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PSEUDOPOTENTIALS AND TOTAL ENERGY CALCULATIONS: APPLICATIONS TO CRYSTAL STABILITY, VIBRATIONAL PROPERTIES, PHASE TRANSFORMATIONS, AND SURFACE STRUCTURES

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July 1984

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PSEUDOPOTENTIALS AND TOTAL ENERGY CALCULATIONS: APPLICATIONS TO CRYSTAL STABILITY, VIBRATIONAL PROPERTIES, PHASE TRANSFORMATIONS, AND SURFACE STRUCTURES

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ABSTRACT

A review of the applications of the pseudopotential method and total energy techniques to the electronic and structural properties of solids is presented. With this approach, it has recently become possible to determine with accuracy crystal structures, lattice constants, bulk moduli, shear moduli, cohesive energies, phonon spectra, solid-solid phase transformations, and other static and dynamical properties of solids. The only inputs to these calculations, which are performed either with plane wave or LCAO bases, are the atomic numbers and masses of the constituent atoms. Calculations have also been carried out to study the atomic and electronic structure of surfaces, chemisorption systems, and interfaces. Results for several selected systems including the covalent semiconductors and insulators and the transition metals are discussed. The review is not exhaustive but focuses on specific prototype systems to illustrate recent progress.

I. INTRODUCTION

In the past decade, it has become possible to compute with good accuracy a number of electronic and structural properties for simple solids and their surfaces without resorting to empirical means. Among the quantities obtainable from these calculations are crystal structures, lattice constants, bulk moduli, shear moduli, cohesive energies, phonon spectra, electron-phonon and phonon-phonon interactions, solid-solid phase transformations, and other static and dynamical properties. This development has opened up many exciting possibilities for the study of condensed
matter since one is now in a position to predict properties of systems which were formerly inaccessible to theory or experiment. Possible applications are numerous—prediction of new materials; determination of the structure of surfaces, interfaces, and defects in solids; study of phase stability at high pressure; study of alloy stability; and so forth.

Several factors have contributed to the present success of ab initio calculations for real materials systems. These include the development of approximations to the density functional formalism, refinements in band structure calculational techniques, invention of the ab initio pseudopotentials, and development of techniques for calculating total energies. Equally important, of course, is the availability of modern high speed computers.

This set of lectures reviews some of the many recent theoretical accomplishments in this area. Experimental results are discussed only in so far as they bear on a theoretical result. In addition, in order to limit the scope of this review, emphasis will be placed on a few theoretical techniques—primarily the pseudopotential approach. Specific prototype systems are considered to illustrate the accomplishments of the theory for semiconductors, insulators, and transition metals. Some details of the calculations and results will be given, but the reader should go to the original papers for more specifics.

The organization of the lectures is as follows. A brief review of the theoretical techniques is given in Sec. II. This includes a discussion on the density functional formalism, generation of ab initio pseudopotentials, and techniques for band structure calculations. The bulk systems are discussed in Sec. III. The static structural properties are presented in Sec. IIIA. These results establish the accuracy of the calculations. Examples will be given for semiconductors, insulators, and transition metals. The vibrational properties are discussed in Sec. IIIB. Phonon frequencies are calculated using the frozen phonon technique. Complete dispersion curves along symmetry directions in the Brillouin zone are obtained from calculated force constants. Calculations of anharmonic terms and phonon-phonon interaction matrix elements are also presented. In Sec. IIIC, results for solid-solid phase transitions are presented. The stability of group IV covalent materials under pressure is discussed. Also presented is a calculation on the temperature- and pressure-induced crystal phase transitions in Be. In Sec. IV, we discuss the application of pseudopotential calculations to surface studies. Silicon and diamond surfaces will be used as the prototypes for the covalent semiconductor and insulator cases while surfaces of niobium and palladium will serve as representatives of the transition metal cases. In Sec. V, the validity of the local density approximation is examined. The results of a nonlocal density functional calculation for Si and
II. THEORETICAL TECHNIQUES

In this section, we briefly summarize the major theoretical techniques employed in contemporary pseudopotential calculations. The approach involves the use of ab initio pseudopotentials to compute the electron-core interactions and local density functionals for evaluating electron-electron interactions. Several different basis sets can be used to solve the electron wave equation. The particular choice is determined by the system of interest. Finally, the total energies and forces are calculated using a momentum space scheme.

A. Density Functional Formalism

One major difficulty in ab initio calculations of the properties of electronic systems is an adequate treatment of the many body electron-electron interaction. The most commonly used approach for condensed matter systems is that of the density functional formalism. Hohenberg and Kohn established that the electronic energy of a system of interacting electrons in an external potential \( V_{\text{ext}} \) is a functional of the electron density. This is usually written in the form:

\[
E[n] = T_0[n] + \int d\vec{r} \ n(\vec{r}) \ V_{\text{ext}}(\vec{r}) + E_H[n] + E_{\text{xc}}[n]
\]  

(1)

The first term is the kinetic energy of noninteracting electrons of the same density; the second term gives the energy of interaction with the external potential; the third term is the electrostatic or Hartree energy; and the last term contains the rest, the exchange-correlation energy which is an universal functional of \( n \). Further, the total energy is minimized for the correct ground state density, i.e.

\[
\frac{\delta E}{\delta n} = 0
\]  

(2)

at the physical \( n(\vec{r}) \). Given the energy functional, the problem of finding the ground state energy is reduced to solving a set of effective one electron equations with a local potential, the Kohn-Sham equations (in atomic units):

\[
\{-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) + u_{\text{xc}}[n]\} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})
\]  

(3)

The exchange-correlation part of the effective potential is given by \( u_{\text{xc}} = \delta E_{\text{xc}}/\delta n \) and the density \( n \) is obtained from the one-particle wavefunctions.
where \( N \) is the number of electrons in the system.

This formalism, therefore, reduces the many-body problem to an effective single-particle problem which in principle gives the exact ground state energy. The central difficulty is specification of \( E_{\text{xc}} \). The most widely used approach is the local density approximation (LDA)\(^9\):

\[
E_{\text{xc}}^{\text{LDA}} = \int \, d\mathbf{r} \, n(\mathbf{r}) \, e_{\text{xc}}^{\text{hom}}(n(\mathbf{r}))
\]

where \( e_{\text{xc}}^{\text{hom}}(n) \) is the exchange-correlation energy density of the homogeneous electron gas of density \( n \). Several parameterizations of electron gas data are in common use.\(^{10-14,18}\) The procedure in a typical calculation is: (1) Determine \( V_{\text{ext}} \) from the constituent elements and an assumed geometry. (2) Calculate the electron energies and wavefunctions and determine \( n(\mathbf{r}) \). (3) Evaluate the total energy \( E[n] \).

B. Ab Initio Pseudopotentials

In the pseudopotential approach, \( V_{\text{ext}} \) is replaced by an ionic pseudopotential which combines the nucleus and the core electrons into one inert entity, and the self-consistent field equations (Eqs. 3 and 4) are carried out only for the valence electrons. The ionic pseudopotentials, unlike the all-electron potentials, are nonsingular by construction near the nuclei leading to smooth valence electron wavefunctions which greatly facilitate the calculations. Moreover, since the core electrons which do not influence the properties of the solid phase are removed from the problem, much higher numerical precisions can be achieved. Systems involving heavy atoms are not much more complicated than those with light ones. Table I depicts the precision requirements for calculating various cohesive and structural quantities. The only disadvantage of the pseudopotential approach is that the potential is nonlocal, i.e., angular momentum dependent. This, however, only imposes a small inconvenience in the calculations.

Several simple schemes\(^3-7\) have been formulated to extract ab initio ionic pseudopotentials from atomic calculations. The basic procedure is to generate a potential by inversion of the Kohn-Sham equation. Angular-momentum-dependent screened atomic pseudopotentials, \( V_{\delta} \), are first constructed with the constraints that: (1) the valence eigenvalues from the all-electron calculation and those from the pseudopotential calculation agree for a chosen prototype configuration and (2) the all-electron wavefunctions

\[
n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2
\]
Table I. Precision requirement for various structural quantities.

<table>
<thead>
<tr>
<th>Precision requirement</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>cohesive energy</td>
<td>0.01 Ry/atom</td>
</tr>
<tr>
<td>lattice constant, bulk modulus</td>
<td>0.001 Ry/atom</td>
</tr>
<tr>
<td>phonon frequencies</td>
<td>0.0001 Ry/atom</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total crystal energy (referred to dissociated entities)</th>
</tr>
</thead>
<tbody>
<tr>
<td>all-electron calculation</td>
</tr>
<tr>
<td>pseudopotential calculation</td>
</tr>
</tbody>
</table>

and the pseudowavefunctions agree beyond a chosen core radius, \( r_C \). With these constraints, it can be shown that the potentials have two centrally desirable properties. The electrostatic potential produced outside \( r_C \) is identical for the all-electron and the pseudocharge distribution; the scattering properties of the all-electron atoms are reproduced with minimum error as the electronic eigenvalues move away from the prototype atomic levels. These two properties ensure a good transferability of the pseudopotentials. The final bare-ion pseudopotentials, \( V_{ion}^{\text{bare}} \), are extracted from the neutral potentials by subtracting from each neutral \( V_{ion}^{\text{neutral}} \) the Coulomb and exchange and correlation potentials due to the pseudovalence charge density.

In Fig. 1, the ionic pseudopotential for Si generated using the Hamann-Schlüter-Chiang scheme\(^3\) is depicted. It is evident that much of the strong attractive Coulomb point ion potential near the core is reduced in the pseudopotential formalism. A comparison of the all-electron wavefunction with the pseudowavefunction is illustrated in Fig. 2. It should be remarked that the exact form of the pseudopotential in the core region is nonunique since the potential is only required to reproduce the scattering properties of the ion core outside of a certain radius. The different generation schemes produce very different looking potentials. This feature can, in fact, be well utilized in tailoring the form of the ionic pseudopotential to suit the particular techniques used in a band structure calculation. Figure 3 shows an Si ionic pseudopotential generated using the Kerker scheme.\(^4\) Identical values were obtained from the two potentials for quantities of interest.

The ab initio pseudopotentials together with the local density approximation have proven to yield excellent results as will be illustrated by the examples in this review. The basic assumptions in their construction are the frozen-core approximation and a decoupling of the core charge in the determination of the exchange-correlation potential seen by the valence electrons.
Fig. 1. Nonlocal ionic pseudopotential for Si generated using the Hamann-Schlüter-Chiang scheme Ref. 3). The potentials for angular momentum $l = 0, 1, \text{ and } 2$ are shown. The dash line represents the Coulomb point ion potential.

Fig. 2. Comparison of the 35 pseudowavefunctions and all-electron wavefunction for Si.
Fig. 3. Nonlocal ionic pseudopotential for Si generated using the Kerker scheme (Ref. 4).

Since the local density exchange-correlation functionals\textsuperscript{10-14} are nonlinear in the charge density, the second assumption is not strictly valid when there is a large overlap between the valence and core charge densities or when spin-density-functional calculations are performed. However, this problem can easily be eliminated by the use of nonlinear ionic pseudopotentials\textsuperscript{7} where the core charge density is explicitly carried along in a calculation for the purpose of evaluating the exchange-correlation potentials and energy densities.

C. Basis Sets

To solve the Kohn-Sham equations with pseudopotentials, the standard approach is to expand the electron wavefunctions by a plane wave set in reciprocal space lattice vectors. The electron structure is obtained by diagonalization of the Hamiltonian matrix. This basis set has been mostly employed for semiconductor studies because of the relatively smooth pseudopotentials and delocalized electron wavefunctions of these systems. There are several advantages for using plane waves. The Hamiltonian matrix elements are simple to evaluate. Test of convergence in the basis expansion can be done by simply increasing the number of plane waves used. Moreover, the calculation of Hellmann-Feynman forces is the less involved in a plane wave basis.

For systems with highly localized electrons such as the transi-
tion metals and large-gap insulators, a plane wave basis set would not be suitable. Other more judicious choices of basis functions have to be used. One approach is to use a mixed-basis set.\textsuperscript{15} The electron wavefunction is expanded in a combined set of plane waves and Bloch sums of atom-centered Gaussian orbitals. The mixed-basis set is most suitable for efficient description of systems with both highly localized (atomic-like) electrons and delocalized (plane wave-like) electrons. Another approach is to use a linear combination of atomic-like orbitals (LCAO) basis.\textsuperscript{16} This is probably the most efficient basis for calculating the total energy of complex systems. For some elements, with suitable choices of Gaussian orbitals centered on each atom, the number of basis functions per atom needed to obtain an accurate charge density can be reduced by one or more orders of magnitude as compared with a plane wave expansion. For example, instead of requiring $N \sim 300$ plane waves to describe the carbon pseudowavefunction in diamond, only 12 Gaussian orbitals are needed for each atom. Since, in general, the computer memory required in a calculation is proportional to $N^2$ and the time required to $N^3$, this represents orders of magnitude of savings. Moreover, with the LCAO approach, results can be more easily interpreted in terms of the chemical bonds. Other factors also contribute to the numerical efficiency of this method. With the potential also expanded in Gaussians, all the matrix elements consist of integrals of Gaussians and polynomials. These integrals can be evaluated in closed form. The essential matrix elements are wavevector independent. Thus, once these elements have been determined, they may be stored and retrieved as necessary for the wavevector in question. Furthermore, with the LCAO basis, there are several simplified levels of self-consistency\textsuperscript{19,20} that may be carried out for those complex systems for which full point by point self-consistency would not be practical.

D. Total Energy Expressions

Once the single particle wave equation has been solved, the total energy of the system may be evaluated. It is usually cast in the form

$$E_{\text{total}} = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int V_H(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} - \int u_{xc}[n] n(\mathbf{r}) d\mathbf{r}$$

$$+ \int \varepsilon_{xc}[n] n(\mathbf{r}) d\mathbf{r} + E_{\text{ion-ion}}$$

(6)

where the sum is over all occupied states, $\varepsilon_i$ are the one-electron eigenvalues, $n$ is the self-consistent charge density, $\varepsilon_{xc}$ is the exchange-correlation energy density, and $u_{xc}$ is the exchange correla-
tion potential. $E_{\text{ion-ion}}$ is the electrostatic interaction energy among the bare ions.

The expression in Eq. 6, however, does not have the variational property given by Eq. 2 unless $n$ is the exact fully self-consistent charge density. This is because the sum of electron eigenvalues, the first term on the right of Eq. 6, contains information on both the input charge and the output charge of a particular iterative cycle in the calculation. Thus, $E_{\text{total}}$ is not a functional of a single density. For many applications, an alternate expression which makes explicit use of the density-functional variational principle is desirable. Consider a situation where an initial charge density $n_{\text{in}}$ (e.g., from the superposition of atomic charge densities) is used and the single particle equation is solved to obtain a new charge density $\tilde{n}$. One can show\textsuperscript{16} that the total energy can be written as

$$
E_{\text{total}} = \sum_{i=1}^{N} \varepsilon_i - \int V_H[n_{\text{in}}] \tilde{n}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int V_H[\tilde{n}] \tilde{n}(\mathbf{r}) d\mathbf{r} + \int \mu_{\text{xc}}[n_{\text{in}}] \tilde{n}(\mathbf{r}) d\mathbf{r}
$$

$$
+ \int \varepsilon_{\text{xc}}[\tilde{n}] \tilde{n}(\mathbf{r}) d\mathbf{r} + E_{\text{ion-ion}}
$$

which is accurate to second order in $\Delta n = n - \tilde{n}$. In Eq. 7, all contributions from $n_{\text{in}}$ (and, hence, from the input screening potential) are explicitly removed from the energy expression. The sole function of $n_{\text{in}}$ is to provide a way for obtaining a good approximation to $n$. Often, it is possible to obtain accurate ground-state properties by using the superposition of atomic charge for $n_{\text{in}}$ and only solve the Kohn-Sham equation once to obtain $\tilde{n}$. In this fashion, many self-consistent cycles may be eliminated in obtaining an accurate solution for the total energy.

To evaluate the total energy terms in Eq. 7 for periodic or quasiperiodic systems, it is most convenient to use the formalism of Ihm et al.\textsuperscript{17} This formalism expresses the energy in momentum space and involves the Fourier transform of the potential and charge density. The energy per atom is written as (for the case of an elemental solid with one atom per unit cell)

$$
E_{\text{total}} = \frac{1}{N} \sum_{n_{\text{in}}} n_{n_{\text{in}}} \mathbf{k} - \Omega_a \sum_{G \neq 0} [V_H(n_{\mathbf{G}}) + u_{\text{xc}}(\mathbf{G})] \tilde{n}(\mathbf{G})
$$

$$
+ \frac{1}{2} \Omega_a \sum_{G \neq 0} \tilde{V}_H(\mathbf{G}) \tilde{n}(\mathbf{G}) + \Omega_a \sum_{\mathbf{G}} \tilde{\varepsilon}_{\text{xc}}(\mathbf{G}) \tilde{n}(\mathbf{G})
$$

$$
+ \gamma_{\text{Ewald}} + \alpha Z
$$

(8)
where
\[ \gamma_{\text{Ewald}} = \frac{1}{2} \sum_{\mathbf{R} \neq 0} \frac{Z^2}{|\mathbf{R}|} - \frac{1}{2\pi^2} \Omega_a \int \frac{4\pi Z^2}{|\mathbf{G} + \mathbf{G}_a|^2} d^3r. \]

Here \( \Omega_a \) is the atomic volume in the crystal, \( N \) is the number of atoms in the crystal, and the sum of the first term is over all occupied bands. We use atomic units, and \( \mathbf{G} \) denotes the reciprocal lattice vectors.

III. BULK PROPERTIES

In this section, we describe the applications of the density functional pseudopotential scheme to the bulk properties of solids. Since this is a very active area, only specific prototypical calculations are featured to illustrate major subareas. The results on semiconductors were calculated using the plane wave method whereas results on transition metals and insulators were obtained either using the mixed basis approach or the LCAO approach.

The total energy must be computed very precisely if it is to be used to calculate structural and other ground-state properties. An estimate of the precision requirements for the total energy for calculation of the cohesive energy, the lattice constant or bulk moduli, and phonon frequencies are given in Table I. A major advantage of the pseudopotential method as mentioned in the previous section is that the energies of the core electrons which are of the order of \(-10^3 \) to \(-10^4 \) Ry per atom are removed from the total energies of both the isolated atoms and those of the solid state. This leads to a major enhancement in the precision of a calculation.

A. Static Structural Properties

Calculations have been carried out for a number of solids. The first applications were to the semiconductors.\(^{21,22}\) However, for the purpose of illustration here, we first discuss the results for diamond.\(^{16}\) The calculation was carried out using the LCAO basis with three Gaussian exponents for each of the s, px, py, and pz orbitals totaling 12 basis functions per carbon atom. The calculated total energy as a function of volume \( E(V) \) is present in Fig. 4. The points are the computed values, and the curve is a fit of the results to the Murnaghan\(^{23}\) equation of state. The minimum and curvature of \( E(V) \) near the minimum determine the lattice constant and bulk modulus. The cohesive energy can be evaluated by comparing the energy for the solid including a zero-point motion contribution and the isolated pseudoatom ground-state energy.
Fig. 4. Total energy vs. volume for carbon in the diamond structure. The continuous curve is the Murnaghan equation of state fit to the calculated points. (from Ref. 16)

Fig. 5. Total energy curves for various assumed crystal structures of Si as a function of volume normalized to the observed volume. The dashed line is the common tangent between the diamond and white tin phases. (from Ref. 21)
Table II. Ground-state properties of diamond. (after Ref. 16)

<table>
<thead>
<tr>
<th>Ground state</th>
<th>Experiment</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LCAO</td>
<td>Plane waves</td>
</tr>
<tr>
<td>Cohesive energy (in eV)</td>
<td>7.37</td>
<td>7.84</td>
</tr>
<tr>
<td>Lattice constant (in Å)</td>
<td>3.567</td>
<td>3.560</td>
</tr>
<tr>
<td>Bulk modulus (in Mbar)</td>
<td>4.42</td>
<td>4.37</td>
</tr>
<tr>
<td>Pressure derivative of bulk modulus</td>
<td>4</td>
<td>3.54</td>
</tr>
</tbody>
</table>

Further, by fitting the calculated points to an equation of state such as the Murnaghan form:

\[
E(V) = \frac{B_0 V}{B'_0 (B'_0 - 1)} \left[ B'_0 \left(1 - \frac{V}{V_0}\right) + \left(\frac{V}{V_0}\right)^{B'_0} - 1 \right] + E(V_0) \tag{9}
\]

we obtain both the equilibrium bulk modulus \(B_0\) and its pressure derivative \(B'_0\). The results\(^{16}\) are compiled in Table II together with the experimental values and results from a self-consistent plane wave calculation.\(^{24}\) There is excellent agreement between theory and experiment and between the two theoretical calculations. The LCAO total energy was evaluated using the variational expression (Eq. 7) with \(n\) obtained from a potential generated using superposition of carbon sp\(^3\) atomic charges. This and the fact that only 12 basis functions per atom were used account for the slight difference in the cohesive energy between the two calculations. We note that because of the localized nature of the carbon bond in diamond approximately 250 plane waves per atom were used for the plane wave basis.

In Fig. 5, the total energy of Si is given as a function of volume for seven different crystal structures.\(^{21}\) As expected and consistent with experiment, the diamond structure has the lowest energy. Since these curves were generated with the atomic number and several assumed crystal structures as the only input, the method can be used to predict crystal structures and to study solid-solid structural phase transformations. The calculated structural results\(^{21}\) for Si and Ge in the diamond structure are
Table III. Comparison of calculated and measured static properties of Si and Ge. (from Ref. 21)

<table>
<thead>
<tr>
<th></th>
<th>Lattice constant (Å)</th>
<th>Cohesive energy (eV/atom)</th>
<th>Bulk modulus (Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Calculation</td>
<td>5.451</td>
<td>4.84</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>5.429</td>
<td>4.63</td>
</tr>
<tr>
<td>Ge</td>
<td>Calculation</td>
<td>5.655</td>
<td>4.26</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>5.652</td>
<td>3.85</td>
</tr>
</tbody>
</table>

Table IV. Static properties for some III-V semiconductors. (from Ref. 22)

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>GaP</th>
<th>AlAs</th>
<th>AlP</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>th</td>
<td>5.570</td>
<td>5.340</td>
<td>5.641</td>
<td>5.420</td>
</tr>
<tr>
<td>exp</td>
<td>5.653</td>
<td>5.451</td>
<td>5.662</td>
<td>5.451</td>
</tr>
<tr>
<td>$B_0$ (10^10 N m^-2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>th</td>
<td>7.25</td>
<td>8.97</td>
<td>7.41</td>
<td>8.65</td>
</tr>
<tr>
<td>exp</td>
<td>7.48</td>
<td>8.87</td>
<td>7.70</td>
<td>8.60</td>
</tr>
</tbody>
</table>

summarized in Table III. Agreement with experiment to within 1% is found for the lattice constants; the cohesive energies and bulk moduli are given to around 10%.

Structural calculations have not been limited to the group IV elements. The plane wave calculations have been extended to the III-V semiconductors and the simple metals like Be, Na, and Al. Some results for these crystals are listed in Tables IV and V. In the case of Be, it was possible to calculate the Poisson ratio and the c/a ratio. Using the LCAO approach, these calculations have also been extended to study the transition metals. Some representative results are presented in Table VI for the cases of Mo and W. The transition metals are much more difficult to
Table V. Static structural properties of Al and Be. (after Refs. 25 and 26)

<table>
<thead>
<tr>
<th>Material</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aluminum</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>B₀ (x 10¹² dyne cm⁻²)</td>
<td></td>
</tr>
<tr>
<td>Theory</td>
<td>4.01</td>
<td>0.715</td>
</tr>
<tr>
<td>Experiment</td>
<td>4.02</td>
<td>0.722</td>
</tr>
<tr>
<td><strong>Beryllium</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>c (Å)</td>
<td>c/a</td>
</tr>
<tr>
<td>Theory</td>
<td>2.25</td>
<td>3.57</td>
</tr>
<tr>
<td>Experiment</td>
<td>2.2858</td>
<td>3.5842</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theory</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>Experiment</td>
<td>-0.01 - -0.05</td>
<td></td>
</tr>
</tbody>
</table>

deal with because of their much stronger potentials and their very localized electrons. The LCAO method, nevertheless, yields results as accurate as those of the semiconductors which are considered state-of-the-art. Similar calculations have also been carried out using the mixed basis method.²⁸

The accuracy of the results for all the materials mentioned are, therefore, comparable and, in general, in very good agreement with experiment. For special cases like Na,⁷ which has a small cohesive energy and low electronic density so that correlation effects are important, the results are sensitive to the choice of the LDA exchange-correlation potential. For most systems, the use of different exchange-correlation potentials only results in a few percent change in the computed values. In addition to the structural properties, the LDA pseudopotential calculations provide very accurate valence charge densities n(r). This is illustrated by Fig. 6 in which the calculated charge density of graphite²⁹ is compared with the experimental density obtained from x-ray measurements.³⁰

B. Vibrational Properties

Given the capacity to evaluate total energy for arbitrary crystal structures, it is clear that we should be able to probe energy changes with atomic positions and, therefore, be able to cal-
Table VI. Comparison of calculated and measured static properties of Mo and W. (from Ref. 27)

<table>
<thead>
<tr>
<th></th>
<th>Lattice constant (Å)</th>
<th>Cohesive energy (eV/atom)</th>
<th>Bulk modulus (Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Calculation</td>
<td>3.09</td>
<td>7.16</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>3.15</td>
<td>6.82</td>
</tr>
<tr>
<td>W</td>
<td>Calculation</td>
<td>3.12</td>
<td>8.56</td>
</tr>
<tr>
<td></td>
<td>Experiment</td>
<td>3.16</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Fig. 6. Contour plots of valence-electronic-charge density for graphite: (A) Present results and (b) results from analysis of x-ray data. Contour values are given in units of 0.1 e/Å³. Atomic positions are denoted by filled circles. Two planes are shown—one containing an a axis and the other containing the c axis and both intersecting at 90° along a C–C bond. In (a), the dashed circle denotes the pseudopotential radius. (from Ref. 29)
1. Phonon Dispersions. The frequency and eigenvector of an individual phonon mode can be obtained using the frozen phonon technique. In this approach, the usual Born-Oppenheimer approximation is made. The electrons are assumed to be in the ground state defined by the instantaneous ionic configuration. In the calculation, the crystal is distorted with atomic displacements corresponding to a particular phonon mode (For simplicity, we specialize to the case of one atom per unit cell), for example,

$$\mathbf{u}_k = u_0 \hat{\mathbf{e}}_k \cos(k \cdot \mathbf{R}_i + \delta_k)$$

(10)

where \(\mathbf{R}_i\) is the equilibrium position of the \(i\)th atom, \(u_0\) is the amplitude of the distorted wave, and \(\delta_k\) is the phase factor. If the wave vector \(k\) is commensurate with the bulk reciprocal lattice, the resultant deformed lattice is just another crystal with reduced symmetry. The energy difference per atom between the two crystals can be calculated as a function of the displacement amplitude \(u_0\) and fit to the expansion

$$\Delta E = \frac{1}{2!} K_2 u_0^2 + \frac{1}{3!} K_3 u_0^3 + \frac{1}{4!} K_4 u_0^4 + \ldots$$

(11)

\(K_2\) as shown below is related to the phonon frequency

$$\frac{M u_k^2}{K} = K_2$$

(12)

for a zone center or zone boundary phonon and

$$\frac{1}{2} \frac{M u_k^2}{K} = K_2$$

(13)

for a phonon mode of arbitrary \(k\). The higher order terms \(K_3\) and \(K_4\) are the anharmonic terms which give rise to the phonon-phonon interactions.

Thus, from Eqs. 12 and 13, the phonon frequency can be evaluated from the curvature of the calculated energy vs. displacement curve for small displacements. These results can be extended to the case of compounds and to general wave vectors where the lack of symmetry requires the calculation and diagonalization of the dynamical matrix to obtain the phonon frequencies and polarization vectors. Moreover, this approach allows a detailed investigation of the role of core-core, electron-core, electron kinetic, and electron-electron energies to determine the vibrational frequencies of the solids examined. This kind of information has been valuable in analyzing and understanding phonon anomalies in semiconductors and transition metals.

Figure 7 illustrates the changes in the crystal total energy as a function of the amplitude for a \(k = 0\) optical phonon frozen...
Fig. 7. Frozen-phonon energy vs. bond displacement. (from Ref. 16)

into the diamond crystal. The atomic motions for this phonon mode are particularly simple. The motion may be taken to be a constant volume uniaxial distortion of the diamond crystal along the <111> direction. From the quadratic term of the curve in Fig. 7, the zone center optical phonon frequency was obtained to within 1% of the experimental value. Compared to the structural properties calculations, the only additional input is the ionic masses. The calculated phonon frequencies for some selected phonon modes are presented in Table VII and Table VIII for diamond and Si respectively. As seen in Table VIII, phonon mode Grüneisen parameters have also been obtained. It is probably fair to say that phonon calculations using this ab initio approach give results which are more accurate than most empirical fits. In addition to obtaining accurate frequencies, the calculations are of great value because they allow detailed analysis of the electronic response to lattice distortions and, hence, the mechanisms causing phonon anomalies. The calculations also provide microscopic information not obtainable otherwise and provide benchmarks for the validity of phenomenological models.

The frozen phonon technique has been applied with equal success to the metals. The only added complication in these calculations is that a large number of k-points in the Brillouin zone is needed to sample over the Fermi surface for convergent results because of the small energies involved.

It is also possible to obtain whole phonon dispersion curves along some direction in k-space from the ab initio calculations. This can be done in two equivalent ways. One way is
Table VII. Frozen phonon calculations of phonon frequencies for selected modes of diamond. (from Ref. 35)

<table>
<thead>
<tr>
<th>Mode</th>
<th>( \omega_{\text{theory}} ) (cm(^{-1}))</th>
<th>( \omega_{\text{expt.}} ) (cm(^{-1}))</th>
<th>( \Delta \omega ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTO(( \Gamma ))</td>
<td>1346.5</td>
<td>1332</td>
<td>15</td>
</tr>
<tr>
<td>LO(( \Gamma = 1/3 ) to X)</td>
<td>1353.3</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LO(( \Gamma = 2/3 ) to X)</td>
<td>1328.2</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>LOA(X)</td>
<td>1219.5</td>
<td>1185</td>
<td>34</td>
</tr>
<tr>
<td>TO(X)</td>
<td>1173.9</td>
<td>1069</td>
<td>104</td>
</tr>
<tr>
<td>TA(X)</td>
<td>772.1</td>
<td>807</td>
<td>-35</td>
</tr>
</tbody>
</table>

Table VIII. Total energy calculations of phonon energies and Gr"uneisen parameters for a few phonon frequencies of Si. (from Ref. 31)

<table>
<thead>
<tr>
<th>Phonon frequencies (THz)</th>
<th>LTO(( \Gamma ))</th>
<th>TA(X)</th>
<th>TO(X)</th>
<th>LOA(X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{\text{calc.}} )</td>
<td>15.16</td>
<td>4.45</td>
<td>13.48</td>
<td>12.16</td>
</tr>
<tr>
<td>( F_{\text{expt.}} )</td>
<td>15.53</td>
<td>4.49</td>
<td>13.90</td>
<td>12.32</td>
</tr>
<tr>
<td>Deviation</td>
<td>-2.4%</td>
<td>-0.9%</td>
<td>-3.0%</td>
<td>-1.3%</td>
</tr>
</tbody>
</table>

Gr"uneisen parameter

| \( \gamma_{\text{calc.}} \) | 0.92 | -1.50 | 1.34 | 0.92 |
| \( \gamma_{\text{expt.}} \)  | 0.98 | -1.40 | 1.50 | ~0.90 |

by computing the Hellmann-Feynman forces on atoms resulting from displacing a plane of atoms. This is done by considering a supercell of \( N \) layers and, thus, obtaining the first \( N \) nearest neighbor force constants. Results\(^{38}\) for Si in the [100] direction of the Brillouin zone calculated this way are given in Fig. 8. Another equivalent way which does not involve the Hellmann-Feynman forces directly is to perform several frozen phonon calculations along a \( k \)-direction for a given branch. Given the calculated frequencies, one can invert the dynamical matrix to obtain the planar force constants up to several nearest-neighbor planes until convergence is achieved. Results\(^{35}\) for the longitudinal branches of diamond in the [100]
Fig. 8. Calculation of phonon dispersions for Si in the [100] direction using Hellmann-Feynman forces. The dashed line is the result when plane waves up to an energy of 6 Ry are used; the solid line is for 10 Ry. The triangles and dots represent measured points. (from Ref. 38)

direction obtained using this scheme are given in Fig. 9.

2. Anharmonic terms and phonon-phonon interactions. As seen from Eq. 11, in addition to the phonon frequencies, the frozen phonon calculations yield higher order anharmonic terms and, hence, information on phonon-phonon interactions. They are extremely valuable information since these terms are often not directly measurable and cannot be reliably gotten from phenomenological models.

To illustrate the kind of useful information that can be obtained, we consider here in some detail one example—calculation of the optical phonon-phonon interactions in diamond. This will serve both to illustrate the power of the method and to shed some light into the phenomenon of two-phonon Raman anomaly in diamond. It was observed that the two-phonon Raman spectrum of diamond has an anomalous sharp peak (not seen for Si and Ge) at 2667 cm⁻¹ which is at an energy 3 cm⁻¹ higher than twice the optical phonon frequencies at Γ. Despite a number of theoretical works, the nature and origin of this peak is still a mystery. One particularly intriguing explanation was the two-phonon bound state theory by Cohen and Ruvalds. They proposed that a two-phonon bound state is formed
Fig. 9. Calculation of phonon dispersions for diamond in the [100] direction by extracting force constants from frozen-phonon results. Only the longitudinal modes are plotted. The squares are frozen-phonon results. The triangles and dots represent measured points. (from Ref. 35)

giving rise to a split-off level at the anomalous peak position if the optical phonons near the Brillouin zone center interact through a positive quartic anharmonic interaction $\Phi$

$$
\begin{align*}
\vec{k}' & \rightarrow -\vec{k}' \\
\vec{k} & \rightarrow -\vec{k}
\end{align*}
$$

which is greater than certain critical value. For 15 years, this theory was neither confirmed nor disproved because of the lack of information on the optical phonon anharmonic terms.

In the following, we summarize a calculation on $\Phi$ for the optical phonons at $\vec{k} = 0$. For simplicity, we again specialize our discussion to one basis atom per unit cell and later generalize to the case of the diamond structure. The total energy of the crystal is expanded in a series in the atomic displacements $\xi$ from the equilibrium positions.

$$
E_{\text{tot}} = E_0 + (T + E_2) + E_3 + E_4 + \ldots 
$$

(14)

where
\( T \) = kinetic energy

\( E_0 \) = constant

\[
E_2' = \frac{1}{2T} \sum_{\mathbf{m}, \mathbf{n}} \phi_{ij}^{\mathbf{m}, \mathbf{n}} \xi_i^m \xi_j^n
\]

\[
E_3 = \frac{1}{3!} \sum_{\mathbf{m}, \mathbf{n}, \mathbf{j}} \phi_{ijk}^{\mathbf{m}, \mathbf{n}} \xi_i^m \xi_j^n \xi_k^p
\]

\[
E_4 = \frac{1}{4!} \sum_{\mathbf{m}, \mathbf{n}, \mathbf{j}, \mathbf{k}} \phi_{ijkl}^{\mathbf{m}, \mathbf{n}} \xi_i^m \xi_j^n \xi_k^p \xi_l^q
\]

With \( i, j, \ldots = \) cartesian indices and \( \mathbf{m}, \mathbf{n}, \ldots = \) real space lattice vectors. If we denote the eigenvectors of the harmonic part, \( T + E_2' \), by

\[
\mathbf{Q}_{m} = \frac{1}{\sqrt{N}} \mathbf{e}_{i}^m \mathbf{e}^{ik} \mathbf{e}^{ik} \quad (15)
\]

where \( \lambda \) is the polarization index, then the normal mode coordinates \( a' \)'s are given by

\[
\xi_i^m = \sum_{\mathbf{k}, \mathbf{l}} \mathbf{Q}_{\mathbf{m}}^{\mathbf{k}, \mathbf{l}} a_\mathbf{k}^m \quad (16)
\]

The energy terms in Eq. 14 may be written as

\[
E_2' = \frac{1}{2T} \sum_{\mathbf{k}, \mathbf{l}} \phi_{\mathbf{k}, \mathbf{l}}^{' \mathbf{k}'} \mathbf{a}_{\mathbf{k}}^{\mathbf{l}} \mathbf{a}_{\mathbf{k}'}^{\mathbf{l}'} \quad (17a)
\]

\[
E_3 = \frac{1}{3!} \sum_{\mathbf{k}, \mathbf{l}, \mathbf{m}} \phi_{\mathbf{k}, \mathbf{l}, \mathbf{m}}^{' \mathbf{l}'} \mathbf{a}_{\mathbf{k}}^{\mathbf{l}} \mathbf{a}_{\mathbf{k}'}^{\mathbf{l}'} \mathbf{a}_{\mathbf{m}}^{\mathbf{l}''} \quad (17b)
\]
and

\[ E_4 = \frac{1}{4!} \frac{1}{N} \sum_{kk'k''k'''} \phi^{kk'}^{\lambda_{\lambda'}}^{k''_{k''_{k'''}}} a_{\lambda} a_{\lambda'} a_{\lambda''} a_{\lambda'''} \]  \hspace{1cm} (17c)

The \( \phi \)'s are then the generalized elastic constants. The third and fourth order \( \phi \)'s are directly proportional to the matrix elements for the three- and four-phonon processes respectively.

For example, since the \( a \)'s are the normal mode coordinates,

\[ \phi^{kk'}_{\lambda\lambda'} = \delta_{k,-k'} \delta_{\lambda,\lambda'} \kappa(\tilde{k},\lambda) \]  \hspace{1cm} (18)

Therefore,

\[ E_2' = \frac{1}{2} \sum_{k\lambda} \kappa(k,\lambda) a_{\lambda}^* a_{\lambda} \]  \hspace{1cm} (19)

Also, the kinetic energy is given by

\[ T = \frac{M}{2} \sum_{k\lambda} a_{\lambda}^* a_{\lambda} = \frac{M}{2} \sum_{k\lambda} \omega^2(k,\lambda) a_{\lambda}^* a_{\lambda} \]  \hspace{1cm} (20)

Equating \( E_2 = T \) mode by mode, one obtains

\[ \omega(k,\lambda) = \sqrt{\frac{\kappa(k,\lambda)}{M}} \]  \hspace{1cm} (21)

For the purpose of understanding the two-phonon bound state problem, we are interested in the \( k \approx 0 \) phonons and their interactions. We, therefore, need to calculate \( \phi^{\lambda_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}} \) and \( \phi^{\lambda_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}} \) where \( \lambda \) denotes the various optical modes. For example, \( \phi^{\lambda_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}} \) gives the amplitude for the process

\[ \lambda'' \]
\[ \lambda \]
\[ \lambda' \]

and \( \phi^{\lambda_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}}_{\lambda''_{\lambda'''}} \) the amplitude for

\[ \lambda'' \]
\[ \lambda'' \]
\[ \lambda' \]
\[ \lambda'' \]
\[ \lambda' \]
Here, we will focus on calculating only these $\mathbf{k} = 0$ terms. Generalization to other cases involving finite $\mathbf{k}$'s can be done straightforwardly.

In a frozen-phonon calculation, instead of traveling waves

$$
\xi^\dagger_i = \frac{1}{\sqrt{N}} \sum_{k\lambda} a^k_\lambda \tilde{e}^k_{i\lambda} e^{i \mathbf{k} \cdot \mathbf{m}} \tag{22}
$$

standing waves of the form

$$
\xi^\dagger_i = \sum_{k\lambda} u^k_\lambda \tilde{e}^k_{i\lambda} \cos(\mathbf{k} \cdot \mathbf{m}) \tag{23}
$$

are considered. For the case of diamond and $\mathbf{k} = 0$, a standing wave consisting of a linear combination of the optical modes is used. We may choose the three polarization vectors to be $\hat{x}$, $\hat{y}$, and $\hat{z}$. Then, the atomic displacements for the two carbon atoms in the unit cell are of the form

$$
\begin{align*}
\mathbf{\xi}^\dagger (1) &= \mathbf{u} \cos(\mathbf{k} \cdot \mathbf{m}) \\
\mathbf{\xi}^\dagger (2) &= -\mathbf{u} \cos(\mathbf{k} \cdot \mathbf{m}) \tag{24}
\end{align*}
$$

where $\mathbf{u} = (u_x, u_y, u_z)$. The frozen wave is equivalent to having

$$
\mathbf{a}^\dagger_{\lambda} = \begin{cases} \sqrt{2N} \ u_{\lambda} & \text{for } \mathbf{k} = 0, \ \lambda = x, y, z \\ 0 & \text{otherwise} \end{cases}
$$

and the various energy terms (per atom) in Eq. 17 become

$$
\begin{align*}
E_2 &= \frac{1}{2} \left( \frac{1}{2N} \right) \phi_{\lambda\lambda}^0 a^0_{\lambda} a^0_{\lambda'} = \frac{1}{2} \phi_{xx}^0 (u_x^2 + u_y^2 + u_z^2) \\
E_3 &= \frac{1}{3!} \left( \frac{1}{(2N)^{3/2}} \right) \sum_{\lambda\lambda'\lambda''} \phi_{\lambda\lambda\lambda''}^0 a^0_{\lambda} a^0_{\lambda'} a^0_{\lambda''} \\
&= \frac{1}{3!} \left\{ \phi_{xyz}^0 \ u_x u_y u_z + \phi_{xxx}^0 \ u_x u_x u_x + \ldots \right\} \\
E_4 &= \frac{1}{4!} \left( \frac{1}{(2N)^2} \right) \sum_{\lambda\lambda'\lambda''\lambda'''} \phi_{\lambda\lambda\lambda''\lambda'''}^0 a^0_{\lambda} a^0_{\lambda'} a^0_{\lambda''} a^0_{\lambda'''} \\
&= \frac{1}{4!} \left\{ \phi_{xxxx}^0 \ u_x u_x u_x u_x + \ldots \right\} \tag{25}
\end{align*}
$$
Comparing the above expression with a general Taylor's series expansion for $E_{\text{total}}$, we see that the $\Phi$'s are simply the various order derivatives of $E_{\text{total}}$ with respect to the $u_i$'s, for example,

$$
\Phi^{oo} = \frac{\partial^2 E}{\partial x^2} = E_{xx}
$$

$$
\Phi^{ooo} = \frac{\partial^3 E}{\partial x \partial y \partial z} = E_{xyz}, \text{ etc.}
$$

The symmetry of the diamond crystal structure dictates that many of the $\Phi$'s are zero. One can easily show that the only terms up to fourth order not required by symmetry to vanish are the following:

$$
E_{xx} = E_{yy} = E_{zz} \equiv \kappa
$$

$$
E_{xyz} = \gamma
$$

$$
E_{xxxx} = E_{yyyy} = E_{zzzz} \equiv \alpha
$$

$$
E_{xxzz} = E_{yyzz} = E_{xxyy} \equiv \beta
$$

(26)

All other terms that are not related to the above terms by permutation of the indices are zero. As noted before, $\kappa$ gives the optical phonon frequency; $\gamma$ gives the amplitudes for three-phonon processes; and $\alpha$ and $\beta$ give the amplitudes for the bare four-phonon processes.

To obtain $\kappa$, $\gamma$, $\alpha$, and $\beta$, several $\vec{u}$'s of different magnitudes and directions are used to calculate the total energy of distorted crystals. Figure 10 illustrates the calculation of $\kappa$, $\alpha$, and $\beta$. Plotted are curves for $\Delta E/u^2$ vs. $u$ for $\vec{u}$ along the (001), (110), and (111) directions. (For the (111) direction, the plotted values are those averaged over positive and negative $\vec{u}$'s. This is to remove the third-order component in the energy. There is no third-order contribution for the other two directions because of symmetry.) The intercept at $u = 0$ is the value for $\kappa$. The slopes of the curves correspond to $\alpha$, $\alpha/2 + 3\beta/2$, and $\alpha/3 + 2\beta$ for the (100), (110), and (111) directions respectively. Also, by plotting $\Delta E/u^2$ vs. $u$ for the (111) direction, one extracts the value for the third-order term $\gamma$. The calculated results are summarized in Table IX.

The theoretical value for $\alpha$ is negative whereas for $\beta$ it is positive and small compared to the magnitude of $\alpha$. This implies that the phonon-phonon interaction of the form

$$
\begin{align*}
&x \\
&x
\end{align*}
$$

$$
\begin{align*}
&x \\
&x
\end{align*}
$$
Fig. 10. Plots of $\Delta E/u^2$ vs. $u^2$ for $\vec{k} = 0$ frozen-optical phonons in diamond (see text). ($\Delta E$ is energy/cell.) (from Ref. 35)

Table IX. Bare harmonic and anharmonic parameters for $k = 0$ optical phonons in diamond (see text). (from Ref. 35)

<table>
<thead>
<tr>
<th>2k</th>
<th>2\gamma</th>
<th>2\alpha</th>
<th>2\beta</th>
</tr>
</thead>
<tbody>
<tr>
<td>2!</td>
<td>3!</td>
<td>4!</td>
<td>4!</td>
</tr>
<tr>
<td>22.36</td>
<td>-24.49</td>
<td>-28.98</td>
<td>2.08</td>
</tr>
</tbody>
</table>

is attractive, but interaction of the form

\[
\begin{align*}
\begin{array}{cc}
x & y \\
x & y
\end{array}
\end{align*}
\]

is weakly repulsive.

The parameters $\alpha$ and $\beta$, however, only describe the direct four-phonon terms. To address the two-phonon bound state question, we have to consider other possible four-phonon diagrams of comparable
strength. They may be obtained using perturbation theory. Diagrams up to order $\gamma^2$ are given in Fig. 11. These are phonon-phonon interactions via an exchange of a third phonon. It turned out that because of symmetry the diagrams in Fig. 11 do not effect processes of the type $xx \rightarrow xx$. Therefore, $\alpha$ remains unchanged. However, processes of the type $xy \rightarrow xy$ or $xx \rightarrow yy$ will have other contributions in addition to the direct term. Thus, the parameter is renormalized. For scattering of the type $xy \rightarrow xy$, four additional diagrams contribute (c-f in Fig. 11) leading to a renormalized value

$$\beta' = \beta - \frac{2\gamma^2}{3\kappa}$$

(27)

and for scattering of the type $xx \rightarrow yy$, also four additional diagrams contribute (a-d in Fig. 11) leading to a renormalized value

$$\beta'' = \beta - \frac{2\gamma^2}{\kappa}$$

(28)

There are now three effective four-phonon interactions of the types

$$\alpha \quad \beta' \quad \beta''$$

The values for $\alpha$, $\beta'$, $\beta''$ are tabulated in Table X. Note that all parameters are now negative.

Fig. 11. Diagrams for phonon-phonon scattering via exchange of another phonon.
Table X. Renormalized fourth-order anharmonic parameters for \( \vec{k} = 0 \) optical phonons in diamond (see text).

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2a/4!</td>
<td>2b'/4!</td>
<td>2b''/4!</td>
</tr>
<tr>
<td>-28.98</td>
<td>-11.33</td>
<td>-38.16</td>
</tr>
</tbody>
</table>

This work contributed in two major ways. First, the calculation shows that it is now possible for the first time to calculate from first principles phonon-phonon interaction parameters that are inaccessible from experiment. Second, since all the effective four-phonon terms (direct plus mediated processes up to \( \gamma^2 \)) are attractive for the \( \vec{k} = 0 \) optical phonons in diamond, the formation of the two-phonon bound state is unlikely in this system.

C. Structural Phase Transformations

In this subsection, we describe several examples of applications of the total energy pseudopotential method to structural phase transformations induced either by pressure or temperature.

By calculating the total energy of an element or compound at various crystal structures, one can determine the relative stability among the structures considered. For example, in Fig. 5, the total energy for Si as a function of volume for seven common crystal structures is displayed. The diamond structure curve has the lowest energy minimum. Hence, it is the stable structure for Si as found in experiment. At small volumes which can be achieved under pressure, the diamond structure energy is no longer the lowest. A solid-solid structural phase transition to a lower energy structure should occur.

Near the experimental equilibrium volume, the theoretical curves (Fig. 5) show that Si in the hexagonal diamond (homopolar wurtzite) structure has energy closest to the cubic diamond curve. However, since the hexagonal diamond curve lies higher in energy than cubic diamond over the whole range of volumes, no pressure-induced transition is predicted. This is again consistent with experimental observations. On the other hand, at volume smaller than 0.82 of normal volume, the \( \beta \)-Sn structure has lower energy than the cubic diamond structure. Therefore, a structural transformation should occur as a function of pressure.
At zero or low temperatures, the critical pressure at which Si transforms from the diamond structure into the β-Sn structure can be calculated by examining the enthalpy

\[ H = E + PV \]  \hspace{1cm} (29)

for the two structures. The transition occurs at a pressure when the enthalpy of the two phases is equal, that is, when

\[ P = - \left( \frac{E_2 - E_1}{V_2 - V_1} \right). \]  \hspace{1cm} (30)

From the definition of \( P \), we see that the diamond-β-Sn transition occurs at the volume where the first common tangent (Gibbs line) can be drawn between the diamond curve and the β-Sn curve. In Fig. 5, the Gibbs line is given by the dashed line. Thus, the points 2 and 3 label the transition volumes between the structures and the slope of the Gibbs line provides the transition pressure. A calculation of the energetics of Ge in various crystal structures showed that Si and Ge behave very similarly under pressure. Both materials transform to a metallic β-Sn phase at a pressure around 100 kbars. The theoretical results (Table XI) are in excellent agreement with experiment particularly for the transition volumes. These results are remarkable considering that the only input to

| Table XI. Comparison of the calculated and measured transition volumes (\( V_{t}^{d}, V_{t}^{B} \)) of the diamond and β phases, their ratios (\( V_{t}^{B}/V_{t}^{d} \)), and the transition pressures (\( P_{t} \)) for Si and Ge. Volumes are normalized to the measured zero-pressure volumes. (from Ref. 21) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | \( V_{t}^{d} \) | \( V_{t}^{B} \) | \( V_{t}^{B}/V_{t}^{d} \) | \( P_{t} \) (kbar) |
| Si              |                 |                 |                 |                 |
| Calculation     | 0.928           | 0.718           | 0.774           | 99              |
| Experiment      | 0.918           | 0.710           | 0.773           | 125             |
| Deviation       | 1.1%            | 1.1%            | 0.1%            | -20%            |
| Ge              |                 |                 |                 |                 |
| Calculation     | 0.895           | 0.728           | 0.813           | 96              |
| Experiment      | 0.875           | 0.694           | 0.793           | 100             |
| Deviation       | 2.3%            | 4.9%            | 2.5%            | -4%             |
Fig. 12. Total energy versus volume (normalized to the experimental volume) for six structures of carbon. Vertical arrows denote the minimum energy in each structure. (from Ref. 24)

the calculations are the atomic numbers and an assumed set of crystal structures.

Carbon\textsuperscript{24,42-44}, on the other hand, behaves differently under pressure among these three group IV covalent elements. Fig. 12 shows that carbon remains in the diamond structure over a very large volume (and pressure) range. No transition to the $\beta$-Sn structure or to another structure was predicted. This is consistent with observations that diamond remains unchanged up to megabars pressure range. More recent calculations\textsuperscript{22-44}, however, showed that diamond will transform to a BC-8 structure, a structure of distorted tetrahedrons with eight atoms per unit cell, at about 12 Mbars. Hence, carbon is predicted to be stable in the open diamond structure up to extremely high pressure at least for the structures considered. Comparing Si and Ge with diamond, the extraordinary stability of carbon in the tetrahedral structure is probably attributable to the large bond-bending restoring forces of the sp\textsuperscript{3} carbon bond which may be traced back to the lack of d states nearby the sp complex. The diamond structure is, of course, only a metastable state of carbon whose lowest energy phase is that of graphite. The energy difference between these two phases is extremely small, and at present, it is not completely clear how the graphite-diamond transition occurs. Calculations of the kind discussed here should help in understanding such transitions.

Several calculations along the same line have also been performed
Table XII. Transition pressures and structures for III-V semiconductors. (after Ref. 22)

<table>
<thead>
<tr>
<th>Material</th>
<th>Transition Pressure (kbar)</th>
<th>Structure</th>
<th>Theory</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theory</td>
<td>Exp.</td>
<td>Theory</td>
<td>Exp.</td>
</tr>
<tr>
<td>GaAs</td>
<td>160</td>
<td>160-190</td>
<td>β-Sn rocksalt NiAs</td>
<td></td>
</tr>
<tr>
<td>GaP</td>
<td>217</td>
<td>200-240</td>
<td>β-Sn rocksalt</td>
<td></td>
</tr>
<tr>
<td>AlP</td>
<td>93</td>
<td>140-170</td>
<td>rocksalt NiAs</td>
<td></td>
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<tr>
<td>AlAs</td>
<td>76</td>
<td>---</td>
<td>rocksalt NiAs</td>
<td></td>
</tr>
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</table>

For the III-V semiconductors and metals under pressure. For the metals, high pressure phase transitions were predicted by comparing the total energies for the fcc, bcc, and hcp phases, and the results are consistent with experiment and with those using other techniques. For the III-V compounds, several high pressure phases were calculated to have approximately the same energy. Hence, at present, for some of the III-V compounds, it was not possible to decide the appropriate high-pressure phase, but the pressure of the transition was predicted (Table XII), and agreement with experiment was found in cases where data is available.

Another important class of studies is to investigate temperature-induced structural transitions. This has been performed for the metal Be. At ambient pressure, Be transforms from a low temperature hexagonal close-packed (hcp) structure to a high temperature body-centered cubic (bcc) structure at approximately 1530 K before it melts at about 1560 K. This transition is interesting in several respects: there is a large entropy difference between the two phases at the transition, and the bcc phase exists only for a very small range of temperature. The structural transition temperature decreases with increasing pressure. Furthermore, although the face-centered cubic (fcc) phase is calculated to have a lower energy than the bcc phase at zero temperature and zero pressure, the transition is from hcp to bcc.

In order to study structural phase transitions at finite
temperature and pressure, the Gibbs free energy \( G(P,T) \) must be considered. The most stable crystal phase at a given \( T \) and \( P \) is the one with the lowest Gibbs free energy

\[
G(P,T) = H - TS = E + PV - TS
\]  

where \( E \) is the internal energy and \( S \) is the entropy and both are dependent on \( T \). Within the adiabatic approximation, \( G(P,T) \) of a crystal can be separated into two contributions, a static lattice part \( G_{st} \) and a vibrational part \( G_{ph} \). \( G_{st} \) includes the electronic energy and the static Coulomb interaction between the ions fixed at their equilibrium positions. \( G_{ph} \) includes both the zero-point motion and the phonon contribution.

In the work of Lam et al., the Gibbs free energies for the hcp, fcc, and bcc structures were calculated. Several approximations were used to make the calculation tractable. First, the temperature dependence of \( G_{st} \) is neglected. The justification is that electronic excitations are negligible compared with phonon excitations at temperatures which are small compared to the Fermi temperature of the metal. Hence,

\[
G_{st}(P) = E_{st}(T = 0) + P_{st}V
\]

which is just the zero temperature enthalpy and is calculated using

\[ (31) \]

\[ (32) \]

Fig. 13. Static lattice energy differences, fcc-hcp (A) and bcc-hcp (B), as functions of normalized volume (full curves) and energy differences with zero-point energy included (broken curves). (from Ref. 48)
the *ab initio* total energy method as discussed (Fig. 13). Second, the contributions to the pressure from the phonons is recognized to be very small compared with that from the static lattice energy and is, therefore, neglected in the calculation of $G_{\text{ph}}$. Thus,

$$G_{\text{ph}}(T) = E^0_{\text{ph}} + E_{\text{ph}}(T) - TS_{\text{ph}}$$

(33)

where $E^0_{\text{ph}}$ is the zero-point energy. This is just the expression for the Helmholtz free energy which can be evaluated within the harmonic approximation using\textsuperscript{31}

$$G_{\text{ph}}(T) = \sum_1 \frac{\Omega_i}{2} + k_BT \sum_1 \ln \left(1 - \exp \left(-\frac{\Omega_i}{k_BT}\right)\right)$$

(34)

where $\Omega_i$ is the phonon frequency. Finally, since a completely *ab initio* calculation of the full phonon spectrum was not practical, the above expression was evaluated in the following way. An approximate phonon spectrum was obtained by representing the phonon frequency with a finite Fourier series. The coefficients of the series were determined to give the correct sound velocities calculated from the elastic constants. For the hcp phase, experimentally determined elastic constants were available and were used. The elastic constants for the fcc and bcc phases were computed by calculating the static lattice energy for the appropriate distortions of the lattice (Table XIII).

The calculated differences in Gibbs free energy for the three structures at $P = 0$ are presented in Fig. 14. At zero temperature and zero pressure, the most stable phase is the hcp phase as observed experimentally. As the temperature increases, the Gibbs free energy for the bcc phase decreases relative to the hcp value and becomes the lowest one at temperature approximately equal to 1500 K. The observed transition is at about 1530 K. The high temperature bcc phase is, thus, stabilized by the large entropy term, $-TS_{\text{ph}}$. The origin of this large entropy is associated with the presence of low-energy (soft) phonon modes. These soft phonon modes exist in the bcc phase because the $C_{11}-C_{12}$ elastic constant is anomalously small in this phase (see Table XIII). Also, the calculation showed that although the fcc Gibbs free energy is lower than that of the bcc phase at $T = 0$ and $P = 0$, its phonon free energy is considerably larger than that of the bcc phase. Therefore, the fcc phase is never stabilized by temperature.

These total energy methods should be applicable to the study of other solid-solid structural transitions such as the $\omega$-phase of Zr. A goal in the future in this area would be to attempt to predict crystal structures and to suggest experimental studies which might give rise to new materials with desirable properties. For example, as mentioned above, although graphite has a lower energy, diamond does exist. One aim would be to understand transitions of
Table XIII. Elastic constants of Be (10^{12} dyne cm^{-2}). (after Ref. 48)

<table>
<thead>
<tr>
<th></th>
<th>HCP‡</th>
<th>FCC‡</th>
<th>BCC‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{11}</td>
<td>2.95</td>
<td>2.20</td>
<td>1.20</td>
</tr>
<tr>
<td>C_{12}</td>
<td>0.26</td>
<td>0.63</td>
<td>1.10</td>
</tr>
<tr>
<td>C_{44}</td>
<td>1.71</td>
<td>1.86</td>
<td>1.70</td>
</tr>
</tbody>
</table>

‡Experimentally determined elastic constants from Silversmith and Averbach (1970).
§Calculated elastic constants.

Fig. 14. Differences in the Gibbs free energy (A: fcc-hcp; B: bcc-hcp) as a function of temperature at P = 0. (from Ref. 48)

this kind and attempt to predict others.

IV. SURFACES AND CHEMISORPTION SYSTEMS

Research in the properties of surfaces and related systems
represents a major area in condensed matter science. The present interests in these systems are generated both by their fascinating fundamental properties and by their practical importance in fields such as catalysis and device applications. However, despite a great deal of activity in the past decades, an understanding of the electronic and structural properties of surfaces of real materials remains a challenge for both theory and experiment. In this section, we discuss several representative examples of surface studies using pseudopotential methods.

Among the goals for theoretical work in this area are: determination of the geometric structures, understanding of the nature of surface electronic states and chemisorption bonds, theory for mechanisms for surface atomic rearrangements (relaxations and reconstructions), prediction of chemisorption energetics, and analysis of spectroscopic and other experimental data. Most of the past studies have been centered on the search for surface states and characterization of their properties. However, with the advance of the total energy methods such as those described in the previous sections, recent work begins to address the questions of surface geometries and energetics.

One major constraint in theoretical surface calculations is the lack of translational symmetry because of the surface. This can be overcome in two ways. One approach is to match extended electronic wavefunctions from the bulk crystal to decay states representing the surface. Another is to use a thin slab of the crystal to model two surfaces. Further, if a supercell geometry is employed with the slabs, standard band structure techniques may be used. The slab approach is most common and is the method employed for the studies discussed in this section. Another constraint in surface studies is the requirement of somewhat detailed self-consistency in the calculations because of the asymmetrical rearrangement of charge near the surface. Quantities such as work functions, atomic rearrangements, and surface state energies are sensitive to such charge rearrangements.

A. Surfaces of Semiconductors and Insulators

Theoretical research in this area has been focused mainly on the group IV and the III-V materials. In this subsection, for illustration purposes, we describe in some detail two surfaces, the (111) surfaces of silicon and diamond, and briefly mention others.

The (111) surfaces of the tetrahedral elements C, Si, and Ge are found to undergo a remarkable variety of surface reconstructions. A possible common denominator is the apparent occurrence of a 2x1 reconstruction on all three surfaces. The similarity of the angle-resolved photoemission results suggests that a common structure may be responsible.
Fig. 15. Total valence electron charge density for the Si(111)-(1×1) surface. A (110) plane is shown with the top of the diagram representing the semiconductor surface. The cores are shown as shaded discs, and heavy lines represent bonds. Charge density contours are normalized to e/\(n_c\) where \(n_c\) is the bulk unit cell. (from Ref. 53)

The Si(111) surface is probably the most studied semiconductor surface. Yet, the details of the atomic and electronic structure are still considered open subjects. Experimental interest remains high because it is possible to cleave Si in vacuum and produce clean surfaces which can be studied with a host of techniques. Theoretically, this surface is considered to be the prototype semiconductor surface.

In the 1970's, the ideal 1×1 Si(111) surface was studied using the self-consistent pseudopotential method. The charge density was found to smooth out and "heal" the cut bonds (Fig. 15). A dangling-bond surface state band with wavefunctions highly localized at the cut bonds was found to lie in the semiconductor energy gap. Since there is one broken bond per surface unit cell and each has one electron, the surface dangling-bond band is half full leading to a metallic surface. Experimentally, however, Si(111) is semiconducting. The nonmetallic nature is generally believed to be associated with reconstructions or movements of the atoms at the surface. Low energy electron diffraction (LEED) measurements show that Si(111) reconstructs into a metastable 2×1 pattern when cleaved and into
a stable 7×7 pattern upon annealing. Laser-annealed surfaces, on the other hand, show a 1×1 pattern; however, the surface may not be well ordered and the exact interpretation is controversial.

Because of the complexity of the 7×7 geometry, most theoretical research has been directed to the 2×1 reconstruction. Until recently, the commonly accepted model for this surface was a buckling model in which alternate rows of surface atoms are raised and lowered. This model has two inequivalent atoms per surface unit cell and, hence, should give rise to a semiconducting surface if the displacement were large enough. Calculations using the buckling model as input gave results consistent with this picture. The correctness of the buckling model, however, has been challenged. Angle-resolved photoemission measurements give an energy dispersion curve, E(k), for the surface states which is in disagreement with theory constrained to a buckled 2×1 reconstruction. Recently, total energy and force calculations also show that the buckling model is unfavorable.

In the ab initio surface calculations, as in the bulk cases discussed in Sec. III, the exact geometry is no longer a required input. The surface structure is determined by minimizing the total energy with respect to the coordinates of atoms in the first several layers for a given topology. An equivalent approach is to calculate the Hellmann-Feynman forces on each atom and move the surface atoms until all forces are zero. In either approach, the calculation must be done iteratively since when atoms are moved, new forces

![Diagram](Side View of 2 x 1 Buckling Distortion)

**Fig. 16.** Side view of a 2x1 buckling distortion used to test the stability of the ideal 1x1 Si(111) surface. (from Ref. 58)
Fig. 17. Energy as a function of relaxation of the surface layer, the antiferromagnetic $2\times1$ and the paramagnetic $1\times1$ states of Si(111). The zero of energy is the ideal paramagnetic surface. (from Ref. 63)

develop on their neighbors. Several cycles are usually needed to achieve a minimum energy, zero force structure. When this approach was used for Si(111),$^{58}$ the surface was found to resist buckling. Forces developed on a buckled surface to restore the atoms back to a relaxed $1\times1$ configuration (Fig. 16).

A possible state in which the surface behaves electronically semiconducting and yet remains in the $1\times1$ geometry is one with a gap arising from electron-electron interaction. An antiferromagnetic phase for the $1\times1$ Si(111) surface has been predicted$^{58,60-62}$ but not observed. The most recent calculation$^{63}$ placed the antiferromagnetic phase at a lower energy than the paramagnetic phase (Fig. 17) for the ideal geometry, but with relaxation, it is difficult to determine whether the occurrence of this state is feasible. As seen in Fig. 17, the difference in total energy between the paramagnetic and the antiferromagnetic phases is very small. Also, it is sensitive to the approximations used in the calculations.$^{63}$

Since the $1\times1$ geometry is predicted to be stable with respect to buckling, this suggests that the observed $2\times1$ structure may result from a distortion of a different kind. Motivated by the angle-resolved photoemission data, Pandey$^{54}$ suggested that the $2\times1$ structure is a $\pi$-bonded chain geometry. A schematic ball and stick model of the ideal and the $\pi$-bonded chain structures are shown in Fig. 18. The characteristic six-fold ring geometry of
the ideal 1x1 structure and its decomposition into five-fold and seven-fold rings for the 2x1 \(\pi\)-bonded chain surface are depicted. It is evident that the two structural models have very different topologies. Thus far, the \(\pi\)-bonded chain geometry gives the lowest calculated total energy among the various models proposed in the literature.\(^{59}\) This geometry is stabilized by the dangling bonds moving into near-neighbor positions where they can participate in \(\pi\) bonding. It has also been shown that at least one path existed going from the ideal geometry to the \(\pi\)-bonded chain with a barrier of only \(-0.01\) eV.\(^{59}\) The cleaving process could easily supply enough energy for this transition to occur. The resulting chain geometry is lower in energy by \(-0.2\) eV than the relaxed ideal (1x1) geometry.

One can also compare the calculated surface state dispersion with experimental results for confirmation once a minimum energy structure is determined. The theoretical surface state bands\(^{59,64}\) were found to be in good agreement with angle-resolved photoemission data (Fig. 19). The agreement of the \(k\)-dependent of the surface state energies with experiment is impressive considering that only the atomic number and some geometrical restrictions went into the theory. The absolute position of the experimental points in Fig. 19 has been shifted up rigidly by 0.3 eV for ease of comparison. This kind of discrepancy arises from using local density functional
Fig. 19. Calculated electron energy dispersion curve for Si(111) in the energy optimized π-bonded chain structure. The experimental points have been shifted upwards by 0.3 eV so that the theory and experiment are aligned at the J point. (after Ref. 59)

theory which is well-known to give excellent ground-state properties but too small excitation energies. Calculations for the 2×1 Ge(111) surface also showed that the π-bonded chain geometry has the lowest energy and a surface band dispersion similar to Si. We should note that agreements between theory and experiment for E(k) for a low energy structure are necessary conditions for determining surface reconstructions but not sufficient conditions. Other geometries may give similar E(k) curves, and at present, there are no certain tests to determine that a given structure corresponds to the absolute minimum and not a local minimum in energy.

Total energy calculations have also been carried out to study a variety of proposed reconstructions on the diamond (111) surface. For this case, the LCAO basis was used because of the localized nature of the carbon electron wavefunctions. Both a 1×1 phase obtained by polishing and a 2×2/2×1 phase obtained by annealing to above ~1000 C were observed by LEED. (LEED cannot distinguish between a true 2×2 or disordered domains of 2×1 for this surface; the similarity of the angle-resolved photoemission to that of Si and Ge suggests the latter.) No surface states were observed in the gap for the 1×1 diamond surface. However, recent experiments have shown that this is a hydrogen-terminated surface. The 2×2/2×1 surface, on the other hand, is believed
Table XIV. Calculated total energies of C(111) 1×1 and 2×1 surface reconstruction models. (from Ref. 66)

<table>
<thead>
<tr>
<th>Surface model</th>
<th>Energy eV/(surface atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal 1×1</td>
<td>0.00</td>
</tr>
<tr>
<td>Relaxed 1×1</td>
<td>-0.37</td>
</tr>
<tr>
<td>Buckled (Δz = ± 0.26 Å)</td>
<td>0.35</td>
</tr>
<tr>
<td>Chadi π-bonded molecule</td>
<td>0.28</td>
</tr>
<tr>
<td>Seiwatz single chain</td>
<td>1.30</td>
</tr>
<tr>
<td>Ideal Pandey π-bonded chain</td>
<td>-0.05</td>
</tr>
<tr>
<td>Relaxed Pandey π-bonded chain</td>
<td>-0.47</td>
</tr>
<tr>
<td>Same with ±2% dimerization</td>
<td>-0.46</td>
</tr>
<tr>
<td>Same with ±4% dimerization</td>
<td>-0.43</td>
</tr>
<tr>
<td>Same with ±6% dimerization</td>
<td>-0.38</td>
</tr>
<tr>
<td>Fully relaxed Pandey chain</td>
<td>-0.68</td>
</tr>
</tbody>
</table>

to be hydrogen free and clean, and unlike Si and Ge whose 2×1 phases are metastable, the diamond 2×2/2×1 structure appears to be thermodynamically stable.

Similar to the case of the Si(111) surface, many models have been proposed for the 2×1 diamond surface. Results of the total energy calculation for these models are summarized in Table XIV. The energy per surface atom for the ideal 1×1 model is used as a zero of energy. Relaxing the first two surface bonds (Fig. 20(a)) lowers the energy by 0.37 eV. Four topologically distinct 2×1 models have been tested: the buckling model, the Pandey π-bonded chain model, the Chadi molecule model, and the Seiwatz single-chain model. As in Si, buckling of the 1×1 surface is found to raise the energy. Of the other three models, the Pandey chain model clearly has the lowest energy. The Chadi molecule model, in second place, has not been relaxed further because the calculated surface state dispersion is inconsistent with angle-resolved photoemission data.

The energy of the Pandey chain model shown in Fig. 18 was minimized by adjusting the four surface-most bond lengths to give the "relaxed" structure of Fig. 20(b) lowering the energy to -0.47 eV. A surprising feature of the resulting geometry was the 8% lengthening of the subsurface interlayer bond. The surface chain bond, on the other hand, was only contracted by 4% to a value approximately midway between that of graphite and diamond. Contrary to some speculations, dimerization of the
Fig. 20. Illustration of bond length changes (with respect to bulk) which occur upon relaxation of (a) 1×1 and (b) 2×1 Pandey chain models for the diamond (111) surface. (from Ref. 66)

chain does not lower the surface energy. However, the structure can be further relaxed by allowing the atoms below the first two layers to move. This further relaxation relieves some of the bond angle strains on the third layer atoms. The final geometry has an energy lowered by an additional 0.21 eV per surface atom.

It is instructive to compare the diamond results with those of Si where the ideal and relaxed Pandey chain models have energies (per surface atom) of -0.22 and -0.36 eV respectively compared to the ideal 1×1 surface. In diamond, the ideal Pandey model is less favorable, but relaxations are more important. This can be attributed to the highly directional nature of the carbon sp³ bonds which implies that bond angle variations are more costly. (The ratio of the bond-bending force constant to the bond-stretching force constant is twice as large in diamond than that in Si.) Evidently, the large bond angle distortions in the third layer are more costly in diamond and the relaxations which relieve bond angle strains more important. This is consistent with the 8% expansion of the diamond subsurface interlayer bond which can be ascribed to bond weakening resulting from bond angle distortion.
Figure 21 shows the calculated surface band structure for the fully relaxed Pandey chain model. Experimental angle-resolved photoemission data are shown for comparison. The dispersion of the calculated surface band is in good agreement with experiment. However, the calculated band is too high by a rigid shift of ~1 eV. As mentioned before, such a shift is also observed for the surface bands of Si and Ge (by 0.3 and 0.8), and a correlation effect may perhaps be invoked to explain this discrepancy.59,65

From these calculations, it is, therefore, fair to conclude that, taken both total energies and spectroscopic data into consideration, a Pandey π-bonded chain topology is most likely to be the correct structure for the 2x1 phase of the (111) surfaces of diamond, Si, and Ge.

The methods described here have been applied to the other surfaces of the group IV elements such as the Si(100) surface74,75 and to other semiconductor surfaces.76 One important application which we have not discussed is the study of chemisorption, both on the geometry and energetics of adsorbates on surfaces. Figure 22 illustrates the result from a study of Al on the GaAs(110) surface.76 Energy surfaces for Al atoms adsorbed on the surface were determined and comparisons made between various possible
adsorbate sites. Another important application is to use the total energy methods to calculate microscopic interaction parameters among the various structural units on a surface. These parameters can then be used in the study of statistical, temperature-dependent properties of the surface employing techniques such as the renormalization group method. This kind of analysis has recently been done for the structural properties and phase diagram of the Si(100) surface. Yet, another area which we have not discussed is defects on surfaces. It is likely that total energy studies will be applied in the near future to determine the lowest energy reconstructions near defects such as steps.

B. Surfaces of Transition Metals

In recent years, research in metal surfaces has been focused primarily on the transition metals because of their richness in phenomena and their technological importance. Compared to the semiconductor surfaces, transition metals surfaces are much more difficult to treat theoretically owing to the coexistence

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Fig. 22. Three-dimensional plot of the total energy for an Al atom adsorbed on the GaAs(110) surface. Two favorable paths for the surface migration of Al atoms are indicated as 1 and 2. It is clear in the figure that channel 1 follows the valleys and channel 2 traces plateaus. Corresponding atomic positions for the first two surface layers are also illustrated. (from Ref. 76)
of the localized d-electrons and the delocalized sp electrons. As a consequence, the theoretical study of these surfaces has lagged somewhat behind that of semiconductor surfaces. Virtually all work has been done only on the electronic properties. Ab initio determination of surface structures via total energy calculations similar to those discussed in the previous subsection is yet to be done. From the electronic structure calculations, one can, nevertheless, still gain much insight into the nature of these surfaces and, in many cases, provide detailed explanations of experimental observations. Our discussion here will, thus, be limited to surface electronic structures.

Several methods have been developed to calculate the surface electronic structure self-consistently for transition metal systems. All of these involve modeling the surfaces by thin slabs (or by repeated slabs in the case of the supercell approach) and expanding the electron wavefunctions in some basis sets. In conjunction with pseudopotentials, the mixed basis or the LCAO basis are most commonly employed. With basically the surface geometry as input, these calculations yield the work function, surface states, adsorbate states, surface charge densities, densities of states, and often information on preferred sites of adsorption. Surface states are shown to be important in the interpretation of spectroscopic measurements, and chemisorption studies give valuable information concerning the nature of the surface chemical bond.

We discuss below the Nb(001) and Mo(001) surfaces as examples of bcc transition metal surfaces and the Pd(111) surface as an example of an fcc transition metal surface. As an illustration for chemisorption, we consider the case of hydrogen on the Pd(111) surface. Except for the case of the Nb(001) surface which was done with a plane wave basis, the calculations were performed using the mixed basis method in a repeated slab geometry with slab size usually 7 to 11 atomic layers thick.

The calculated surface energy band structure for the Nb(001) surface is presented in Fig. 23 along high symmetry directions in the two-dimensional Brillouin zone. The vertical and horizontal crosshatching shows the allowed bulk states (the projected band structure) of various symmetries. The dash curves are the surface bands (either bona fide or strong resonance). These results demonstrated, in a fully self-consistent calculation, that transition metal surfaces support a variety of surface states. The surface states can have different angular momentum character and exist over a wide range of energies and over different portions of the two-dimensional Brillouin zone.

The characters of the surface states shown in Fig. 23 are mainly atomic d-like and are highly localized in the surface
Fig. 23. Surface bands (dashed curves) and the projected band structure for the Nb(001) surface. (from Ref. 77)

Fig. 24. Charge density distribution of a Tl (see Fig. 23) surface state at $\overline{k} = (3/8,1/4)2\pi/a_c$ (with $a_c$ the bulk crystal lattice constant) plotted on (a) the (110) plane and (b) the (100) plane. Charge density is given in relative units. (from Ref. 77)
region. The charge density (square of the wavefunction) of one of the prominent surface states is presented in Fig. 24. This state is associated with the band labeled Tl in Fig. 23 which extends over a large region in the two-dimensional Brillouin zone and has very flat dispersion. As seen in Fig. 24, states in the Tl surface band are \( d_{3z^2-r^2} \)-like and are highly localized on the surface layer with practically no overlap between neighboring surface atom consistent with the weak \( k \)-dependent of this band.

Calculation for the Mo(001) surface \(^8^4\) yielded a surface electronic structure qualitatively similar to that of the Nb surface. Surface states of a variety of character are found to exist in roughly the same energy ranges and positions in \( k \)-space. It is found that the existence of some of these states are sensitive to the details of the self-consistent potential. The calculated surface states have been successfully used to interpret many of the surface sensitive spectral features observed in angle-resolved photoemission experiments.

One important prototypical study in this area is that on the Pd(111) surface and the interaction of hydrogen with this surface. \(^7^8,^8^6,^8^7\) This system is of great interest because of its fundamental importance in chemisorption theory and in technological areas such as catalysis, hydrogen storage, and hydrogen embrittlement.

The calculated surface state bands for the clean Pd(111) surface are shown in Fig. 25 together with that of a monolayer of hydrogen adsorbed on the surface three-fold sites. \(^7^8,^8^6\) The computed work function of 5.8 eV agrees well with the measured value of 5.6 eV. There is a significant surface charge rearrangement in going to self-consistency so that the ad hoc constraint of atom-by-atom neutrality used in many non-self-consistent calculations is likely too rigid. Figure 25 shows that, as in the case of bcc metals, many surface states exist with most of them d-like and highly localized. An interesting exception is the surface state at \(-2\) eV above the Fermi level which is sp-like and penetrates some distance into the bulk.

The calculation also yielded valuable information on the symmetry and origin of the individual surface states. Knowing the symmetry of the surface state wavefunctions would greatly facilitate the identification of these states in experiment by use of selection rules. High resolution angle-resolved photoemission measurements \(^8^7,^8^8\) have recently been performed to search for the surface states predicted in Fig. 25. The agreement between experiment and theory is very good for both the energy positions and the wavefunction symmetry of the states (Table XV). Furthermore, it is shown \(^8^9,^9^0\) that one can understand the surface states on other (111) surfaces for the nearby elements in the Periodic
Table in terms of the Pd(111) results using a rigid-band interpretation.

The surface states strongly affect the spectroscopic properties of the surface. Figure 26 shows the calculated local density of states (LDOS) for the fourth layer from the surface, the second layer from the surface, the surface layer, and a region one layer thick beyond the surface layer for the Pd(111) surface. The LDOS gives the energy spectrum for electrons in a particular region \( \Omega_i \) and is defined

\[
N_i(E) = \sum_{\mathbf{k}_\parallel, n} \int_{\Omega_i} |\psi_{\mathbf{k}_\parallel, n}(\mathbf{r})|^2 \, d^3r \, \delta(E - E_n(\mathbf{k}_\parallel))
\]  

(35)

where \( k_\parallel \) is the wavevector parallel to the surface, \( n \) is the band index, and \( \psi \) is the electron wavefunction. As seen from the figure, the fourth layer LDOS is virtually identical to the bulk Pd DOS, but the surface layer LDOS is very different. It is enhanced in the region from 0 to \(-2\) eV below the Fermi level \( E_F \) and is noticeably narrower. This enhancement arises from the existence of the many surface states near \( E_F \) (Fig. 25).
Most importantly, these results explain a characteristic adsorbate-independent reduction of photoemission signal from 0-2 eV below $E_F$ observed when different adsorbate species are chemisorbed on the Pd(111) surface. (Similar effects are seen in Ni and Pt.) It is interpreted that this reduction is largely due to the removal (shifting to lower energies) of surface states and resonances by the adsorbates since angle-integrated measurements basically probe the surface LDOS. Figure 27(a) shows the difference between the layer 4 LDOS and that of the surface layer. The negative parts of the curve correspond to regions where there are excess state density at the surface. This is to be compared with the curves in Fig. 27(b) which are the observed differences in photoemission intensity between the clean and the adsorbate-covered surfaces. The deficit can, therefore, clearly be associated with the removal of surface states. The effect is adsorbate-independent because the states involved are characteristic of the substrate. This picture has since been confirmed in detail by a direct calculation of H chemisorbed on the Pd(111) surface.

Experimentally, hydrogen dissociates as the molecule adsorbs on the Pd(111) surface and forms a (1×1) monolayer at low tempera-

### Table XV. Localized states on the Pd(111) surface. (Energies are in eV measured relative to $E_F$.) Experimental data from Refs. 87 and 88. (after Refs. 78 and 86)

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<tbody>
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<td>1.7</td>
<td>-1.3</td>
<td>-1.2</td>
</tr>
<tr>
<td></td>
<td>-0.2</td>
<td>-0.3</td>
<td>-3.2</td>
<td>-3.1</td>
</tr>
<tr>
<td></td>
<td>-2.0</td>
<td>-2.2</td>
<td>-7.5</td>
<td>-7.9</td>
</tr>
<tr>
<td></td>
<td>-4.1</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$\bar{\Gamma}$</td>
<td>-1.0</td>
<td>-0.3</td>
<td>-0.8</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>-1.9</td>
<td>-2.1</td>
<td>-2.8</td>
<td>-2.8</td>
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<tr>
<td></td>
<td>-3.0</td>
<td>---</td>
<td>-6.3</td>
<td>-5.9</td>
</tr>
<tr>
<td>$\bar{\Theta}$</td>
<td>---</td>
<td>-1.0</td>
<td>-0.6</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>-3.8</td>
<td>---</td>
<td>-6.8</td>
<td>-6.4</td>
</tr>
</tbody>
</table>
The exact structure, however, is not determined. In the calculations, three possible structural models were considered for monolayer coverage: (A) H on top of every surface Pd atom; (B) H on a three-fold site over a hole in the second layer; and (C) H on a three-fold site over an atom in the second layer. The H-Pd bond length was fixed at the sum of the Pd metallic and the H covalent radii.

The calculated densities of states were compared with angle-integrated photoemission data to distinguish the three possibilities. The first possibility, site A, was ruled out as the preferred site. The two three-fold sites B and C produce very similar spectra which agree well with the experimental data and are essentially indistinguishable from one another.

The calculated surface band structure for H on site C is shown in Fig. 25. The H adatoms induce extensive changes in the surface electronic structure of the clean Pd(111) indicating a strong surface chemical bond. The two most striking H-induced features are the narrow H-Pd bonding adsorbate band which appears about 2 eV below the Pd bulk d bands, and the 4 eV wide anti-bonding H-Pd band just above $E_F$ in a gap in the projected band structure.
Fig. 27. (a) Calculated difference in LDOS between layer 4 and the surface layer for the Pd(111) surface. (b) Adsorbate-induced differences in photoemission intensities from Ref. 92. The dash curves indicate the estimated attenuation if uniform attenuation of the d-band were to occur. (from Ref. 78)

Fig. 28. Charge density contour plots for adsorbate states at $\bar{R}$ at (a) -6.3 eV and (b) 4.1 eV [H/Pd(111) at C sites]. The charge densities are given in relative units and plotted for a (110) plane. (after Ref. 86)
Fig. 29. Calculated LDOS for (a) bulk Pd and (b) Pd(111) surface with and without a monolayer of H in the C site. (from Ref. 86)

near Κ. The intrinsic surface states of clean Pd(111) are strongly affected by H adsorption—some disappear and contribute to the H-Pd adsorbate states, some have their character intact but move to lower energies, and some change their character.

An examination of the charge distribution of the H-Pd adsorbate states shows that the wavefunctions of these states are almost completely localized on the H atoms and the first Pd layer (Fig. 28). The strong bonding at the surface is predominantly from the interaction between the Pd 4d and the H ls orbitals. The highly localized nature of the H-substrate interaction explains the virtually identical surface band structures for the sites B and C.

The calculated surface density of states is presented in Fig. 29 together with the bulk density of states. The bonding Pd-H band appears as a distinct peak at -6.5 eV. The reduction of the amplitude of the density of states near EF is primarily due to removal of intrinsic surface states from this energy region. This can also be seen in Fig. 25 which shows that near EF all intrinsic surface states are shifted to lower energies confirming the interpretation given above on the universal reduction of photoemission intensity in this region. Another important result from the calculation is the absence of a well-defined peak corresponding to anti-bonding H-Pd states as would be predicted by simple chemisorption models. This is a band structure effect.

Because of the symmetry of the surface, the anti-bonding states
can only exist in a limited portion of the two-dimensional Brillouin zone. The large band width of these states also contributed to their invisibility in the spectrum.

The theoretical difference spectra $\Delta N$ for the three chemisorption geometries are presented in Fig. 30 together with the experimental curve. The theoretical $\Delta N$'s are evaluated from the LDOS with final-state and matrix element effects ignored. As seen in the figure, the most prominent feature (structure (d)) in the experimental curve is well reproduced in all three theoretical curves. This structure as discussed above mainly results from the removal of surface states/resonances from this particular energy region; it is, hence, insensitive to the nature of the adsorbate or to its position. The comparison clearly rules out the case with H on each Pd atom. The spectra for sites B and C, on the other hand, are very similar and reproduce remarkably well the experimental spectrum. These results, therefore, show that hydrogen prefers a three-fold site and interacts strongly with the Pd d-states.

In addition to the low-temperature angle-integrated photoemission data, the surface state dispersions for H on Pd(111) have been measured recently by high resolution angle-resolved photoemission

Fig. 30. Comparison of the calculated H-induced photoemission difference spectra with the experimental difference curve. (from Ref. 86)
techniques at temperatures ranging from nitrogen to above room temperature. The predicted surface band structure is shown to be in excellent agreement with the low temperature data. A comparison between theory and experiment is shown in Fig. 31. (Also, see Table XV.) The only possible discrepancy is for states near $\overline{M}$ at which experiment also has a larger uncertainty. These calculations, which have treated both the clean and the adsorbate-covered surfaces in equal footing, give, as a consequence, a complete and very accurate description of the chemisorption process at low temperature.

The situation at higher temperature is, however, more complex. Experiments indicate that there appear to be two H/Pd(111) phases with the more stable high temperature phase showing no sign of any H-induced features, at least in near normal emission spectra. Although the exact H coverage is not certain, these results suggest a structural transformation with the H moving from the low-temperature three-fold sites into some other positions as the temperature rises. The same phenomenon is also observed for H on the (111) surfaces of Ni and Pt. At present, there is no satisfactory model for the high temperature phase. Total energy calculations on these systems would help in clarifying the situation.

Fig. 31. Calculated and measured surface states for the H(1×1) Pd(111) surface at low temperature phase. The shaded regions are the calculated projection of the bulk bands. The heavy lines are calculated surface states or resonances; the circles are data. The open circles indicate experimental peaks with some uncertainty. (after Ref. 87)
V. BEYOND LOCAL DENSITY APPROXIMATION

In the previous sections, we have seen that pseudopotential local density calculations give impressive results for a variety of ground-state properties. There are, however, some systematic discrepancies. The cohesive energy is quite generally overestimated, a result usually attributed to the failure of the local density approximation (LDA). Also, when the eigenvalues from the Kohn-Sham equations are interpreted as quasiparticle energies, the minimum gaps for semiconductors and insulators are consistently underestimated by 30-50%.95-97

The problem of the cohesive energy, in principle, can be corrected with a better exchange-correlation functional. The band gap problem is more difficult because density functional formalism does not explicitly provide information on the excitation energies. The quasiparticle energies should, in general, be obtained from the one-particle Green's function.98,99 However, recently Sham and Schlüter100 have shown that there is a formal relationship between the minimum gap \( E_g \) of an insulator and the Kohn-Sham gap \( E_g \) obtained from a difference in eigenvalues:

\[
E_g = E_g + \Delta
\]

where \( \Delta \) is the discontinuity in the functional derivative of the exchange-correlation functional across a gap. Since there is not yet a calculation for \( \Delta \) for a real material, there remains the important question of whether the discrepancy for the LDA results arises largely from inadequacies of the LDA or the neglect of \( \Delta \).

It is, therefore, important from both practical and fundamental points of view to carry out the calculation beyond the LDA. In this section, we discuss one such calculation101 on Si and Ge using a generalized weighted density functional scheme.

The usual LDA is based on an intrinsically metallic system, the limit of a nearly homogeneous electron density. A semiconductor differs from this limit in two respects—the charge density is localized in bonds and the electron spectrum has a gap which changes the screening properties qualitatively from those of the metals. Several schemes going beyond the LDA have been proposed for overcoming the first: gradient corrections,8,102 self-interaction corrections,103 and the weighted density approximation (WDA).104-106 With the exception of the WDA calculations reported in Refs. 101 and 106, none of these schemes have been carried out fully for semiconductors. In particular, structural properties have only been investigated beyond the LDA in one study.101 The semiconductor screening aspect of the problem has been addressed partially by calculating the exchange-correlation energy of a
model electron gas which reproduces the characteristic screening of a semiconductor arising from the gap, but the resulting LDA exchange-correlation functional only gave small improvements for the spectrum of Si.

In a complete formulation, both the inhomogeneity and the effect of the gap should be treated on an equal footing. Table XVI summarizes the band energies at selected points for Si and Ge calculated using the WDA both with metallic screening and with semiconductor screening in the exchange-correlation functional. In this approach, the exchange-correlation energy of an interacting electron system is expressed in terms of the exchange-correlation hole charge \( n_{xc} \) (in Ry units):

\[
E_{xc}[n] = \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\]

This hole arises from the exchange and dynamical Coulomb interactions between electrons which lead to a local depletion of electron density around a given electron. The exchange-correlation hole is related to a pair correlation function

\[
n_{xc}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}')G_n(\mathbf{r}, \mathbf{r}')
\]

and the exchange-correlation hole must contain precisely one unit of charge

\[
-1 = \int d\mathbf{r}' n_{xc}(\mathbf{r}, \mathbf{r}')
\]

In the LDA, \( E_{xc} \) is approximated by replacing the exact \( G_n \) by the homogeneous electron gas result evaluated for the local density. The argument of the density prefactor in Eq. 38 is further changed to the local point \( \mathbf{r} \):

\[
n_{xc}^{LDA}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})G_{hom}^{LDA}\left(\left|\mathbf{r} - \mathbf{r}'\right|; n(\mathbf{r})\right)
\]

The LDA exchange-correlation hole is, therefore, spherically symmetric and centered on the electron by construction. The LDA is successful for ground-state properties despite these limitations because \( E_{xc} \) depends only on the spherical average of the hole charge and because the sum rule (Eq. 39) is satisfied leading to some systematic cancellation of errors.

In the WDA, a better description of the exchange-correlation hole is attempted. The proper density prefactor is retained, and \( G_{hom} \) is evaluated for a density averaged essentially over the size of the hole:
The parameter $\bar{n}$ is determined at each point by requiring the sum rule (Eq. 39) to be satisfied. The exchange-correlation hole needs no longer remain centered on the electron and depends nonlocally on the charge density which may be highly inhomogeneous.

Because simple formulations of $G^{\text{hom}}$ are not available, the calculations were carried out with the analytic ansatz proposed by Gunnarsson and Jones:

$$G(x; \bar{n}) = C(\bar{n}) \left[ 1 - \exp\left(-[\lambda(\bar{n})/x]^{5}\right) \right]$$

The parameters C and $\lambda$ are determined by demanding that G in Eq. 42 reproduces the homogeneous limit. Effectively G is constructed to have the same zeroth and inverse r moment as some $G^{\text{hom}}$. In Table XVI, three sets of calculations are presented together with the experimental values. The first column shows the results of LDA calculations with the Ceperley-Alder (CA) exchange-correlation data which agree well with previous calculations. The second column (labeled WDA(CA)) shows the results for calculations where $C(n)$ and $\lambda(n)$ are determined from usual electron gas data (CA). Results including semiconductor screening using the Levine-Louie (LL) model are given in the third column (labeled WDA(LL)). For both Si and Ge, the discrepancy with experiment for the minimum gap is significantly reduced. The conduction band energies at X and L are consistently improved. However, the direct gaps are not substantially improved. As seen from Table XVI, the improved description of charge density inhomogeneity and that of electron screening both appear to play equally important roles.

There is a clear qualitative difference between the LDA and the WDA. Figure 32 shows the exchange-correlation hole (Eq. 38) for an electron at the antibonding site in Si. In the LDA, as discussed earlier, the hole is spherically symmetric and centered on the electron (Fig. 32(a)). In the WDA, the hole is shifted towards the bond charge by the proper density prefactor in Eq. 41 (Fig. 32(b)). The exchange-correlation potential and, hence, the spectrum are affected. The effect on the structural properties is shown in Table XVII. The results for the WDA(LL) are, indeed, as good as the LDA results and compare favorably to experiment and results discussed in Sec. III. The importance of treating inhomogeneity and the effects of the gap on screening on an equal footing is again emphasized as the WDA(CA) does not give results as well as either the LDA or WDA(LL). We also note that the cohesive energy in the WDA(CA) is underbound by ~30%. The overestimation of cohesive energies found generally in LDA calculations is often attributed to underbinding in the atomic calculation.
Table XVI. Comparison of the calculated band energies at selected points to experiment for Si and Ge. Energies are reported in eV and relative to the valence band maximum. (from Ref. 101)

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>WDA(CA)</th>
<th>WDA(LL)</th>
<th>EXP.\textsuperscript{a}</th>
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<tr>
<td><strong>Si</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_g$</td>
<td>0.56</td>
<td>0.71</td>
<td>0.90</td>
<td>1.17</td>
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<tr>
<td>$\Gamma_{25',v}$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$\Gamma_{15,c}$</td>
<td>2.57</td>
<td>2.69</td>
<td>2.81</td>
<td>3.40</td>
</tr>
<tr>
<td>$\Gamma_{2,c}$</td>
<td>3.29</td>
<td>3.27</td>
<td>3.34</td>
<td>4.2</td>
</tr>
<tr>
<td>$X_4,v$</td>
<td>-2.86</td>
<td>-2.80</td>
<td>-2.74</td>
<td>-2.9</td>
</tr>
<tr>
<td>$X_{1,c}$</td>
<td>0.71</td>
<td>0.87</td>
<td>1.06</td>
<td>1.30\textsuperscript{c}</td>
</tr>
<tr>
<td>$L_{3',v}$</td>
<td>-1.21</td>
<td>-1.18</td>
<td>-1.16</td>
<td>-1.2±2</td>
</tr>
<tr>
<td>$L_{1,c}$</td>
<td>1.55</td>
<td>1.62</td>
<td>1.73</td>
<td>2.1\textsuperscript{d}</td>
</tr>
<tr>
<td>$L_{3,c}$</td>
<td>3.40</td>
<td>3.54</td>
<td>3.68</td>
<td>3.9±1\textsuperscript{b}</td>
</tr>
<tr>
<td><strong>Ge</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_g$</td>
<td>0.52</td>
<td>0.60</td>
<td>0.69</td>
<td>0.74</td>
</tr>
<tr>
<td>$\Gamma_{25',v}$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Gamma_{2,c}$</td>
<td>0.74</td>
<td>0.74</td>
<td>0.78</td>
<td>0.89</td>
</tr>
<tr>
<td>$\Gamma_{15,c}$</td>
<td>2.58</td>
<td>2.71</td>
<td>2.79</td>
<td>3.25±1</td>
</tr>
<tr>
<td>$X_4,v$</td>
<td>-3.03</td>
<td>-2.97</td>
<td>-2.92</td>
<td>-3.15±2</td>
</tr>
<tr>
<td>$X_{1,c}$</td>
<td>0.80</td>
<td>0.95</td>
<td>1.11</td>
<td>1.3±2</td>
</tr>
<tr>
<td>$L_{3',v}$</td>
<td>-1.38</td>
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<td>-1.33</td>
<td>-1.4±3</td>
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<tr>
<td>$L_{1,c}$</td>
<td>0.52</td>
<td>0.60</td>
<td>0.69</td>
<td>0.74</td>
</tr>
<tr>
<td>$L_{3,c}$</td>
<td>3.74</td>
<td>3.88</td>
<td>3.99</td>
<td>4.3±2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ref. 109 except where noted.
\textsuperscript{b}Ref. 110
\textsuperscript{c}Estimated from conduction band minimum and longitudinal effective mass.
\textsuperscript{d}Ref. 111
Fig. 32. Contour plot of the exchange-correlation hole charge for an electron at the anti-bonding site in the (110) plane of Si (electron location denoted by +) for the LDA (a) and for the WDA(LL) (b). The contour interval is 1.25 electrons per unit cell. (from Ref. 101)

In the case of the WDA(CA), most of the change in the cohesive energy is due to an enhanced binding in the atom. There is a relative small change in the total crystalline energy as one goes from the LDA to the WDA(CA). The LL model is not directly applicable to isolated atoms, so the cohesive energy was not obtained.

The above calculation, thus, demonstrates that by going beyond the LDA, a minimum gap in Si and Ge much closer to experiment can be obtained without degrading the description of structural properties in the solid state. However, for accurate quantitative cohesive energies and excitation energies, much improvement is still needed in the theory.

VI. SUMMARY AND CONCLUSIONS

The aim of this article was to review some of the recent progress in calculating the electronic and structural properties of condensed matter using the ab initio pseudopotential density functional approach. Specific examples have been given for a variety of properties and systems. These include the static structural properties, the vibrational properties, phonon-phonon interactions, solid-solid structural phase transitions, surface
Table XVII. Comparison of the calculated equilibrium structural properties to experiment for Si and Ge (after Ref. 101)

<table>
<thead>
<tr>
<th></th>
<th>Lattice constant A</th>
<th>Bulk modulus (kbar)</th>
<th>Cohesive energy (eV)</th>
</tr>
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<tr>
<td><strong>Si</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>5.40</td>
<td>940</td>
<td>5.28</td>
</tr>
<tr>
<td>Present work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WDA(CA)</td>
<td>5.48</td>
<td>850</td>
<td>3.19</td>
</tr>
<tr>
<td>WDA(LL)</td>
<td>5.39</td>
<td>940</td>
<td>--</td>
</tr>
<tr>
<td>Exp.</td>
<td>5.43</td>
<td>990</td>
<td>4.63</td>
</tr>
<tr>
<td><strong>Ge</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>5.60</td>
<td>730</td>
<td>4.67</td>
</tr>
<tr>
<td>Present work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WDA(CA)</td>
<td>5.68</td>
<td>620</td>
<td>2.64</td>
</tr>
<tr>
<td>WDA(LL)</td>
<td>5.61</td>
<td>700</td>
<td>--</td>
</tr>
<tr>
<td>Exp.</td>
<td>5.65</td>
<td>770</td>
<td>3.85</td>
</tr>
</tbody>
</table>

electronic and geometric structures, and so forth. The method is shown to be equally applicable to semiconductors, insulators, simple metals, and transition metals. With basically the atomic number and atomic mass of the constituent elements as input, many of the above properties have been calculated to within a few percent of experiment.

Currently, there is considerable activity in applying and extending these methods to study other systems and properties. Only a subset of the applications have been discussed here. Several important areas have been omitted. One area is defects in solids. Calculations in impurities, vacancies, interstitials, line defects, and plane defects have been performed using similar methods. Another area is interfaces. Applications are being made to the metal-semiconductor interfaces (Schottky barriers), semiconductor-semiconductor interfaces (heterojunctions), and superlattices. The study of molecules and clusters is a third area. Also, since the method can be used to calculate electron-phonon couplings, phenomena such as resistivity, superconductivity, ultrasonic attenuation, and so forth, can now be studied using these ab initio methods. Results from research in all these areas have been impressive and very encouraging.
The use of the density functional formalism, however, restricts the applications to properties and phenomena related to the ground state (or differences in ground states). Excited states or quasi-particle energies, at present, cannot be justifiably extracted from these calculations. As discussed in Sec. V, the calculated energy band gaps for most semiconductors and insulators are too small by 30-50% compared to observed values when a local density approximation is used. Many workers are currently investigating modifications to the LDA or exploring other new avenues to extend these calculations to excited states.

New ideas and refinements to present methods will surely continue to develop for this important field. However, even if one limits the studies to ground-state properties, future applications are numerous and exciting. With the availability of modern supercomputers, this general approach should have the power to predict the existence of new materials, novel properties and phenomena, and to extend the study of materials to physical situations (such as those at extreme pressures or at complex interfaces) which are difficult or impossible to examine experimentally.

ACKNOWLEDGMENTS

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90. N. A. W. Holzwarth and J. R. Chelikowsky (to be published).
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