

Total energies in the pseudopotential theory

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A new approximation is proposed for total-energy calculations in semiconductors. The various contributions to the total energy are separately analyzed on the basis of a simple model of the interatomic interactions. The model allows a direct connection to be found between the valence-band eigenvalues and the lattice energy of a solid. The theory correctly describes total energies and zone-center optical-phonon frequencies for a number of elemental and binary tetrahedral semiconductors. Elastic properties such as the bulk modulus can also be computed and are shown to give a good agreement with experiment in the case of Si.

I. INTRODUCTION

Very satisfying results¹⁻³ have been recently obtained by employing the self-consistent pseudopotential method⁴ to calculate the structural properties of semiconductors. This method, however, requires very accurate and time-consuming numerical computations which tend to obscure the physical interpretation of the experimentally observed trends. Good as they are, therefore, these results do not eliminate the quest for simpler approaches. In the following we propose a simple approximation scheme which allows for a direct connection between the sum of the valence-band eigenvalues and the total energy of a semiconductor.

The starting point of our method is a reasonable guess of the form of the interatomic interactions in a solid. As is described in Sec. II we assume that the field which acts on an atom in a solid is just the field "felt" by its valence electrons. Accordingly we write it in terms of a screened pseudopotential so that the lattice energy can be easily computed. The total energy is then obtained by adding the sum of the valence-band eigenvalues plus the exchange and correlation energy as given by electron-gas theory.

It must be noted that what we call lattice energy is quite different from the cohesive energy as usually defined.⁵ By definition, in fact, the latter quantity is obtained by subtracting from the total energy the sum of the ionization energies of the isolated atoms. As a consequence our lattice energy is substantially greater than the cohesive energies and is therefore more suitable for approximate

computations.

A further feature of our method is that the total energy is effectively separated into a structure-independent and a structure-dependent part. The point is that in our scheme too, as in Harrison's⁶ recently developed tight-binding approach, and bypassing the calculation of Madelung energies turns out to be a very effective way to get good simplified formulations. In fact, as we show in Sec. III, the total energies of a number of elemental and binary semiconductors can be predicted just by using one numerical constant. As an even more interesting result we show that with the same value of the constant and with no additional parameter the zone-center optical phonons can be analogously determined. This result is particularly relevant since it offers a proof of the direct connection between electronic and total energy which is the basis of our scheme.

Finally, we discuss in Sec. IV how our theory can be successfully extended to the study of other elastic properties such as the bulk modulus. Again, this can be done without introducing additional parameters. The calculations have been done in the case of Si and they show, besides a good agreement between experimental and theoretical value of the bulk modulus, that our theory can be used as a guide for building realistic pseudopotentials.

II. ANALYTIC FORMULATION

The usual way to compute total energy is to have it divided into ionic and electronic parts.

Only the former part, namely Madelung energy, can be computed exactly, while because of the critical balance that occurs among the electronic contributions, self-consistent methods have to be used for the latter one. If one wants to avoid these cumbersome, though successful, methods and look for effective approximations, an alternative scheme can be found by looking at a solid as a periodic structure of interacting atoms (instead of ions). In this case the total energy per atom can be written as an atomic part E_A (the electronic energy of an atom in its bonding state) plus a lattice part E_L (the interatomic interaction energy). For weakly interacting systems E_A is very close to the sum of the isolated atom ionization energies, so that E_L almost coincides with the cohesive energy E_C . This is no longer true for strongly interacting systems such as covalent semiconductors: E_L is here substantially greater than E_C because it corresponds to the separation of a solid into isolated atoms in excited states.

Let us now confine the following discussion to monatomic solids, since generalizing to polyatomic situations is straightforward. The first thing to be pointed out is the short-range character of the interatomic forces, as opposed to the long-range Coulomb nature of the ionic interactions. This fact allows the potential experienced by an atom in a solid to be approximated by the potential felt by its outer electrons. This is the main advantage of our scheme, since all the achievements of pseudopotential theory can be fully exploited.

To be more precise let us further assume that the interatomic forces can be described by a two-body potential $W(r)$ given by the usual pseudopotential $V(r)$ times the valence Z . Accordingly, E_L can be conveniently written as the convergent sum

$$E_L = W(0) + \frac{1}{2} \sum_{\vec{g}} S^*(\vec{g}) S(\vec{g}) W(g), \quad (1)$$

the factor $\frac{1}{2}$ entering so that each atom pair shall not be counted twice. As usual, $W(g)$ is the Fourier transform of $W(r)$ and $S(\vec{g})$ is the structure factor, \vec{g} being a reciprocal-lattice vector. The total electronic energy of an atom in its bonding state is equal to the sum of the valence-band eigenvalues, divided by the number of atoms, minus the double counting energy. To second-order perturbation theory it is simply given, double-counting correction included, by

$$E_A = ZV(0) + E_{BS} + \sum_{|k| < k_F} \frac{\hbar^2 k^2}{2m}, \quad (2)$$

where the band-structure energy E_{BS} is given by⁵

$$E_{BS} = \sum_{\vec{g}} S^*(\vec{g}) S(\vec{g}) F(g), \quad (3)$$

and $F(g)$ by⁵

$$F(g) = - \frac{\Omega_0 g^2 V_0^2(g) [\epsilon(g) - 1]}{8\pi e^2 \epsilon(g)}. \quad (4)$$

As usual, $V_0(g)$ denotes a bare ionic pseudopotential, Ω_0 the atomic volume, and $\epsilon(g)$ a suitable dielectric function. It must be remembered that because of our basic approximation we identify $V(g)$ with $W(g)/Z$.

The close similarity between E_L and E_{BS} strongly suggests that one should be able to derive one of them from the knowledge of the other. To this end let us notice that the approximations leading to both equations can be considered roughly equivalent. In fact, using second-order perturbation theory for E_{BS} is very much like approximating the interatomic forces by a two-body potential. It is reasonable, therefore, to suppose that the same connection between E_{BS} and E_L should be found in rigorous treatments as is found in approximated ones. As a further simplification let us take for $W(g)$ a simple screened Coulomb form

$$W(g) = \frac{W^0(g)}{\epsilon(g)} = - \frac{4\pi Z^2 e^2}{\Omega_0 g^2 \epsilon(g)}. \quad (5)$$

Again, it is reasonable to suppose that the results obtained with this choice should have a wider validity than the assumption itself, since E_{BS} and E_L should be equally affected.

Substituting Eq. (5) for $W(g)$ in Eqs. (1) and (4) gives

$$E_L = W(0) - \sum_{\vec{g}} \frac{S^*(\vec{g}) S(\vec{g}) 2\pi Z^2 e^2}{\Omega_0 g^2 \epsilon(g)}, \quad (6)$$

and

$$E_{BS} = - \sum_{\vec{g}} \frac{S^*(\vec{g}) S(\vec{g}) 2\pi Z^2 e^2}{\Omega_0 g^2 \epsilon(g)} [\epsilon(g) - 1]. \quad (7)$$

A comparison of Eqs. (6) and (7) would lead immediately to the relation

$$E_L = W(0) + E_{BS} / (\bar{\epsilon} - 1), \quad (8)$$

if the dielectric function would be independent of g and equal to some average value $\bar{\epsilon}$. Though clearly this is not the case, Eq. (8) cannot be too incorrect

an approximation to the true relationship between E_L and E_{BS} . As we shall see in Sec. III, on the contrary, quite good results can be obtained just by using the same $\bar{\epsilon}$ for a number of elemental and binary semiconductors.

The total energy can now be obtained by adding to E_L as given by Eq. (8) the energy of the electron system. This should include exchange and correlation as well as kinetic and band-structure energy. A consistent way of doing this is to take E_{kin} and E_{xc} from electron-gas theory⁷ and to set $V(0)$ equal to minus two-thirds of the Fermi energy E_F , as is true for any Coulomb potential screened by the Lindhard dielectric function. Accordingly, our final result is

$$E_{tot} = -\frac{4Z}{3}E_F + E_{BS}/(\bar{\epsilon}-1) + \frac{3Z}{5}E_F - Z \left[\frac{0.916}{r_s} - 0.115 + 0.031 \ln r_s \right] + E_{BS}, \quad (9)$$

where it is implied that energies are in Ry/atom.

Equation (9) gives us a practical recipe for total energy calculations whose only input, apart from atomic volume, is E_{BS} . In the case of metals one could simply use Eq. (3). For semiconductors, however, second-order perturbation theory does not work too well, so a better evaluation of E_{BS} is needed. Since E_{BS} cannot be obtained directly from ordinary band calculations we propose the approximation

$$E_{BS} = E_B - \frac{2.21Z}{r_s^2}, \quad (10)$$

where E_B is the sum of the valence-band eigenvalues at the Baldereschi point.⁸ In this way we neglect to correct for double counting but the error should only be reflected in the choice of $\bar{\epsilon}$. In fact, neglecting double-counting corrections we underestimate E_{BS} , so that $\bar{\epsilon}$ should turn out to be somewhat lower than the value one would expect. However, the general trends should be unchanged, apart from a slight bias which should occur because we have used in Eq. (10) the free-electron kinetic energy instead of the actual one.

III. NUMERICAL RESULTS

Our band calculations have been done by using the pseudopotentials chosen by Cohen and Berg-

stresser.⁹ Fifty plane waves have been included exactly in the expansion of the wave function at the Baldereschi point. The average value $\bar{\epsilon}$ of the dielectric function has been taken to be 1.3 for all semiconductors. Doubling the number of plane waves would lead to quite analogous results with only a slightly higher value of $\bar{\epsilon}$.

As can be seen from Fig. 1 the overall agreement between theoretical and experimental values is quite good. It must be noted that the straight line which gives the best fit is not exactly the line $E_{tot}^{theor} = E_{tot}^{expt}$. As has been already suggested this slight difference is due to the approximation leading to Eq. (10). It stands to reason, in fact, that the kinetic part of the valence-band eigenvalues in II-VI compounds should be less than the corresponding part in III-V compounds. The net result of including such a correction would be to improve the agreement between the two lines.

On the whole, therefore, our approximation scheme seems to be quite sound, the more so because the value of $\bar{\epsilon}$ turns out to be, as expected, somewhat lower than the typical values of $\epsilon(g)$ for the relevant reciprocal-lattice vectors. For instance the values of $\epsilon(1,1,1)$ for Si, Ge, and Sn are, respectively, 1.59, 1.61, and 1.70, if one uses Lindhard's dielectric function with Hubbard's correction⁷ included. Moreover, the fact that the use of only one value of $\bar{\epsilon}$ suffices to give good results for a whole group of semiconductors is very encouraging since it ensures that our theory is not critically dependent on the choice of this parameter.

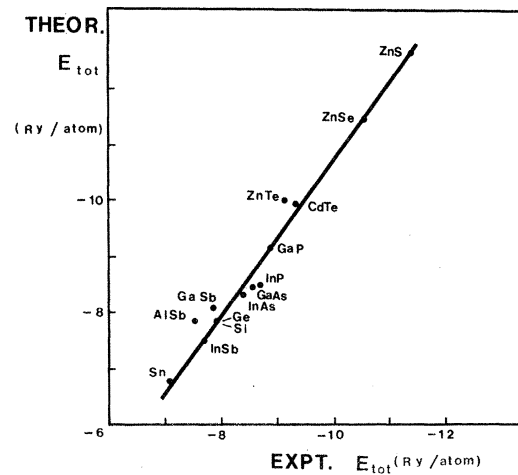


FIG. 1. Experimental vs theoretical values of the total energy, according to Eq. (9), with $\bar{\epsilon}=1.3$. Experimental data from Ref. 13.

A quite independent check on the reliability of our scheme can be obtained by using Eq. (9) to compute the phonon frequencies for the same semiconductors considered in Fig. 1. This can be done without problems for purely covalent semiconductors. In this case, in fact, the zone-center optical phonons can be most simply computed just by a proper modification of the structure factors with no need to increase the size of the unit cell. For polar compounds, however, the energy increase due to the phonon distortion should be partially compensated by an accompanying variation of the charge transferred from more electropositive to more electronegative atoms. This variation should act in the sense of lowering the total energy and should be accounted for by a suitable modification of the pseudopotential form factors. Since the effect should be proportional both to the energy of the phonon distortion and to the ionicity of the compound we propose to account for it simply by multiplying the energy of the phonon distortion by the factor $1 - f_i$, where f_i is the Phillips¹⁰ ionicity.

As is shown in Fig. 2 the above empirical factor leads to excellent values of the longitudinal optical phonons, instead of the transverse ones, as would seem more natural. The reason must lie in the empirical character of f_i , which seems to be better suited to the description of longitudinal vibrations. Anyway, the important feature is that a consistent set of phonon frequencies can be obtained without the introduction of any new disposable parameters.

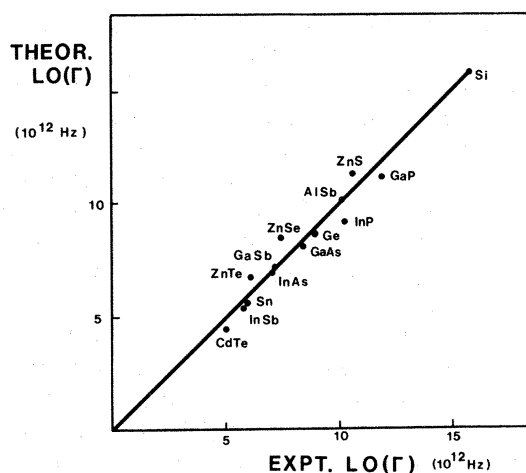


FIG. 2. Experimental vs theoretical values of the longitudinal-optical phonons at Γ , computed with $\bar{\epsilon}=1.3$. Experimental data from Ref. 14.

In fact the band calculations have been done in the same way as in Fig. 1, and with the same value of $\bar{\epsilon}$. Moreover, since the kinetic energy gives almost no contribution to the vibration frequencies the variation of E_{BS} with the phonon distortion can be substituted by the corresponding variation of E_B with practically no loss of accuracy. As a consequence the use of Eq. (10) should not introduce any bias in the case of phonon frequencies. As can be seen from Fig. 2 this is indeed what happens.

IV. FURTHER DEVELOPMENTS AND CONCLUSIONS

In Sec. III we used Eq. (9) to compute phonon frequencies as well as total energies, thus showing that our scheme can describe distorted as well as perfect structures. It is a natural development, therefore, to try and apply our approach to compressed or expanded crystal structures, thereby gaining information about important elastic properties such as the bulk modulus. To this aim, however, we need volume-dependent pseudopotential form factors so as to be able to compute valence-band eigenvalues for different values of the lattice constant. Furthermore, since we are not dealing with a self-consistent procedure, the form factor variation should include the volume dependence of the screening.

A set of pseudopotential form factors that meets the above requirements is the general model pseudopotential developed by Aymerich, Meloni, and Mula¹¹ (AMM). In fact its analytic formulation allows an easy calculation of the bare form factors for any value of the lattice constants. Moreover, AMM pseudopotentials are screened through the use of a suitable semiconductor dielectric function,¹² so that the volume dependence of the screening can also be easily accounted for.

We have used the AMM pseudopotential to compute the total energy of Si for various values of the lattice constant. Our results are summarized in Table I, where the separated contributions are also displayed. We have used Eq. (9) with $\bar{\epsilon}=1.42$, at variance with the $\bar{\epsilon}=1.3$ which has been used in Sec. III for Cohen and Bergstresser pseudopotentials. We remark that the change in $\bar{\epsilon}$ is closely connected with the introduction of AMM pseudopotentials, since they give E_{BS} values which are consistently higher (in absolute value) than in the former case. A higher value of $\bar{\epsilon}$ is accordingly needed in order to obtain for AMM pseudopo-

TABLE I. Total energy contributions (in Ry/atom) for different values of the lattice constant for Si. Calculations according to Eqs. (9) and (10) with $\bar{\epsilon}=1.42$.

a_0 (Å)	5.03	5.23	5.43	5.63	5.83
E_{kin}	2.56082	2.36871	2.19743	2.04408	1.90624
E_{BS}	-0.63376	-0.73084	-0.81692	-0.89151	-0.95580
E_B	1.92706	1.63787	1.38051	1.15257	0.95044
E_{xc}	-2.35524	-2.27499	-2.20048	-2.13110	-2.06633
$2W(0)$	-5.69058	-5.26368	-4.88306	-4.54230	-4.23600
E_L	-4.35424	-4.37194	-4.38658	-4.39379	-4.39371
E_A	-3.27347	-3.26896	-3.26150	-3.24968	-3.23389
E_{tot}	-7.62771	-7.64090	-7.64808	-7.64347	-7.62760

tentials analogous results to the ones shown in Fig. 1. The particular value $\bar{\epsilon}=1.42$ has been chosen in order to bring the minimum of the total energy curve in correspondence with the observed value of the lattice constant.

Besides a reasonable value for the total energy (-7.65 Ry/atom against the experimental -7.919 Ry/atom) the results shown in Table I allow the determination of the bulk modulus with a quite good accuracy: $B_{\text{theor}}=1.1 \times 10^{12}$ dyn/cm² to be compared with the experimental¹ $B_{\text{expt}}=0.99 \times 10^{12}$ dyn/cm². In addition, again with the AMM pseudopotential and with $\bar{\epsilon}=1.42$, we have computed the optical-phonon frequency at Γ obtaining $\text{LO}(\Gamma)=14.7 \times 10^{12}$ Hz. These results show that our scheme is an effective recipe for the calculation of the structural properties of semiconductors. In order to get a better understanding of how it works let us do a critical review of our approximations.

Basically our starting point might be considered as equivalent to the Chadi's¹⁵ decomposition of the total energy of an electron-ion system into a band-structure term plus a short-range pair potential term. The effectiveness of such a decomposition has been demonstrated by Chadi's success¹⁵ in describing the pair potential term with the use of a simple two-parameter force-constant model. Our second step, and our main approximation, is to write the pair potential as a screened pseudopotential, thus being able to derive an analytical relation between the pair-potential energy and the band-structure energy. This is at variance with Chadi's approach but our approximations work exactly as his do, namely because of the short-range nature of

the pair potential. In fact, our assumption that the field experienced by an atom in a solid is just the field felt by its valence electrons, can only hold in the case of short-range potentials.

Our remaining approximations stem from the use of the electron gas theory to compute quantities such as $V(0)$, E_{kin} , E_{xc} . We believe that all these are minor approximations because the related errors should be compensated by the choice of $\bar{\epsilon}$. The important point is that all these quantities should be mainly dependent on the average electron density so that their approximate computation should not introduce spurious trends [apart, of course, from the already discussed case of the free-electron kinetic energy in Eq. (10)].

As a conclusion we would like to point out that our theory allows for a very simple and direct connection between structural and electronic properties. Information about the former field can thus be used for the latter one and vice versa. This can be done meaningfully because we have shown that one value of $\bar{\epsilon}$ suffices for a whole group of semiconductors and for different properties. It must be noted that the above result is independent of the particular kind of pseudopotential used. Within our scheme, in fact, the arbitrariness of the pseudopotentials is compensated by the choice of $\bar{\epsilon}$. This arbitrariness, moreover, can be exploited to try to find some "best" set of pseudopotentials, capable of best accounting for both types of physical properties. Such an approach should be most useful for studying solid solutions, since the use of a common value for $\bar{\epsilon}$ should be a guarantee of the compatibility of the fitting procedures chosen for the end compounds.

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