc}(x)$ (see Ref. 6). This slope determines 1) the 'elevation' $4\pi\sigma u$ of the

Fig. 5a. Variation of potential created by *longitudinal* displacement of Fig. 1 in a *polar* crystal (GaAs) - schematic representation. Periodic repetition of dipole layers produced a *macroscopic field* in large part of each supercell¹⁶. The supercell periodicity is respected and the (supercell-)averaged electric field is zero.

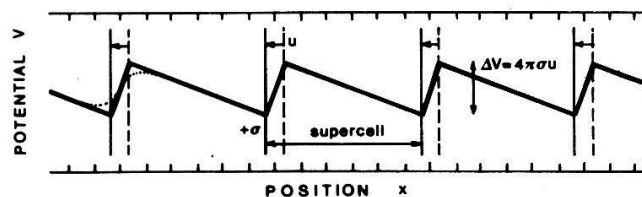
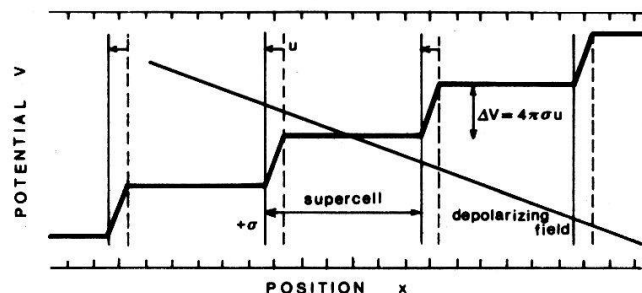


Fig. 5b. Potential of Fig. 5a can be graphically represented as a sum of two contributions: 1) Potential produced by each dipole-layer considered separately, like in Fig. 4b - which, however, does not obey the periodic boundary conditions. 2) Depolarizing field, constant over crystal, which compensates the net potential difference at the two ends of crystal¹⁷.



'saw' - from here e_L^* is found, like in Section 3.1; 2) the intensity E^{macro} perceived in the 'central' elementary cells of each supercell. Contribution of the macroscopic field to the force 'felt' by an atom is $F(\kappa) = e_T^*(\kappa) E^{\text{macro}}$ and, as our experience on GaAs shows, this is the *only* force felt by the atoms distant $\geq 5a/4$ from the displacement, i.e. at the 'central' sites in each supercell. (The atoms close to the displacement perceive, in addition, the short-range distortion of electronic distribution, i.e. the force which was our main concern in Section 2.1.) Applying the Hellmann-Feynman theorem to the self-consistent charge density, we obtain the force on central atom and find e_T^* . The results $|e_L^*| = 0.163 \pm 0.002 |e|$, $|e_T^*| = 1.87 \pm 0.14 |e|$ and $\epsilon \equiv e_T^*/e_L^* = 11.4 \pm 1.6$ compare with the experimental values 0.198, 2.16, 10.9 respectively, and with $|e_L^*| = 0.158 \pm 0.005$ determined in Section 3.1. Note that all these results arose out of determination of phonon dispersion in GaAs, from merely understanding the behavior of fields, and did not require any additional self-consistent calculation.

3.3. External macroscopic field. The dielectric constant was determined in previous Section indirectly, by comparing two different responses (\vec{P} and \vec{F}) to a displacement. Obviously, this approach only applies to polar crystals and, for finding e.g. ϵ of Ge, one has to be able to deal directly with a macroscopic field imposed from outside. There is no reason not to put external potentials into the basic equations of LDF - except for the potential of a field at $\vec{k} = 0$: as it is constant in space, the potential of such field is a monotonic function and its addition destroys lattice periodicity. This difficulty is general and has been encountered in different branches of solid state physics⁵.

The issue we have proposed in Ref. 13 is shown in Fig. 6a: on a sufficiently large supercell repeating the elementary cell a number of times, we impose a saw-like potential which is periodic on supercell and yet it represents a constant field in large regions of space. We can imagine that we had incorporated into the crystal plates of capacitor, a periodic sequence charged alternately + and -. For all practical purposes, we smooth out the cusps, as shown by dotted lines, which physically corresponds to spreading the charge slightly around the 'plates' and which allows us to deal with shorter than infinite Fourier expansions.

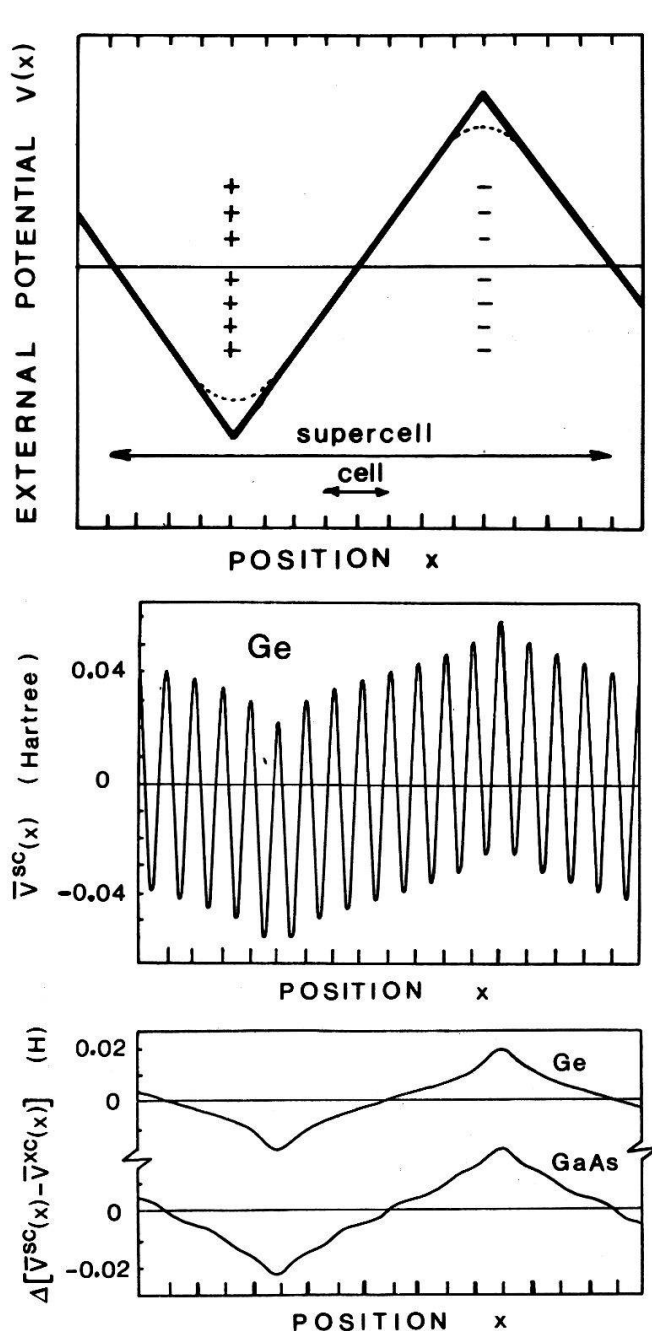
The self-consistency makes the electrons to adapt to V^{ext} and an example of the resulting self-consistent potential is plotted in Fig. 6b.

We find the usual oscillations, the new feature, the underlying saw-like shape, results from the perturbation V^{ext} . So as to visualize the *screened macroscopic field* we remove the fast oscillations in Fig. 6b by subtracting the self-consistent potential of the unperturbed case; their difference (Fig. 6c) is the screened V^{ext} of Fig. 6a. Comparison of the average slopes in Figs. 6a, 6c yields the dielectric constant, from its definition; our present results¹³, 19.1 for Ge and 13.6 for GaAs, are 20 % above the experiment.

Unlike V^{ext} , the screened potential Fig. 6c is not represented by perfectly straight lines; the bumps, barely visible in Ge but clearly apparent in GaAs, are *not* computational noise and they reflect a well defined physical effect: *microscopic variation of local fields*. By treating in the same way $n(\vec{r})$ instead of $V^{\text{sc}}(\vec{r})$, one obtains the analogous local variation of electronic charge density (not shown here); it reflects the off-diagonal elements

Fig. 6. Treatment of *external macroscopic* electric fields. (From Ref.13.)

- a) Saw-like potential, periodic on supercell, used for producing the *constant* electric field in at least one *elementary* cell. The potential can be imagined by incorporating into the system a sequence of capacitor plates, charged alternately + and -. By allowing the charge to spread out of the plates slightly, the sharp edges get rounded and Fourier expansions shortened¹⁷.
- b) The actual self-consistent potential calculated for Ge in the external field shown in Fig. 6a¹⁸.
- c) Screened saw-like potential of Fig. 6a, obtained when the fast atom-to-atom oscillations are removed from Fig. 6b by subtracting the unperturbed self-consistent potential. The ratio of slopes between a) and c) determines the dielectric constant of the material. Small deviations from straight-line shape reflect the microscopic variations of *local fields*¹⁹.



of the dielectric matrix and is in excellent agreement with calculations on perfect infinite crystals, with macroscopic field treated as perturbation within linear response theory¹⁴.

4. CONCLUSION

The apparent novelty of the direct methods consists in dealing with phonons and related quantities in *direct space*. The approach became feasible since Local Density Functional provided a sufficiently accurate scheme for evaluation of total energy of an arbitrary configuration of atoms; in return, numerous successful applications confirmed the validity of the LDF itself. Originally directed to phonon energies, the direct methods then turned to dealing with forces and presently they are extending to fields which have seemed to be a preserve of the response-function approach: to direct treatment of some *dielectric properties*. On the other hand, predictions of quantities inaccessible to experimental determination became possible.

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15. Local pseudopotential used in the calculation is the average of those for Ga and As; exchange and correlation of Slater, other details like in Ref.6
16. The sharp edges are rounded (dotted lines) if the charge is not strictly confined at each plane.
17. Note that the potential V felt by electron is plotted, which has the opposite sign than the electrostatic potential ϕ .
18. $V^{sc}(\vec{r})$ was averaged over y - and z - coordinates, i.e. in the planes parallel with (100).
19. Note that the Hartree potential, rather than the self-consistent one, is used for comparison of slopes.