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Theory of structural properties of covalent semiconductors

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We describe a method to calculate structural properties of semiconductors from the electron-ion Hamiltonian using density-functional expressions for the total energy. The method is applied to Si using an ionic pseudopotential with a plane-wave basis and considering TO (Γ), TA(X), and $C_{11} - C_{12}$ lattice distortions. Harmonic and anharmonic forces and Grüneisen coefficients are shown to be in reasonable agreement with experiment except that additional steps toward self-consistency appear to be essential for the very sensitive TA(X) mode. Charge densities for the distorted crystals show the nature of the electronic forces and the relation to phenomenological models.

I. INTRODUCTION

In this paper we describe a practical method to calculate the charge density and total energy of crystals as a function of the atomic positions.[1] The purpose is to derive structural properties directly from the electron-ion Hamiltonian. The basic starting point is the density-functional approach of Hohenberg, Kohn, and Sham[2,3] which gives, in principle, exact expressions for the charge density and the total energy. Here we apply the method to representative phonon modes in Si and predict changes in the charge density and total energy, determining both harmonic and anharmonic coefficients.

The density functional has now been well established as a method to compute total energies, for example, in the work of Moruzzi *et al.*,[4] on elemental metals. However, to our knowledge the only other calculation for covalent semiconductors is that of Ohkashi and Shindo.[5] Also, we note the closely related work of Goroff and Kleinman[6] on diamond. The above-mentioned work has all been restricted to the calculation of the total energy as a function of volume with resulting predictions of the equilibrium lattice constant and bulk modulus. There is another category of calculations in which harmonic phonon energies are calculated from perturbation theory, which can be cast[7] in terms of the inverse dielectric-function matrix ϵ^{-1}. Relevant work in this area has been summarized by Sinha[8] and by Sham,[8] in addition to several more recent papers.[9-13] Louie and Cohen[9] have carried out the full calculations for the zone-center optic mode. Others have used physically motivated approximations to the ϵ^{-1} matrix; we note in particular the work of Turner and Inkson,[10] who report excellent agreement with experiment for harmonic frequencies of the elemental semiconductors. In these calculations it is implicitly assumed, but not checked, that the lattice is at equilibrium. Also, there have been a number of calculations of particular energies based upon empirical tight-binding methods[14,15] and the "chemical pseudopotential"[16].

The present work is quite different from previous calculations on covalent crystals. Here, various structural energies are determined directly as the difference in total energies of distorted and undistorted crystals. Therefore, we are not limited to small displacements and we can calculate anharmonic forces. Second, we determine various representative restoring forces and the equilibrium conditions for the same Hamiltonian, which has not been done in other calculations. The approach of directly calculating energy differences is similar to that of Refs. 15 and 16; however, unlike Refs. 15 and 16, we determine explicitly ion-ion and electron-electron interactions which must be added to the band-structure contributions to properly determine the total energy.

Two features are inherent in the present method: (i) The calculations for the distorted crystal in general must be carried out self-consistently. Here we carry the calculations to partial self-consistency and show that for most cases the results are essentially convergent. For very sensitive modes, in particular the soft transverse-acoustic mode, the results are not very convergent. (ii) The periodicity of the distorted crystal is utilized to reduce the computations through the use of "special points"[17] to carry out the integrals over the Brillouin zone. Hence our method is practical only for distortions which give rise to small unit cells, e.g., zone-center or zone-boundary phonons. One result of this paper is that by examining charge densities and various contributions to the energies for such displacement patterns, one can analyze the important structural properties of crystals such as Si.

Silicon is chosen as the prototype for covalent semiconductors because its electronic properties at equilibrium are well understood in terms of ionic pseudopotentials,[18,19] and calculations of phonon energies have been reported using various approximations for the electronic states[8-16] as well as a host of phenomenological models.[8,20] In a recent paper,[21] the electron-ion pseudopotential Hamiltonian and local-density functional used throughout the present work were shown to satisfactorily describe the equilibrium electronic bands and the effects of atomic displacements upon the energy bands, i.e., deformation potentials. In this paper we describe calculations of representative distortion energies, harmonic and anharmonic, including the pressure dependence of phonon energies, and show relations of these structural energies to the electronic properties. We also analyze the charge density of the distorted crystals, which is the proper quantum-mechanical distribution that has previously been approximated by classical shells or bond charges.[20]

The basic equations for calculation of the total energy are given in Sec. II. There we show the relation to the ϵ^{-1} formalism[7] and demonstrate the equivalence of our method for small displacements, i.e., harmonic energies. One consequence of this equivalence is that local-field effects[7] are included to all orders in the present work. The electronic Hamiltonian for Si is described in Sec. III and the results are given in Sec. IV, where we see that the energies calculated with no adjustable parameters are in rather good agreement with experiment. In Sec. IV we also present charge densities which aid in understanding the forces and their relation to phenomenological models.[20]

II. FORMULATION

Structural properties of an array of atoms are derived from the total energy E_{tot} of the system as a function of the positions of its constituent atoms. E_{tot} is the sum of an electronic part E_{el} and an ionic part E_{ion} corresponding to the direct Coulomb interaction of the ions in a uniform negative background. E_{el} is due to the valence electrons moving in the potential of the ions and interacting with each other. It can be formally expressed in the "density-functional form" of Hohenberg and Kohn (HK).[2] They proved that E_{el} is a unique functional of the charge density $n(r)$, i.e.,

$$E_{\text{el}}[n]=\int v(r)n(r)\,d^3r+F[n]\,, \tag{1}$$

where $v(r)$ is the ionic potential and $F[n]$ is the energy functional comprising the kinetic and interaction energies of the electrons with density distribution $n(r)$. It is useful to decompose $F[n]$ according to[3]

$$F[n]=\frac{1}{2}\int d^3r\int d^3r'\,\frac{n(r)n(r')}{|r-r'|}+T_s[n]+E_{xc}[n]\,, \tag{2}$$

where the Hartree term and the part of the kinetic energy $T_s[n]$ due to independent Fermions of density $n(r)$ (both intrinsically nonlocal) are treated separately. The term $E_{xc}[n]$ is the exchange and correlation energy of the interacting many-electron system with density $n(r)$. HK have shown that $E_{\text{el}}[n]$ is minimum for the correct charge density of the many-particle ground state. According to our definition, a structural energy is then just the change of the ionic energy ΔE_{ion} plus the difference of the electronic energies calculated from Eq. (1) using the ground-state charge densities $n'(r)$ and $n(r)$ of distorted and undistorted systems, respectively:

$$\Delta E_{\text{tot}}=\Delta E_{\text{ion}}+(E_{\text{el}}[n']-E_{\text{el}}[n])\,. \tag{3}$$

It is relevant to note that Eqs. (1)–(3) give exact expressions[2] for lattice energies within the adiabatic approximation[7]; this is in contrast to the approximations[3] needed to derive single-particle electronic energies from the density functional. Equations (1)–(3) are the central relations used throughout the paper and the relations derived in Sec. III will be immediate consequences of these equations.

The method is not restricted to small perturbations; however, it is useful to first consider the case where the changes in v and n are small. For a small perturbation of the electronic density, let $n^{(0)}(r)$ be the density of the unperturbed system, and $n'(r)=n^{(0)}(r)+n^{(1)}(r)$ [with $\int d^3r\,n^{(1)}(r)=0$] that of the perturbed one. According to HK, for each density $n(r)$ there is a unique external potential $v(n(r))$; let us define $v'(r)=v(n'(r))=v^{(0)}(r)+v^{(1)}(r)$. Then to second order in $n^{(1)}(r)$, the electronic contribution to the structural energy becomes[22]

$$\begin{aligned}\Delta E_{\text{el}}=&\int d^3r\,v^{(1)}(r)[n^{(0)}(r)+n^{(1)}(r)]\\&+\int d^3r\left(v^{(0)}(r)+\frac{\delta F}{\delta n(r)}\bigg|_{n^{(0)}}\right)n^{(1)}(r)\\&+\frac{1}{2}\int d^3r\int d^3r'\,\frac{\delta^2F}{\delta n(r)\delta n(r')}\bigg|_{n^{(0)}}\\&\times n^{(1)}(r)n^{(1)}(r')\,,\end{aligned} \tag{4}$$

where δ indicates a functional derivative and the subscript $n^{(0)}$ indicates that the quantities are evaluated at the unperturbed charge density. The variational principle applied to the unperturbed system with potential $v^{(0)}(r)$ requires that the term in large parentheses vanishes at every point r. Furthermore, applying the variational theorem to the perturbed system, i.e., the condition $(\delta\Delta E_{\text{el}})/\delta n^{(1)}(r)=0$, leads to

$$-v^{(1)}(r)=\int d^3r'\,\frac{\delta^2F}{\delta n(r)\delta n(r')}\bigg|_{n^{(0)}}n^{(1)}(r')\,. \tag{5}$$

Inverting this equation we obtain

$$n^{(1)}(r)=\int d^3r'\,\chi(r,r')v^{(1)}(r')\,, \tag{6}$$

with

$$\chi(r,r')=\left(-\frac{\delta^2F}{\delta n(r)\delta n(r')}\right)^{-1}_{n^{(0)}}\,. \tag{7}$$

Thus $[-\delta^2F/\delta n(r)\delta n(r')]^{-1}$ relates the first-order change in the external potential to a linear change in the charge density, i.e., $[-\delta^2F/\delta n(r)\delta n(r')]^{-1}$ is the (static) density-response function which plays the central role in the general linear-response theory.[7] The total potential acting upon an electron induced by the applied potential $v^{(1)}(r)$ is

$$\phi^{(1)}(r)=v^{(1)}(r)+\int d^3r_1\int d^3r_2\,\frac{1}{|r-r_1|}\chi(r_1,r_2)\times v^{(1)}(r_2)\,. \tag{8}$$

Defining the dielectric function $\epsilon(r,r')$ in the usual way as

$$\phi^{(1)}(r)=\int d^3r'\,\epsilon(r,r')v^{(1)}(r')\,, \tag{9}$$

we find

$$\epsilon^{-1}(r,r')=\delta(r-r')+\int d^3r_1\,\frac{1}{|r-r_1|}\chi(r_1,r')\,. \tag{10}$$

Equation (10) demonstrates the relation of the density functional to the exact dielectric function. In particular, it shows that $\epsilon^{-1}(r,r')$ and thus $\epsilon(r,r')$ are functionals of the charge density $n(r)$, and that the density-functional form includes local-field effects, i.e., $\epsilon^{-1}(r,r')$ is a function of r and r', which leads to off-diagonal terms for ϵ^{-1} in reciprocal space. Thus we have established the equivalence of density-functional equation (1) to linear response or dielectric theory for small charge-density perturbations in a general array of ions and electrons.

The expressions for harmonic restoring forces derived in Ref. 7 for crystals can be straightforwardly derived from Eqs. (3)–(7), and (10). First, we rewrite Eq. (10) by operating on each side with the Laplacian ∇_r^2:

$$4\pi\chi(r,r')=\nabla_r^2[\epsilon^{-1}(r,r')-\delta(r-r')] \tag{11}$$

so that Eqs. (3) and (4) can be written

$$\Delta E_{\text{tot}}=\Delta E_{\text{ion}}+\int d^3r\,v^{(1)}(r)n^{(0)}(r)+\frac{1}{8\pi}\int d^3r\int d^3r'\,v^{(1)}(r)\nabla_r^2\times[\epsilon^{-1}(r,r')-\delta(r-r')]v^{(1)}(r')\,. \tag{12}$$

The further simplifications of this equation are derived by assuming that the ions are nonoverlapping, in which case the ion-ion interaction potential is Coulombic and is the same as the ion-electron potential $v(r)$ for r outside the ion-core radius, so that $\nabla_r^2v(r)=4\pi n_{\text{ion}}(r)$. Equation (12) may then be written

$$\Delta E_{\text{tot}}=\frac{1}{8\pi}\int d^3r\int d^3r'\,v^{(1)}(r)\times\nabla_r^2\,\epsilon^{-1}(r,r')v^{(1)}(r')\,, \tag{13}$$

along with the equilibrium condition

$$\int d^3r\,v^{(1)}(r)[n^{(0)}(r)+n_{\text{ion}}^{(0)}(r)]=0\,. \tag{14}$$

These equations completely determine the harmonic restoring forces and are self-consistent solutions to harmonic order. It would be straightforward but tedious to extend such equations to higher orders.

The perturbation analysis can also be used to estimate errors in cases where the charge density $n'(r)$ is not self-consistent with the external potential $v'(r)$. In this case, we do not restrict ourselves to small $n^{(1)}$ or $v^{(1)}$, but rather consider small deviations of the approximate charge density $\tilde{n}^{(1)}$ from the actual $n^{(1)}$, and define $\delta n^{(1)}=\tilde{n}^{(1)}-n^{(1)}$. Without loss of generality, we can assume that the equilibrium configuration is self-consistent.[23] It follows from Eq. (4) that the error in the structural energy is

$$\delta E_{\text{tot}}=\frac{1}{2}\int d^3r\int d^3r'\left(\frac{\delta F}{\delta n(r)\delta n(r')}\right)_{n^{(0)}}\times\delta n^{(1)}(r)\delta n^{(1)}(r')\,. \tag{15}$$

The important aspects of Eq. (15) are: (i) there is no linear term in the error $\delta n^{(1)}$, so the approximate ΔE_{tot} is correct to first order in $\delta n^{(1)}$, and (ii) the error δE_{tot} is positive definite, so that the approximate ΔE_{tot} is always greater than the exact ΔE_{tot}. Therefore, any calculation starting from a self-consistent solution for the equilibrium can set an upper limit on the exact ΔE_{tot} caused by any perturbation, including the displacement of atoms considered in this paper.

After having studied the functional approach for small density perturbations in an arbitrary system, let us return to Eqs. (1)–(3). Up to now we have not specified $E_{xc}[n]$. In general, one cannot give a simple exact expression for the functional; however, a common approximation for $E_{xc}[n]$ has the local form

$$E_{xc}[n]=\int d^3r\,n(r)\epsilon_{xc}(n(r))\,, \tag{16}$$

where $\epsilon_{xc}(n(r))$ is the exchange and correlation energy per electron of a uniform electron gas of density n. Kohn and Sham[3] have proved that the ground-state density $n(r)$ is then given by

$$n(r)=\sum_i |\psi_i(r)|^2 , \tag{17}$$

where $\psi_i(r)$ is the self-consistent solution of the Schrödinger equation,

$$[-\tfrac{1}{2}\nabla^2+\phi(r)]\psi_i(r)=\epsilon_i\psi_i(r) , \tag{18}$$

with

$$\phi(r)=v(r)+\int d^3r'\, n(r')(r-r')^{-1}+\mu_{xc}(n(r)) , \tag{19}$$

where $\mu_{xc}(n(r))=d[n(r)\epsilon_{xc}(n)]/dn$ is the exchange and correlation contribution to the chemical potential of a uniform gas of density n. In this form, the total energy may be expressed in terms of the sums of the eigenvalues of occupied states and a correction term for electron-electron interactions:

$$E_{\text{tot}}=E_{\text{ion}}+E_{\text{BS}}[n]-E_{ee}[n] , \tag{20}$$

where

$$\begin{aligned} E_{\text{BS}}[n]&=\sum_i \epsilon_i \\ &=-\frac{1}{2}\sum_i\int d^3r\,\psi_i^*(r)\nabla^2\psi_i(r)+\int d^3r\, v(r)n(r) \\ &\quad+\int d^3r\int d^3r'\,\frac{n(r)n(r')}{|r-r'|}+\int d^3r\, n(r)\mu_{xc}(n(r)) , \end{aligned} \tag{21}$$

and

$$\begin{aligned} E_{ee}[n]&=\frac{1}{2}\int d^3r\int d^3r'\,\frac{n(r)n(r')}{|r-r'|} \\ &\quad+\int d^3r\, n(r)[\mu_{xc}(n(r))-\epsilon_{xc}(n(r))] . \end{aligned} \tag{22}$$

The division of the energy as shown in Eq. (20) has been discussed by many authors,[24,25] and is convenient because it clearly separates out a single-particle term. The calculation of the total energy in the approximation of Eq. (16) therefore is expressed in terms of the solutions of the self-consistent (SC) equations (17)–(19).

In this paper we describe calculations of structural energies of crystals in Eqs. (17)–(22). We consider cases in which atoms are displaced in periodic patterns so that both the distorted and undistorted systems are crystalline, and we find ΔE_{tot} as the difference between two crystalline calculations. For valence bands of crystals, the quantum numbers denoted by i in Eqs. (17), (18), and (21) become band and wave-vector indices n, k. Within the local-density approximation, Eqs. (17)–(22) give exact expressions for the energy and charge density. In addition, $\epsilon_{n,k}$ and $\psi_{n,k}$ are often identified as one-electron eigenvalues and vectors. This is rigorously correct only at the Fermi level.[3] The local-density approximation has been shown to work well for small band-gap semiconductors, so that the $\epsilon_{n,k}$ are closely related to the band structure,[18,19,21] hence the subscript BS in Eq. (21).

One crucial point in carrying out the calculations is the integral over k in evaluating the band-structure energy E_{BS} and the charge density which enters E_{BS} and E_{ee}. For an insulator, these integrations can be carried out with a minimum of computation by choosing special points[17] in the Brillouin zone (BZ) so that Eqs. (17) and (21) become sums over a lattice of a few points in the BZ. The irreducible set of special points depends upon the symmetry; in particular, upon the distortion considered. We follow the approach of Chadi and Cohen and of Monkhorst and Pack.[17] In each case the calculation of energies reduces to carrying out band-structure calculations at a few points in the BZ. Moreover, in the Appendix we show that the convergence in the spacing of the special-point lattice indicates the range of interactions in real space.

Finally, we calculate the change density only to partial self-consistency. In Sec. III we use a screening anasatz as a starting point for $\phi(r)$, from which $n(r)$ is calculated. The density-functional expressions [Eqs. (21) and (22)] are then used to calculate E_{BS} and E_{ee}. The analysis of errors in our cases are given in Sec. III. The important point here is that we have shown that the corrections to our calculated ΔE_{tot} are *second order* in the error in charge density $\delta n(r)$, and are given by Eq. (15).

III. APPLICATION TO Si

The general class of wide-band covalent semiconductors was chosen for this work because the bands are well understood, using a pseudopotential electron-ion interaction and a local exchange-correlation function.[18,19,26,27] This simplifies the calculations, which can readily be carried to convergence by using a plane-wave basis. Nevertheless, it is well known that their structural properties are intimately related to the covalent bonding. Our task is to derive such structural properties directly from the electron Hamiltonian, a job which has not previously been completed successfully.

We chose Si because it is the simplest of the semiconductors from a computational point of view: it has the high-symmetry diamond structure and, unlike C, Ge, or Sn, it can be rather well represented using a local pseudopotential.[18,19,26] This restriction to a local potential of the Appelbaum-Hamann (AH) form is convenient; however, it is probably the largest source of discrepancy with experiment (see the discussion of the equilibrium lattice constant in Sec. IV). From a structural point of view, the properties of Si are very similar to all the tetrahedral semiconductors, and we expect our conclusions to apply to all these materials.

For the electron-ion potential we use the model pseudopotential[18] of Appelbaum and Hamann. They found a potential which is smooth in both direct and reciprocal space and which yields the correct band structure with a self-consistent calculation. For exchange and correlation they used

$$\epsilon_{xc}(n) = 0.76(-\tfrac{9}{8})(3n/\pi)^{1/3}\,, \tag{23}$$

Note that we have adopted 0.76 rather than the $\frac{2}{3}$ used by Kohn and Sham. Furthermore, they found that the self-consistent total potential ϕ in the band equations (18) is very close to their starting approximation

$$\phi(G) = v(G)/\epsilon_f(G)\,, \tag{24}$$

where G is a reciprocal-lattice vector and ϵ_f is the "free-electron" dielectric constant derived[18,21] from Eqs. (7) and (10) using a uniform potential $v(r)$ = const in Eq. (1). This is very useful, since the self-consistent solution is close to the simple starting point. The model ion potential has the form of the Coulomb potential of a Gaussian charge distribution $\rho(r) = 4(\alpha/\pi)^{3/2}\exp(-\alpha r^2)$ plus a parametrized core-repulsion part,

$$v(r) = \int d^3r'\, \rho(r')(r - r')^{-1} + (v_1 + v_2 r^2)\exp(-\alpha r^2)\,. \tag{25}$$

In our calculations we use the values $\alpha = 0.57$, $v_1 = 3.04$, and $v_2 = -1.32$, in atomic units, which are slightly different from those of AH. The difference is caused by the fact that we include more plane waves than AH, and had to change the potential slightly to have agreement with experiment for the band structure.[21]

We solve the band equations with a plane-wave basis including all waves with $(k+G)^2 < 9$ (in units of $2\pi/a$) exactly and all waves with $9 \leq (k+G)^2 < 35$ in Löwdin perturbation theory. For all zone-center calculations, this means we diagonalize ~27×27 matrices. Although it is important to include the other plane waves (~200), the perturbation theory was found to be adequate. For the zone-boundary calculation, the unit cell is doubled, i.e., reciprocal-lattice vectors are halved and the matrix to be diagonalized then contains 54×54 elements. Since the matrix treated exactly is still small in comparison to many calculations, larger unit cells could be considered. The total energy is calculated as in Eqs. (20)–(22) by Fourier transforming the integrals in Eqs. (21) and (22) and explicitly carrying out the sums over the reciprocal-lattice vectors, including all Fourier components with $(k+G)^2 < 35$. For the exchange and correlation terms we approximate $n^{4/3}$ by a Chebyshev polynomial,

$$[n(r)]^{4/3} = \bar{n}^{4/3}(0.9975 + 1.2963\delta + 0.2428\delta^2)\,, \tag{26}$$

where $\delta = [n(r) - \bar{n}]/\bar{n}$. Equation (26) is a very good approximation to $n^{4/3}$; e.g., <2% deviation for n varying from ~$0.15\bar{n}$ to ~$2.5\bar{n}$. This greatly simplifies the resulting calculations.

The ion-ion interaction is calculated directly as the energy of Gaussian ions in a uniform negative background excluding the ion self-energy. The direct ion-ion interactions are equivalent to those of point charges with the addition of a weak attractive nearest-neighbor interaction because of the small overlap of neighboring ions. It is important to use this form of ion-ion interactions in order to be consistent with the electronic calculations where we must use nonpoint ions in order to have convergence. (We note that the attractive terms do not effect the final results for the very sensitive shear-constant and zone-boundary mode discussed below.) For displacement of the ions in which the volume is constant, as in the case for the phonons and shear constants, the changes in ion-ion energy are independent of the background and involve only the direct ion-ion terms.

The uniform background is essential for charge neutrality, and must be included in the energy as a function of the volume. Since the background is the average electron density, the term which we label "ion-ion" in fact includes the dominant part of the ion-electron and electron-electron Hartree energies. We use the method of Fuchs[28] with results in good agreement with the expressions of Goroff and Kleinman[6] for the Madelung constant with nonpoint ions. Finally, the zero Fourier component of the non-Coulombic part of v_{ion} in Eq. (25) contributes to the volume-dependent energy, and we separate this part of the total energy per cell explicitly as

$$E_{\text{ion}}(0) = (N_e/\Omega_{\text{atom}})(\pi/\alpha)^{3/2}(v_1 + \tfrac{3}{2}\alpha v_2)\,, \tag{27}$$

where Ω_{atom} is the volume per atom and N_e is the number of electrons per cell.

The expressions so far have been in terms of the results of self-consistent calculations. In practice it is very difficult to carry out such calculations to the accuracy needed for finding small energy differences. Here we describe our calculations in terms of the usual self-consistent procedures. We start from the bare ionic potential v or v' of Eq. (1) and define the zeroth-order charge distributions $n^{(0)}$ or $n^{(0)\prime}$ by considering the entire atomic potentials v or v' only to lowest order, i.e., linear screening. This yields the crystal potential $\phi^{(0)}$ for the electrons given by Eq. (24). $\phi^{(0)}$ is entered into the band equations (18). Diagonalization leads to eigenvalues $\epsilon_i^{(1)}$ and the wave functions generate $n^{(1)}(r)$. A self-consistent procedure would now use $n^{(1)}(r)$ to establish a new crystal potential $\phi^{(1)}$, diagonalize the corresponding band equations, etc., until convergence in $n(r)$ is achieved. This procedure yields successive approximations to $\Delta E_{\rm tot}$. In particular, we define $\Delta E_{\rm tot}^{(2m)}$, $m \geqslant 0$, to be the energy calculated from Eqs. (1)–(3) and (21)–(23) using $n^{(m)}$ or $n^{(m)\prime}$ in the functional $E_{\rm el}(n)$. Note that $\Delta E_{\rm tot}^{(0)}$ is simply the second-order perturbation expression for a free-electron gas perturbed by v or v'. This is commonly called the free-electron approximation.[24] It is also advantageous to define other approximations $\Delta E_{\rm tot}^{(2m-1)}$, $m \geqslant 1$, which depend upon the eigenvalues $\epsilon_i^{(m)}$ in the mth step but the charge density of the $(m-1)$th step. If we expand our expressions to lowest order in the difference $n^{(m)} - n^{(m-1)}$, we find

$$\Delta E_{\rm tot}^{(2m-1)} = \Delta E_{\rm ion} + \sum_i \epsilon_i^{(m)} - E_{ee}[n^{(m-1)}] . \qquad (28)$$

This form is particularly useful for the $m=1$ step in which case $\Delta E_{\rm tot}^{(1)}$ is found simply from $n^{(0)}$ and the eigenvalues $\epsilon_i^{(1)}$. It is not essential to calculate the wave functions $\psi_i^{(1)}$ and the resulting $n^{(1)}(r)$ which involves many steps in non symorphic crystals.

In our work, we calculated $\Delta E_{\rm tot}^{(r)}$ for $r=0$, 1, 2, and the results are presented in the Sec. IV. We conclude from the convergence in these cases what the effects of self-consistency are and what the probable results for completely self-consistent calculations would be. The most accurate results correspond to $\Delta E_{\rm tot}^{(2)}$, which we found from $n^{(1)}$, which in turn is calculated from the band equations [Eq. (18)]. We find that the total energies calculated are remarkably insensitive to the step in the consistency loop, with the exception of the low-frequency TA(X) mode discussed in Sec. IV. Therefore, we conclude that the non-self-consistent calculations are adequate for many cases of interest, but additional calculations are needed for special cases, particularly ones involving low-frequency modes.

An important aspect of the present work is that electronic and structural properties are considered together. We have shown in a previous paper[21] that the band structure at equilibrium and for the strained crystal are in good agreement with experiment when we used the screening approximation, Eq. (24), for $\phi^{(0)}(r)$. In this paper we use exactly the same Hamiltonian to calculate the structural properties.

IV. RESULTS

In this section we discuss calculations of structural energies of Si from the electron-ion Hamiltonian described in Sec. III. We first consider the energy as a function of volume to establish the equilibrium conditions. This is very important, since calculations for theoretical lattices which are not at equilibrium give spurious contributions to harmonic force constants, as discussed below. This has been emphasized in the formal papers on the dielectric-function formalism.[7] However, to our knowledge none of the calculations using this approach have checked the equilibrium conditions.[8-13] To eliminate the spurious contributions, we introduce an *ad hoc* term to satisfy the equilibrium condition exactly. In the remainder of this section, we consider lower-symmetry distortions of primary interest in this paper.

For the energy as a function of volume, one must include the $G=0$ Fourier components of the ion pseudopotential [non-Coulombic part given in Eq. (27)], the background contributions included in $E_{\rm ion}$, and the average exchange and correlation energy included in $E_{\rm BS}$ and E_{ee}. These terms do not enter any of the phonon modes where volume is conserved. Table I gives the various contributions to the total energy, the first derivative, and the bulk modulus B at the observed lattice constant $a=5.431$ Å. The primary result from Table I is that the totals are similar for each approximation 0, 1, or 2, from which we conclude that the total energy in calculation 2 is essentially at convergence. Indeed, Appelbaum and Hamann have found very similar results in a fully consistent calculation.[29] The presence of the linear term shows that our theoretical lattice is not in equilibrium at the observed lattice constant. Approximate calculations show that the theoretical equilibrium is for $a \sim 4.7$ Å. The bulk modulus calculated with *no parameters* is ~28% lower than the observed value.

We believe the primary source of the discrepancy with experiment is caused by the model potential. In order to fit the bands with the local potential chosen by AH,[18] it is necessary for the potential to be too attractive at distances of order one-half the bond length. This leads to the negative value of $E_{\rm ion}(0)$, which should be repulsive by the usual pseudopotential core-orthogonalization arguments.[26] Evidence of this appears in the

TABLE I. Total energy E_{tot}, linear term $a(dE_{\text{tot}}/da)$, and bulk modulus B at $a=5.431$ Å decomposed into the contributions of Eqs. (20)–(22), and (27). $E_{\text{ion}}(0)$ is the contribution of Eq. (27), and is important only for distortions which change the volume.

	E_{tot} (eV)			$a(dE/da)$ (eV)			$B(10^{11}$ dyne/cm$^2)$		
	0	1	2	0	1	2	0	1	2
II	–192.93	–192.93	–192.93	126.0	126.0	126.0	–4.0	–4.0	–4.0
BS	–32.69	–37.98	–32.96	–42.9	–56.1	–66.3	11.6	15.5	10.8
EE	7.55	7.55	5.85	–63.5	–63.6	–48.3	1.6	0.3	5.0
$E_{\text{ion}}(0)$	–9.04	–9.04	–9.04	27.2	27.2	27.2	–4.7	–4.7	–4.7
Total	–227.11	–232.41	–229.08	46.8	33.6	38.6	4.5	7.0	7.0
Exp	···	···	···	0	0	0	9.8	9.8	9.8

charge density. Our result is given in Fig. 1(a) and is very similar to that calculated from a local empirical potential by Walter and Cohen.[27] The charge-density contours in the bond region are elliptic with the long axis perpendicular to the bond axis, which is opposite to experiment[30] and to the nonlocal calculations of Chelikowsky and Cohen.[19] The shape of the "bond charge" in our calculation allows the atoms to approach more closely than in a more correct nonlocal calculation.

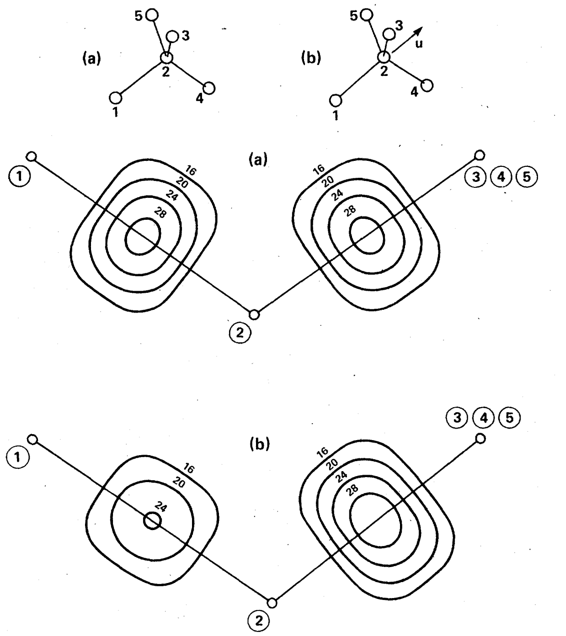

FIG. 1. Charge density in bond regions for Si: (a) undistorted and (b) with atoms displaced along the [111] direction in a zone-center transverse-optical-mode pattern as shown in the inset labeled (*b*). The bonding charge density decreases in the bond 1-2, which is extended, whereas it increases in the three bonds 2-3, 2-4, and 2-5, which are compressed. The magnitude of the displacement is $|u|=0.03a$, where is the lattice constant. For the undistorted crystal, the results are close to those of Ref. 27, and for the distorted, to those reported in Refs. 1 and 37.

We do not attempt to correct this discrepancy in the energy as a function of volume since we are primarily interested in the form of the results for distortions in which the volume is constant. Nevertheless, it is essential to satisfy the equilibrium condition in order to avoid spurious contributions in the calculations, and we introduce an *ad hoc* linear repulsive force between nearest neighbors to stabilize the lattice at $a=5.431$ Å. Since we assume this additional stabilizing force acts only between nearest neighbors and is linear in the bond length τ_i, the contribution to the total energy can always be written

$$\Delta E_{\text{tot}} = -\tfrac{1}{4}\left(a\frac{dE}{da}\right)\sum_i\left(\frac{\Delta\tau_i}{\tau}\right), \tag{29}$$

where $\Delta\tau_i = \tau_i - \tau$ is the change in length of bond i for the given displacement pattern u. It is straightforward to show that, for volume-conserving phonons, the energy ΔE_{tot} in Eq. (29) is always second order in the displacement u. For the energy as a function of volume, the added term satisfies the equilibrium condition while making no contribution to the bulk modulus. The correction to ΔE_{tot} from Eq. (29) is calculated for each mode using $a(dE/da)$ from Table I, and is denoted by CE in Table II and Figs. 2 and 3.

The different contributions to E_{tot} are also given in Table I. The notation *II* denotes the ionic energy including the negative background; BS, the band-structure terms exclusive of the zero Fourier component $E_{\text{ion}}(0)$; and *EE*, the electron-electron *correction* in Eq. (20), i.e., it is the *negative* of the energy E_{ee} given in Eq. (22). The magnitude of E_{tot} is dominated by *II*, which becomes less important as the order of the derivative increases. For the second derivative there are large cancellations between the various terms. We see that our most realistic charge density of calculation 2 leads to a total energy smaller than the one labeled 0, which is the free-electron approximation. In the spirit of the variational principle inherent in HK, this demonstrates that the covalent-charge density $n^{(1)}(r)$ is a better "trial" distribution than the homogeneous metallic charge density

TABLE II. Comparison of calculated and experimental harmonic-force constants for the TO(Γ), TA(*X*), and $C_{11}-C_{12}$ modes in Si (in eV/Å^2). The cubic-anharmonic force k_{xyz} (in eV/Å^3) for TO(Γ) is also given. It is compared with a value derived from Ref. 36. The steps toward self-consistency denoted 1 and 2 are defined in the text. *II*, BS, and *EE* correspond to the separation of terms in Eq. (20), where *EE* denotes $-E_{ee}$. CE is the correction discussed in the text.

	$m\omega^2_{\mathrm{TO}(\Gamma)}$		$2a(C_{11}-C_{12})$		$m\omega^2_{\mathrm{TO}(X)}$		k_{xyz}	
	1	2	1	2	1	2	1	2
II	21.56		−29.25		−24.35		−69.92	
BS	−2.42	−5.76	29.29	27.62	24.09	20.70	7.21	18.62
EE	−2.03	2.71	17.46	16.26	14.08	15.45	15.20	−1.16
CE	−4.04	−4.66	−6.06	−6.98	−6.06	−6.98	0	
Total	13.07	13.85	10.82	7.65	7.76	4.82	−47.51	−52.46
Exp	14.00		7.32		2.33		(−40.51)	

of calculation 0. The difference shows the importance of an inhomogeneous charge distribution in Si. Comparison of the perturbational calculation 1 with calculation 0 shows that linear accounting for the inhomogeneity of $n(r)$ decreases the total energy. However, comparison with calculation 2 demonstrates that higher-order corrections to the total energy increase its value. At this point we want to stress that this finding does not contradict the statement that calculation 2 is our best calculation and should thus lead to the lowest value for the total energy. Indeed, calculations 0 and 2 evaluate Eqs. (20)–(22) rigorously for the given charge densities, whereas calculation 1 uses only an approximate form of these equations. It is interesting to note that although the totals in Table I are well converged, the band structure and electron-electron terms separately are not. This shows the importance of considering the total energy to which the variational condition applies rather than the separate parts.

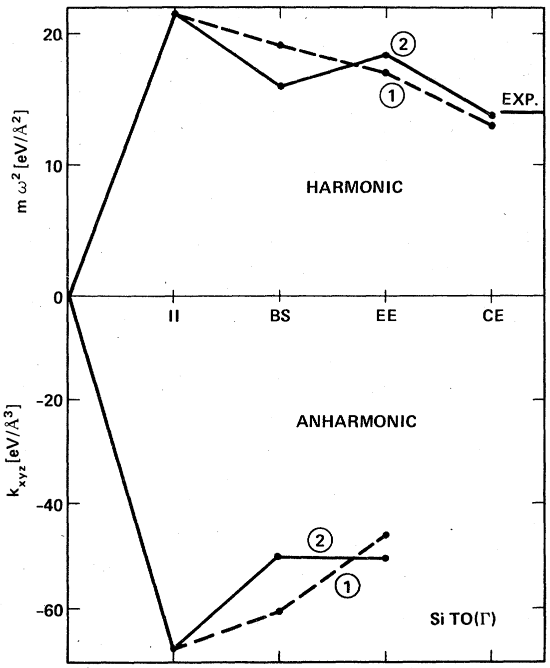

FIG. 2. Contributions of the various forces to harmonic and anharmonic energies defined in Eq. (30) for the TO(Γ) phonon and given in Table II. The point II represents only ion-ion contributions; at BS the band structure term of Eq. (21) is added; at *EE* the electron-electron correction of Eq. (22) is added; the CE includes the linear correction determined by using Eq. (29). The labels 1 and 2 denote the approximations $\Delta E^{(1)}$ and $\Delta E^{(2)}$ described in the text. As shown in Table II, the calculated anharmonic value is close to that derived from Keating's phenomenological model (Ref. 36). This figure is a corrected version of one given in Ref. 1 in the conference proceedings where the BS point for k_{xyz} was plotted erroneously. The final result is the same. It is evident that ion-ion forces dominate this model, and the electronic forces make smaller contributions.

For distortions lowering the crystal symmetry, we choose distortion patterns corresponding to a TO phonon at Γ, a $C_{11}-C_{12}$ elastic deformation, and a TA phonon at *X*. These phonons are recognized to be representative of the tetrahedral covalent crystals. In phenomenological models, the TO phonon is determined primarily by central nearest-neighbor forces, whereas $C_{11}-C_{12}$ and the TA phonon require directional covalent forces. Furthermore, the flattening of the TA modes considered as anomalous when related to the shear elastic constants of the same symmetry shows that the directional forces have complex long-range character.[20, 31, 32]

In the TO mode the two sublattices may be displaced relative to each other by u along [111] (cf. inset in Fig. 1). The symmetry of this model allows a cubic term, and thus in the lowest order of anharmonicity the structural energy can be written

$$\Delta E_{\mathrm{tot}} = \tfrac{1}{2}(\tfrac{1}{2}m_{\mathrm{Si}})\omega^2_{\mathrm{TO}}u^2 + k_{xyz}(u/\sqrt{3})^3 + \cdots . \qquad (30)$$

The harmonic and cubic force constants are calculated following the discussion above in the approximations denoted 1 and 2, and the results are listed in Table II and depicted[33] in Fig. 2. We have

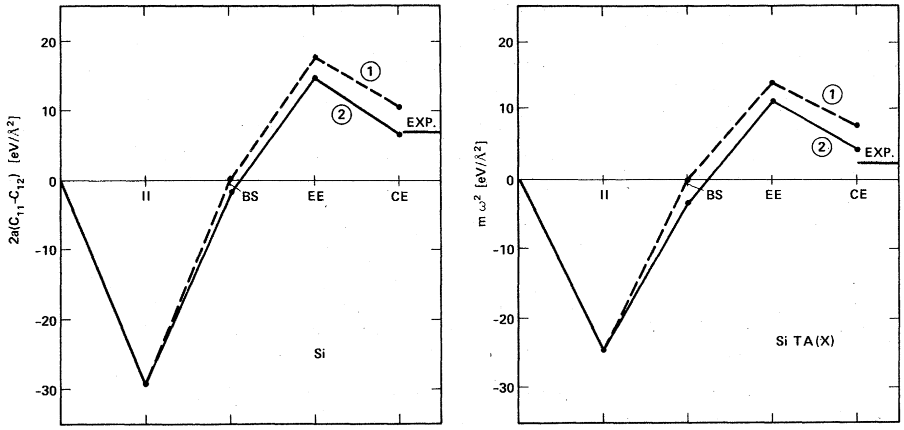

FIG. 3. Contributions to the energies for $2a(C_{11}-C_{12})$ and $m\omega_{TA}^2$ as given in Table II. See caption to Fig. 1 for explanation of symbols. For these shear modes, the ion-ion interactions destabilize the modes, and only the electronic-bonding restoring forces stabilize the structure.

decomposed the force constants into the contributions according to Eq. (20). That means the point labeled *II* corresponds to the force constant we would get by taking into account only the direct ion-ion interaction. At BS we add the contribution arising from the band-structure calculation. The value at *EE* is the result after adding all the contributions from Eq. (20). We obtain our final result CE by including the nearest-neighbor correction term from Eq. (29). This term contributes to $m\omega_{TO}^2$ due to the change of the nearest-neighbor bond length to second order in the atomic displacements. From Fig. 2 we deduce that the harmonic restoring force for the TO phonon is dominated by the direct interaction of the ions. Ion-electron and electron-electron interaction play only a secondary role.[34] The calculations of types 1 and 2 lead to final results that are close to each other. However, there are small qualitative differences in the composition of the contributions BS and *EE*. As was pointed out in Sec. II, the total energy converges rapidly because it is near a minimum as a functional of n, whereas there is no such argument for BS and *EE* separately. The closeness of the final results for the two calculations suggests that the precise form of the valence charge is not important for this distortion. Indeed, the present zeroth-order calculations, as well as previous calculations,[9,20,35] lead to a very similar result. Altogether, our calculated ω_{TO} is in good agreement with experiment (Table II).

For the cubic anharmonicity, the electronic contributions in both calculation types 1 and 2 become slightly more important than for the harmonic force constant. For the harmonic force, BS and *EE* contributions are about 14% of *II*, and for the anharmonic force they are about 25% of the ion-ion interaction. Both calculations 1 and 2 lead to results very close to each other. It is remarkable that in the most exact calculation 2 the electron-electron interaction nearly vanishes. In Table II, for comparison, we give a value of k_{xyz} calculated from Keating's parameters,[36] which he derived by fitting experimental third-order elastic constants.

The k-integration in this case was convergent for $q=2$ in the notation of Monkhorst and Pack[17] given in the Appendix [requiring only (4) 6 special points for the (un)distorted lattice]. As shown in the Appendix, this accounts for interactions up to a distance of $\sqrt{2}a$, which demonstrates that the dominant forces involved in the TO distortion are short range.

The redistribution of valence electrons in this mode[1,37] is shown in Fig. 1, where we see that the charge density in the stretched bond decreases when compared to the equilibrium, and the charge density in the compressed bond increases. This means the magnitude of the bond charge varies inversely with the bond length, which corresponds to the behavior one expects from an overlap of bond orbitals in a localized picture. Similar results have been found by Baldereschi and Maschke.[37]

We have also calculated the hydrostatic Grüneisen coefficient $-d(\ln\omega^2)/d(\ln V)$ by carrying out the calculations for different lattice constants. The results are given in Table III, where we see that all contributions tend to increase the frequency with pressure, with the largest effect from BS. There is reasonable agreement with experiment, considering that there are no adjustable parameters in our calculations. The large magnitude of the calculated value is probably due to the form of the potential which led to the small predicted lattice constant. The difference between calculations 1 and 2 indicates that the results for the Grüneisen constant are not well convergent, and additional steps in self-consistency will change the final result.

Restoring forces for shear modes represented in our paper by ω_{TA} at X and $C_{11}-C_{12}$ are directly related to the directional covalent bonding.[8,20,31,32,35]

TABLE III. Grüneisen coefficients $(-d\ln\omega^2)/d\ln V$ and $(-d\ln c)/d\ln V$ for photon distortions TO(Γ), TA(X), and $C_{11}-C_{12}$.

	TO(Γ)		$C_{11}-C_{12}$		TA(X)	
	1	2	1	2	1	2
II	1.12	1.06	−3.46	−4.90	−2.82	−4.55
BS	2.56	2.08	3.52	2.49	1.44	−0.52
EE	1.48	0.53	0.15	2.87	−1.58	0.32
Tot	5.16	3.65	0.21	0.46	−2.96	−4.75
Exp	1.96 ± 0.12[a]		0.0014[b]		−2.8 ± 0.6[a]	

[a] Reference 39. [b] Reference 38.

These modes are sensitive to the form of the electronic interactions, as evidenced by the fact that they are unstable in the free-electron approximation.[35] Also, it is interesting to compare $2a(C_{11}-C_{12})$ and $m\omega_{\mathrm{TA}}^2$ because the large difference between these two quantities found experimentally implies forces beyond second neighbors.[20, 31, 32] It is these long-range forces which have led to the adiabatic shell and bond-charge models.[20]

We calculate $C_{11}-C_{12}$ from the energy of the crystal compressed along [001] and expanded along [100] and [010] to keep the volume exactly constant. We use the relation

$$\Delta E_{\mathrm{tot}} = 6\Omega_{\mathrm{atom}}(C_{11}-C_{12})\epsilon^2 \tag{31}$$

with Ω_{atom} the volume per atom and $\epsilon = \frac{1}{3}\Delta(c/a)$. In Fig. 3 we plot $2a(C_{11}-C_{12})$ in order to facilitate comparison with ω_{TA}^2 below. In contrast to the TO calculation, we find that the direct ion-ion interaction (*II*) tends to destabilize the crystal. This is because the nearest-neighbor distance increases to second order in the strain. The indirect interaction of the ions via the valence electrons, i.e., the band-structure contribution (BS), compensates the negative ion-ion interaction. Furthermore, it is only with the inclusion of the electron-electron correction *EE* that this mode is even stable. This finding is especially interesting in view of the fact that many tight-binding models neglect the *EE* as well as the *II* terms completely.[14-16] The correction term CE lowers the calculated energies, and makes the results closer to the experimental value.

The comparison of the calculations denoted 1 and 2 shows that the convergence is similar to that for the TO; however, the fractional effect upon the final result is much greater. The difference in the quantity $E_{\mathrm{BS}}+E_{ee}$ between calculations 1 and 2 is only ~6%, but this leads to a difference of ~25% in the final value. Further steps in the self-consistency loop would be expected to lower $E_{\mathrm{BS}}+E_{ee}$ by an amount of $\lesssim$6%, so that result 2 is close to convergence as well as to the experimental value. We have also calculated the Grüneisen constant, with the result given in Table III. Here the cancellations are even larger, and the experimental value[38] is a very small positive coefficient. The calculated value is also small but still larger than experiment. Therefore, we conclude that the model-ion pseudopotential calculation we have carried out adequately explains the shear modulus $C_{11}-C_{12}$ at Si and its relation to the electronic states. However, it is not sufficiently accurate for Si to predict in detail results for modes in which the cancellations are largest, namely, the Grüneisen constant.

Another important result is that convergence for the structural energy could only be obtained by integration over a large set of special points [denoted by $q=4$ in the Appendix, requiring (10) 20 points in the (un)distorted case], implying that interactions between $3a/\sqrt{2}$ and $4a/\sqrt{2}$ are important. Therefore, the microscopic calculation shows that $C_{11}-C_{12}$ is highly influenced by long-range interactions. This is in agreement with phenomenological models such as those of Refs. 31 and 32. There it is shown that four-body forces involving third to sixth neighbors contribute ~$\frac{2}{3}$ of the restoring forces for $C_{11}-C_{12}$.

The crystal formed by displacing the atoms in a TA(X) pattern is shown in Fig. 4. It has four atoms per cell and a tetragonal Bravois lattice with basis vectors $(1,1,0)a/\sqrt{2}$, $(1,1,0)a/\sqrt{2}$, and $(0,0,1)a$. The harmonic frequency is calculated from

$$\Delta E_{\mathrm{tot}} = \tfrac{1}{2}(\tfrac{1}{2}m_{\mathrm{Si}})\omega_{\mathrm{TA}}^2 u^2 , \tag{32}$$

where ΔE_{tot} is the change in energy per atom pair, and u is the displacement magnitude. Because the displacements u are perpendicular to the bond vec-

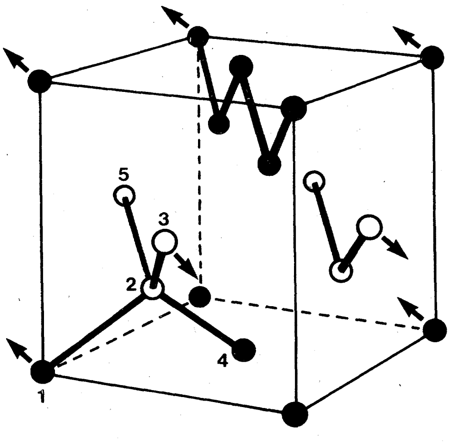

FIG. 4. Displacement pattern for TA(X) phonon mode. The labeling of the atoms corresponds to that used in Fig. 5. All white atoms move together to the lower right, and all black atoms to the upper left.

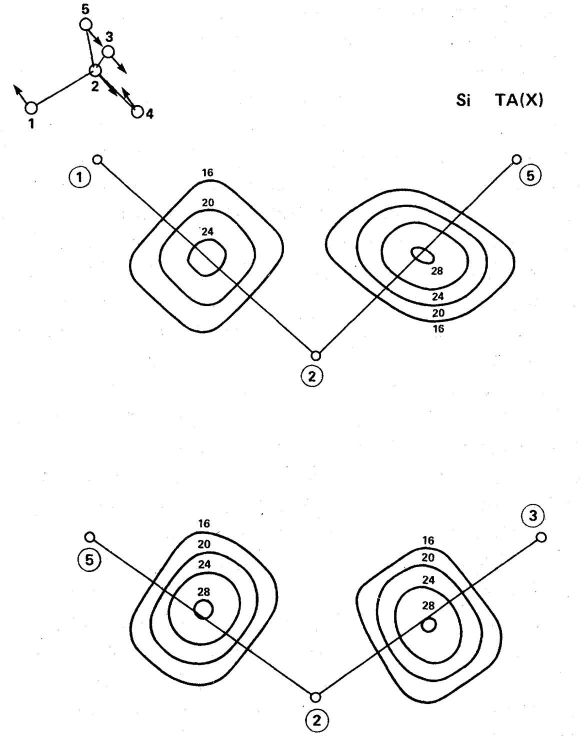

FIG. 5. Charge density for a crystal with a TA(X) displacement pattern. The inset and the larger set of atoms shown in Fig. 4 define the labeling of the bonds. A center of symmetry is maintained for bonds 1-2 and 2-4, but is lost for bonds 2-3 and 2-5. The "rotation" of the bonds is apparent in the 3-2-5 plane in the lower figure, and the change in shape is clear in each drawing.

tors, the restoring forces are angular in character. Since the TA(X) mode belongs to the same symmetry as the $C_{11}-C_{12}$ shear deformation, and the local environment of the atoms is similar, the contributions to the two modes are also similar, as shown in Fig. 3 and Table II. The results demonstrate that $m\omega_{\mathrm{TA}}^2$ is reduced compared to $2a(C_{11}-C_{12})$, which is in agreement with the experimental fact that ω_{TA} is anomalously low, but the amount of the reduction is not as great as found experimentally. The convergence is very similar for $2a(C_{11}-C_{12})$ and $m\omega_{\mathrm{TA}}^2$; however, because $m\omega_{\mathrm{TA}}^2$ is smaller, the fractional effect is larger. We conclude that a fully self-consistent result would lower the calculated ω_{TA} and would explain the "anomalous" softening.

The mechanism for the softening of the TA can already be seen in our calculations. Consider the changes in the charge density of the distorted crystal shown in Fig. 5. For the TA distortion there are two inequivalent types of bonds. Type I maintains inversion symmetry (the bond between atoms 1 and 2 in Fig. 4) and only the magnitude of the bonding charge decreases due to a change in bond length of second order in the atomic displacement. (All bonds are of this type for the $C_{11}-C_{12}$ shear.) For the bonds of type II, the center of symmetry is lost, allowing an off-center charge relaxation reminiscent of a bond-charge displacement.[20] We see also that the shape as well as the magnitude of the bond charge changes. It is this off-center motion and asymmetric change in the shape of the charge which allows the crystal to lower its energy for a TA mode relative to that for the $C_{11}-C_{12}$ elastic mode.

The results for the TA mode were at convergence in the lattice of special points for the set of points mapped from the $q=3$ set in the fcc (see Appendix). Since $C_{11}-C_{12}$ required that $q=4$, we see that ω_{TA} involves only forces of range shorter than those in $C_{11}-C_{12}$. This is in agreement with the phenomenological models,[31,32] where it is found that ω_{TA}^2 is determined solely by the simple second-neighbor bond-bending forces, whereas $C_{11}-C_{12}$ is greatly affected by longer-range forces.

Results for the Grüneisen coefficient are given in Table III. The primary result is the large negative value which has been found experimentally for Si and other tetrahedral semiconductors.[39] This has been interpreted[39] as a tendency toward the phase transition to the β-Sn structure which is analogous to the dramatic softening of ω_{TA} in the sequence of elements C-Si-Ge-Sn. In our calculations, the effect is primarily due to the negative ionic contribution which increases in magnitude as the lattice is compressed. The electronic contributions to the Grüneisen coefficient are small in contrast to the result for $C_{11}-C_{12}$. We see that the final result is qualitatively correct but considerably larger than experiment.

The calculated energies for $C_{11}-C_{12}$ and ω_{TA} may be compared with the empirical tight-binding results of Ref. 15. There, only the band-structure energy was considered for the case where the nearest-neighbor distance τ did not change. The present results are for constant volume, in which case τ increases to second order in the displacements. The additional positive contribution to ΔE_{BS} from $\Delta\tau$ qualitatively explains the large value of ΔE_{BS} found here compared to that reported in Ref. 15. The ion-ion and electron-electron terms also contribute in the present work, and lead to a final answer close to that of Ref. 15.

We conclude that the model ionic pseudopotential and local-density-functional approach for Si is adequate to predict the basic structural properties of Si such as the elastic constants and optical-mode frequencies. In the present form, it is apparently not accurate enough to predict the constants to better than ~20%, or to predict very sensitive quantities such as $d(C_{11}-C_{12})/dV$. It does predict the softening and the strong pressure dependence of the TA(X) frequency. However, for the TA mode the cancellations are so extensive that there is a large fractional error in the final value due to lack of convergence in the present steps toward self-consistency. For this mode, further calculations are required to definitively describe the TA restoring forces and the relation to charge density.

V. CONCLUSION

In conclusion, we have described a practical method to calculate the charge density and total energy of insulators as a function of the atomic positions without any adjustable parameters. The method is based on the local-density-functional formalism,[2,3] and relies upon the special-point technique.[1,17] Our scheme is not restricted to small displacements and in general involves the solution of self-consistent equations. Here, special attention was given to the formal and practical aspects of the scheme with respect to small distortions and small deviations from self-consistency. In particular, we derived the relation to the dielectric-function ϵ formalism and we showed that deviations of the charge density from the self-consistent density give rise to an error of the total energy only to second order in the deviation. We also demonstrated how the number of special points needed for convergence shows the range of interactions involved.

Results were calculated for Si employing a rigid-ion model potential for the Si^{4+} ion[18] together with a plane-wave basis. Computations were carried only to first order in self-consistency with careful analysis of the effects of self-consistency. Our calculated lattice constant was too small by ~13% and the bulk modulus by about 28%, indicating the need for a better (possibly nonlocal) potential in order to describe symmetry-conserving distortions. We stabilized the theoretical crystal at the experimental lattice constant by means of an *ad hoc* linear repulsive term between nearest neighbors. For distortions which lower the crystal symmetry, we then investigated TO(Γ), $C_{11}-C_{12}$, and TA(X) distortions and predicted the harmonic energies of these modes, their pressure coefficients, and the cubic force associated with the TO(Γ) mode. Predicted theoretical results were found to be close to experiment, except for the TA(X) harmonic energy and $d\ln(C_{11}-C_{12})/d\ln v$, for which the corresponding experimental values are extraordinarily small. Our investigations showed those cases to be very sensitive because of near cancellations, so that they require better convergence in self-consistency than obtained in our calculations. From the convergence of the special-point summations, the forces involved were found to be of short range in TO(Γ) and TA(X), and of longer range for the elastic $C_{11}-C_{12}$ deformation. One important result was that the proper inclusion of electron-electron interactions was vital for stability against shear. Altogether, the theoretical considerations and calculational results presented here are encouraging for the investigation of structural properties of semiconductors. They also indicate hope for other calculations in which periodicity can be used, for example, determining the equilibrium properties of crystalline surfaces.

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APPENDIX

Here we discuss the relation of the range of forces to the convergence in a number of special points. It is most convenient to follow the approach of Monkhorst and Pack,[17] although the generator methods of Chadi and Cohen[17] may be used as well. The range of forces may be determined by examining the energy as a function of the displacement of atoms in the various low-symmetry distortions. First, we consider a distortion which reduces the point-group symmetry to the identity, i.e., the lowest point-symmetry possible. In the special-point approach, the energy (as well as the charge density) is approximated by

$$E(\vec{k})=\sum_{\vec{m}} E_{\vec{m}} e^{i\vec{k}\cdot\vec{R}_{\vec{m}}}\,, \qquad \text{(A1)}$$

where $\vec{m}\equiv(m_1,m_2,m_3)$ and $\vec{R}_{\vec{m}}=\sum_{i=1}^{3} m_i\vec{R}_{\vec{i}}$ is a direct-lattice vector. Let the grid of special points be defined by the vector of integers $\vec{r}=(r_1,r_2,r_3)$ according to

$$\vec{k}_{\vec{r}}=\sum_{i=1}^{3} u_{\vec{r}}^{i}\vec{G}_i\,, \qquad \text{(A2)}$$

where the $\vec{G}_i$ are the reciprocal-lattice basis vectors and the $u_{\vec{r}}^{i}$ are given by the values

$$u_{r_j}^{i}=(2r_j-q-1)/2q,\quad r_j=1,\ldots,q\,. \qquad \text{(A3)}$$

The grid of points is specified by the integer q, where the grid spacing is inversely proportional to q.

Monkhorst and Pack[17] showed that the integrals over $\vec{k}$ implied in Eqs. (17) and (21) may be written

$$\Delta E=\int d^3k\,E(\vec{k})=\sum_{\vec{r}} E(\vec{k}_{\vec{r}})+{\sum_{\vec{m}}}' E_{\vec{m}}S_{\vec{m}}\,, \qquad \text{(A4)}$$

where $\sum'$ excludes the $\vec{m}=0$ term, and the final term is given by

$$S_{\vec{m}}=\begin{cases}(-1)^{(m_1+m_2+m_3)(q+1)/q} & \text{whenever each } m_i \text{ is a multiple of } q\\ 0 & \text{otherwise}\end{cases} \tag{A5}$$

In this paper we have evaluated the first term on the right-hand side of Eq. (A4) as a function of q, and varied q until convergence was reached. That is, we found the value of q for which the final term is negligibly small. It is clear from the derivation that this means that all $E_{\vec{m}}\approx 0$ for $\vec{m}$ for which $S_{\vec{m}}\neq 0$. The smallest lattice vector $\vec{R}_{\vec{m}}$ for which $S_{\vec{m}}\neq 0$ is $\vec{R}_{(q,0,0)}=q\vec{R}_1$. Therefore, convergence for a given value of q implies that interactions in the Hamiltonian for atoms separated by $q\vec{R}_1$ or larger vectors is negligible. In the case of distorted fcc crystals, this is the range $qa/\sqrt{2}$ which was used in the text in Sec. IV.

We note that for cases with higher symmetry, the above considerations are not sufficient. In that case, the upper identify in Eq. (A5) has to be replaced by

$$S_{\vec{m}}=\sum_{C_{\vec{m}}^*}(-1)^{(m_1+m_2+m_3)(q+1)/q}\,, \tag{A6}$$

where the sum is over the star $C_{\vec{m}}$ or $\vec{m}$ or $\vec{R}_{\vec{m}}$, respectively. The summation in Eq. (A6) may lead to a cancellation between terms which are opposite in sign. Thus the range of the interactions which are taken into account exactly in the special-point sum is greater. The range is always increased, never decreased, by these cancellations. For example, in the undistorted fcc case, the very large range of interactions accounted for by only a small set of reciprocal points, as shown by Chadi and Cohen,[17] can be readily derived by examining the cancellations in the sum in Eq. (A6).

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