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Interatomic interactions in covalent and ionic solids

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The total energy in tight-binding theory is obtained to second order in the ratio of the width of the bonding band to the bonding-antibonding splitting. This is the reciprocal of the expansion parameter appropriate to metals. No other important approximation on the minimal-basis, nearest-neighbor, tight-binding Hamiltonian is required for the periodic lattice. This leads to a simple theory of covalent bonding that is more accurate and much more general than bond-orbital methods. The lowest-order term is a bonding term that is a square root of a sum over neighbors performed at each atom. Writing the total bonding energy as a sum of such terms evaluated locally becomes an approximation in nonperiodic systems, but gives the total-energy estimate directly in terms of local interactions. The interesting second-order term, a chemical "grip," is a sum over pairs of neighbors to each atom, depending upon the angle they subtend. A radial overlap repulsion of the form $A/d^3+B/d^{12}$ is added, and fitted to the observed equilibrium spacing and bulk modulus. The resulting form is used for a number of covalent systems to predict spacings and relative energies in competing structures. The bonding term always favors high coordination, but the grip, larger for small atoms and nonpolar systems, determines the tetrahedral structure for semiconductors and the graphite structure for carbon. An elastic shear constant in the tetrahedral structure is also obtained. The method generalizes directly to other systems such as transition-metal compounds and SiO_2. It also gives directly short-ranged interatomic forces, which could be used in molecular dynamics.

I. INTRODUCTION

In metals it has proven possible, using pseudopotential perturbation theory, to calculate the total energy of the metal and transform the result so that it was given in terms of two-body interatomic interactions.[1] The form of the result is quite surprising. In the simplest approximation (Fermi-Thomas screening) it is given[2] by a simple repulsion $V_0(d)=Z^2e^2\cosh^2(\kappa r_c)e^{-\kappa d}/d$ in terms of the internuclear distance d. The parameter κ is the Fermi-Thomas screening parameter[3] and r_c is the empty core–pseudopotential core radius.[3] These repulsions are balanced in pseudopotential theory by a volume-dependent energy. In a more complete theory this volume-dependent energy would be replaced by a complicated many-body interaction but that interaction appears to have so little structure that in most systems it is absorbed in the boundary conditions, or in systems with gross inhomogeneities it could be included by calculating the two-body repulsions locally.

One could not have anticipated, without pseudopotential theory, that the form of the interaction would be purely repulsive, and all of the usual phenomenological models (Lennard-Jones, etc.) had attractive regions near the equilibrium spacing. The fact that the system was not in equilibrium under the radial interactions of pseudopotential theory alone explained the observed deviations from the Cauchy relations;[2] such deviations did not arise, as had been anticipated, from angular three-body forces. Thus in the case of simple metals the microscopic theory suggested interatomic interactions of a totally different form than those which had been anticipated intuitively.

It has not seemed possible to make the corresponding first-principles calculation of the total energy for covalent systems in the form of interatomic interactions. It could not be meaningfully done in terms of pseudopotential perturbation theory since the small quantity, the appropriate expansion parameter, was the kinetic energy, not the pseudopotential.[3] Because of a crossing and repopulation of levels in the formation of the covalent solid, the extrapolation from the free-electron gas implicit in the perturbation theory is qualitatively incorrect. The same qualitative statement can be made in the tight-binding framework: we cannot proceed with perturbation theory based upon localized atomiclike states since a transformation to bondlike states is required; interatomic interactions cannot be treated as the expansion parameter.[3]

Here we utilize an alternative expansion parameter, the width of the occupied band of states, which would seem to be appropriate for any insulating or semiconducting system. We may again expect a repulsion similar to the V_0 given above for metals, which was a repulsion between overlapping "pseudoatoms," but the attractive interaction, and particularly the structure-dependent part, will be found to be quite different from the volume-dependent term of the theory of metals.

Our formulation is in terms of tight-binding atomic states, though in principle it could be done in terms of pseudopotentials, and the total energy is obtained using a moments method.[4] If we expanded the resulting energy in the interatomic interactions, it would be appropriate for metals, but for covalent solids we must expand in the bandwidth, which in the atomic context is from the splitting between the atomic *s* and *p* states. That is exactly the expansion made in bond-orbital methods in which the covalent energy, representing the coupling between sp^3 hybrids and causing the bonding-antibonding splitting, is regarded as large and the metallic energy, arising from the *sp* splitting, is treated in perturbation theory. The new feature is the more accurate evaluation of the total energy and the independence of the formulation upon a specific structure, such as the diamond structure. The most essential feature of the method is not the use of moments; in fact an essentially equivalent formulation could be made in terms of the special-points method[5] for obtaining average band energies. For that reason we would prefer to call the method the band-width expansion method, rather than a moments method.

In tight-binding theory of *sp*-bonded systems the electronic eigenstates are written in terms of a minimal basis set consisting of a single *s* state and three *p* states on each atom.[3] The corresponding one-electron eigenvalues are then obtained by diagonalizing an $N \times N$ Hamiltonian matrix based upon these N orbitals. A principal contribution to the total energy is the sum of the eigenvalues of the occupied states. In all of the eight-electron *AB* compounds which we shall consider this consists of the lowest half of the eigenvalues. We shall see that this generalizes directly to systems such as SiO_2 and transition-metal systems. Thus we seek the average of the lower half of the eigenvalues, as measured from the average of all of the eigenvalues. A simple, but crude, estimate can be taken as the square root of the second moment of the eigenvalues (again with eigenvalues measured from the average over all). If, in fact, the true eigenvalues had the same magnitude, with half positive and half negative, this estimate would be exact. Thus we take this as the lowest-order estimate and shall then correct for the effect of the spread in the upper and lower values using the fourth moment.

To obtain the total energy we must add an overlap repulsion which in the tight-bonding context arises principally from nonorthogonality of neighboring orbitals and which is expected to be additive. We shall see that the interaction given above for metals is approximately correct for silicon, which is perhaps not so surprising; the band structure of silicon is sufficiently free-electron-like that this gross feature might carry over. We shall find, however, that if we directly take the formula, with previously determined core radius r_c, an equilibrium spacing small by some 9% is predicted. Since we need to make an adjustment in any case, it seemed best to use one of the algebraic forms used earlier. These also have some theoretical justification and have proven successful before. The simplest form is[6] A/d^4, with d the internuclear distance and A adjusted such that the total energy is at a minimum at the observed spacing. Then all properties are calculated in terms of the observed internuclear distance. We shall use this form for interpreting our predictions in Sec. VI. For quantitative predictions in Sec. V, we use the form suggested by Bechstedt and Harrison,[7] the form $A/d^3 + B/d^{12}$, with A and B adjusted to give the correct internuclear distance *and* bulk modulus. To be useful for molecular dynamics, the A/d^3 term would need truncation; here we include the repulsion only for nearest neighbors.

II. ESTIMATING THE AVERAGE BAND ENERGY

We consider a distribution of eigenvalues, as illustrated in Fig. 1. It consists of an antibonding band above, and a bonding band below, the zero of energy, taken as the average of all eigenvalues. Thus the average energy of the lower band is equal to the negative of the average energy of the upper band, ε_b. It is the value of that average,

$$\varepsilon_b = (2/N) \sum_{i>0} \varepsilon_i \; , \tag{1}$$

which we seek. Here we have indexed the eigenvalues with positive i for the $N/2$ eigenvalues in the upper band and negative i for the lower band.

In order to estimate this average we calculate the sum of the squares of all of the eigenvalues of the Hamiltonian matrix:

$$\sum_i \varepsilon_i^2 = \sum_{i,j} H_{ij} H_{ji} \; . \tag{2}$$

This equality holds because the trace of a matrix is in-

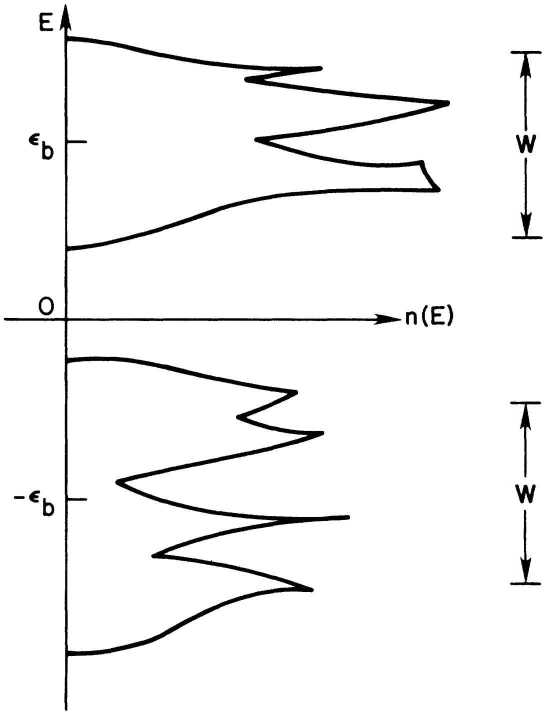

FIG. 1. A schematic representation of the density of electronic states as a function of energy, measured from the average of all, in a covalent solid. The upper band, of average energy ε_b, is empty. The lower, of average energy $-\varepsilon_b$, is full. An average bandwidth W is defined in terms of the second moments of the individual bands. The approach used here obtains the sum over occupied states as an expansion in $W/2\varepsilon_b$, carried to second order.

variant under a unitary transformation and such a transformation could be used to diagonalize the squared matrix, $\sum_k H_{ik}H_{kj}$, the matrix which has eigenvalues equal to the square of each eigenvalue of the Hamiltonian matrix. Similarly we calculate the sum of the fourth power of the eigenvalues,

$$\sum_i \varepsilon_i^4 = \sum_{i,j,k,l} H_{ij}H_{jk}H_{kl}H_{li} \ . \tag{3}$$

A convenient way to proceed is to write the expressions in terms of ε_b. The sum over the upper band of the squared eigenvalues becomes

$$\sum_{i>0} \varepsilon_i^2 = (N/2)\varepsilon_b^2 + 2\varepsilon_b \sum_{i>0} (\varepsilon_i - \varepsilon_b) + \sum_{i>0} (\varepsilon_i - \varepsilon_b)^2 \ . \tag{4}$$

The corresponding expression for the sum of eigenvalues to the fourth power can also be written. It has coefficients $N/2$, 4, 6, 4, and 1. Both can be checked by expanding the terms and canceling. The term linear in $\varepsilon_i - \varepsilon_b$ vanishes in both equations by the definition, Eq. (1), of ε_b. In the expression for the sum of eigenvalues to the fourth, we also drop the terms of third and fourth order in $\varepsilon_i - \varepsilon_b$. These terms are of higher order in the bandwidth W defined by

$$W^2 = (2/N) \sum_{i>0} (\varepsilon_i - \varepsilon_b)^2 \tag{5}$$

and thus are to be neglected.

The only remaining sums in Eq. (4) and the corresponding fourth-power expression are of the form of Eq. (5). Thus we can add the corresponding sum (with the square of differences from the average over the lower band) and let W represent the average of the upper and lower bandwidths. The second and fourth moments become

$$M_2 \equiv \sum_i \varepsilon_i^2/N = \varepsilon_b^2 + W^2 \ , \tag{6}$$

$$M_4 \equiv \sum_i \varepsilon_i^4/N = \varepsilon_b^4 + 6W^2\varepsilon_b^2 \ . \tag{7}$$

We subtract the square of the expression in Eq. (6) from the expression in Eq. (7) and drop the higher-order term, W^4, leaving $4\varepsilon_b^2 W^2$. This gives us an estimate of W^2 in terms of the sums in Eqs. (2) and (3). We substitute this back into Eq. (6) and solve for ε_b^2:

$$\varepsilon_b^2 = M_2 - (M_4 - M_2^2)/(4M_2) \ . \tag{8}$$

This was our goal, to obtain the average energy of the bonding or antibonding band in terms of the sums which can be obtained from Eqs. (2) and (3). We shall see that the first term alone will give a radial interaction and is the dominant term. The small correction term will lead to angular forces. Note that to keep terms only to lowest order in our expansion, we may expand the square root when we obtain ε_b and the final term in that expansion will be $(M_4 - M_2^2)/(8M_2^{3/2})$ and we shall see in Sec. VI that in a weak-coupling limit this becomes equivalent to the "chemical grip" description of angular forces introduced in Ref. 3 (pp. 459ff). We shall test the accuracy of Eq. (8) for some simple examples in the following section and then turn to the evaluation of Eqs. (2) and (3) for *sp*-bonded systems.

III. TEST OF THE METHOD FOR SAMPLE DISTRIBUTIONS

As indicated in the Introduction, the second moment gives an exact estimate of the average if the bandwidths, Eq. (5), are zero. In this case, the Eqs. (6) and (7) obtain with $W=0$ and the right side of Eq. (8) gives exactly ε_b^2 as it should. We may take the other extreme, in which the state distributions are not peaked at all, but uniformly distributed with a state density $N/2\varepsilon_0$ for $-\varepsilon_0 < \varepsilon_i < \varepsilon_0$ and zero otherwise. Then $\sum_i \varepsilon_i^2/N$ equals $\varepsilon_0^2/3$ and $\sum_i \varepsilon_i^4/N$ equals $\varepsilon_0^4/5$. Equation (8) leads to the estimate $\varepsilon_b^2 = (\frac{1}{3} - \frac{1}{15})\varepsilon_0^2$ or $\varepsilon_b = 0.516\varepsilon_0$, compared to the exact average of $0.500\varepsilon_0$ which can be obtained immediately for this distribution. That is very good accuracy indeed, and significantly better than the estimate obtained directly from the second moment itself [the first term in Eq. (8)] of 0.577 ε_0. Even when the bands are very broad, the narrow-band approximation is working very well.

We may construct an example which may be more relevant to *sp*-bonded materials, as we shall see. We let the average of the upper and lower bands be plus or minus V_2 and let three-quarters of the levels in each case lie V_1 above the average and the other quarter lie $3V_1$ below the average. This differs from the previous example in that the distribution has a third moment, which is neglected in our analysis. For this case, $\sum_i \varepsilon_i^2/N$ becomes $V_2^2 + 3V_1^2$ and $\sum_i \varepsilon_i^4/N$ becomes $V_2^4 + 18V_1^2V_2^2 + 21V_1^4$. These may be substituted into Eq. (8) and the result can be written in terms of a metallicity defined by

$$\alpha_m = 2V_1/V_2 \ , \tag{9}$$

which is a measure of the bandwidth relative to the separation. Note that the metallicity goes to 0 for narrow bands and approaches 1 as the band gap goes to 0. In terms of metallicity, Eq. (8) gives

$$\varepsilon_b^2 = V_2^2[1 + \tfrac{3}{8}\alpha_m^4/(1 + \tfrac{3}{4}\alpha_m^2)] \ . \tag{10}$$

The exact value of the average is of course V_2, and the α_m^4 term in Eq. (10) represents the error in the method. If the metallicity becomes small, the error also becomes small. Even if the metallicity approaches 1 and the gap goes to 0, as for gray tin, the correction term in Eq. (10) is only $\frac{3}{14}$, corresponding to a 10% error in the estimated energy. Use of the second moment alone, $V_2^2 + 3V_1^2$, without correction for the bandwidth, leads to $V_2^2(1 + \frac{3}{4}\alpha_m^2)$ for the right side of Eq. (10) and an error of 32% in the energy. With the correction from the second moment, the errors from the method would seem to be comparable to the errors in the tight-binding theory and the approach would seem to be justified.

IV. PARAMETERS FOR *sp*-BONDED MATERIALS (REF. 8)

We utilize universal tight-binding parameters, consisting of Hartree-Fock term values for the diagonal terms and forms

$$V_{ll'm}=\eta_{ll'm}\hbar^2/md^2 \tag{11}$$

for interactions between nearest-neighbor orbitals. The first two subscripts indicate the orbitals coupled and the last indicates the component of angular momentum around the internuclear axis. The coefficients are $\eta_{ss\sigma}=-1.32$, $\eta_{sp\sigma}=1.42$, $\eta_{pp\sigma}=2.22$, and $\eta_{pp\pi}=-0.63$.

Use of these parameters beyond the realm of tetrahedral solids may be questionable; Van Schilfgaarde and Harrison[9] have found that these do not transfer well to other coordinations but that if one includes the effects of nonorthogonality, the matrix elements of the nonorthogonal orbitals do transfer but that one must include then explicitly the effects of nonorthogonality for higher coordinations. The difficulty is partly that the tight-binding basis orbitals are treated as orthogonal in solving for the electronic energies. Though matrix elements between atomic orbitals might be expected to be transferable, those between orthogonalized atomic orbitals might not. Even taking the couplings between the original nonorthogonal orbitals as transferable led to bands which become too broad with high coordination.[9] For this reason, we shall not go higher in coordination than the 6 of the simple cubic structure, but even there transferability may be questionable.

It will ease the interpretation if we write the parameters in terms of the parameters of bond-orbital theory for tetrahedral solids,[3] and no approximation is involved in that. In that theory we constructed sp^3 hybrids which differ in energy from the average of all atomic term values in the system by $+V_3$ for the metallic atom (the atom from columns I–IV in the Periodic Table) and $-V_3$ for the nonmetallic atom (the atom from columns IV–VII in the Periodic Table). The *sp* splitting is written $4V_{1+}$ for the metallic atom and $4V_{1-}$ for the nonmetallic atom. Thus relative to the average of all eigenvalues, the *p*-state energy of the metallic atom is given by $+V_3+V_{1+}$, the *s*-state energy is $+V_3-3V_{1+}$, the *p*-state energy on the nonmetallic atom is $-V_3+V_{1-}$, and its *s*-state energy is $-V_3-3V_{1-}$. We may immediately write the sums of the squares of the diagonal elements of the *N*-by-*N* Hamiltonian matrix by squaring these (including three terms for each *p* state) to obtain $N[V_3^2+3(V_{1+}^2+V_{1-}^2)/2]$.

We may also immediately obtain the contributions from off-diagonal terms. They arise entirely from the coupling between orbitals on neighboring atoms since there is no coupling between atomic orbitals on the same atom. For a particular pair of neighbors the sum $\sum_{i,j}H_{ij}H_{ji}$ is invariant under unitary transformations of the states on either atom so for that sum the states may be taken as σ oriented or π oriented and the sum is then obvious, $V_{ss\sigma}^2+2V_{sp\sigma}^2+V_{pp\sigma}^2+2V_{pp\pi}^2$. Each of these terms is of the same form, Eq. (11), and the appropriate squared coefficient may be added up to give V_2^2, where V_2 is a covalent energy defined to be

$$V_2=(V_{ss\sigma}^2+2V_{sp\sigma}^2+V_{pp\sigma}^2+2V_{pp\pi}^2)^{1/2}=3.39\hbar^2/md^2\ , \tag{12}$$

with *d* of course the internuclear distance between the atoms in question. This is slightly larger than the covalent energy of bond-orbital theory, $3.22\hbar^2/md^2$, which was defined to be the coupling between two hybrids directed into the same bond. This is as expected. The square covalent energy we define here is the squared matrix element between these two hybrids, plus the sum of the squares of the other couplings between hybrids on these two atoms, all of which are neglected in the bond-orbital approximation.[3]

This V_2^2 is to be summed over the neighbors to each of the $N/4$ atoms, and summed over those atoms. For the present we let there be *n* nearest neighbors to every atom and let all of the spacings be identical so the contribution to the trace of the squared matrix is $nNV_2^2/4$. Then we may add this to the diagonal contribution and divide by the number of orbitals, *N*, to obtain

$$\sum_i \varepsilon_i^2/N=V_3^2+3(V_{1+}^2+V_{1-}^2)/2+nV_2^2/4\ . \tag{13}$$

This result for the second moment is rather remarkable in itself. We could take the square root of the right side as an estimate of the average electron energy (relative to the average of the atomic levels) for a tetrahedral semiconductor ($n=4$). The corresponding estimate obtained in the bond-orbital approximation, in which all coupling is neglected except for that between two hybrids in the same bond, is $(V_2^2+V_3^2)^{1/2}$, equal to what is obtained from Eq. (13) if the metallic energies (to which we shall return) are dropped. We have in Eq. (13) a slightly larger covalent energy and if in fact we expand to lowest order in the difference we see that the result is of the form of the appropriate correction, in perturbation theory, for the neglected coupling between bonds and neighboring antibonds, corrections which we have called "interatomic metallization."[3] Similarly, if we expand the square root of Eq. (13) in terms of $V_{1+}^2+V_{1-}^2$, we see that the result is of the same form as the corrections which we earlier called (intra-atomic) metallization. Both corrections are overestimated by writing the average energy as the square root of Eq. (13), and our correction for bandwidth will approximately remove that overestimate. An interesting point is that the simple form, Eq. (13), will include corrections which are ordinarily omitted in bond-orbital theories and could be more accurate, even without bandwidth corrections, than bond-orbital theory.

The evaluation of the fourth moment is more complicated. The sum of the diagonal terms is straightforward and gives

$$M_4(1)=\sum_i H_{ii}^4/N=V_3^4+9V_3^2(V_{1+}^2+V_{1-}^2)+\tfrac{21}{2}(V_{1+}^4+V_{1-}^4) \tag{14}$$

(equal to the model result given earlier if $V_{1+}=V_{1-}$). The 1 in parentheses indicates one-atom terms.

There are off-diagonal terms involving two, three, and four neighboring atoms. Those involving only two atoms may be obtained by taking the i in Eq. (3) to represent an orbital on a particular atom and j, k, and l to be orbitals either on that atom or a particular neighbor, but always including at least one orbital on each atom. These can be averaged with terms with i corresponding to the neighbor atom. There are a large number of terms which must be collected. They lead to

$$\begin{aligned}M_4(2)=&(V_{ss\sigma}^4+4V_{ss\sigma}^2V_{sp\sigma}^2-4V_{ss\sigma}V_{sp\sigma}^2V_{pp\sigma}+2V_{sp\sigma}^4+4V_{sp\sigma}^2V_{pp\sigma}^2+V_{pp\sigma}^4+2V_{pp\pi}^4)/4\\&+V_{ss\sigma}^2[V_3^2+3V_3(V_{1-}-V_{1+})+9(V_{1+}^2+V_{1+}V_{1-}+V_{1-}^2)]/2\\&+V_{sp\sigma}^2[V_3^2+V_3(V_{1-}-V_{1+})+5(V_{1+}^2+V_{1-}^2)-3V_{1+}V_{1-}]\\&+(V_{pp\sigma}^2+2V_{pp\pi}^2)[V_3^2-V_3(V_{1-}-V_{1+})+V_{1+}^2+V_{1+}V_{1-}+V_{1-}^2]/2\ .\end{aligned}\tag{15}$$

These are to be summed over all atoms and over all neighbors to that atom. The 2 in parentheses on the left side indicate two-atom terms. For homopolar systems, for which $V_3=0$, this can be rewritten simply as $0.215V_2^4+4.032V_1^2V_2^2$ by substituting the appropriate coefficients for each $V_{ll'm}$ and V_i. These terms contribute to a central-force two-body interaction.

The terms involving three atoms are the most interesting. They may be organized and evaluated by thinking of the terms in Eq. (3) as paths moving from state i to state j to state k to state l; we must return to state i at the end. In a tetrahedral structure two neighbors to any one atom are quite far from each other ($\sqrt{3}d$) and the coupling between orbitals on those two atoms is small enough to be neglected. Thus no paths contain a triangle, but must have a central atom and two ligands with negligible coupling between them. Similarly, second neighbors in a simple-cubic structure are separated by $\sqrt{2}d$ and it has been usual to neglect their couplings, so again there are no triangular paths. They occur only in the structures of higher coordination, which we have omitted because of the question of transferability of the matrix elements. Thus for all of the three-atom paths which we consider, there is a central atom and two ligands with negligible coupling between them. Then we can begin a path at the central atom with any one of four states, move to any one of four states on the first ligand, return to the central atom to any one of four states, and move to any one of the four states on the second ligand for a total of 256 different paths. However, we may begin with i designating any of the states on the path and proceed in either direction. For example, if we select p states which are oriented perpendicular to the plane of the three atoms, they couple to each other and to no other states. Thus there is only one path which may proceed either way from the center or begin at either ligand, leading to four terms, each equal to $V_{pp\pi}^4$ per electron. We associate all such paths with the central atom so when we divide by N (equal to four times the number of atoms), as in Eq. (6), we obtain a contribution of $V_{pp\pi}^4$. For the remaining terms, we include first only terms with σ-oriented states on the ligands. When these involve a p state on the central atom, we may orient it along the vector to the first ligand, giving σ-matrix elements, but then its σ-oriented component along the vector to the second ligand is $\cos\theta$, with θ the angle subtended by the two ligands at the central atom. We must keep these angular factors as we evaluate these terms. Each path will give eight identical terms when two different states on the central atom enter. Finally, we add the terms with one or two π-oriented (but in the plane of the three atoms) states on the ligands. These many terms can be collected and combined, noting that each term contains four matrix elements, two with one neighbor and two with another, to give a three-atom contribution to the fourth moment of

$$\begin{aligned}M_4(3)=&(V_{ss\sigma}^2+V_{sp\sigma}^2)^2+2(V_{sp\sigma}^2+V_{pp\sigma}^2)V_{pp\pi}^2+V_{pp\pi}^4+2V_{sp\sigma}^2(V_{ss\sigma}-V_{pp\sigma})^2\cos\theta+(V_{sp\sigma}^2+V_{pp\sigma}^2-V_{pp\pi}^2)^2\cos^2\theta\\=&(0.150+0.382\cos\theta+0.324\cos^2\theta)V_2^2(d_1)V_2^2(d_2)\ .\end{aligned}\tag{16}$$

To obtain the final form we substituted the values of the matrix elements given in Eq. (11) and noted that $V_{ss\sigma}$ and $V_{pp\sigma}$ are of opposite sign, so the two terms add. d_1 and d_2 are the two internuclear distances involved. This is the form we shall use in our analysis. It will be interesting to note later that the final form has a minimum at 126°.

Up to this point we have taken all internuclear distances the same so $d_1=d_2$ and we have added this particular ligand pair for every atom before dividing by the number of electrons N. We must still sum over each ligand pair to the atom in question. For the tetrahedral structure, for example, there are $4\frac{3}{2}=6$ ligand pairs, each with $\cos\theta=-\frac{1}{3}$. When we construct general interatomic interactions we shall add such terms for every atom.

Finally we turn to terms involving four nearest-neighbor atoms. These do not occur in the tetrahedral structure, but they do in the rocksalt structure where the paths are square. Consider first paths based entirely upon s states. Let i in Eq. (7) reside on a particular atom. There are 12 square paths starting with that state. Each can be traversed in two directions so each path contributes $2V_{ss\sigma}^4$. There is one such contribution for each right-angle three-atom path which was included in Eq. (16). This contribution does not change if the angles deviate from 90°. Other contributions from this collection of four atoms do depend upon the angles, but for a square the contributions are $8V_{ss\sigma}V_{sp\sigma}^2V_{pp\pi}$, $4V_{pp\sigma}^2V_{pp\pi}^2$, and $2V_{pp\pi}^4$ contributions for a total of $0.052V_2^4$ for each of the 12 paths. We shall only require the contribution of the square in the present analysis.

V. RELATIVE ENERGIES OF THE STRUCTURES

The first application is to perfect-crystal structures. The second moment is given in Eq. (13). The fourth moment contains the one-center terms of Eq. (14). It also contains the two-center terms in Eq. (15), which are to be multiplied by the number of neighbors, n, and can be combined using the expressions Eqs. (12) and (13) for $V_{ll'm}$ and V_2 as

$$M_4(2)=n[0.214V_2^4+0.5V_2^2V_3^2+0.154(V_{1-}-V_{1+})V_2^2V_3+1.808(V_{1+}^2+V_{1-}^2)V_2^2+0.405V_{1+}V_{1-}V_2^2] . \tag{17}$$

The three-center term is obtained by summing the final form of Eq. (16) over pairs of neighbors for each structure. We write the result, again using Eqs. (12) and (13),

$$M_4(3)=C_nV_2^4 . \tag{18}$$

For the tetrahedral structures there are six combinations of ligand pairs, each having the angle such that $\cos\theta=-\frac{1}{3}$. Thus we obtain $C_4=0.352$. For the graphite structure, with three combinations of neighbor pairs, each with $\cos\theta=-\frac{1}{2}$, we obtain $C_3=0.120$. For a chain of atoms, with neighboring bands separated by $\theta=126°$, the angle at which Eq. (16) is a minimum, we obtain $C_2=0.037$. For the simple-cubic structure, the sum contains 12 pairs at $\theta=90°$ and three with $\theta=180°$, for a value of 2.076. However, for this one case there is also a contribution of four-neighbor terms, 12 paths at $0.052V_2^4$, giving $0.624V_2^4$, for a total contribution of the form of Eq. (18) with $C_6=2.700$. We do not go to higher coordination because of question of transferability of the couplings discussed earlier for high cooordinations. These are collected as $M_4=M_4(1)+M_4(2)+M_4(3)$ and the energy ε_b is written using Eq. (8). We may readily evaluate these for silicon, obtaining $M_2=31.60$ eV^2 and $M_4=1938$ eV^4, so indeed $(M_4-M_2^2)/(4M_2)=7.4$ eV^2 is small compared to M_2, as we have assumed. The expansion would seem to be reasonable.

It is most convenient to obtain the energy per atom pair, so this ε_b is to be multiplied by -8. To obtain the energy relative to isolated atoms, we must add a promotion energy, $\varepsilon_p-\varepsilon_s=4V_1$, for each atom in homopolar systems, which shifts the atom from an s^2p^2 to an sp^3 configuration. For III-V compounds we must also shift an electron from a p state on the column-V atom to one on the column-III atom, to obtain both in an sp^3 configuration, requiring an additional $-V_{1-}+2V_3+V_{1+}$. Twice this transfer energy is required for II-VI compounds and three times it for I-VII compounds, but for the I-VII compounds no $\varepsilon_p-\varepsilon_s$ is required on the column-I atom. Thus the promotion energy per atom pair is given by

$$E_{\rm pro}=\begin{cases} 8V_1 & \text{for column-IV compounds ,}\\ 5V_{1+}+3V_{1-}+2V_3 & \text{for III-V compounds ,}\\ 6V_{1+}+2V_{1-}+4V_3 & \text{for II-VI compounds ,}\\ 3V_{1+}+V_{1-}+6V_3 & \text{for I-VIII compounds .}\end{cases} \tag{19}$$

We must also add the coordination, n, times the repulsion, $nV_0(d)$, to obtain an energy per atom pair of

$$E_{\rm pair}=-8\left[M_2-\frac{M_4-M_2^2}{4M_2}\right]^{1/2}+nV_0(d)+E_{\rm pro} . \tag{20}$$

For silicon we tried the form $V_0(d)$ given for metals in the Introduction, with $\kappa=(4e^2k_Fm/\pi\hbar^2)^{1/2}$ based on the free-electron Fermi wave number for silicon and $r_c=0.56$ Å (Ref. 3). Minimizing the total energy with respect to d gave $d=2.17$ Å, in rather poor agreement with the observed 2.35 Å. This r_c also led to a bulk modulus of about three-quarters of the observed value. It may be gratifying that the theory predicts this well with so little adjustment of parameters, but in order to use the method, we will wish to adjust the overlap potential to give both the spacing and bulk modulus correctly. We use

$$V_0(d)=A/d^3+B/d^{12} , \tag{21}$$

of the form used by Bechstedt and Harrison.[7]

Our procedure then is to adjust A and B in the $V_0(d)$ of Eq. (21) such that the energy is a minimum at the observed spacing in the observed tetrahedral structure, and also gives $\partial^2E_{\rm pair}/\partial d^2=4k$, where k is the bond-stretching force constant, given by $4d\sqrt{3}$ times the bulk modulus in the tetrahedral structure. Then using the same A and B, the energy is obtained from Eq. (20) for the other structures, as illustrated in Fig. 2, and minimized with respect to d for each of those structures. The input parameters and resulting A and B are given in Table I for two series of systems—C, Si, Ge, Sn, and Ge, and GaAs, ZnSe, and CuBr—to obtain dependences on the two familiar variations in covalent systems, namely the variation of metallicity (or row of the Periodic Table) and of polarity (or difference in the column of the Periodic Table for the two constituents). In Table II is given the predicted equilibrium spacing and total energy, relative to free atoms, for structures of different coordination.

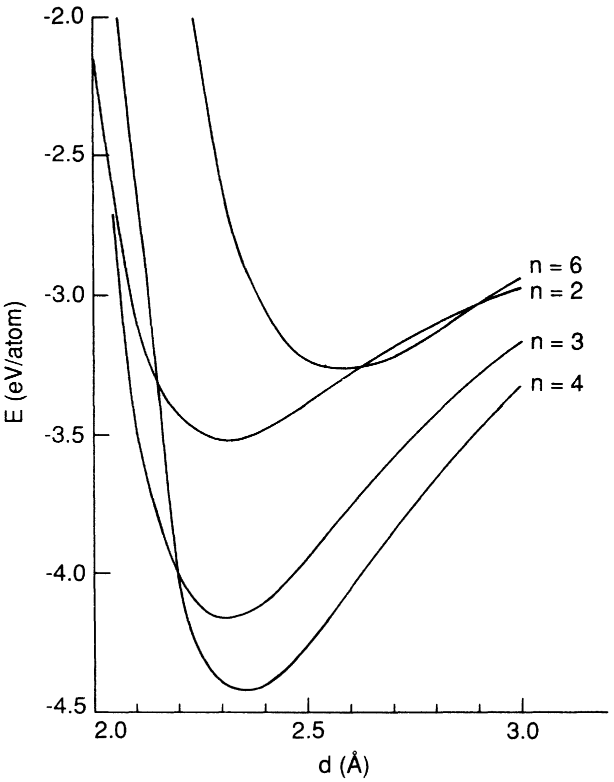

FIG. 2. The energy per atom, relative to free atoms, for silicon as a function of the internuclear distance d in the carbyne ($n=2$) structure, the graphite ($n=3$) structure, the diamond ($n=4$) structure, and the simple-cubic ($n=6$) structure, all based on Eqs. (20) and (21), with A and B adjusted to give the correct equilibrium spacing and bulk modulus for $n=4$.

The values for the case of silicon can be matched with the minima in Fig. 2. We see that, remarkably, the correct structure is obtained in each case (tetrahedral except for carbon). The predicted cohesive energies are very roughly in accord with experiment. The experimental[7] values are 7.36, 4.64, 3.88, and 3.12 eV/atom for C, Si, Ge, and Sn, to be compared with the magnitude of the energy in the $n=4$ structure, and 7.76, 6.52, 5.16, and 5.80 eV/atom pair for Ge, GaAs, ZnSe, and CuBr. The values are sensitive to the form of the overlap repulsion; softer repulsions[3,6,7,9] give smaller cohesive energies, so one should be cautious about attaching too much importance to the agreement with these values, though it is encouraging that the trends are not badly given.

It is also of interest to note that the energy difference between the fourfold and sixfold structures decreases with increasing atomic number (4.61, 1.15, 0.86, and 0.26 eV/atom for C, Si, Ge, and Sn) and with polarity (1.73, 1.31, 0.77, and 0.40 eV/atom pair for Ge, GaAs, ZnSe, and CuBr. Indeed, tin is stable in a more close-packed metallic structure, and some noble-metal halides are stable in the sixfold (rocksalt) structure.

We made similar calculations for three compounds which occur in the rocksalt structure, namely LiF, NaCl, and CaO. The corresponding results appear in Tables I and II. It is disappointing that we find LiF and NaCl stable in structures of lower coordination, again representing an overestimate of $n=6$ energy relative to $n=4$ energy. One effect which comes immediately to mind is our neglect of second-neighbor repulsions, which become important in the rocksalt structure.[11] Inclusion of these would, however, further increase the energy in that structure, worsening the agreement with experiment.

It may not be surprising that we do not obtain correct structures in all cases with such a simple theory. Nonetheless, the principal trends among the semiconductors are correctly given without any adjustment of the bonding contribution represented by the first term in Eq. (20), and with some adjustment it may provide a good representation of the true interatomic interactions.

Another test which may readily be made is of the angular rigidity, reflected in the elastic shear constant $(c_{11}-c_{12})/2$ for the tetrahedral structure. We do this by applying a strain $e_1=-e_2=\varepsilon$. We then obtain the change in angle θ between a pair of neighboring internuclear vectors $\mathbf{d}_1$ and $\mathbf{d}_2$ from $\cos\theta=\mathbf{d}_1\cdot\mathbf{d}_2/(d_1 d_2)$, obtaining two angles each with $\cos\theta=-\frac{1}{3}\pm\frac{4}{3}\varepsilon$ plus terms of order ε^3. Two other angles have $\cos\theta=-\frac{1}{3}-\frac{2}{3}\varepsilon^2$. All changes in bond length are the same and of order ε^2, giving a negligible change in total energy of order ε^4. Thus the second moment does not change, and only the θ dependence of Eq. (16) enters. The sum over paths of $\cos\theta$ changes by $-\frac{4}{3}\varepsilon^2$, and the sum over $\cos^2\theta$ changes by $8\varepsilon^2$ and M_4 changes by $(-\frac{4}{3}\times 0.382+8\times 0.324)V_2^4\varepsilon^2=2.08V_2^4\varepsilon^2$. Using the parameters for silicon, this yields a change in energy per atom of $3.20\varepsilon^2$ eV. Equating this to the elastic energy of $(c_{11}-c_{12})\varepsilon^2$ times the atomic volume yields $(c_{11}-c_{12})/2=1.28\times 10^{11}$ ergs/cm^3. This is well below the experimental value of 5.1×10^{11} ergs/cm^3, and is not as close as values obtained in the bond-orbital approximation.[3] However, we shall see that trends from material to material are better described here. Before considering these trends, it is appropriate to try some simplification of method which makes those trends more apparent.

VI. SIMPLIFICATION AND INTERPRETATION

Our basic approach has been an expansion in the bandwidth divided by ε_b, the term $(M_4-M_2^2)/(4M_2)$ under the square root in Eq. (20) being the correction to M_2 as the value of ε_b^2. Thus, to the order we work, it is legitimate to expand the square root as $\sqrt{M_2}-(M_4-M_2^2)/(8M_2^{3/2})$, dropping higher-order terms. If we make this approximation, we find that generally the predicted structures do not change and the predicted cohesion is not affected greatly. The predicted elastic constant is decreased by 15%, slightly worsening the agreement with experiment. On the scale of the apparent inaccuracies of the method, it would seem to be a well-justified approximation, and indeed it simplifies the form of the interatomic interactions. It will also make it somewhat simpler to understand the origin of predicted trends.

In this expanded form we see that the leading term in the energy per electron, $-\sqrt{M_2}$

$=-[3(V_{1-}^2+V_{1+}^2)/2+nV_2^2/4+V_3^2]^{1/2}$, provides a radial interaction, though one which depends on the environment of the atom in the crystal through the coordination number, n. This is essentially the dependence of the interaction on bond order discussed recently by a number of authors.[12–17] We see, in fact, that the one- and two-body terms in M_4 similarly give a radial interaction, which is expected to be considerably smaller than the leading term, and which also depends on the environment of the atom.

In addition to these radial terms are the three-body terms which, for V_2 small compared to V_3, approach the fourth-order perturbation-theory correction which we introduced for ionic crystals earlier (Ref. 3, p. 459) and called the "chemical grip." Since it raised the energy, it needed to be distinguished from the bonding contributions and a new name seemed appropriate. It is the leading term in the angular interaction and is here extended to systems such as silicon, where the perturbation theory is not applicable, as well as to a variety of other systems.

Although the one- and two-body terms in M_4, as well as the M_2^2 which partially cancelled against them, depend upon the environment, it is reasonable to drop them and hope that the difference is largely made up by the overlap interaction, $V_0(d)$, which must now be readjusted to fit the observed spacing and bulk modulus. Then only the θ-dependent $M_4(3)$ term of Eq. (18) (the chemical grip) remains and the magnitude of the bond energy for the undistorted crystals becomes $\varepsilon_b=\sqrt{M_2}-C_nV_2^4/(4M_2)^{3/2}$. This step, in fact, eliminates a small repulsive interaction which is larger for higher coordination, and it was large enough that dropping it changed the predicted stable structure for silicon to the graphite structure, and that for carbon to the carbyne structure, and increased the predicted cohesive energy a few electron volts per atom, significantly decreasing the agreement with experiment. Thus this additional approximation is not justified quantitatively, but will give us a simple enough picture to understand easily the trends predicted by the more complete energy of Eq. (20), or that form with only the first term kept in the expansion of the square root. The energy per pair becomes

$$E_{\text{pair}}\approx-8\sqrt{M_2}+C_nV_2^4/M_2^{3/2}+nV_0(d)+E_{\text{pro}}\ . \tag{22}$$

The overlap repulsion $V_0(d)$ is the same, but the coefficients must be redetermined with the new expression for E_{pair}, and E_{pro} is from Eq. (19) as before. The first two terms represent the effect of the electronic structure and we note that the properties of the constituent elements, the $V_{1\pm}$ and V_3, enter only through $\sqrt{M_2}$; the C_n depends only on structure, and $V_2=3.39\hbar^2/md^2$ is a simple function of distance. Thus the two trends among semiconductors which we mentioned earlier, variations of properties with metallicity (or row in the Periodic Table) and polarity (or column in the Periodic Table), are now a single trend, that with covalency,

$$\alpha_c=V_2/[3(V_{1-}^2+V_{1+}^2)/2+nV_2^2/4+V_3^2]^{1/2}\ , \tag{23}$$

which can be reduced either by the metallic or the polar energies. That was not so apparent in the bond-orbital model. The values of α_c are 0.949, 0.832, 0.788, and 0.771 for C, Si, Ge, and Sn in the tetrahedral structure. They are 0.721, 0.591, and 0.472 for GaAs, ZnSe, and CuBr.

It is of interest first to consider the form of the energy, Eq. (22), with the simplest form[6] of $V_0(d)$, given by A/d^4. The first step for any system is to fix the value of A by minimizing the energy with respect to d at the observed spacing. If we first neglect the three-body term $C_nV_2^4/M_2^{3/2}$, which arises from the bandwidth, we note that $nV_0=nA/d^4$ is given by a constant times nV_2^2 and the only dependence of Eq. (22) upon bond length is through the expression nV_2^2 in the $-8\sqrt{M_2}$ and the nV_0, so a single value of nV_2^2 provides the minimum for all coordinations. It follows that, for the same system in different structures,

$$d\propto n^{1/4}\ . \tag{24}$$

Even if we include the $C_nV_2^4/M_2^{3/2}$ term, C_n as a sum over pairs of neighbors is approximately proportional to n^2, so that the argument still applies. It is a familiar qualitative fact that d increases with coordination, and this yields a tentative quantitative expression. It is very approximate because the A/d^4 form is very crude. It predicts a spacing in graphite of $(\frac{3}{4})^{1/4}$ times the diamond spacing, or 1.43 Å, close to the observed 1.42 Å.

Taking A to give the correct spacing in the observed structure and substituting the universal value of nV_2^2 back into Eq. (22) then leads to the same E_{pair} for all values of n, again only approximately if the $C_nV_2^4/M_2^{3/2}$ term is included, since C_n is not really proportional to n^2. By finding all energies equal, we fail to predict the structure. As pointed out by Pettifor,[18] this is a general feature of models for which the repulsion is proportional to the square of the interatomic matrix elements. To understand the structure, we must improve the model in two regards: First, we must use a more appropriate form for V_0 and, second, we must use the correct values of C_n.

Fitting the Bechstedt form,[7] or any other form, of V_0 to obtain the observed bulk modulus as well as the observed spacing gives a value different from $\nu=4$ for the expression

$$\nu=-(d/V_0)(\partial V_0/\partial d)\ , \tag{25}$$

corresponding to a V_0 varying as $1/d^\nu$. [This is the ratio relevant to the determination of structures, though what we have actually fitted to experiment is a different ν, equal to $-(\partial^2V_0/\partial d^2)/(\partial V_0/\partial d)-1$.] A value of ν larger than 4 favors high n, while a value lower than 4 favors low n. C_n, on the other hand, increases more rapidly with n than n^2 [it is more nearly as $n(n-1)$] which always favors lower coordination. This effect of this three-body term proportional to C_n becomes smaller as the covalency decreases. Both should be considered in order to understand the trends.

Values of ν obtained from Eq. (25) using the repulsion given by Eq. (12) and Table I are 3.20, 4.09, 4.12, and 4.99 for C, Si, Ge, and Sn. This correctly suggests that,

TABLE I. Experimental bond length d, and $k=\frac{1}{4}\partial^2 E_{\text{pair}}/\partial d^2$ (k is the experimental interatomic force constant) and parameters of the repulsion of Eq. (21). Experimental parameters are from the collection in Ref. 7.

	d (Å)	k (eV Å^2)	A (eV Å^3)	B (eV Å^{12})
C	1.54	29.69	46.20	54.30
Si	2.35	9.94	46.31	12 788.0
Ge	2.44	8.01	43.43	18 965.0
Sn	2.80	6.43	35.70	107 425.0
GaAs	2.45	7.89	41.03	19 506.0
ZnSe	2.45	6.33	35.47	16 548.0
CuBr	2.46	4.13	30.53	12 767.0
LiF	2.01	2.53	26.47	484.7
NaCl	2.82	1.27	26.30	26 960.0
CaO	2.41	4.83	17.57	10 649.0

relative to the tetrahedral structure, on the basis of the overlap repulsion, only carbon should have lower coordination, as we found in Table II, but it does not explain why the carbyne structure is not even more stable than graphite and, in fact, the full solution of Eq. (22), rather than Eq. (20), did give the carbyne structure lower in energy. The effects of V_0 also contribute to the increasing stability of the simple-cubic structure relative to tetrahedral structures with increasing atomic number. The effects of the C_n term are always to favor low coordination, but they drop rapidly (as α_c^4) with dropping covalency and thus become quite small in tin, also supporting the tendency toward close packing for systems low in the Periodic Table.

Values of v are very nearly the same for Ge, GaAs, ZnSe, and CuBr, so the tendency toward higher coordination with increasing polarity may be attributed entirely to decreasing of the three-body C_n term with decreasing covalency. Note that there are no effects in this theory from the Madelung energy, which we regard as a small effect with effective charges typically of order $\pm 0.5e$.

Finally, we should return to the angular rigidity as reflected by the elastic constant $(c_{11}-c_{12})/2$. This arose entirely from the angular chemical-grip term, $M_4(3)$, which in our full analysis gave a change in energy $\delta E_{\text{pair}}=\delta M_4/\{M_2[M_2-(M_4-M_2^2)/(4M_2)]^{1/2}\}$. In the simplified form this is modified only by replacing the $[M_2-(M_4-M_2^2)/(4M_2)]^{1/2}$ in the denominator by $M_2^{1/2}$ (so that $\delta E_{\text{pair}}=\delta M_4/M_2^{3/2}$), decreasing the estimate by a factor of 0.87. Our estimate was already much too small, and this makes it slightly worse.

This was disappointing since the bond-orbital estimates were much closer, but we recall[3] that the bond-orbital model predicted a variation from material to material in proportion to covalency, α_c, equal to that defined in Eq. (23) without the term $3(V_{1-}^2+V_{1+}^2)/2$. Experimentally, and theoretically with the inclusion of interatomic metallization, the true behavior was more nearly as α_c^3. It is of interest to compare the ratios of the elastic constants with the present theory. In the simplified form the elastic constant, as derived at the end of the preceding section, becomes

$$\frac{c_{11}-c_{12}}{2}=\frac{1}{4\Omega_0}\frac{\delta M_4}{M_2^{3/2}\varepsilon^2}=0.338\frac{V_2\alpha_c^3}{d^3}\ . \tag{26}$$

This is immediately evaluated using the α_c values listed after Eq. (23) and the d from Table I. The predicted ratios for each system to the value for germanium (and the corresponding experimental number in parentheses) for each system are C, 17.44 (11.80); Si, 1.42 (1.26); Ge, 1 (1); Sn, 0.47 (0.49); GaAs, 0.75 (0.80); ZnSe, 0.41 (0.40); and CuBr, 0.22 (0.13).

It is remarkable indeed that the trends are very well given over an extraordinary range of values and variety of materials, though the individual predicted elastic constants are in error by a factor of more than 4. This would suggest that though the parameters of the theory are not so accurate in this instance for direct quantitative predictions, with an adjustment of the numerical coefficients entering the final form of $M_4(3)$ in Eq. (16) the theory may give good trends over a wide variety of systems.

TABLE II. Predicted nearest-neighbor distance (Å), and energy (eV/atom for elemental systems, eV/atom pair for compounds) in structures of varying coordination (2, carbyne at $\theta=126°$; 3, graphite; 4, diamond; and 6, simple cubic). The spacing in the stable structure has been fitted to experiment.

Material	$n=2$	$n=3$	$n=4$	$n=6$
C	1.39, −8.19	1.45, −9.37	1.54, −8.81	1.95, −4.20
Si	2.30, −3.52	2.31, −4.17	2.35, −4.42	2.58, −3.28
Ge	2.43, −3.47	2.41, −3.97	2.44, −4.21	2.65, −3.34
Sn	2.80, −3.14	2.78, −3.69	2.80, −4.09	2.96, −3.83
GaAs	2.40, −7.50	2.41, −8.39	2.45, −8.83	2.65, −7.53
ZnSe	2.39, −8.69	2.41, −9.23	2.45, −9.51	2.62, −8.74
CuBr	2.41, −7.08	2.43, −7.31	2.46, −7.41	2.61, −6.85
LiF	1.77, −15.71	1.79, −15.80	1.82, −15.63	2.01, −13.92
NaCl	2.67, −9.82	2.68, −9.93	2.71, −9.99	2.82, −9.76
CaO	2.33, −13.11	2.33, −13.67	2.35, −14.16	2.41, −14.54

VII. GENERALIZATION TO OTHER SYSTEMS

The formulation of the total energy required that the energy levels in the solid be split up and down, with the lower half occupied, so that we could use the second moment to estimate the average energy of occupied states. This applied to *sp*-bonded *AB* compounds with eight electrons per atom pair, but not to most other systems. It is nevertheless possible in many cases to proceed. The procedure for doing this is perhaps clearest for transition-metal systems.

A. Transition-metal compounds

In many transition-metal compounds the important electronic levels are the *d* states of the transition metal and the *p* states of the nonmetallic constituent. In *AB* compounds they ordinarily form in the rocksalt structure so that the important coupling is the V_{pdm} coupling between them. In such a situation with l degenerate levels coupled to l' degenerate levels there will be $|l'-l|$ nonbonding levels with energy equal to that for the majority levels (*d* levels, in this case). [This is simply because it is possible to select $|l'-l|$ combinations for which the coupling with the minority levels cancels out. Imagine, for example, $l'>l$. Then we seek a linear combination (with coefficients u_i) of the l' states for which $\sum_i H_{ij}$ is equal to zero for l values of j. This is seeking the simultaneous solution of l equations with l' unknowns. If l' were equal to l, there would only be the trivial solution with all $u_i=0$, but for each integer by which l' exceeds l, there is an additional solution, corresponding to a state uncoupled to the set of l levels. All that is required is that the diagonal elements of the l' states be equal so that these nonbonding combinations are also uncoupled to the other states of the set of l']. The remaining levels will then split upward and downward and if the lower half are occupied, our approach is again applicable. Such an approach was taken by Harrison and Straub[19] for treating transition-metal compounds using only the second-moment contribution to the energy, without introduction of the chemical grip. Then the combination of couplings, $V_2^2=V_{ss\sigma}^2+2V_{sp\sigma}^2+V_{pp\sigma}^2+2V_{pp\pi}^2$, which we introduced in Sec. IV, is replaced by $V_2^2(pd)=V_{pd\sigma}^2+2V_{pd\pi}^2$, which was written in terms of universal parameters. With three levels coupled per atom, the expression $V_2^2/4$ of Eq. (13) becomes $V_2^2/3$; there is no $V_{1\pm}$ with only one energy value per atom. The form of the chemical grip is also modified but can be directly written down.

Even in the rare case without half occupation of the bands, such as the cuprate superconductors, we could use the fourth moment to estimate the width of the bands and using a model form of the density of states estimate the average energy of the occupied states.

B. The role of peripheral states

We might be concerned about the neglect of the effect of *s* states on the metallic atom in the transition-metal compounds, but since the corresponding bands are well removed from the occupied states it should be adequate to treat them in perturbation theory. Then in lowest order they simply add terms to the radial interaction which should be adequately treated by absorbing them in the fit overlap repulsion, as were many terms in Sec. VI here. Similarly we might be concerned about the role of peripheral *s* or *d* states in the *sp*-bonded materials, but for *s* states they may again be absorbed in the overlap repulsion. For *d* states there are many terms which can be absorbed in the overlap repulsion and the remaining terms could be included as an angular contribution similar to the angular terms in Eq. (16). The fact that so many of the contributions we are dropping can be absorbed in the overlap repulsion explains to some extent why the theory based upon a minimal basis set has been as successful as it has.

C. Silicon dioxide

In silicon dioxide, and related compounds, there are three oxygen *p* states on each of two atoms coupled to four silicon atomic states. Thus if we omit, as a first step, any role of the oxygen *s* states we may describe the electronic structure in terms of two nonbonding bands, at the energy of the oxygen *p* state, four bonding bands and four antibonding bands. We may then add the oxygen *s* states in perturbation theory and, to second order in the coupling, these simply add a radial interaction. We need not specify the coefficients for the nonbonding states. Thus again the second moments can be used to estimate the energy. We define a covalent energy

$$\begin{aligned} V_2(\mathrm{SiO_2}) &= [V_{sp\sigma}^2+V_{pp\sigma}^2+2V_{pp\pi}^2)]^{1/2} \\ &= 2.78\hbar^2/md^2 . \end{aligned} \tag{27}$$

The second moment is a sum of $V_2^2+V_3^2+3V_{1+}^2/2$, with V_3 being half the difference between the silicon hybrid energy and the oxygen *p*-state energy and V_{1+} being one quarter of the silicon *sp* splitting, over all atoms and over all neighbors to each atom, divided by the number of formula units times eight for the number of orbitals involved per molecular unit. The negative of the square root of it is an estimate of the average energy of the band relative to the average of the atomic levels involved.

We have a choice when we write the total energy of the system in terms of locally calculated moments. For the perfect crystal we could evaluate the moment for one formula unit (one silicon and two oxygens in which case the sum over V_2^2 contains eight identical terms and is divided by 8) and multiply the negative of the square root by 8 for the number of electrons per molecular unit. We could instead evaluate the moment at each oxygen (with a sum over two neighbors and a division by 2), multiply each by 2, and add the negative of the square root of the moment at the silicon (with a sum over four neighbors and a division by 4) multiplied by 4. The same $V_3^2+3V_{1+}^2/2$ enters each second moment so the result is the same, but the latter form extends more naturally to nonperiodic structures and we would choose that. The total energies obtained are not identical for a nonperiodic structure because limiting the number of terms under the square root eliminates cross terms between them, most of which we expect correspond to unphysical interactions which would be eliminated by including more moments. In particular, summing over molecular units would include interactions between some sets of bonds but not other equivalent sets.

The chemical grip contribution also generalizes directly to the SiO_2 structure. However, in eliminating the oxygen s states from the problem we change its form and the minimum energy in terms of the angle at the oxygen occurs at $\theta = 90°$ rather than 126°. Thus we predict too small an angle at oxygen. This occurred also in the earlier tight-binding analysis of this system.[3] Adding the effect of the oxygen s state would increase the equilibrium angle, but it would appear not enough.

VIII. INTERATOMIC INTERACTIONS FOR MOLECULAR DYNAMICS

The total energy of a system is obtained, in the simplified theory, by summing the $\frac{1}{2}E_{\text{pair}}$ of Eq. (22) over all atoms. In this sum, and in obtaining M_2 from Eq. (13), the coordination n is replaced by a sum over neighbors. The force on any atom, then, is the partial of this total energy with respect to the position of that atom. We look first at the term $-4\sqrt{M_2}$. A change in that term is given by $-4/\sqrt{M_2}$ times half the change in the sum of $V_2^2/4$. Each term involves one neighbor, and the corresponding force on the central atom is

$$F = 2V_2^2/\sqrt{M_2}d \qquad (30)$$

in the direction of that neighbor and $\sqrt{M_2}$ is evaluated for the central atom. Thus although this is a radial two-body force, it depends upon the environment of the atom. There is another contribution to the interaction between this pair, in the same direction, and given by the same formula but with $\sqrt{M_2}$ evaluated for the neighbor. The two forces may not be equal but when added they give equal and opposite forces on the two atoms. The overlap repulsion gives a second, simpler, contribution to the radial two-body interaction.

The bonding force drops from neighbor to neighbor as $1/d^5$ and is thus, hopefully, of short enough range that summing over neighbors is not a serious problem. If the contribution to any calculation of neighbors beyond the first shell becomes significant, it is appropriate to cut off the force since such a cutoff was made in the solid before fitting the parameters of Eq. (11) and the overlap repulsion of Eq. (21).

The grip term in Eq. (22) is already in the form of a valence force field with an angular dependence (from the C_n). The $M_2^{3/2}$ in the denominator is to be evaluated at the central atom and again θ is the angle between the two vectors, $\mathbf{d}_1$ and $\mathbf{d}_2$, to the neighbors. Each pair is counted only once, not $\mathbf{d}_1,\mathbf{d}_2$ and $\mathbf{d}_2,\mathbf{d}_1$. There is some extra complexity in the forces resulting from the grip due to the variation of the $M_2^{3/2}$ in the denominator as the position is varied to obtain the force. It may sometimes be legitimate, as we suggest in the example below, to neglect that extra complexity. Another interesting feature of the grip is that a chain of atoms tends to zigzag with a predicted 126° angle; if each atom has a third neighbor at the same distance the angle decreases to 120°. Bringing a fourth atom tends to pucker the plane.

Finally, we may note that there are many generalizations which may be made, such as allowing additional electrons locally, which may be ignored if as in SiO_2 they are nonbonding, or may be included reducing the factor 4 in the $-4\sqrt{M_2}$ bonding term if they are in antibonding states. We are not so much offering a specific detailed scheme for calculating interactions as offering a method of approach to the problem. In the same vein, the general approach should be applicable to the wide variety of dielectric and other properties of semiconductors, though some steps such as the dropping of two-center terms in the fourth moment would need to be reconsidered. Similarly, the specific parameters we have used are not sacred, but there seems to be reason to believe that the form of Eq. (20) does well at representing the form of the real interatomic interactions in nonmetallic systems.

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