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Overlap interactions and bonding in ionic solids

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The virial theorem is used with tight-binding theory to show that the overlap repulsion should vary as $1/d^4$ in covalent solids, as $1/d^8$ in ionic solids, and as $1/d^{12}$ in inert-gas solids. The $1/d^8$ form is used to predict equilibrium spacings in alkali-metal halides and alkaline-earth chalcogenides. It is then combined with the equilibrium condition to obtain analytic formulas in terms of the tight-binding parameters for the cohesive energy, bulk modulus, and Grüneisen constant for these systems.

I. INTRODUCTION

Tight-binding theory provides electronic energy levels and a theory of the cohesive forces in covalent[1] and ionic[1,2] solids. It ordinarily treats the atomic states as orthogonal and then yields total energies which decrease monotonically with decreasing spacing. It is the nonorthogonality of atomic states on adjacent atoms which leads to a repulsion between atoms and stabilizes the lattice against collapse. That repulsion is called the *overlap interaction.* Such contributions arise since the orthogonality between states on adjacent atoms requires a modification of the wave functions, increasing the kinetic energy of the electrons, this being ultimately responsible for the stability of condensed matter against collapse.

In the present analysis we combine this nonorthogonality description with the density-functional theory of the same interaction, and the virial theorem, to obtain an algebraic form for the overlap interaction. With a power-law dependence for the repulsion, the equilibrium condition can be used to eliminate the coefficient and obtain the volume dependence of the energy entirely in terms of the parameters of the electronic structure, a covalent energy of coupling V_2 between nearest-neighbor atomic states and a polar energy V_3 obtained from a difference in free-atom term values.

II. OVERLAP INTERACTION FROM DENSITY-FUNCTIONAL THEORY

In density-functional theory, the formulation of the total energy, and the needed repulsion, is based upon the proof by Hohenberg and Kohn[3] that the total energy of a system of atoms in the ground state can be written as a function of the electron density $n(\mathbf{r})$. Kohn and Sham[4] then noted that this energy could be approximated by writing the functional of $n(\mathbf{r})$ as a simple *function* of $n(\mathbf{r})$. They took the energy density to be the energy density of a uniform electron gas at that density and then integrated over volume. (They actually calculated the electronic kinetic energy by a more accurate procedure but, in the subsequent evaluation of the overlap interaction which we shall discuss, the free-electron formula is used also for kinetic energy.)

Nikulin[5] and Gordon and Kim[6] approximated the electron density of a collection of closed-shell atoms by the superposition of free-atom densities, which were obtained from a Hartree-Fock calculation, and used existing approximations for the energy density for a free-electron gas. An examination of their results[2] shows that the dominant term in the repulsion is the excess kinetic energy of the overlapping charge densities, as suggested by the argument given above.

This calculation of overlap repulsion can be carried out approximately[2] for the limiting case of widely spaced atoms (and will be extrapolated down to small spacings) using the asymptotic form of the electronic wave functions for free atoms. That is obtained directly from the Schrödinger equation and is proportional to $r^{\nu}e^{-\mu r}$, where ν is near zero (and equal to zero for states just one Rydberg in energy) and μ is related to the energy ε_i of the atomic state by

$$\hbar^2\mu^2/2m = -\varepsilon_i \ . \qquad (1)$$

Thus we may approximate the electron density by a constant times $e^{-2\mu r}$ and if we further extend the approximation back to small r and require that the integral over that density correspond to one electron (normalize the wave function) we obtain a charge density for each atomic state of $(\mu^3/\pi)^{1/2}e^{-2\mu r}$. Using this form we may write the electron density for the highest-energy occupied states (which dominate the repulsion), for example multiplying by six for a full p shell. We may then carry out the calculation of excess kinetic energy giving the overlap interaction for two atoms separated by a distance d. In fact we may note that we may scale all positions r in the calculation by d and see that the result will be of the form $(\hbar^2\mu^2/2m)f(\mu d)$. A detailed evaluation for two atoms with identical ε_i gave[2]

$$V_0(d) = 70.8(\hbar^2\mu^2/2m)\mu d e^{-5\mu d/3} \ , \qquad (2)$$

which is of course this form.

III. APPLICATION OF THE VIRIAL THEOREM

We may next see that the lowering in energy obtained in tight-binding theory is essentially a potential energy.

We do this using linear combinations of atomic orbitals (LCAO's) for the simplest case, that of two identical atoms, each with a single state. When the atoms are brought together an even and an odd molecular orbital are formed. The expectation values of their energies are

$$\varepsilon^{\pm}=\frac{(\langle 1| \pm\langle 2|)H(|1\rangle \pm |2\rangle)}{(\langle 1| \pm\langle 2|)(|1\rangle \pm |2\rangle)}\ , \tag{3}$$

which may be written out in terms of the atomic energy $\varepsilon_1=\langle 1|H|1\rangle=\langle 2|H|2\rangle$, the matrix element $H_{12}=\langle 1|H|2\rangle=\langle 2|H|1\rangle$, and the nonorthogonality $S=\langle 1|2\rangle=\langle 2|1\rangle$. The difference between the two energies is written $-2V_2$, with V_2 the covalent energy given by $V_2=(H_{12}-\varepsilon_1 S)/(1-S^2)$, which is negative. This gives the splitting in tight-binding theory which results in the bonding of the atoms. It corresponds to orthogonal tight-binding atomic states coupled by V_2. The average of the two molecular orbital energies is ε_1-SV_2. It contains the repulsion arising from the nonorthogonality, SV_2. Also, since H contains the kinetic energy operator T and the potentials $V(1)$ and $V(2)$ from each atom, ε_1 contains a potential shift $\langle 1|V(2)|1\rangle$; detailed evaluation[6,2] has shown this to be small compared to the kinetic energy shift and we neglect it throughout.

We may look further at Eq. (4). Noting that $[T+V(2)]|2\rangle=\varepsilon_1|2\rangle$ if we again neglect the potential shift, we have $\langle 1|H|2\rangle=\langle 1|\varepsilon_1+V(1)|2\rangle=S\varepsilon_1+\langle 1|V(1)|2\rangle$ so V_2 above is given by $\langle 1|V(1)|2\rangle/(1-S^2)$. The numerator is a pure potential energy; the denominator is from a renormalization of the wave function. Thus in this LCAO theory, the covalent energy is purely potential.

For this simple case, with two electrons in the bond, the energy of the system is the atomic energy plus $2V_2-2SV_2$, with V_2 negative. The first term is purely potential energy, the second is predominantly kinetic. At the equilibrium spacing, with no external forces applied, the virial theorem tells us that the second must be half the first. This is the result we sought. A number of approximations have been made, including the neglect of the shift potential in comparison to the shift in kinetic energy in the evaluation of the average energies of the states (the overlap repulsion per electron for closed-shell systems where both odd and even states are occupied). We have also used LCAO theory to place the results in the context of tight-binding theory. This model system represents a simple covalent bond.

Before making use of this result, we may note that it applies also to ionic systems. Then the two coupled states have much different atomic energies ε_1 and ε_2. The energy gain in tight-binding theory can be calculated in perturbation theory in the coupling V_2. In first order the lower-energy state $|1\rangle$ becomes $|1\rangle+|2\rangle V_2/(\varepsilon_1-\varepsilon_2)$ and its energy is shifted by $V_2^2/(\varepsilon_1-\varepsilon_2)$, a change in potential energy of the modified state. The repulsion again is the increased kinetic energy of the overlapping closed-shell atoms. Again at equilibrium we expect the repulsion to be half the attractive term.

IV. USE OF A $1/d^{2n}$ FORM

If we choose to use a power-law form for the repulsion, we see immediately that the virial theorem tells us the value of n for each system. In tight-binding theory we use universal parameters[7] for which couplings V_2 vary as $1/d^2$ near the equilibrium spacing. This was originally derived[8] by noting that near equilibrium the bands were both representable in tight-binding theory and were free-electron-like; the dependence of the couplings on d follows immediately. Thus in the covalent case described above, the dependence of the total energy upon d is of the form $E=-A/d^2+B/d^{2n}$. The equilibrium condition is $\partial E/\partial d=2A/d^3-2nB/d^{2n+1}=0$. Writing the equilibrium d as d_0 this yields $2nB/d_0^{2n}=2A/d_0^2$. If the repulsion is to be half the attraction, $2n$ must be equal to four (and $B=\frac{1}{2}Ad_0^2$).

We had obtained this $1/d^4$ dependence of the overlap interaction earlier[9] in quite a different way. We noted that in extended Hückel theory,[10] the couplings are related to nonorthogonalities by assuming, in our notation, $V_2=KS\varepsilon_1$, with K an empirical constant, frequently taken as 1.75. This also leads to a repulsion $-SV_2$ proportional to V_2^2 and therefore $1/d^4$, but uses an empirical formula to do it. In fact, the derivation given here could be considered as a crude derivation of extended Hückel theory.

The same analysis for ionic solids, where the attractive term varies as $V_2^2/(\varepsilon_1-\varepsilon_2)$, proportional to $1/d^4$, gives an overlap repulsion proportional to $1/d^8$. (We should note that in the tight-binding theory of ionic solids, the electronic terms are regarded as the dominant attraction.[2] The atoms have effective charges, but they are changing rapidly near the observed spacing so that though a force $-e^2/d^2$ would be appropriate at large spacings, the real electrostatic interaction is negligible at the equilibrium spacings.) The same analysis might even suggest that for inert gas solids, where the dominant attraction is a van der Waal's interaction, proportional to $1/d^6$, the repulsion should be proportional to $1/d^{12}$. All of these predictions are in rough accord with the dependences obtained by fitting experimental equilibrium spacings and force constants. This lends strong support to the somewhat intuitive derivation.

A further test of these predictions can be made using the more complete form of the overlap interaction, Eq. (2). We could fit that form to a form A/d^{2n} by matching the value and the derivative at the equilibrium spacing. Matching logarithmic derivatives gives directly

$$2n=\tfrac{5}{3}\mu d-1\ . \tag{4}$$

We may obtain μ immediately from the atomic term values and Eq. (1) and insert the observed spacing for any system to see what values of $2n$ are predicted. For silicon we use the hybrid energy to obtain $2n=5.15$, to be compared with the four obtained with the virial theorem. (Use of p states gives a slightly lower value, 4.93, but the use of hybrids seems appropriate here.) For potassium chloride we use the average of the μ's obtained for the chlorine p state (1.90 Å^{-1}) and the potassium core p state (2.61 Å^{-1}) and the equilibrium spacing of 3.15 Å to obtain $2n=10.85$, compared to the derived 8. For argon, at the observed spacing of 3.76 Å we obtain 11.87, to be compared with the derived 12. The agreement is only semiquantitative, but so also is the tight-binding theory we use and some of the discrepancy may well come from the use of Eq. (2). The increase in the exponent $2n$ from covalent to ionic to inert-gas systems is seen to arise partly from the increasing depth of the atomic states, but mostly from the larger spacing.

Another interesting point may be made using Eq. (2). It may be surprising to be able to derive dependences of such high order as 4, 8, and 12 since it corresponds to coefficients B with peculiar units, energy-length^{2n}. However, we noted in deriving Eq. (2) that the repulsion was of the form $(\hbar^2\mu^2/2m)f(\mu d)$; using Eq. (1), we see that it follows that the form proportional to $1/d^{2n}$ may be written as

$$V_0(d) = -\eta_0' \varepsilon_i (\hbar^2/m\varepsilon_i d^2)^n \ , \tag{5}$$

with η_0', a positive dimensionless constant to be determined (a prime was included to distinguish it from another constant to be introduced) and $n=2$, 4, and 6 for the three solid types.

We might also mention that a familiar form of the interatomic interactions called the *Morse potential* has similar properties. The total interaction energy for a pair of atoms is written $D(1-e^{-\mu(d-d_0)})^2 = D(1-2e^{-\mu(d-d_0)} + e^{-2\mu(d-d_0)})$. Again there is an attractive term and a repulsive term with twice as rapid a variation with distance and with this the repulsive term is half the attractive term at the equilibrium spacing d_0. It is advantageous to have the attractive and repulsive terms of the same form since then formulas for properties can frequently be written in simple analytic form, as we shall see. When we earlier[2] used algebraic forms for the interaction and the exponential [Eq. (2)] for the overlap interaction, numerical calculations of properties were required; they were simple but less informative. Since our attractive terms are algebraic, the algebraic form for $V_0(d)$ is to be preferred here.

This form for the overlap has been used to study cohesion and bonding in covalent solids in the zincblende structure,[9] with good results for the equilibrium spacing, cohesion, and bulk modulus. We extend the theory now to ionic solids in the rocksalt structure.

V. BONDING IN IONIC SOLIDS

In alkali halides there is an energy gain in the formation of the solid equal to $\varepsilon_p - \varepsilon_s$ (negative, for an energy gain) from transferring an electron from the alkali to the halogen. The ε_p of course refers to the nonmetallic atom, the ε_s to the metallic atom. This gain does not depend upon the coupling between neighboring electronic states. In Sec. III we indicated that the gain in energy from the coupling could be included in perturbation theory, proportional to $V_{sp\sigma}^2/(\varepsilon_p - \varepsilon_s)$.

We can, in fact, be more accurate using the special-point method of Baldereschi[11] in which the average energy for a band is approximated by the value at one representative wave number, called a *special point*. In the rocksalt structure with nearest-neighbor interactions, this leads to an energy gain per atom pair, due to the coupling, of[2]

$$E_{\text{coupling}} = \varepsilon_s - \varepsilon_p - 2[(\varepsilon_p - \varepsilon_s)^2/4 + 6V_{sp\sigma}^2]^{1/2} \ . \tag{6}$$

This was obtained by noting that with nearest-neighbor *sp* coupling only, two of the valence bands are flat with energy ε_p. The other valence band has the form

$$E(\mathbf{k}) = \tfrac{1}{2}(\varepsilon_s + \varepsilon_p) - [(\varepsilon_p - \varepsilon_s)^2/4 + f(\mathbf{k})V_{sp\sigma}^2]^{1/2} \ ,$$

where $f(\mathbf{k})$ is a function of wave number, to be evaluated at the special point. We know the value must turn out to be equal to the number of nearest-neighbor atoms so that for small $V_{sp\sigma}$, Eq. (6) becomes $12V_{sp\sigma}^2/(\varepsilon_p - \varepsilon_s)$, the perturbation theory gain in energy with each of the three p states coupled to two neighboring s states by $V_{sp\sigma}$, and doubly occupied. Equation (6) will remain appropriate when the coupling becomes larger in comparison to $|\varepsilon_p - \varepsilon_s|$. We shall not use this modified form for the coupling energy to modify the $1/d^8$ form of the overlap interaction.

It will also simplify our expressions if we introduce a covalent energy V_2 and a polar energy V_3,

$$\begin{aligned} V_2 &= \sqrt{6}V_{sp\sigma} = -3.48\hbar^2/md^2 \ , \\ V_3 &= (\varepsilon_s - \varepsilon_p)/2 \end{aligned} \tag{7}$$

in analogy with covalent solids. Then we may add Eq. (6) to the energy gain $\varepsilon_p - \varepsilon_s$ for the alkali halides to obtain the energy gain per atom pair, E_{bond}. For divalent compound we must add an additional $\varepsilon_p - \varepsilon_s$. The results in terms of V_2 and V_3 are

$$\begin{aligned} E_{\text{bond}} &= -2(V_2^2 + V_3^2)^{1/2} \quad \text{for halides (valence I)} \ , \\ E_{\text{bond}} &= -2V_3 - 2(V_2^2 + V_3^2)^{1/2} \\ &\qquad \text{for chalcogenides (valence II)} \ , \\ E_{\text{bond}} &= \varepsilon_p - \varepsilon_d - 2V_3 - 2(V_2^2 + V_3^2)^{1/2} \\ &\qquad \text{for pnictides (valence III)} \ . \end{aligned} \tag{8}$$

We have noted in the last case that the pnictides form ionic compounds with Sc, Y, the lanthanides (rare earths), and the actinides. The third valence electron in these metals is of d character.

We can also define a polarity $\alpha_p = V_3/(V_2^2 + V_3^2)^{1/2}$ and a covalency $\alpha_c = |V_2|/(V_2^2 + V_3^2)^{1/2}$. Polarities are typically 0.8 or 0.9 for alkali halides, 0.6 to 0.8 for chalcogenides and about the same for pnictides.

In all cases we use an overlap repulsion of the form, Eq. (6), proportional for simple ionic solids to $1/d^8$. Only for predicting lattice constants will we need the detailed form of the coefficient.

A. Lattice distance

Equation (6) was derived for the overlap of states of the same energy ε_i. Here, in KCl for example, the highest-energy occupied states are the valence p states on the nonmetallic atom and the core p states on the metallic atom. The form of the interaction, Eq. (2), is not simple when the two energies are different. A convenient approximation is the use of the valence ε_p for the inert gas atom between the two elements; e.g., ε_p for argon in the case of KCl. For compounds with constituents from different rows we use the geometric mean and write it ε_{ig}. It is also convenient to write the interaction in terms of the $V_2 = -3.48\hbar^2/md^2$ from Eq. (7). Thus the nearest-neighbor overlap interaction of Eq. (5) becomes

$$V_0(d) = \eta_0 V_2^4 / |\varepsilon_{ig}|^3 , \tag{9}$$

with $\eta_0 = \eta_0'/(3.48)^4$. We have found empirically[2] that η_0 depends primarily upon the row of the nonmetallic atom so we define such a value to give the correct spacing of the potassium halide. We shall shortly find 4.69 for the fluorine row, 7.93 for the chlorine row, 9.02 for the bromine row, and 11.48 for the iodine row. We use these for predicting bond lengths for all ionic compounds.

In tetrahedral structures the second neighbors were more distant than the nearest neighbors by a factor $\sqrt{3}$ and we neglected the corresponding overlap interaction. In ionic solids this is inadequate[2] for second-neighbor nonmetallic ions; they are much larger [smaller μ in Eq. (2)] and are only more distant by a factor of $\sqrt{2}$. We use Eq. (9) for the second-neighbor anion interaction also, using the same η_0 since the nonmetallic ion is the same in both cases. However the p-state energy for the nonmetallic ion, ε_{p-}, applies to both interacting ions and is used in the denominator in place of ε_{ig}. For the undistorted structure the second-neighbor spacing is $\sqrt{2}d$. There are twelve, rather than six, neighbors at that distance, but each is to be counted only as a half for each anion, so the overlap interaction energy per ion pair is

$$E_{\text{over}} = 6\eta_0 V_2^4 (1/|\varepsilon_{ig}|^3 + 1/16|\varepsilon_{p-}|^3) . \tag{10}$$

For a cesium chloride structure the numbers of neighbors change and V_2 becomes $\sqrt{8}V_{sp\sigma}$. The ratio of distances also changes and Eq. (10), in terms of the new V_2, becomes

$$E_{\text{over}} = \tfrac{9}{2}\eta_0 V_2^4 [1/|\varepsilon_{ig}|^3 + 243/(2048|\varepsilon_{p-}|^3)] .$$

This specifies all of the parameters needed in the analysis for both structures.

All three expressions for bond energy in Eq. (8) depend upon bond length only through the term $-2(V_2^2 + V_3^2)^{1/2}$, so to predict the bond length we may simply add this to Eq. (10) and minimize the result with respect to V_2. The predicted bond length may then be determined from this value using $|V_2| = 3.48\hbar^2/md^2$ for the rocksalt structure ($4.02\hbar^2/md^2$ for the cesium-chloride structure). A convenient form for the minimization condition for the rocksalt structure is

$$1/V_2^2 = 12\eta_0 (V_2^2 + V_3^2)^{1/2} [1/|\varepsilon_{ig}|^3 + 1/(16|\varepsilon_{p-}|^3)] . \tag{11}$$

The left side is proportional to d^4 and the right side indicates how it depends upon the parameters of the system. V_2 is ordinarily much less than V_3 so neglecting V_2 on the right gives a direct simple prediction for the bond length with explicit dependence upon the parameters of the system.

Here we proceed with greater precision and use Eq. (11) as a rapidly converging iterative procedure for obtaining V_2. The polar energy V_3 is given by $(\varepsilon_{s+} - \varepsilon_{p-})/2$; the ε_{ig} is the geometric mean of the p-state energies for the inert gas atoms adjacent to the anion and the cation, and η_0 depends only upon the row of the anion. The first step is to substitute values for the potassium halide, including the observed d, and solve for η_0. This gives the four values we gave after Eq. (9). We then insert parameters from Ref. 7. We do not include lithium compounds for which there is no core p state and a formulation in terms of core s states would be needed. We shall consider the trivalent compounds, along with the rare-earth and actinide compounds in a separate study. The results of solving Eq. (10) for the monovalent compounds are given in Table I.

Note that η_0 had been set to give the correct value for the potassium halide and the table demonstrates the extent to which the theory predicts the variation among different alkali metals for the same cation. Indeed it does reasonably well except for the fluorides. The cesium compounds are all in the cesium-chloride structure so the calculation involved the modified V_2 and the modified overlap interaction given after Eq. (10).

Perhaps a more interesting test is the direct application to the divalent compounds, without further adjustment of parameters. The results are given in Table II. The agreement again is rather good though we have systematically overestimated the equilibrium spacing by some 5%. The agreement would suggest that the form for the overlap interaction may be appropriate for other properties, such as the other elastic properties or distortions near a defect. In such estimates it would be preferable to adjust the η_0 used for each material such as to give the correct equilibrium spacing for that material, as we shall do in treating other properties of the compounds.

In a recent paper we discussed corrections to the theory from Coulomb interactions between the electrons.[12] We shall discuss their role in cohesion in the following subsection. To a first approximation these add a constant term to the energy which would not affect the estimate of internuclear distances, but they do change the V_3 and do have a weak dependence upon bond length. It is not clear just how to include them in the theory of internuclear distances and to some extent their effect would simply modify the four values of η_0 which we have obtained here. We have not yet attempted it.

TABLE I. Internuclear distances d in Å predicted for alkali halides by Eq. (11) (with a modified form for the Cs compounds, all in the CsCl structure) compared with experimental values in parentheses.

	F	Cl	Br	I
Na	2.36	2.79	2.93	3.15
	(2.32)	(2.82)	(2.99)	(3.24)
K	fit	fit	fit	fit
	(2.67)	(3.15)	(3.30)	(3.53)
Rb	2.79	3.29	3.44	3.70
	(2.82)	(3.29)	(3.45)	(3.67)
Cs	2.97	3.52	3.70	3.98
		(3.57)	(3.71)	(3.95)

TABLE II. Internuclear distances d in Å predicted for divalent compounds in the NaCl structure by Eq. (11) (with η_0 fit to the potassium halides) compared with experimental values in parentheses.

	O	S	Se	Te
Mg	2.27	2.69	2.82	3.04
	(2.10)	(2.60)	(2.73)	
Ca	2.55	3.00	3.15	3.37
	(2.41)	(2.85)	(2.96)	(3.18)
Sr	2.66	3.12	3.28	3.51
	(2.58)	(3.10)	(3.12)	(3.24)
Ba	2.80	3.28	3.44	3.70
	(2.76)	(3.19)	(3.30)	(3.49)

B. Cohesion

Our formalism gives directly a prediction of the cohesive energy, the energy gained in forming the solid from free atoms. Equation (8) gave the electronic energy gain per atom pair in forming the rocksalt structure. To this is added the overlap interaction energy of Eq. (10), this being given by a constant of the material times V_2^4. We may use the minimum condition, that the derivative of the total with respect to V_2 (or equivalently with respect to d) be equal to zero, to show that at equilibrium the overlap interaction is $V_2^2/2(V_2^2+V_3^2)^{1/2}$ (corresponding to adjusting η_0 for each material to give the correct equilibrium spacing). Then the cohesive energy per atom pair for alkali halides in the rocksalt structure is

$$E_{\rm coh}=2(V_2^2+V_3^2)^{1/2}-V_2^2/2(V_2^2+V_3^2)^{1/2} \; . \qquad (12)$$

Divalent compounds have an additional term, $2V_3$; trivalent compounds have a $2V_3+\varepsilon_d-\varepsilon_p$ added to Eq. (12). These estimates for the cohesion appear as the second entry in Table III for alkali halides and in Table IV for alkaline earth chalcogenides; the corresponding experimental values are listed in parentheses.

Because V_2 is considerably smaller than V_3, this estimate is approximately $2V_3=\varepsilon_s-\varepsilon_p$ for the alkali halides. This is just the energy gain in dropping an electron from the alkali-metal s state to the chlorine p state. For the divalent compounds the estimate becomes the energy gained in dropping two electrons from the alkaline earth s state to the chalcogenide p state. These are listed as the first entry in Tables III and IV.

(For the trivalent compounds, which we have not included here, it is the energy to drop two electrons from the metallic s state and one from the metallic d state into the pnictide p state.) We see that these simplest estimates are already in rough accord with experiment, though slightly too large. Adding the bonding terms [by replacing V_3 by $(V_2^2+V_3^2)^{1/2}$] and the smaller overlap interaction energy makes the estimate even larger, and in poorer accord with experiment.

There are, however, Coulomb corrections to the energy which should be included.[12] The point is that by using free-atom term values we have tacitly assumed that the increase, denoted by U, in the energy ε_p on the nonmetallic atom due to the addition of an electron is canceled by the lowering in that ε_p by the Coulomb potential, the Madelung potential $-\alpha e^2/d$, from the other ions. The difference, $U^*=U-1.75e^2/d$ for rocksalt and cesium chloride structures, is in fact small but not negligible. The effect of U^* on the cohesive energy of alkali halides, in the approximation that the coupling V_2 is negligible, is a reduction by U^* for each atom pair; it is by a reduction of $3U^*$ for divalent compounds, and $6U^*$ for trivalent compounds. These U^*'s were evaluated for the monovalent and divalent compounds in Ref. 12. They are subtracted from the second entry in Tables III and IV to give

TABLE III. Cohesive energies in electron volts per atom pair, predicted for monovalent compounds in the rocksalt structure. The first entry is $2V_3$; the second is the more accurate Eq. (12). In the third entry, the Coulomb correction U^* is subtracted from the second entry. Experimental values are in parentheses.

	F	Cl	Br	I
Na	14.91	8.83	7.49	6.02
	17.16	10.08	8.63	7.05
	12.3	8.8	7.2	5.7
	(7.9)	(6.8)	(6.1)	(5.2)
K	15.85	9.77	8.43	6.96
	16.72	10.50	9.13	7.6
	10.3	8.2	7.0	5.5
	(7.6)	(6.9)	(6.2)	(5.4)
Rb	16.11	10.03	8.69	7.22
	16.80	10.63	9.26	7.75
	10.0	8.0	5.8	5.5
	(7.4)	(6.7)	(6.1)	(5.4)

TABLE IV. Cohesive energies in electron volts per atom pair, predicted for divalent compounds in the rocksalt structure. The first entry is $4V_3$. The second is the more accurate Eq. (12). In the third entry, the Coulomb correction $3U^*$ is subtracted from the second entry. Experimental values are in parentheses.

	O	S	Se	Te
Mg	19.68	9.44	7.6	
	23.05	12.20	10.30	
	15.6	12.2	10.3	
	(10.4)	(8.0)		
Ca	22.80	12.56	10.72	8.44
	24.58	14.16	12.31	9.93
	12.6	12.4	10.8	8.1
	(11.0)	(9.7)	(7.3)	
Sr	23.74	13.50	11.66	9.38
	25.06	14.60	12.88	10.66
	11.0	10.7	9.9	8.3
	(10.4)	(9.3)		
Ba	24.86	14.62	12.78	10.50
	25.83	15.53	13.69	11.38
	9.9	10.7	9.5	7.5
	(10.3)	(9.4)	(10.3)	

the third, which is the tight-binding estimate of the cohesion. The effect of U^* is rather small, as was the effect of V_2, and the cross term depending upon both should be even smaller; we neglect it here.

We see that these corrections more than cancel the bonding terms and give an estimate even closer to experiment than the simple $2V_3$ and $4V_3$ estimates, particularly for the fluorides and oxides where the U values are very large. This is probably as accurate a theory as we could hope for from tight-binding theory. Except for the fluorides and oxides, it may even be that the simplest theory, given by the first entry in Tables III and IV, is of more interest.

C. Bulk modulus

We may similarly predict the bulk modulus for each system. It is given by

$$B=\frac{\Omega_{\text{pair}}\partial^2(E_{\text{bond}}+E_{\text{over}})}{\partial\Omega^2_{\text{pair}}}$$

$$=\frac{1}{9}\frac{(d^2/\Omega_{\text{pair}})\partial^2(E_{\text{bond}}+E_{\text{over}})}{\partial d^2}\ ,$$

where Ω_{pair} is the volume per pair. The quantity $E_{\text{bond}}+E_{\text{over}}$ is the total energy per pair. Note that we cannot use Eq. (12) for this purpose since it was explicitly evaluated at equilibrium. Instead we may write

$$E_{\text{bond}}+E_{\text{over}}=-2(V_2^2+V_3^2)^{1/2}+CV_2^4$$

(also for divalent compounds since the difference is independent of d). We set the first derivative with respect to V_2 equal to zero to obtain a value for the constant C, and substitute it in the second derivative with respect to V_2. Then $\partial^2(E_{\text{bond}}+E_{\text{over}})/\partial d^2$ is simply $(-2V_2/d)^2$ times this second derivative. Noting that $\Omega_{\text{pair}}=2d^3$, we obtain

$$B=\tfrac{4}{9}(V_2/d^3)(1-\alpha_p^2)^{1/2}(3-\alpha_p^2)\ , \tag{13}$$

where we have written the result in terms of the polarity,

$$\alpha_p=V_3/(V_2^2+V_3^2)^{1/2} \tag{14}$$

in order to more clearly display the dependences.

TABLE V. The bulk modulus in eV/Å^3 predicted for alkali halides in the rocksalt structure by Eq. (13), compared with experimental values in parentheses. (More usual units are erg/cm^3.)

	F	Cl	Br	I
Na	0.394	0.080	0.073	0.065
	(0.290)	(0.150)	(0.124)	(0.094)
K	0.080	0.041	0.034	0.025
	(0.190)	(0.109)	(0.092)	(0.073)
Rb	0.054	0.029	0.024	0.019
	(0.164)	(0.097)	(0.081)	(0.066)

These values of the bulk modulus are compared with experiment for the alkali halides in Table V. They are not numerically very accurate, generally too small by a factor of two, but have the correct general magnitude and display rather well the trends from one material to another. An earlier analysis (unpublished) using the exponential form of the overlap interaction, Eq. (2) with adjusted coefficient, gave somewhat better agreement, but perhaps not significantly so.

The same formula, Eq. (13), applies to the divalent compounds but we only found experimental values for MgO and CaO. The predictions and experimental values (in parentheses) are 0.580 (0.955) eV/Å^3 for MgO and 0.216 (0.668) eV/Å^3 for CaO. The agreement with experiment for the polyvalent systems appears to be comparable to that for the alkali halides. The predicted values are larger both because of the reduced polarity and the smaller internuclear distance.

We have not yet incorporated the Coulomb interactions in these predictions. This would include two steps:: first is the addition of U^* to the energy as in the cohesion, including its dependence upon d. This neglects coupling between the s and the p states, if we also use the $2V_3$ approximation to the cohesion, and thus treats the effective ionic charges for the alkali halides as unity. Second is the inclusion of U^* in the calculation of the effects of the coupling, V_2. Then the energy difference between levels, $2V_3$, should be calculated self-consistently to obtain the energy gain which replaces the simple $2V_3$. This will require numerical calculation, in contrast to the formulas such as Eq. (13) into which we could directly substitute V_2 and V_3 obtained from free-atom term values and observed internuclear distances.

We have also not yet calculated the shear elastic constants. These cannot be written in such simple terms since the first- and second-neighbor repulsions enter differently and cannot be as simply written as in the CV_2^4 term we used for cohesion and the bulk modulus. It would also seem necessary to include the Coulomb effects in the theory since $\alpha e^2/d$ in U^* varies significantly, and in a well-known way, with shear.[1]

D. Grüneisen constant

Finally we might evaluate the Grüneisen constant γ which is proportional to the derivative of the bulk modulus with respect to volume, $\gamma=-(\Omega/2B)\partial B/\partial\Omega$; the factor of $\frac{1}{2}$ arises since the definition is related to the logarithmic derivative of the vibrational frequencies, proportional to the square root of the elastic constants, with respect to volume. This can also be written in terms of the variation of the total bond energy with respect to bond length. Using also the equilibrium conditions, we obtain

$$\gamma=\frac{1}{2}-\frac{1}{6}\frac{d^3\partial^3E/\partial d^3}{d^2\partial^2E/\partial d^2}\ . \tag{15}$$

Proceeding again with the bond energy $E=-2(V_2^2+V_3^2)^{1/2}+CV^4$, we may evaluate γ and use the equilibrium condition to eliminate C. After some algebra we find

$$\gamma = 3 - \frac{V_3^4}{(V_2^2 + V_3^2)(3V_2^2 + 2V_3^2)} . \tag{16}$$

This is slightly less than three for the alkali halides. The only experimental value we have found is the value $\gamma = 1.60$ for sodium chloride, given by Fritz *et al.*[13] The agreement is not so close, but it is difficult to know what to expect on a third derivative. We note that there was also error of the order of a factor of 2 for the bulk modulus.

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