

## Tight-binding theory of molecules and solids

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**Abstract** - A general tight-binding analysis is described which differs from traditional methods in that 1) analytical forms are derived and utilized for obtaining the coupling parameters, and 2) the calculation of electronic-state energies is simplified sufficiently that they also can be obtained analytically. With these two features it becomes possible to write formulae for a wide range of bonding, dielectric, and electronic properties, in terms of the free-atom term values of the constituent atoms and internuclear distances. Although the resulting predictions are less accurate than full first-principles computations and than empirical scaling theories, they do clearly show the dependences of these properties upon the chemical composition of the system and the geometry of the atomic arrangements. It is illustrated for molecules, covalent solids, ionic solids, and transition-metal systems. Different conceptual bases, but the same fundamental parameters, are required for each of these systems in order to simplify calculation of properties.

### THE MOTIVATION

Tight-binding theory of solids is as old as the doctoral thesis of Felix Bloch (ref. 1). I would like to describe how it has been used in the past several years to give simple estimates of almost the entire range of properties of solids (ref. 2). For the experimentalist such a method is valuable in allowing him to estimate the expected range of any measurement, or to choose which material may be most appropriate for a particular application. Since it displays clearly the trends from one material to another it also allows him to guess which way to turn if one material is not adequate to his purposes. It gives the computational theorist a quick and dirty estimate before he commits himself to a full analysis, or helps him learn ahead of time which system or which geometry may be of most interest.

Such a method does not compete with full calculations for accuracy, nor even with empirical scaling theories if there is enough related data to allow an interpolation. It does however have most of the utility of the more complete theory, and it is frequently much easier to understand the results and the physical origin of each effect.

### THE THEORY AND PARAMETERS

#### Tight-binding theory

The essential idea of tight-binding theory is that the electronic states  $|\psi_k\rangle$  in a

molecule or a solid can be written as a linear combination of atomic states  $|\psi_i\rangle$  of the constituent atoms.

$$|\psi_k\rangle = \sum_i u_i |\psi_i\rangle \quad (1)$$

This becomes a simplification if we also assume that only a *minimal basis set* of such atomic states is needed, only those states from shells which are partially occupied in the free atom, and that is the approximation we make. For most systems this consists of the valence s- and p-states appropriate to the row in the periodic table from which the atom comes. The electronic eigenstates and eigenvalues  $\epsilon_k$  are obtained by minimizing the expectation value of the Hamiltonian for the state  $|\psi_k\rangle$  with respect to the coefficients  $u_i$ . If, when these states are occupied by the number of electrons present, the atoms remain essentially neutral, the sum of the eigenvalues of the occupied states

$$E_{TOT} = \sum_{occ.} \epsilon_k \quad (2)$$

can be regarded as the total energy of the system in the sense that change in energy of the system as the atoms are rearranged (including separating them to free atoms) is equal to the change in this sum of eigenvalues. This provides a simple theory of virtually the entire range of properties of solids, since most properties (cohesion, elasticity, dielectric constants, etc.) can be written in terms of the energy.

#### Values for the parameters

In order to proceed we need values for the tight-binding parameters, which mathematically are the matrix elements of the Hamiltonian matrix in the basis of the atomic states. These parameters include the atomic term values  $\epsilon_i$  (the diagonal matrix elements) which we take as Hartree-Fock free-atom term values; a table is given, for example in Ref. 2. They also include the coupling  $V_{ij}$  between electronic states on neighboring atoms (the off-diagonal matrix elements). It has turned out that to a good approximation those can be neglected except for nearest-neighbor atoms and that these nearest-neighbor couplings can be taken to have universal values given by

$$\begin{aligned} V_{ss\sigma} &= -1.32 \hbar^2/md^2 & V_{pp\sigma} &= 2.22\hbar^2/md^2 \\ V_{sp\sigma} &= 1.42\hbar^2/md^2 & V_{pp\pi} &= -0.63\hbar^2/md^2 \end{aligned} \quad (3)$$

The first two subscripts indicate the angular-momentum quantum number of the atomic state and the third indicates the angular momentum of the two states around the internuclear axis (  $\sigma$  for zero and  $\pi$  for one unit,  $\hbar$  ).

#### A derivation of the coupling

Where do these couplings come from? The question has an interesting answer that also gives us some idea how much confidence we can have in them. Initially these forms came from fitting an analytic form to values obtained from careful band calculations on semiconductors (ref. 3). It was then realized that these forms followed from the fact that semiconductor band structures could be well described by tight-binding theory but at the same time were very free-electron-like (ref. 4).

This is most easily seen for the simplest case: that of a one-dimensional chain of atoms, each containing an atomic s-state. With nearest-neighbor coupling it is easily seen that the energy bands are given by  $\epsilon_k = \epsilon_\sigma + 2V_{ss\sigma} \cos kd$ , where  $d$  is the spacing between atoms and  $k$  varies from  $-\pi/d$  to  $+\pi/d$ . If the spacing were such that the electrons also behaved as free, their energy could also be written  $\epsilon_k = \epsilon_0 + \hbar^2 k^2/2m$ . The total band width, as  $k$  varies from 0 to  $\pi/d$ , is given in tight-binding theory by

$-4V_{ss\sigma}$ , and for free-electrons by  $\hbar^2(\pi/d)^2/2m$ . If these are to be consistent we conclude that  $V_{ss\sigma} = -(\pi^2/8)\hbar^2/md^2$ , of the same form as that given in Eq. 3. In fact, the coefficient  $-\pi^2/8$  is  $-1.23$ . For the three-dimensional diamond lattice an analogous treatment gave the same form for all four interatomic matrix elements listed in Eq. 3 and for  $V_{ss\sigma}$  gave the value  $-9\pi^2/64 = -1.39$ ; the value  $-1.32$  given in Eq. 3 came from fitting the known band structure of germanium. The differences are not so important. It is important, however, that these values cannot be very far off near the equilibrium spacing because in real semiconductors the band structures are quite free-electron-like. It has also turned out that these interatomic matrix elements remain quite the same when the atoms are rearranged, as in an ionic structure, so that it is reasonable to take them as universal.

### The neglect of coulomb effects

We now have all the needed parameters for studying the electronic structure, and therefore the properties, of simple covalent (ordinarily semiconducting) and ionic solids. We should point out, however, what has turned out to be the most serious approximation given above: that is the assumption that each atom remains neutral in the solid. Frequently within the tight-binding context the atoms become charged - a sodium atom in rocksalt is found to have a net charge near 0.8, and this must be taken into account to obtain reasonably accurate predictions of some properties. This has been undertaken, including self-consistent determination of the charges, and significantly improves agreement between theory and experiment (ref. 5). The corrections are not so large as one might at first think since the shift in energy levels on one atom, due to its charge, tends to be cancelled (usually to within 10%) by the shift due to its neighboring atoms which have opposite charge. It is appropriate not to worry about these Coulomb shifts in the present discussion as we discuss the theory of a variety of systems.

## A SIMPLE MOLECULE, $N_2$

### Evaluation of the eigenvalues

We begin by applying the above approach to a simple diatomic molecule, where the calculations are completely trivial, but at the same time show exactly how we may proceed in the solid. We first look up the term values for nitrogen,  $\epsilon_s = -26.22$  eV and  $\epsilon_p = -13.84$  eV. Here we take the internuclear distance from experiment,  $d = 1.09$  Å, although it is possible to extend the theory to estimate these (refs. 5 and 6). We immediately obtain the couplings from Eq. 3, giving for example  $V_{pp\pi} = -4.04$  eV and molecular  $\pi$ -states at energies  $\epsilon_p = \epsilon_p \pm V_{pp\pi} = -17.88$  eV and  $-9.80$  eV. In  $N_2$  only the lower state is occupied. The four  $\sigma$ -states are also immediately obtained by evaluating parameters and solving a quadratic equation.

In spite of the fact that these are reduced to trivial calculations, these results for the occupied states are in rather good accord with more complete theories requiring extensive computer calculations. The predicted value  $-17.88$  eV for the bonding  $\pi$ -state may be compared with the results of a full calculation by Ransil (ref. 7) who obtained  $-16.7$  eV. For the three occupied  $\sigma$ -states we obtain  $-41.1$ ,  $-21.7$ , and  $-21.5$  eV, compared to Ransil's  $-38.6$ ,  $-20.3$ , and  $-15.1$  eV. The empty states here, and in many cases in solids, are not at all well given, but they do not directly enter the ground-state properties. It is necessary to extend the theory if one is interested in the excited states (Ref. 5).

### A Simplification using hybrids

Before proceeding it is interesting to simplify the electronic structure, which will be necessary for solids though it is completely unimportant for the simple diatomic molecule. We introduce the familiar concept of hybrid states. In the calculation of the  $\sigma$ -states we may use as a basis hybrids in the form  $(|s\rangle \pm |\rho\rangle)/\sqrt{2}$  which are oriented on

each atom toward or away from its neighbor. If we again solve the appropriate quadratic equation we obtain precisely the values obtained above. However, we may instead make the approximation of neglecting the coupling of an outward-directed hybrid with any states on the other atom. Then these two states become nonbonding at an energy  $\epsilon_{nb} = (\epsilon_s + \epsilon_p)/2 = -20.0$  eV. Further, the remaining two states are written immediately as  $\epsilon_{nb} \pm (V_{ss\sigma} - 2V_{sp\sigma} - V_{pp\sigma})/2$  with the lower having the value -40.4 eV. We have not lost any appreciable accuracy by this simplification, but of course all we have saved is the solution of a quadratic equation so it is of no importance. Such a simplification in a solid, on the other hand, replaces a major computational task by a trivial estimate such as that in the diatomic molecule. The coupling between hybrids is called a *covalent energy*, in this case given by

$$V_2 = (V_{ss\sigma} - 2V_{sp\sigma} - V_{pp\sigma})/2 = -3.19 \text{ } \hbar^2/\text{md}^2. \quad (4)$$

An analogous expression will apply to covalent solids.

### Cohesion of $N_2$

We may immediately evaluate properties for this diatomic molecule. We need, however, add a repulsion between atoms which arises from the overlap of atomic states on adjacent atoms and a corresponding increase in the kinetic energy of the electrons occupying these states. Without it, the bond energies proportional to  $1/d^2$  would cause the two nitrogen atoms to fall together indefinitely. This is called an *overlap repulsion* and we may guess, on the basis of the virial theorem (ref. 6), that it will vary as twice the power of the attraction, or as a constant divided by  $d^4$ . (Then this kinetic energy will end up half as large as the potential energy arising from the interatomic coupling as appropriate to the virial theorem.) Combining this with the energy of the occupied (and nonbonding) states we obtain a total distance-dependent energy of  $2V_2 + 4V_{pp\pi} + A/d^4$ . (We have used hybrids for this evaluation.) This must be minimum at the observed spacing and that condition gives the value of  $A$  for the nitrogen molecule. We may now substitute that value back and subtract the sum of energies of the occupied states in the molecule from that in the two free atoms to obtain a cohesive energy of  $\epsilon_p - \epsilon_s + V_2 + 2V_{pp\pi} = -16.2$  eV (a negative quantity as defined here). This may be disappointing as compared with the experimental binding energy of -8.7 eV, but this factor of two may be familiar. Extended Hückel Theory (ref. 8), which is another simplified theory but one requiring computer analysis, also has been found ordinarily to overestimate binding energies by a factor of two. Indeed this turns out to be a feature of carbon-row systems. We will find that this factor of two discrepancy is not there for heavier systems. It is not even so much problem since we know to expect just this discrepancy for carbon-row systems. I do not believe that the origin of the discrepancy is known.

We could of course also obtain the interatomic force constant as the second derivative of this total energy with respect to the internuclear distance and obtain the vibrational frequencies, or from the full curve obtain the full set of frequencies including anharmonicity.

### Polarizability of $N_2$

This description of the electronic structure also allows an analysis of the dielectric properties. The effect of the field  $\mathbf{E}$ , in tight-binding theory, is simply to shift the term values on the two atoms with respect to each other by  $-e\mathbf{E}\cdot\mathbf{d}$ . This makes the bond asymmetric, shifting charge to one side. The effect is obtained by solving a quadratic equation and leads to a polarizability for fields along the molecular axis of

$$\alpha = e^2d^2[1/V_2 + 2/V_{pp\pi}] \quad (5)$$

We see that the entire range of properties of the system follows once we have a representation of the electronic structure. The same is true in solids. We begin with semiconductors, covalent solids which have bonds closely analogous to those of  $N_2$ .

## TETRAHEDRAL SEMICONDUCTORS

### The two-center bond

Silicon, gallium arsenide, and other tetrahedral semiconductors all have four valence electrons per atom. Since it is possible to make just four orthogonal hybrids with the four valence orbitals ( $sp^3$ ) per atom, and thus four independent bonds, these four electrons per atom are just enough to fill the bonds if each atom has four neighbors. If we construct these four hybrids (each of the form  $(|s\rangle + \sqrt{3}|p\rangle)/2$ , with the p-state oriented along an internuclear distance) and neglect its coupling with any but the opposite hybrid directed into the same bond, in exact analogy with our treatment of hybrids in  $N_2$ , we may treat the system as consisting of independent bonds, and the analysis becomes as simple as it was for  $N_2$ . The new covalent energy is

$$V_2 = (V_{ss\sigma} - 2\sqrt{3}V_{sp\sigma} - 3V_{pp\pi})/4 = -3.22 \text{ eV} \quad (6)$$

This covalent energy for  $sp^3$ -hybrids is slightly larger than the covalent energy for  $sp$ -hybrids given in Eq. 4. In a polar semiconductor such as gallium arsenide the two hybrids making up the bond have different energy, but we may find the bond energy by solving a quadratic equation, just as we did for  $N_2$  when a field was applied. We obtain

$$\epsilon_b = \frac{\epsilon_h^c + \epsilon_h^a}{2} - \sqrt{\left(\frac{\epsilon_h^c - \epsilon_h^a}{2}\right)^2 + V_2^2} \quad (7)$$

where the hybrid energies are denoted as coming from the cation or anion. Half the difference of the hybrid energies arises so often that it is convenient to define it as the *polar energy*,

$$V_3 = (\epsilon_h^c - \epsilon_h^a)/2 \quad (8)$$

### Metallicity and the energy bands

A third energy which enters many properties is called the *metallic energy*,

$$V_1 = (\epsilon_s - \epsilon_p)/4 \quad (9)$$

In a polar semiconductor there are two metallic energies, one for the anion and one for the cation. The coupling between two hybrids sharing the same atom in a tetrahedral solid can easily be seen to be equal to this metallic energy  $V_1$ . Thus adjacent bonds are coupled by this  $V_1$  (in a nonpolar semiconductor the coupling between bonds is easily seen to be  $V_1/2$ ). Thus it is  $V_1$  which broadens the bonding levels into bands just as the coupling  $V_{ss\sigma}$  broadened the s-levels in the atomic chain discussed above into a band of width  $4V_{ss\sigma}$ .

In a simplest approximation the bonding band, or valence band, width in a tetrahedral semiconductor is given by  $-4V_1$ . In that approximation the band gap between the valence and empty conduction bands is  $-2V_2 + 4V_1$ . (Note that both  $V_1$  and  $V_2$  are negative.) This turns out to be approximately true even in a more complete calculation of the bands. Thus if the metallic energy exceeds half the covalent energy, the gap goes to zero and the system becomes metallic. This occurs in tetrahedral tin; it is the

increase in the ratio  $2V_1/V_2$ , called the *metallicity*, from diamond to silicon to germanium to tin (principally due to the decrease in  $V_2$  from the increased interatomic distances) which provides the main trend in the properties of these systems.

### Cohesion in semiconductors

The calculation of the total energy in terms of the two-center bonds described above is directly parallel to that for the molecular  $N_2$ . It gives in fact  $-2V_1 + V_2$  per bond for nonpolar ( $V_3 = 0$ ) semiconductors in direct analogy with the  $\epsilon_p - \epsilon_s + V_2 + 2V_{pp\pi}$  which we gave for  $N_2$ . Interestingly enough, this goes to zero, as did the gap, as the metallicity approaches one. However, as the metallicity grows, the effects on the energy of the coupling between each bond and the neighboring antibonds becomes important and must be included to get meaningful results. This is quite easily done in perturbation theory giving corrections (called *metallization*) to the cohesive energy proportional to  $V_1^2/V_2$  (ref. 6). The resulting cohesion, for the polar as well as nonpolar semiconductors, is good to approximately 20% (ref. 6), except for carbon-row systems in which we overestimate the cohesion by a factor of two, as indicated above. It may be noted that for tin, the cohesion arises entirely from metallization, since  $-2V_1 + V_2 = 0$ ; the bonding energy ( $V_2$ ) is just cancelled by promotion energy ( $-2V_1$ ).

### The dielectric properties

We may also directly calculate the polarizability of these two-center bonds for fields along the bond, as in  $N_2$ , and average over angles to obtain the dielectric susceptibility of a semiconductor. It is given by (ref. 2)

$$\chi = \frac{\sqrt{3} e^2 V_2^2}{8d(V_2^2 + V_3^2)^{3/2}} \quad (10)$$

This is not one of the most accurate predictions. It tends to be too small by a factor of order one half for the homopolar semiconductors, but it gives quite accurate trends. In particular the ratio of the susceptibilities of the polar semiconductors is quite close. For example, the ratios  $\chi(\text{GaAs})/\chi(\text{Ge})$ ,  $\chi(\text{ZnSe})/\chi(\text{Ge})$ , and  $\chi(\text{CuBr})/\chi(\text{Ge})$  are very close to experiment.

In judging the predictions we should not forget that they have been made without computation, with all of the dependencies upon bond-length and composition directly displayed as in Eq. 10. Furthermore, it is the same three fundamental parameters,  $V_1$ ,  $V_2$ , and  $V_3$ , which determine the dielectric as well as the bonding properties. This is of course because the theory is based upon the fundamental electronic structure, crudely described as it is.

## IONIC CRYSTALS

We turn next to compounds such as rocksalt. If we considered a molecule of NaCl rather than a crystal we could of course proceed with the two-center bond as in  $N_2$ . However, in the crystal each atom has six neighbors and it is not possible to make six independent hybrids from the four orbitals per atom. Nor does it make any sense to try to add higher-energy orbitals such as the d-states in order to do this since in reality the coupling of these d-states to the valence states of the sodium and chlorine pushes them still higher and leaves them still unoccupied. We need a new view of the electronic structure, but fortunately can proceed with the same parameters. Again using Hartree-Fock term values we see that the lowest sodium valence state is far above the highest chlorine valence state,

$$\epsilon_s(\text{Na}) - \epsilon_p(\text{Cl}) = 8.8 \text{ eV} . \quad (11)$$

The coupling between them is quite small, at  $d = 2.82 \text{ \AA}$ , we obtain from Eq. 3 the value  $V_{sp\sigma} = 1.36 \text{ eV}$ . This is characteristic of the ionic solid. Electrons drop from the cation states to the anion states and are little disturbed by the residual coupling.

### Coupling neglected

As a first approximation we can neglect the coupling altogether and treat the system as composed of independent ions. Then the energy gap between occupied and full states is given by the 8.8 eV of Eq. 11, in very good accord with the experimental value of 8.5 eV. It is at first astounding that the answer is even near to correct since we have used an energy near the ionization energy of chlorine for an added electron when the electron affinity, which might seem more appropriate for an added electron, is over ten electron volts higher. However, as we indicated at the outset, the Madelung shift very nearly cancels the intraatomic repulsion giving the difference between electron affinity and ionization energy. The extent of the agreement is perhaps fortuitous. These Coulomb potentials do not quite cancel and there are corrections to the one-electron theory of opposite sign which remove the resulting discrepancy (ref. 5).

We also obtain the cohesion immediately from the differences in one-electron energies. As the solid is formed we gain  $\epsilon_s(\text{Na}) - \epsilon_p(\text{Cl})$  per atom pair from the transfer of the electron. Thus the cohesion is also predicted to be just the 8.8 eV of Eq. 11, again in good accord with the experimental 8.0 eV. In fact this theory has given an empirical rule which we believe is new, that the cohesion of an alkali halide is equal to the gap.

This same almost trivial theory gives quite good trends both for the gap and the cohesion for all of the alkali halides, and similar agreement for the divalent alkaline-earth chalcogenides.

We turn finally to the dielectric susceptibility which, without coupling, we find equal to zero. On the scale of the semiconductor susceptibilities this is not a bad estimate. However, if we wish to obtain values we must incorporate the coupling between levels.

### The inclusion of interatomic coupling

We may first perform a simple band calculation, analogous to that which we did for the atomic chain, and find that at  $k = 0$  the symmetry is high enough that there is no coupling of the s-states to the p-states. Thus our prediction of the gap is unchanged by the inclusion of coupling and remains in good accord with experiment. At other wavenumbers the bands push each other apart.

For other properties it is most appropriate to include this weak coupling in perturbation theory. The coupling of each occupied chlorine p-state to each of two neighbors gives a shift of  $-V_{sp\sigma}^2/(\epsilon_s(\text{Na}) - \epsilon_p(\text{Cl}))$ . Thus the six p-electrons per chlorine have their energy shifted by  $-12V_{sp\sigma}^2/(\epsilon_s(\text{Na}) - \epsilon_p(\text{Cl})) = -2.5 \text{ eV}$ , which is a small contribution to the cohesion. It is partly cancelled by the overlap repulsion which must also be included as it was for the covalent bonds. The independent-ion theory is not importantly affected.

The susceptibility may also be directly calculated in perturbation theory (ref. 2). The coupling of each p-state electron to a neighbor transfers a charge  $V_{sp\sigma}^2/(\epsilon_s(\text{Na}) - \epsilon_p(\text{Cl}))^2$  to that atom. When a field is applied that charge changes, due to the change in  $\epsilon_s(\text{Na}) - \epsilon_p(\text{Cl})$ . The corresponding dipole leads directly to a susceptibility of

$$\chi = 4e^2V_{sp\sigma}^2/[(\epsilon_s(\text{Na}) - \epsilon_p(\text{Cl}))^3d] = 0.06 \quad (12)$$

for NaCl, again nearly a factor of two smaller than the observed 0.10. Again it is of the right order and the formula applies to all of the other alkali halides and alkaline-earth

chalcogenides. Again also, the same theory and the same parameters give us the entire range of properties of these ionic solids.

### TRANSITION-METAL COMPOUNDS

When transition-metal atoms are present we must include their d-states among the valence states. These states have atomic term values near those of the atomic s-state, but the d-states are much more strongly localized near the nucleus; thus their coupling with neighbors tends to be weaker. For our purposes here we shall again neglect Coulomb shifts in the d-states though frequently they are far from negligible ( ref. 5).

Usually the lowest-energy empty states and highest-energy occupied states (in the sense of an ionic crystal) are the metallic d-states and nonmetallic p-states. The coupling between these can be obtained (ref. 2) by a theory analogous to, but somewhat more intricate than, that given above for coupling between s- and p-states. [The d-state theory actually predated the sp-theory and suggested that the latter was a possibility.] The largest coupling is given by

$$V_{pd\sigma} = -2.95 \hbar^2 r_d^{3/2} / m d^{5/2} . \quad (13)$$

The parameters  $r_d$  are known for each transition metal, given for example by 0.80 Å for iron and 0.67 Å for copper (ref. 2). Again we have all the parameters needed to calculate the electronic structure and properties of the compounds.

Frequently the coupling  $V_{pd\sigma}$  is not sufficiently small compared to  $\epsilon_d(M) - \epsilon_p(X)$  that we can use perturbation theory, e. g., in TiC and in the cuprates. We again need a new view. A particularly convenient one is to use the method of moments to estimate the width of the pd-bands which are formed. Then we can approximate the resulting density of states as a constant, as illustrated in Fig. 1. We see that the five atomic d-states, coupled to three atomic p-states, leads to two nonbonding p-bands, three bonding bands and three antibonding bands (just as, in fact, the single sodium s-state coupled to three chlorine p-states gave two nonbonding p-bands, one bonding and one antibonding band).

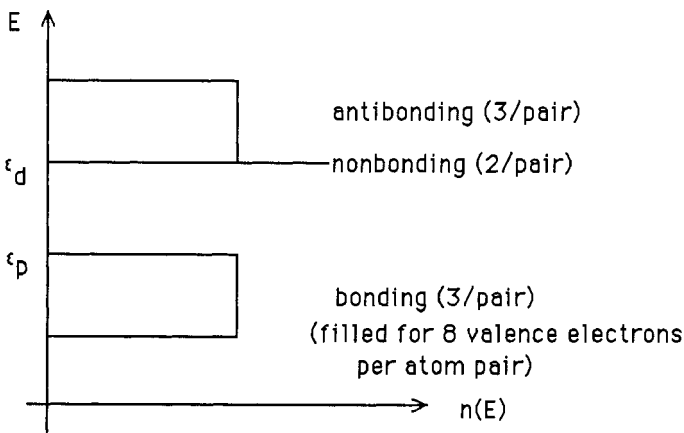


Fig. 1. Simplified pd-density of states for transition-metal compounds.

The average energy of the bonding band, obtained from the second moment, is found to be

$$\langle \epsilon_b \rangle = (\epsilon_d + \epsilon_p) / 2 - [V_2^2 + V_3^2]^{1/2} \quad (14)$$



with  $V_3 = (\epsilon_d - \epsilon_p)/2$  and  $V_2 = \sqrt{n} (1/3 V_{pd\sigma}^2 + 2/3 V_{pd\pi}^2)^{1/2}$ , with  $n$  the number of neighbors, six in the rocksalt structure. Using these forms we can directly proceed with the bonding and dielectric properties of these systems.

It is interesting to view the energy from Eq. 14 as arising from *resonant bonds* (ref. 9). There are three electron pairs forming a bond with a covalent energy and a polar energy, but shared for each atom with six neighbors. Of particular interest is the enhancement of the covalent energy by the factor  $\sqrt{n}$ ; the energy of a resonating bond is enhanced by the square root of the number of bond sites among which it resonates. This resonance energy comes from the theory directly without additional parameters. Similarly the coupling in rocksalt added an energy  $-12V_{sp\sigma}^2/(\epsilon_s(\text{Na}) - \epsilon_p(\text{Cl}))$  for the two electrons in the resonant bond, with the coupling enhanced by a factor of  $\sqrt{6}$ . Similarly also for benzene the resonant  $\pi$ -bond energy is enhanced by  $\sqrt{2}$  in comparison to that in ethane and by a factor of  $\sqrt{3}$  in graphite.

### SUMMARY

We see that tight-binding theory makes it possible to estimate most of the properties of molecules and of covalent and ionic solids; values are available for all of the needed parameters. The estimates become simple if we take an appropriate outlook, and that outlook is different for different systems. Indeed, the outlook in each case is quite close to that traditionally taken for these systems. For full numerical solution of the electronic structure and properties of these systems it would not be necessary to have any understanding, but that understanding, or outlook, is essential if we wish to make the theory simple. For the same reason, our understanding can be enhanced sometimes more by the simple theory than by the full, more accurate, solution.

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