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Instructor's Guide and Solutions Manual for

Electronic Structure and the Properties of Solids

THE PHYSICS OF THE CHEMICAL BOND

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CHAPTER 1. ELECTRONIC STRUCTURE OF ATOMS AND MOLECULES

INTRODUCTION

A course based upon this text can rather easily be adjusted to the background of the students. At the most elementary level one can make quantum-mechanical introduction carefully and isolate the elementary ideas in the rest. One works with hybrids and bond orbitals, lessing the difficulties which are only corrected by full use of the elements V_{so}, V_{sp}, etc. Mixed tetrahedral solids can be omitted together. Ionic crystals are treated simply as collections of with small corrections giving ion softening, ion distortion, and chemical grip; complexities associated with excitons and with band theory can be neglected. In simple metals the most elementary aspect can be emphasized, with some practice using the empty-core potential. The pseudopotential theory of covalent solids can be developed, and only the qualitative aspects of transition-metal compounds transition metals discussed. It still provides a general understanding of solid-state chemistry, the ability to estimate a wide range properties, and familiarity with a source for further understanding specific problems.

At the more advanced level, one can skip the quantum formulation to emphasize the general use of LCAO theory, with approximations appropriate to the problem. Even at this level, deviations from one-electron behavior are a side issue. The origin of pseudopotentials, discussed in the appendix, can be studied in depth. The understanding valent solids in terms of pseudopotentials is a beautiful unifying which can be explored. Even with very able students, large segments of material will need to be dropped if the course is to be kept e.

Just how one organizes a course out of the material is a subject question and very dependent upon the lecturer and the audience. I would not try to anticipate the many ways of doing it. This guide discuss briefly for each chapter some aspects I think particularly important and in some cases how I like to present them in class. It also indicate sections which can be omitted without destroying continuity. It will then give problem solutions. Many, but not all, class-tested. Thus there may be numerical errors but it may neverless be useful to have what I think is the correct solution. There also suggested additional problems.

I have found it most rewarding to be able to bring students in an contrary way to the forefront of today's research. I hope this text help provide that opportunity to others. Good luck!

Presenting the quantum mechanics which is needed for all of the theory done in the course may bring along some students whose background is weak. The formulation is I think novel: we define a wavefunction for an electron, an operator for an observable with energy being the most important, and then give the statement which contains all the physical content. That is that the average energy measured for an electron in a state $|\psi\rangle$ is $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle$.

The approach used for most of the book is to approximate the wavefunction by a linear combination of known functions and most of our calculation will be manipulating the coefficients of this expansion. I like to follow through a derivation of Eq. 1-10 in class, illustrate it with energy-level diagrams for diatomic molecules, and give the results for perturbation theory. I then discuss atomic states and work through Li₂ with matrix elements and only s-states. This gives two levels, -7 eV and -4 eV (different from Table 1-1 since that included p-states). I then outline the calculation with s- and p-states and assign Problem 1-3 to complete it.

Problem 1-1. Elementary quantum mechanics

a) $\langle\psi|\psi\rangle = A^2 \int_{4\pi r}^2 e^{-2r/a_0} dr = \pi a_0^3 A^2 = 1$

So $A = (\pi a_0^3)^{-1/2}$

b) P.E. = $\langle\psi|V|\psi\rangle = A^2 \int_{4\pi r}^2 e^{-2r/a_0} (-e^2/r) dr$
 $= -\pi a_0^2 A e^2 = -e^2/a_0$

c) K.E. = $\frac{\hbar^2}{2m} A^2 \int_{4\pi r}^2 \left(-\frac{1}{a_0}\right)^2 e^{-2r/a_0} dr = \frac{\hbar^2}{2m a_0^2}$
 $d) \frac{d}{da_0} \left[\frac{P.E. + K.E.}{a_0} \right] = \frac{d}{da_0} \left[-\frac{e^2}{a_0} + \frac{\hbar^2}{2ma_0^2} \right]$
 $= \frac{e^2}{2} - \frac{\hbar^2}{3a_0^2} = 0 . \text{ Thus } a_0 = \hbar^2/m e^2 .$

The second derivative is $e^2/a_0^3 > 0$ so it is a minimum.

$$\begin{aligned} & -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial^2}{\partial r^2} \frac{\partial}{\partial r} \psi - \frac{e^2}{r^2} \psi \\ & = -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(-\frac{1}{a_0} \right) r^2 e^{-r/a_0} \right] - \frac{e^2}{r} \frac{\partial}{\partial r} e^{-r/a_0} \\ & = -\frac{\hbar^2}{2ma_0^2} Ae^{-r/a_0} = -\frac{\hbar^2}{2ma_0^2} \psi . \end{aligned}$$

Q.E.D.

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The potential described here is not a pseudopotential. It is an approximation to the true potential of lithium with the effect of two nuclear charges and the two core electrons replaced by a square-well potential.

It would be possible to substitute the Hamiltonian and evaluate $\langle \psi | H | \psi \rangle$ for each state, but that would be a big job. It is best to calculate the correction. Thus $E = -e^2/(8a_0) + \langle \psi | V_{\text{core}} | \psi \rangle$.

$$\begin{aligned} \text{For the s-state, } & \langle \psi_{2s} | V_{\text{core}} | \psi_{2s} \rangle = \frac{4\pi}{32\pi a_0^3} \int_0^{a_0} \left(4r^2 + \frac{4r^3}{a_0} + \frac{r^4}{a_0^2} \right) e^{-r/a_0} \left(-\frac{2e^2}{a_0} \right) dr \\ & = \frac{1}{8} \left(8 - \frac{21}{e} \right) \left(-\frac{2e^2}{a_0} \right) = -0.0686 \frac{e^2}{a_0} = -1.87 \text{ eV} \end{aligned}$$

Note the single e is the mathematical constant; e^2 is the square of the electron charge.

For the p-state the angular average gives $\langle x^2 \rangle = r^2/3$, so

$$\begin{aligned} \langle \psi_{2p} | V_{\text{core}} | \psi_{2p} \rangle &= \frac{4\pi}{32\pi a_0^3} \frac{1}{3a_0^2} \left(-\frac{2e^2}{a_0} \right) \int_0^{a_0} r^4 e^{-r/a_0} dr \\ &= \frac{1}{24} \left(24 - \frac{65}{e} \right) \left(-\frac{2e^2}{a_0} \right) = -0.00732 \frac{e^2}{a_0} = -0.20 \text{ eV} \end{aligned}$$

The p-state is only slightly lowered. For total energies we get $\epsilon_s = -3.40 - 1.87 = -5.27 \text{ eV}$ compared to -5.48 from the Solid State Table and $\epsilon_p = -3.60 \text{ eV}$, probably too deep as guessed by extrapolating B, Be, Li.

The integrations above are somewhat of a pain and maybe not really worth it.

Problem 1-3. Diatomic molecules

In the problem statement were given the equations

$$\begin{aligned} (\epsilon_s - E)u_1 + V_{ss\sigma}u_2 + 0 + V_{sp\sigma}u_4 &= 0 \\ V_{ss}u_1 + (\epsilon_s - E)u_2 - V_{sp\sigma}u_3 + 0 &= 0 \\ 0 - V_{sp\sigma}u_2 + (\epsilon_p - E)u_3 - V_{pp\sigma}u_4 &= 0 \\ V_{sp\sigma}u_1 + 0 - V_{pp\sigma}u_3 + (\epsilon_p - E)u_4 &= 0 \end{aligned}$$

The low energy solution has $u_2 = u_1$ and $u_4 = u_3$. The first two equations both become

$$(\epsilon_s - E + V_{ss\sigma})u_1 - V_{sp\sigma}u_3 = 0$$

A

The last two become

$$-V_{sp\sigma}u_1 + (\epsilon_p - E + V_{pp\sigma})u_3 = 0$$

B

The solution is equivalent to that of Eq. 1-34 and is

$$E = \frac{\epsilon_s + \epsilon_p + V_{ss\sigma} + V_{pp\sigma}}{2} \pm \sqrt{\left(\frac{\epsilon_s + V_{ss\sigma} - \epsilon_p - V_{pp\sigma}}{2} \right)^2 + V_{sp\sigma}^2}$$

For the C_2 molecule we have from Table 1-1 that $d = 1.24 \text{ \AA}$ (smaller than that for diamond), so using Table 2-1

$$V_{ss\sigma} = -1.40 \times 7.62 \text{ eV}/(1.24)^2 = -6.94 \text{ eV}$$

Similarly $V_{pp\sigma} = 16.06 \text{ eV}$ and $V_{sp\sigma} = 9.12 \text{ eV}$. From Table 2-2 for carbon $\epsilon_s = -17.52 \text{ eV}$, $\epsilon_p = -8.97 \text{ eV}$ and our energies become $E = -24.72 \pm 9.12 = -33.9 \text{ eV}$, -15.6 eV . The values in Table 1-1 are -33.9 eV and -14.5 eV corresponding perhaps to rounding off in a different order.

The odd solutions, $u_2 = -u_1$ and $u_4 = u_3$ are obtained from

$$(\epsilon_s - V_{ss\sigma} - E)u_1 + V_{sp\sigma}u_3 = 0$$

$$+ V_{sp\sigma}u_1 + (\epsilon_p - V_{pp\sigma} - E)u_3 = 0$$

and are

$$E = \frac{\epsilon_s + \epsilon_p - V_{ss\sigma} - V_{pp\sigma}}{2} \pm \sqrt{\left(\frac{\epsilon_s - \epsilon_p - V_{ss\sigma} + V_{pp\sigma}}{2} \right)^2 + V_{sp\sigma}^2}$$

$$= -1.75 \pm 12.70 \text{ eV}$$

$= -14.5 \text{ eV}$, $+11.0 \text{ eV}$, about equal to the -15.6 eV and $+11.0 \text{ eV}$ of Table 1-1.

To obtain the s-character we need u_1 and u_3 . We return to Eq. A

$$u_3 = (\epsilon_s + V_{ss\sigma} - E)u_1/V_{sp\sigma} = \frac{(-17.52 - 6.94 + 33.9)u_1}{9.12}$$

$$= 1.04 u_1$$

$$\frac{u_1^2 + u_2^2}{u_1^2 + u_2^2 + u_3^2 + u_4^2} = \frac{u_1^2}{u_1^2 + u_3^2} = \frac{1}{1 + (1.04)^2} = 0.48$$

s-state, 52% p-state. It is near 50-50, as an sp-hybrid. One have expected more s-character but $\frac{\epsilon_p + V_{pp\sigma}}{V_{ss\sigma}} < \frac{\epsilon_s + V_{ss\sigma}}{V_{pp\sigma}}$.

The LCAO approach gives a nice generalization of the splitting of atomic levels in the molecule to the production of bands of states in the solid, with total number of levels conserved. CsCl, viewed as a simple cubic structure, and the s-bands in particular, give the simplest illustration and are worth carrying through in lecture. The p-band results can be directly added and are plausible if one understood the s-band calculation. The relationship of these LCAO bands to the free-electron bands shown in Fig. 2-2 has turned out in the end to be one of the most important results in the chapter. It leads in Section 2-D to theoretical formulae for the LCAO matrix elements used throughout the book. Though only added at the final stage of publication, they did not need to change the calculations coming later in the book; we continued to use the adjusted parameters ' $\eta\omega_m$ '. A good problem to illustrate this relationship is a derivation of $\eta\omega_m$ by equating the s-band width for a [110] direction in a simple cubic structure to the lowest free-electron band for the corresponding structure; it gives $-\pi^2/8$. Just as does the corresponding fit for a [100] direction, carried out in the text.

The Solid State Table introduced in this chapter provides an organization of the subject of the text and deserves emphasis, as does the concept of level crossing which is central to covalent solids. I like the discussion of electron dynamics, but only the results are needed.

Problem 2-1. One-dimensional bands

If a student has had this in another course it goes very fast and helps familiarize him with the notation used here; the effort isn't wasted even for him.

We take the derivative, noting that in the V_2 term each u_α^* appears once with a $u_{\alpha+1}$ and once with a $u_{\alpha-1}$. Of course u_{N+1} is to be read as u_1 and u_{-1} is to be read as u_N , by periodic boundary conditions. We obtain,

$$\frac{\partial E}{\partial u_\alpha} = \frac{\epsilon u_\alpha - V_2(u_{\alpha+1} + u_{\alpha-1})}{<\psi|\psi>} - \frac{<\psi|H|\psi>}{<\psi|\psi>} u_\alpha = 0$$

where we have used, for example, $<\psi|\psi>$ and $\sum_\alpha u_\alpha^* u_\alpha$ as interchangeable.

We cancel out one factor of $<\psi|\psi>$ and write $<\psi|H|\psi>/<\psi|\psi>$ as E to obtain

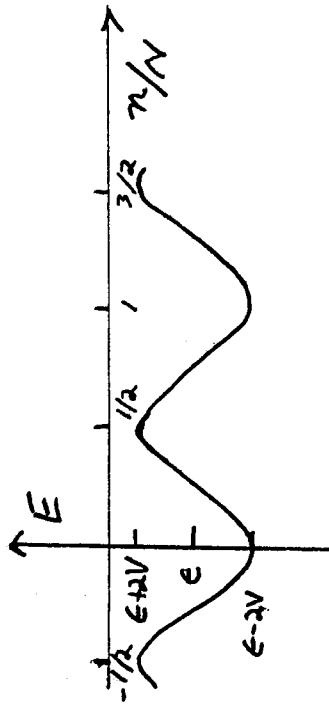
$$\epsilon u_\alpha - V_2(u_{\alpha+1} + u_{\alpha-1}) = Eu_\alpha \quad A$$

a) Then $u_{\alpha+1} = ue^{2\pi i n/N}$ and $u_{\alpha-1} = ue^{-2\pi i n/N}$. We substitute these in A and cancel a factor of u to obtain

$$E = \epsilon - 2V_2 \cos 2\pi n/N$$

This is independent of α so satisfying it satisfies the equation A for all α .

b) E is given in Eq. B above. A sketch of the result is



c) The normalization integral is

$$\sum_{\alpha} u_{\alpha}^* u_{\alpha} = A^* A \sum_n e^{-2\pi i n / N} e^{2\pi i n / N} = A^* A N = 1$$

The phase of A is arbitrary and its magnitude is $N^{-1/2}$.

d) For given n , $u_{\alpha}(n) = A e^{2\pi i n / N}$. But $u_{\alpha}(n+N) = A e^{2\pi i \alpha(n+N) / N}$

$$= u_{\alpha}(n) e^{2\pi i \alpha} = u_{\alpha}(n).$$

Problem 2-2. Electron dynamics

From Eq. 2-11, in one dimension we have

$$k = -|e\mathcal{E}|/\hbar$$

Integrating from $k = 0$ at $t = 0$ we obtain

$$k = -e\mathcal{E}t/\hbar$$

Letting k go outside the Brillouin Zone does not change the physical properties (it doesn't change E or $\partial E / \partial k$). So

$$E(t) = -V_2 \cos e\mathcal{E}at/\hbar$$

$$v = \frac{1}{\hbar} \frac{\partial E}{\partial k} t = + \frac{V_2 a}{\hbar} \sin ka = - \frac{V_2 a}{\hbar} \sin(e\mathcal{E}at/\hbar)$$

$$x = \int_0^t v dt = \frac{V_2 [\cos(e\mathcal{E}at/\hbar) - 1]}{e\mathcal{E}}$$

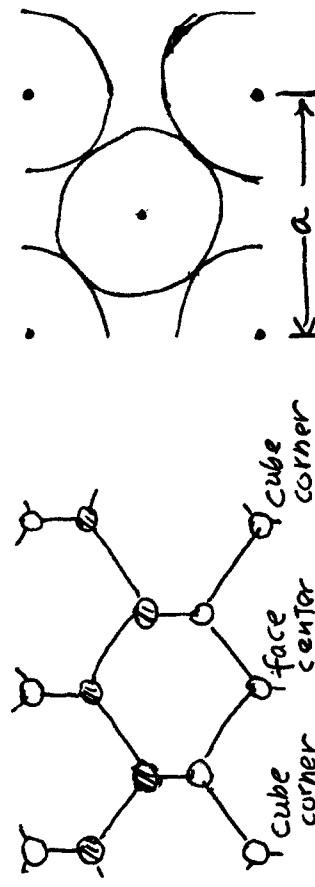
The maximum is $2V_2/e\mathcal{E} = 2 \times 2 \text{ eV}/100 \text{ volts/cm} = 0.04 \text{ cm}$ or 2×10^{-6} lattice distances.

If you choose to vary the order of discussion slightly it works well to discuss the structure and the band calculation as indicated in Fig. 3-7. I do this incompletely but give the results and then describe the process as a unitary transformation on the Hamiltonian matrix. I then indicate that this can also be done as a series of unitary transformations, an approach which will prove useful when we wish to go beyond bands and beyond perfect crystals. The transformation from atomic orbitals to hybrids to bond orbitals is such a series. I represent it in parallel as a change of basis orbitals and as a transformation on the Hamiltonian matrix and as a set of energy-level diagrams (which correspond to the diagonal elements of the Hamiltonian matrix). This is very important and should be reinforced using Problem 3-2. (That requires introducing the graphite structure, Section F, in class.)

It is also important to emphasize how unitarity, combined with the Bond Orbital Approximation, allows us to sum energy and other one-electron properties bond-by-bond. I indicate that this is always qualitatively correct but not always accurate. Perturbation theory in the bonding-antibonding matrix elements can be used to improve the calculation, but it is not necessary at this point to go through the Extended Bond Orbitals. By the end of this a student should have a feeling for the hybrid covalent energy, the hybrid polar energy, and the metallic energy; the details of metallicity are not so important.

Problem 3-1. Tetrahedral crystal structures

This is designed to force a student to sort out the tetrahedral structure and may not be necessary. The (110) projection of the diamond structure is as below.



The packing fraction is best computed in terms of the cube edge a . On the right above is shown a (100) projection of the face-centered cubic structure, but with the atoms expanded to contact the nearest

metals. The spheres touch so the $r = \frac{4}{3}a$, where there are four spheres per cube of edge a so the packing fraction is

$$f = 4 \times \frac{4\pi}{3} \left(\frac{\frac{4}{3}a}{2}\right)^3 / a^3 = 0.74$$

In diamond the radius of contracting spheres is reduced to $\frac{1}{2}a/8$ but there are twice as many so the packing fraction is

$$f = 2 \times 4 \times \frac{4\pi}{3} \left(\frac{\frac{1}{2}a}{8}\right)^3 / a^3 = 0.34$$

There is room between the spheres to fit an equal number more, forming a body-centered cubic lattice with twice the packing fraction, 0.68, near that of face-centered cubic and hexagonal close-packed.

Problem 3-2. Hybrid and bond orbitals in graphite

$$(a) |h_1\rangle = \frac{1}{\sqrt{3}} (|s\rangle + 2^{\frac{1}{2}} |p_x\rangle)$$

$$|h_2\rangle = \frac{1}{\sqrt{3}} \left(|s\rangle - \frac{1}{2} |p_x\rangle + \frac{1}{2} |p_y\rangle \right)$$

$$|h_3\rangle = \frac{1}{\sqrt{3}} \left(|s\rangle - \frac{1}{2} |p_x\rangle - \frac{1}{2} |p_y\rangle \right)$$

$$(b) \epsilon_k = \langle h_1 | H | h_1 \rangle = \frac{1}{3} (\langle s | + 2^{\frac{1}{2}} \langle p_x |)$$

$$\begin{aligned} & \times (\epsilon_s |s\rangle + 2^{\frac{1}{2}} \epsilon_p |p_x\rangle) \\ & = (\epsilon_s + 2\epsilon_p)/3 \end{aligned}$$

$$V_1 = -\langle h_2 | H | h_1 \rangle$$

$$= -\frac{1}{3} \left(\langle s | - \frac{1}{2} \langle p_x | + \frac{1}{2} \langle p_y | \right)$$

$$\times (\epsilon_s |s\rangle + 2^{\frac{1}{2}} \epsilon_p |p_x\rangle)$$

$$= (\epsilon_p - \epsilon_s)/3$$

Note we have taken the $|s\rangle$ and $|p_x\rangle$ and $|p_y\rangle$ states to be eigenstates of H

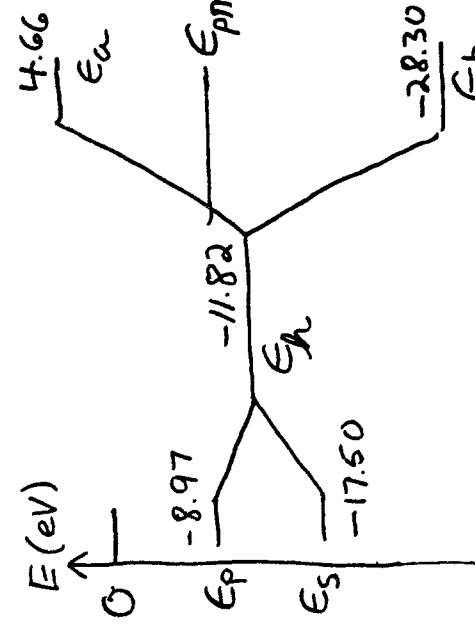
$$\left. \begin{aligned} \epsilon_k &= (-17.52 - 2 \times 8.97)/3 = -11.82 \text{ eV} \\ V_1 &= (-8.97 + 17.52)/3 = +2.85 \text{ eV} \end{aligned} \right\} \text{graphite}$$

(c) Writing hybrids in the same bond as $|h_1\rangle$, $|h_1'\rangle$, we have

$$V_2 = -\langle h_1' | H | h_1 \rangle = -\frac{1}{3} (\langle s' | + 2^{\frac{1}{2}} \langle p_x' |) H (|s\rangle + 2^{\frac{1}{2}} |p_x\rangle)$$

with the primed and unprimed orbitals on nearest neighbor atoms. We are choosing signs so V_2 is positive.

$$\begin{aligned} V_2^h &= -\frac{1}{3} (V_{ss} + 2(2^{\frac{1}{2}}) V_{sp} + 2V_{pp\sigma}) \\ &= \frac{\hbar^2}{md^2} (0.47 + 1.73 + 2.16) = \frac{\hbar^2}{md^2} 4.36 = 16.48 \text{ eV} \end{aligned}$$



Problem 3-3. Band energies in graphite

The results here are used in Problems 4-1 and 5-2. Graphite w $d = 1.42 \text{ \AA}$ gives

$$\begin{aligned} V_{ss\sigma} &= -5.29 \text{ eV} \\ V_{pp\sigma} &= +12.24 \text{ eV} \\ V_{pp\pi} &= -3.06 \text{ eV} \\ \epsilon_p &= -8.97 \text{ eV} \\ \epsilon_s &= -17.52 \text{ eV} \end{aligned}$$

for carbon. The matrix element between the central orbital shown a

Band Type	Painter-Ellis	Here
s antibond	+ 1.0	- 1.5
π antibond	- 1.0	+ 0.2
p σ antibond	- 3.0	+ 4.8
p σ bond	-13.0	-23.0
π bond	-17.0	-18.0
s bond	-27.0	-33.4

Not bad, except for the overestimate of $V_{pp\sigma}$ mentioned in the problem. You might want to use a smaller $V_{pp\sigma}$ for graphite in later problems but I did not do that here. Most answers would come out better.

Problem 3-4. Hybrid polarity in hexagonal BN

An sp^2 hybrid is of the form

$$|h\rangle = 3^{-1/2} (|s\rangle + 2^{1/2} |p\rangle)$$

The corresponding hybrid covalent energy is

$$\begin{aligned} V_2^h &= \langle h' | H | h \rangle = \frac{1}{3} (V_{ss\sigma} - 2V_{sp\sigma} - 2V_{pp\sigma}) \\ &= 4.36 \frac{\hbar^2}{md} = 16.48 \text{ eV} \end{aligned}$$

to the upper right requires decomposing the p-state into $p\sigma$ - and states. It is

$$V_x = \left(\frac{3}{2}\right)^2 V_{pp\sigma} + \left(\frac{1}{2}\right)^2 V_{pp\pi}$$

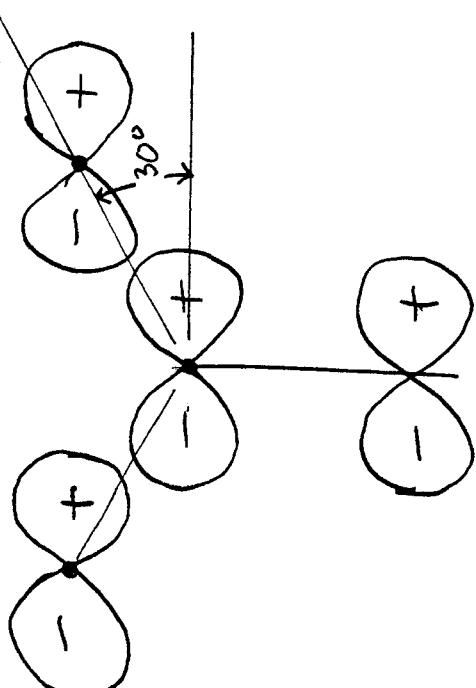
h orbitals are of p_x -type but are not translationally equivalent. need to construct two Bloch sums, Eq. 3-19, which for $k=0$ take form

$$\chi_a = N^{-1/2} \sum_i |\psi_{x,i}\rangle$$

summed over atoms of one type each. The matrix element between the Bloch sums is obtained by focusing, for example, on one atom in the giving the right-hand wavefunction in the matrix element; let it be atom in the center in the figure above. There are contributions from three neighbors (one gives $V_{pp\pi}$) and there are N_p terms in the sum. The matrix element becomes

$$\langle \alpha | H | \beta \rangle = 2V_x + V_{pp\pi} = \frac{3}{2} V_{pp\sigma} + \frac{3}{2} V_{pp\pi} = 13.77 \text{ eV}$$

corresponding two bands at Γ have energies $\epsilon \pm 13.77 \text{ eV} = 4.80 \text{ eV}$, -22.74 eV . The p_z -bands have the same energies at Γ . The bands have energies $\epsilon_s \pm 3V_{ss\sigma} = -1.52 \text{ eV}$, -33.39 eV . The resulting band energies, with the corresponding energies from Painter and Ellis are



neighbors shown below.

It has been natural to give considerable attention to the dielectric constant here because it was so central to the development of understanding and misunderstanding of covalent solids. Some controversy remains and the term "oscillator strength" is still used interchangeably for matrix elements of x , for matrix elements of $\partial/\partial x$, and the dimensionless oscillator strength through the three show very different trends. Thus it has seemed to me necessary to retain a fairly complete discussion in the text. On the other hand, most students will prefer to understand the central points and essential trends and class discussion can be confined to that. This chapter begins the treatment of properties. The previous ones focused on electronic structure.

I like to write down Eq. 4-3 for $\chi_2(\omega)$, which can be made plausible to a knowledgeable student and accepted by others. It is also not difficult to see in terms of perturbation theory why $\chi_1(0)$ should be related to it and equations such as 4-5 and 4-7 obtained. We are ultimately most interested in $\chi_1(0)$ but the more complete description of the response, $\chi_2(\omega)$, enables us to learn what contributions are most important.

Figure 4-1 indicates that there are no mysteries and Figs. 4-3 and 4-4 enable us to identify features and see that the energy difference which is probably going to dominate the χ_1 arises from the pp-matrix elements, not the hybrid matrix element V_{12} ; i.e., if we are to make a two-level approximation to the valence and conduction bands the splitting should be determined by a different V_2 . It would have been nice if a single covalent energy had sufficed for all properties, but we were not that lucky; a different is needed for dielectric than for bonding properties.

The derivation of the form 4-26 for the dielectric constant is carried out with matrix elements in order to identify what we learn about the dielectric properties in this chapter with the bond-dipole derivation in the next.

At this stage it may become convenient to combine problems. As an example we may give a composite problem, the solution to which can be obtained from the solutions of each of the problems making it up:

Example: A composite of Problems 3-3, 4-3, and 5-1

Find the splitting of the p-states at Γ for graphite, which may be equated to $2V_2$ for graphite in analogy with the tetrahedral structure. Also in analogy with that structure, the V_2 will be given by the sum of the matrix elements between the central p-state and its

neighbors shown below.

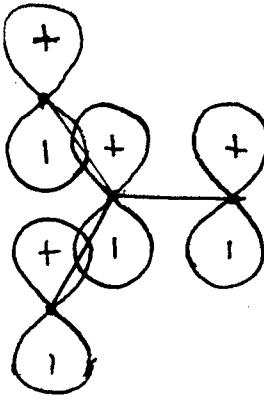
You may note from the derivation of Eq. 5-6 that it is applicable also for graphite. Use it to derive the σ -contribution to $\chi_1(0)$ for graphite for fields in the plane of the graphite. The angular average is different from that in the tetrahedral structure. To calculate the total electron density you need the spacing between layers, 3.4 \AA ; three quarters of the electrons are σ -electrons. Take γ to be the same as for diamond and obtain a value for the contribution to the susceptibility.

Problem 4-1. Features in the optical spectra

Rewriting Eq. 3-39

$$E_0 = -\frac{1}{2} \left[\epsilon_p^c - \epsilon_s^c + \epsilon_p^a - \epsilon_s^a \right] + \left[\left(\frac{\epsilon_s^c - \epsilon_s^a}{2} \right)^2 + \left(\frac{42.67}{d} \right)^2 \right]^{1/2} \\ + \left[\left(\frac{\epsilon_p^c - \epsilon_p^a}{2} \right)^2 + \left(\frac{16.46}{d} \right)^2 \right]^{1/2}.$$

We get 1.91 eV , 2.89 eV , 5.49 eV for Ge, GaAs, ZnSe [using 2.45 \AA for GaAs, ZnSe. 2.44 \AA is O.K. but gives 2.96 eV and 5.55 eV instead of 2.89 eV and 5.49 eV]. These particular cases give a factor of two discrepancy with experiment but predicted (observed) for Si is 3.68 (4.18) for SiC $9.26(7.75)$, for InSb $1.84(0.50)$, etc. Rewriting Eq. 4-15,



This result is used in Problem 5-2. The matrix element giving the splitting of the p-like states at Γ was found in Problem 3-3 to be

$$E_2 = 2 \left[\left(\frac{\epsilon_p - \epsilon_a}{2} \right)^2 + \left(\frac{16.46}{d^2} \right)^2 \right]^{1/2}$$

We get 5.53 eV, 6.26 eV, 8.24 eV for Ge, GaAs, ZnSe (6.30 and 8.27 if we use 2.44 \AA for GaAs and ZnSe).

Problem 4-2: Polarity in BN

This result is used in Problem 5-2. The matrix element giving the splitting of the p-like states at Γ was found in Problem 3-3 to be

$$\begin{aligned} V_2 &= -\frac{3}{2} V_{pp\sigma} + \frac{3}{2} V_{pp\pi} = 13.77 \text{ eV} \\ V_3 &= (\epsilon_p^c - \epsilon_p^a)/2 = (-6.64 + 11.47)/2 = 2.42 \text{ eV} \end{aligned}$$

$$\alpha_p = V_3 / (V_2^2 + V_3^2)^{1/2} = 0.17 ,$$

compared to the hybrid polarity of the 0.20 (see Problem 3-4).

Problem 4-3. The dielectric susceptibility

For a bond making an angle θ with the field (in the x-direction) the matrix element is again

$$\langle a|x|b\rangle = \gamma(d/2)(1-\alpha_p^2)^{1/2} \cos \theta$$

The cosine was $3^{-1/2}$ in the tetrahedral structure. We could treat the three bond orientations separately here or can make use of Eq. 4-23 with the squared matrix element averaged over field directions in the plane of the graphite; the $\cos^2 \theta$ averages to one half. The susceptibility becomes

$$\chi_1(0) = \frac{\frac{N}{2} \epsilon^2 d^2 \gamma^2 (1-\alpha_p^2)^2}{8(V_2^2 + V_3^2)^{1/2}}$$

For graphite, the σ -electron density N is 3 times the atom density, $N_\sigma = 4/(\sqrt{3} d c)$ with $c = 3.4 \text{ \AA}$. We should use the covalent energy based upon p-states, seen in Problem 3-3 to be

$$-\frac{3}{2} V_{pp\sigma} + \frac{3}{2} V_{pp\pi} = 13.77 \text{ eV} .$$

Then for graphite

$$\chi_1(0) = \frac{4 \epsilon^2 d^2 (1.13)^2}{8 \times 3^{1/2} d^2 \cdot 3.4 \text{ \AA} \cdot 13.77 \text{ eV}}$$

$$e^2 = 27.2 \text{ eV Bohr radii} = 14.4 \text{ eV \AA} ; \quad \chi_1(0) = 0.11 .$$

This result is used in Problem 5-2. The calculation can readily be extended to BN if desired. $\chi_1(0)$ is reduced by a factor of

$$V_2^3 / (V_2^2 + V_3^2)^{3/2} = (13.77)^3 / \left[13.77^2 + \left(\frac{11.47 - 6.64}{2} \right)^2 \right]^{3/2} = 0.96 .$$

CHAPTER 5. OTHER DIELECTRIC PROPERTIES

Problem 5-2. Effective atomic charge

It is best to add up the electrons on, say, nitrogen and subtract the nuclear charge rather than guess a generalization of Eq. 5-18. The polarity of the σ -electron bonds was obtained as $\alpha_p = 0.17$ in Problem 4-2. The squared coefficient of the bond orbital on the nitrogen, times two for spin, puts $1+\alpha_p$ electrons on the nitrogen from each of the three bonds surrounding it, a total of 3.51 electrons.

We also need an α_p^π for the π -electrons. The corresponding V_3 is 2.42 eV, as for the σ -states. The coupling is $3V_{pp\pi} = -3 \times (3.06 \text{ eV})$ (Problem 3-3). Thus

$$\alpha_p^\pi = 2.42 / \left(2.42^2 + 9.18^2 \right)^{1/2} = 0.25$$

putting $1+\alpha_p^\pi = 1.25$ electrons on each nitrogen (and 0.75 on each boron for a total of one per atom). Subtracting the valence nuclear charge of 5, we obtain

$$Z^* = 3.51 + 1.25 - 5 = -0.24$$

times the electron charge. Thus it is positive, a surprise, but use of a smaller V_2 as suggested in Problem 3-3 would presumably increase α_p sufficiently to make the nitrogen negative. Again this kind of difficulty is peculiar to the carbon-row elements.

The study of higher order susceptibilities brings us for the first time to the forefront of current research, but unfortunately also indicates how the approximations can become inaccurate as we push them further and harder. The central concept of "screening" is important though the details are less so. The main point of the treatment of anomalies is to indicate the wide applicability of the methods without necessity of further assumptions.

The calculation of the diamagnetic susceptibility is a pretty application but is out of the mainstream of the other treatments and can be omitted without affecting later discussions. It may be noted that the diamagnetic susceptibility inevitably appears with an m_c^2 , of order 0.5×10^6 eV, in the denominator. The corresponding energy in the numerator is of order of an eV leading to very tiny values in comparison to the dielectric susceptibility; thus the diamagnetic susceptibility is inessential to the optical properties.

Problem 5-1. Local theory of susceptibility

Since Eq. 5-6 still applies, so does the linear term, Eq. 5-7.

(We refer to Eq. 5-6 since we could also do nonlinear susceptibilities for graphite or hexagonal BN, another possible homework problem.)

Early the susceptibility will be the same for all field directions in the plane of the structure so we may average over bond orientations. For fields in the x -direction, p_x is proportional to $(\vec{d} \cdot \vec{e})^2/e^2$, which averages to $\frac{1}{2}d^2e^2$. We obtain the contribution

$$p_x = \frac{e^2 \gamma (1 - \alpha_p^2) d^2 e^2}{4(V_2^2 + V_3^2)^{1/2}}$$

per bond. To get the contribution to the susceptibility we must multiply by the bond density, or by half the σ -electron density N_σ leading

$$\chi_1(0) = \frac{N_\sigma e^2 d^2 \gamma^2 (1 - \alpha_p^2)}{8(V_2^2 + V_3^2)^{1/2}}$$

; in Problem 4-3.

The problem only asks for the graphite result, obtained by setting and V_3 equal to zero.

CHAPTER 6. THE ENERGY BANDS

Problem 6-1. Calculation of the π -bands in graphite

I have intentionally postponed the discussion of the details of energy bands to emphasize the fact that they are not necessary to understand most properties of the system. They represent fundamental electronic structure of the material but they must be suppressed, as in the Bond Orbital Approximation, if we are to calculate other properties. At the same time, it was the accurate band structures which provided us with the approximate parameters given in Solid State Table, and whenever we address a genuinely new material it is appropriate as a first step to inspect the bands if they are in the book to put them. This has seemed a good place in the book to do this.

I like to focus on Fig. 6-1 and discuss trends: the general occurrence of direct gaps except for Si and Ge and a few compounds, the increase in band gap with increasing metallicity, the opening up of band gap with increasing polarity (approaching anion s- and p-bands at high h increasing polarity (approaching anion s- and p-bands at high polarity). Having discussed the bands earlier in the Bond Orbital model (left panel in Fig. 6-3), and conduction bands of the same shape higher energy), it is easy to see how V_X broadens the valence bands and collapses the conduction band (middle panel in Fig. 6-3) and the V_4 matrix element gives curvature to the upper p-bands. The latter effect essentially comes from $V_{pp\pi}$ and reflects a bonding-antibonding splitting of π -type (bonding at X and anti-bonding at Γ). However, in the diamond structure the entire band is occupied so it does not affect the total energy.

In connection with the fitting of the bands it is nice to note the empirical finding of the d^{-2} dependence shown in Fig. 6-5. It is also nice to note the dependence of effective masses upon the same oscillator strengths as entered the susceptibility; this indicates additional coherence in the subject though I tend not to discuss this detail. Similarly, the basic idea of the Wannier exciton can be given briefly and not discussed in detail.

For this chapter, as for others, it is rather easy to generate additional problems or problems for exams. I like to give exam problems similar to those for the homework so that a student who understands the homework can do well on the exam. One for this chapter which I found appealing was the carrying out of a band calculation for the energies at Γ for germanium in the graphite structure. I scaled the Ge bond lengths down by 8%, as in going from diamond to graphite. Students could then guess how the bands went along the line ΓP by looking at Figure 3-13 in Problem 3-3, though it isn't obvious how the conduction bands go in detail since the degenerate, nondegenerate levels are interchanged at Γ . (It turns out that in graphite the parameters we use would lead to noncrossing σ bands; Sverre Froyen, a student in my course, carried out the calculation.) It is interesting, and can be seen without knowing the details, that the bands found give a conduction band minimum well below the middle of the π -bands, suggesting that there would be lots of electrons in the antibonding bands and one should not expect germanium to be stable in this structure.

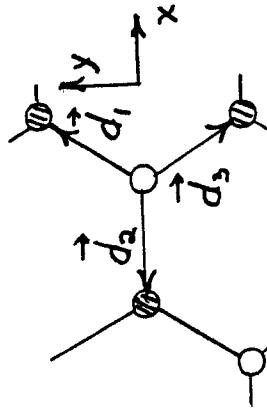
This problem contains all the features of a full LCAO band calculation without the attendant complexity. The two types of atoms correspond to the empty and full circles in Fig. 3-10. We construct the two Bloch sums of π -states as indicated and compute the matrix element between them,

$$H_{12} = \langle \chi_1(\vec{k}) | H | \chi_2(\vec{k}) \rangle$$

For each orbital on the right we include matrix elements $V_{pp\pi} = -3.06$ eV with each of the three neighbors appearing in the wavefunction on the left; these enter with a phase factor differing from the right-hand orbital by $\exp(i\vec{k} \cdot \vec{d}_i)$. Finally the sum over the N_p terms on the right cancels the N_p in the denominator to give

$$H_{12}(\vec{k}) = V_{pp\pi} \left(e^{\rightarrow \vec{k} \cdot \vec{d}_1} + e^{\rightarrow \vec{k} \cdot \vec{d}_2} + e^{\rightarrow \vec{k} \cdot \vec{d}_3} \right)$$

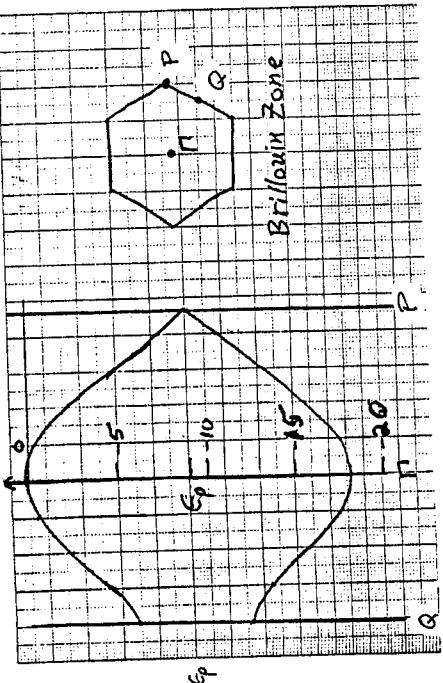
with vectors indicated below.



The bands are obtained from solution of the two-by-two Hamiltonian matrix based upon these two Bloch sums and are

$$E_k = \epsilon_p \pm |H_{12}| = \epsilon_p \pm V_{pp\pi} \left| e^{\rightarrow \vec{k} \cdot \vec{d}_1} + e^{\rightarrow \vec{k} \cdot \vec{d}_2} + e^{\rightarrow \vec{k} \cdot \vec{d}_3} \right|$$

A coordinate system as illustrated above allows the full evaluation. The resulting bands to the zone edge Q and to the zone corner Γ are given below. Note that replacing the \vec{d}_2 by $-\vec{d}_2$ (as with a different crystal orientation) would not change the results.



Problem 6-2. π -bands in BN

Taking the same bond length, we get the same $V_{pp\pi}$; at the Zone center ($\vec{k} = 0$) this gives $H_{12} = 3V_{pp\pi} = -9.18$ eV. With $\epsilon_p(B) = -64$ eV and $\epsilon_p(N) = -11.4$ eV, we obtain $\epsilon = -9.06$ eV and $\epsilon_p(B) - \epsilon_p(N) = 2.42$ eV. At Γ we obtain $-9.06 \pm (2.42)^{1/2} + 9.18^{1/2} + 0.43$ and -18.55 eV. At the zone corner $H_{12} = 0$ and we obtain -06 ± 2.42 or -6.64 and -11.48 eV. The effort involved in the problem is trivial but it requires understanding what has been done in the tetrahedral calculation.

Problem 6-3. σ -bands in the Bond Orbital Approximation

Each bond orbital is $2^{-1/2}$ times a sum of the two hybrids. The matrix element between adjacent bonds has a contribution then of $2^{-1/2}(-V_1)$ from the two hybrids which share the intervening atom. In Problem 3-2 we had $V_1 = 2.85$ eV (or this could be re-evaluated if that problem wasn't done). We may evaluate H_{12} by focusing on a bond of type 2 in the problem figure and note that there are contributions from the bond of type 1 from the right and the left with phase factors $\exp(i\vec{k}d/4)$ and $\exp(-i\vec{k}d/4)$, respectively. Distances \vec{k} measured from the bond centers and components taken along \vec{k} .

$$H_{12} = -\frac{1}{2}V_1 2 \cos(3kd/4) = -V_1 \cos(3kd/4)$$

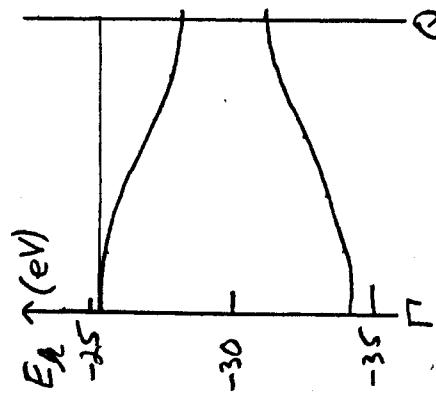
Further $H_{13} = H_{31} = H_{21} = H_{12}$. However, adjacent bonds of types 1 and 3 are in a plane of constant phase (a plane perpendicular to \vec{k}) and the phase factors are unity. The Hamiltonian matrix becomes

$$\begin{pmatrix} \epsilon_b & -V_1 \cos(3kd/4) & -V_1 \\ -V_1 \cos(3kd/4) & \epsilon_b & -V_1 \cos(3kd/4) \\ -V_1 \cos(3kd/4) & -V_1 \cos(3kd/4) & \epsilon_b \end{pmatrix}$$

To get the energy of the solution $(|x_1\rangle, |x_2\rangle)/2^{1/2}$ we can multiply the vector $(u, 0, -u)$ or $(2^{-1/2}, 0, -2^{-1/2})$ by the Hamiltonian matrix, obtaining the same vector multiplied by V_1 ; thus V_1 is the eigenvalue. The corresponding multiplication of the other solution given in the problem by the Hamiltonian matrix gives two equations to be solved for the eigenvalue, and finally,

$$E_k = \epsilon_b - \frac{V_1}{2} \pm \sqrt{\frac{V_1^2}{4} + 2V_1^2 \cos^2 \left(\frac{3kd}{4}\right)}$$

at $\vec{k} = 0$ this gives $\epsilon_b + V_1$ and $\epsilon_b - 2V_1$ (too deep by some 8 eV because $(-17.52 - 2 \times 8.97)/3 = -16.48 = -28.30$ eV of the large V_2 .) A plot is given below.



Problem 6-4. Effective masses

The upper band is completely flat (in the Bond Orbital Model) corresponding to an infinite mass. The other two are obtained by expansion for small k

$$\begin{aligned} E_k &\approx \epsilon_b - \frac{V_1}{2} \pm \left(\frac{9V_1^2}{4} - 2V_1^2 \left(\frac{3kd}{4} \right)^2 \right)^{1/2} \\ &\approx \epsilon_b - \frac{V_1}{2} \pm \frac{3V_1}{2} \mp \frac{3V_1}{2} k^2 d^2 \end{aligned}$$

$$\text{so } \frac{k^2 d^2}{2m^*} = \mp \frac{3V_1}{8} k^2 d^2 \quad \text{or} \quad \frac{m^*}{m} = \mp \frac{4}{3} \frac{d^2}{V_1^2} = \mp \frac{4}{3} \frac{7.62 \text{ eV} \cdot \text{\AA}^2}{(1.42 \text{ \AA})^2 \cdot 2.85 \text{ eV}} = \mp 1.77$$

, negative for the upper band, positive for the lower.

CHAPTER 7. THE TOTAL ENERGY

difference $0.02 \frac{\hbar^2}{md^2}$ to the radial interaction energy. We can also add the suggested π -bonding energy $V_{\text{pp}\pi} = -0.81 \frac{\hbar^2}{md^2}$ for a total of $-0.79 \frac{\hbar^2}{md^2} = -2.54 \text{ eV } \frac{d_0^2}{d^2}$. We add the radial energy and set the derivative with respect to d equal to zero,

$$\frac{70.4(d-d_0)}{d^2} + \frac{5.08}{d} \frac{d^2}{d_0} = 0$$

In this chapter we see that the cohesive energy can be divided into a promotion energy (a negative contribution to the cohesion which is not of principal interest), a radial interaction which we call the overlap interaction, and the bond-formation energy which follows naturally from the discussion of the preceding few chapters. The overlap interaction is the repulsive term which prevents collapse of the system; it arises ultimately from the increase in kinetic energy of the electrons from overlapping the atomic electron distributions. In contrast to most aspects we treat, this one requires major computational effort even in the Nikulin-Gordon-Kim model. The extension of that model to covalent solids given here does not provide a numerically useful overlap interaction but does confirm the origin of the interaction and describes semiquantitatively the decrease of cohesive energy per bond with increasing polarity and with increasing metallicity. The weak link is the overlap interaction which we will take from experiment – just as convenient as taking it from a machine calculation if that calculation had been successful. Figure 7-2 summarizes the experimental cohesive energies but should not allow us to confuse the attempt made in this text at calculating properties in terms of the electronic structure with the widespread efforts simply to empirically interpolate properties as done in that figure. The bulk moduli are of order a few eV/(volume per electron) and scale as -5.

Problem 7-1. Cohesion in graphite

In promotion three electrons are given the hybrid energy $2\varepsilon_p/3 + \varepsilon_s/3$. In the atom their total energy was $2\varepsilon_s + \varepsilon_p^2/3$. The difference is the promotion energy per atom; we multiply by $2/3$ to obtain the promotion energy per bond,

$$E_{\text{pro}} = 2(\varepsilon_p - \varepsilon_s)/3 = 5.7 \text{ eV for graphite}$$

The bond formation energy, for two electrons per bond, is

$$\begin{aligned} E_{\text{bond}} &= 2V_2^h = -\frac{2}{3}(|s| + 2^{\frac{1}{2}}|p|) \text{ H } (|s'\rangle + 2^{\frac{1}{2}}|p'\rangle) \\ &= -\frac{2}{3}(V_{ss\sigma} - 2\sqrt{2}V_{sp\sigma} - 2V_{pp\sigma}) = 8.72 \frac{\hbar^2}{md^2} = 32.95 \text{ eV for graphite.} \end{aligned}$$

Two factors of $3^{\frac{1}{2}}$ appeared in the denominator from normalization of the hybrids. The signs are best determined from a sketch of the orbitals.

Problem 7-2. Equilibrium spacing in graphite

We imagine starting with a bond in diamond, in equilibrium with an energy variation due to deviations from the bond length $d_0 = 1.54 \text{ \AA}$ given by $35.2 \text{ eV } (d - d_0)^2/d_0^2$. This was fit to experiment and thus includes the bond formation energy of diamond. We now modify the bond energy variation from the diamond value, $2V_2^h(\text{diamond}) = 2 \times 4.37 \frac{\hbar^2}{md^2} = 8.74 \frac{\hbar^2}{(md)^2}$ while for graphite it was $2V_2^h(\text{graphite}) = 8.72 \frac{\hbar^2}{(md)^2}$. (These are negative energies, energies gained.) We can add the

difference $0.02 \frac{\hbar^2}{md^2}$ to the radial interaction energy. We can also add the suggested π -bonding energy $V_{\text{pp}\pi} = -0.81 \frac{\hbar^2}{md^2}$ for a total of $-0.79 \frac{\hbar^2}{md^2} = -2.54 \text{ eV } \frac{d_0^2}{d^2}$. We add the radial energy and set the derivative with respect to d equal to zero,

$$\frac{70.4(d-d_0)}{d^2} + \frac{5.08}{d} \frac{d^2}{d_0} = 0$$

The solution is $d = 1.39 \text{ \AA}$. Various approximations could be made such as setting the second term equal to $5.08/d_0$, leading to 1.43 \AA and are good enough. This accounts well for the observed reduction from 1.54 \AA to 1.42 \AA .

Problem 7-3. Overlap interaction

This is a thought problem rather than a written exercise. For graphite, three electrons are promoted to sp^2 -hybrids, corresponding to the same charge density as a single s-electron and two p-electrons. The fourth electron is in a p-state perpendicular to the plane, say a P_z -state. Thus the electron density corresponds to a single P_z electron, single P_x - and P_y -electrons and one s-electron, exactly as in diamond where all four electrons are promoted into sp^3 -states. Thus the overlap interaction, as calculated in the Nikulin-Gordon-Kim scheme would be identical. This is also in accord with the success of the bond-length estimate of Problem 7-2.

Problem 7-4. Cohesion in BN

The hybrid energy is

$$\begin{aligned} \varepsilon_h &= \frac{1}{3}(\varepsilon_s + 2\varepsilon_p) = -8.61 \text{ eV for B} \\ &= -15.33 \text{ eV for N.} \end{aligned}$$

It may be interesting to carry graphite along for comparison, $\varepsilon_h = -11.82 \text{ eV}$. The values for B and N give a V_3 of 3.36 eV .

To obtain the promotion energy we start in boron with the n -electron (which doesn't change) plus two s-electrons. Thus the promotion is from $2\varepsilon_s = -25.08 \text{ eV}$ to $2\varepsilon_h = -17.22 \text{ eV}$, or a cost of 7.86 eV per boron atom. In nitrogen two s-electrons and two p-electrons are promoted to hybrid states, going from $2\varepsilon_s + 2\varepsilon_p = -69.02 \text{ eV}$ to $4\varepsilon_h = -61.32 \text{ eV}$, costing 7.70 eV . In graphite the promotion energy is higher than either at $3\varepsilon_h - (2\varepsilon_s + \varepsilon_p) = 8.55 \text{ eV}$. Thus the promotion energy for BN is $(7.86 + 7.70)/3 = 5.19 \text{ eV per bond}$. For graphite it is $(2/3)8.55 = 5.70 \text{ eV per bond}$.

We had a hybrid covalent energy of 16.48 eV for graphite which we take to be the same in BN. Then the bond formation energy is

$$2(V_2^h + V_3^h)^{\frac{1}{2}} - 2V_3/3 = 31.40 \text{ eV/bond.}$$

Here the second term involved transferring one electron between each

pair of atoms, costing $2V_3$, and counting three bonds per atom pair. (don't worry if students give results as an energy per atom or per electron as long as it is labeled as such.)

A good extension of the problem is to indicate that if the overlap interaction is taken the same, as suggested by Problem 7-3 and by the equal bond length, we may estimate the difference in cohesion between BN and graphite and ask if the σ -bonding contribution decreases with polarity as in the tetrahedral case. All necessary values are given above. We compare the bond formation energy minus the promotion energy for BN, $31.40 - 5.19 = 26.21$ ev per bond, with its value, $32.96 - 5.70 = 27.26$ ev per bond, for graphite. It does decrease with polarity.

We could also sort through the contribution of the π -bonding using some approximation such as that given in Problem 7-2.

CHAPTER 8. ELASTICITY

We note first that the elastic constants are understood in the sense that accurate machine calculations of the total energy of distorted crystals have been made in terms of LCAO energy bands. (These used the special points method, analogous to taking a survey by the ideal typical man.) Our goal is to simplify the theory so that we may address more complicated problems simply.

It is desirable to discuss the rigidity associated with c_{11} – c_{12} , for which rigid hybrids are seen to be appropriate; an outline of the calculation and the result, Eq. 8-14 may suffice. Use of the Bond Orbital Approximation has made this derivation clear and simple. The result describes well the rigidity of the homopolar semiconductors with no scale factor needed. However, the Bond Orbital Approximation for this property becomes increasingly inaccurate for increasing polarity. A proportionality to covalency cubed, suggested by the zig-zag chain model, is much more appropriate than the proportionality to covalency derived using the BOA.

A qualitative description of other appropriate corrections may suffice in class. The ion deformation which softens the noble-metal halides is easy to understand qualitatively. So also are the four additional complications which arise in treating the rigidity associated with c_{44} . Then a clear physical picture emerges, given in the last paragraph of Section C.

I like then to introduce the simplest valence-force field and outline the determination of internal displacements. This can be reinforced by Problem 8-3. Problems 8-1 and 8-2 are appropriate for theoretically inclined students but are not so central to the applications we are to make in Chapter 9.

Problem 8-1. Angular rigidity in the Bond Orbital Approximation

We must decompose the p-states, like vectors, into σ -oriented and π -oriented components with coefficients of cosine and sine of $(\psi - \pi/2)/2$, respectively. This reduces the matrix element between adjacent p-states by a factor of $\cos^2(\frac{1}{2}\psi - \pi/4) = \frac{1}{2}(\sin\psi + 1)$. In the Bond Orbital Approximation the bond energy becomes

$$\epsilon_b = - \left[V_3^2 + V_2^2 \left(\frac{\sin\psi + 1}{2} \right)^2 \right]^{1/2}$$

measured with respect to the average p-state energy; this is to be multiplied by 2 electrons per bond.

This is clearly a minimum where $\sin^2\psi$ is maximum, at $\psi = \pi/2$. Expanding to total energy for small deviations from $\pi/2$ we obtain

$$2\epsilon_b = -2(V_2^2 + V_3^2)^{1/2} + \frac{1}{2}V_2^2(\psi - \frac{\pi}{2})^2 / (V_2^2 + V_3^2)^{1/2} .$$

This corresponds to a

$$c_1 = v_2 \alpha_c$$

is proportional to $\alpha_c = V_2/(V_2 + V_3)^{1/2}$ is the same as in the tetrahedral case. Note that in this model, with only p-states, the distinction between covalent and hybrid covalent energies disappears.

Problem 8-2. Corrections to the Bond Orbital Approximation

The formulation has been given in the problem statement. Proceeding as indicated,

$$\begin{aligned} \langle a' | H | b \rangle &= \left(-u_b^2 \cos \theta \sin \theta - u_a^2 \frac{1}{\sin \theta \cos \theta} \right) v_{pp\sigma} \\ &= \left[-\left(\frac{1+\alpha_p}{2}\right) + \left(\frac{1-\alpha_p}{2}\right) \right] v_2 \sin \theta \cos \theta \\ &= -v_2 \alpha_p \sin \theta \cos \theta \end{aligned}$$

en, by second-order perturbation theory, including shifts from coupling to the antibonding state to the right and the left, we obtain

$$\delta E_b = \frac{2 \langle a' | H | b \rangle^2}{E_b - E_a} = \frac{v_2^2 \alpha_p^2 \sin^2 \theta \cos^2 \theta}{(V_2 + V_3)^2}$$

multiply by the two electrons per bond and expand for small θ . In converting to an expansion in $\psi - \frac{1}{2}\pi$ we obtain a contribution to the total energy,

$$\delta E = -\frac{1}{2} V_2 \alpha_p^2 \alpha_c (\psi - \frac{1}{2}\pi)^2$$

which corresponds to a correction to C_1 of $-V_2 \alpha_p^2 \alpha_c$. When added to the value from Problem 8-1, this gives a corrected C_1 of $V_2 \alpha_c^3$, as indicated in the text.

Problem 8-3. Calculation of internal displacements using force constants

This problem is completely straightforward and mostly geometry; many students seem to have difficulty with it; presumably a civil engineer would not.

We focus on a shaded atom and take our origin of coordinates there. Its neighbor to the right is displaced to the right by $\frac{3}{2}d$ by the strain equation; that to the left, by $-u$. That

below has no displacement in the x-direction. The shaded atom may have an upward displacement by v with respect to the empty atoms, but the empty atoms have no vertical displacements with respect to each other. This should be intuitively obvious and it follows from symmetry. Taking components of the displacements, the fractional change in bond length to the neighbor on the right is

$$\frac{d - d_o}{d_o} = \frac{3^{1/2}}{2} \frac{u - 1}{d}$$

to first order in the strain. Similarly the rotation of the bond is

$$\theta = \frac{u}{2d} + \frac{3^{1/2}v}{2d}$$

to first order. The change in length and angle of the bond to the left is the same. The change in length to the one below is $d - d_o = v$ and there is no change in orientation. Thus we may immediately write the change in energy, to second order in the strain, as

$$\begin{aligned} \delta E &= \frac{1}{2} C_o \left[2 \left(\frac{3^{1/2}}{2} \frac{u}{d} - \frac{1}{2} \frac{v}{d} \right)^2 + \left(\frac{v}{d} \right)^2 \right] \\ &\quad + \frac{1}{2} C_{12} \left(\frac{u}{2d} + \frac{3^{1/2}v}{2d} \right)^2 \end{aligned}$$

per atom pair. This included three bond stretches, two bond angle changes of θ at each atom and one of 2θ at each atom. For a given u this is to be minimized with respect to v . We set the derivative with respect to v equal to zero and solve for v . I get

$$\frac{v}{d} = \frac{C_o - 6C_1}{C_o + 6C_1} \frac{3^{1/2}u}{3d} = \frac{1}{2} \left(\frac{C_o - 6C_1}{C_o + 6C_1} \right) \epsilon$$

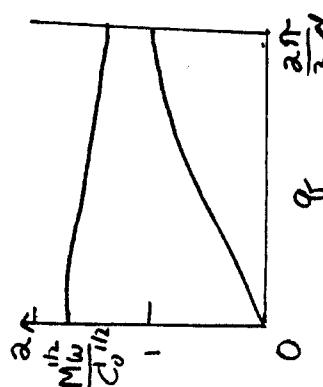
graphite is the special case $M_1 = M_2$, is

$$\omega^2 = \frac{C_o}{M} \left\{ \frac{3}{2} \pm \left(\frac{9}{4} - \frac{2\bar{M}^2}{M_1 M_2} \sin^2 \frac{3kd}{4} \right)^{1/2} \right\}$$

with

$$\frac{\bar{M}}{M} = \frac{2M_1 M_2}{M_1 + M_2}$$

This was written in the \sin^2 form. A plot for the homopolar case is given below.



By working in terms of a force-constant model we have removed the theory one step from the electronic structure. Thus the calculation of the spectrum or of the specific heat in terms of it could as well be in a solid state physics course as in a solid state chemistry course. If most students take both we can save time here by covering these in the other course (or the other way around). However, the origin of and the effect of the long-range forces transmitted through the bonds is very much to the point here. The qualitative idea illustrated in Fig. 9-4 is easy to convey though formal treatment in terms of perturbation theory on the band states is somewhat subtle.

The effective charges, and particularly the very large differences in transverse and piezoelectric charges, is very important. The significance of transverse charges, illustrated in Fig. 9-9, and the resulting arbitrariness of static charges are important to understand, particularly since the failure to understand them has seriously confused much of the earlier thinking about polar covalent solids. There is very good reason to assign Problem 9-3.

Problem 9-1. Lattice dynamics

The mathematics here is of course the same as in the LCAO calculation of the electron states with M_0^2 entering in place of an electron energy. We focus on the atom with the displacement u_1 indicated in the problem figure. We calculate the force on that atom due to the relative displacements of its three neighbors and equate that force to the mass times the acceleration, $-M_0 u_1$. Taking components gives two factors of 1/2 for the bonds to the right. We obtain

$$-M_0^2 u_1 = C_o \left\{ 2(u_2 e^{iqd/2} - u_1) \frac{1}{4} + u_2 e^{-iqd} - u_1 \right\}$$

Similarly for the atom with the displacement u_2 we have

$$-M_0^2 u_2 = C_o \left\{ 2(u_1 e^{-iqd/2} - u_2) \frac{1}{4} + u_1 e^{iqd} - u_2 \right\}$$

It is elementary algebra to solve the corresponding secular equation (equivalent to eliminating u_1 and u_2 between the two equations and solving for ω^2). We obtain

$$\omega^2 = \frac{C_o}{M} \left\{ \frac{3}{2} \pm \left(\frac{5}{4} + \cos \frac{3qd}{2} \right)^{1/2} \right\}$$

$$k_D = (9 \times 3^{1/2} \pi^2/4)^{1/3}/d = 1.38 \times 10^8 \text{ cm}^{-1} \text{ for GaAs}$$

This is a rather trivial problem but following it through requires sorting through the dispersion curves given in the chapter and organizing factors of two, etc. Hopefully a student will check the formulae listed in the problem to see that he understands them.

Substituting for N_p in the equation for k_D leads to

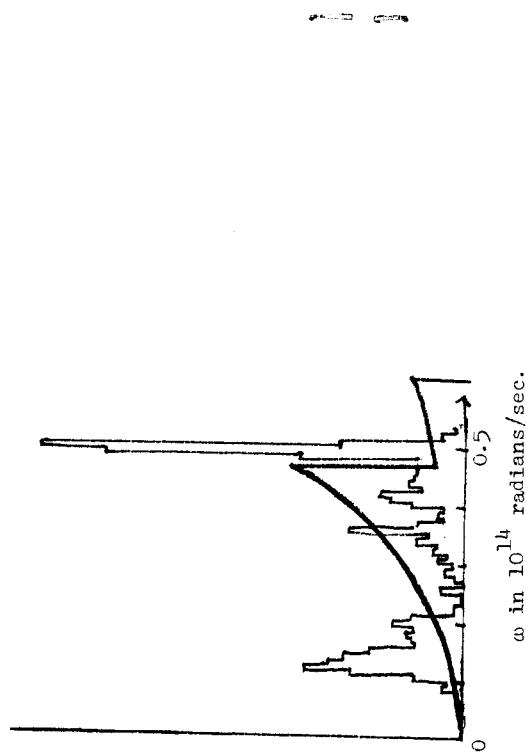
I read the speed of longitudinal sound from the figure as $0.25 \times 10^{14} / (\pi/a) = 0.45 \times 10^6 \text{ cm/sec}$ so $\omega_D = 0.62 \times 10^{14} \text{ sec}^{-1}$. The speed of transverse sound appears to be about $3/4$ of this leading to an ω_D of 0.47×10^{14} . The density of modes is the sum of two parabolas, with the area under the transverse one twice that under the longitudinal one. That result, plotted along with the curve in Fig. 9-6 is given below.

It is not a very significant generalization to carry this same calculation out for BN by keeping two masses. The result, of which

$1/u$ of this is added to the static charge

$$e_T^* = z^* + 3\alpha_p (1 - \alpha_p^2) = 1.02 .$$

If we made instead a vertical displacement the component of the displacement along each bond would be $u3d/2$ but the distance the charge was displaced would have been $3d$ rather than $3d/2$. The result is the same.



Problem 9-3. Transverse charge

As in the tetrahedral case we use the V_2 and V_3 based upon states. From Problem 5-1 they are $V_2 = 13.77$ eV and $V_3 = 2.42$ eV, a polarity of 0.17. On the nitrogen we are putting two π -electrons and the three σ -electrons contribute $3(1 + \alpha_p) = 3.52$ electrons. We subtract the valence nuclear charge of 5 to obtain $z^* = 0.52$, with boron positive. This is not a very realistic treatment of the electrons but it gives a positive boron which is probably correct. This has compensated for the suggestion we have made on earlier problems that the V_{pp} is probably being overestimated by a factor of two in graphite and here.

The displacement \vec{u} shown in the problem figure shortens the bonds to the right by $\delta d = -u/2$, shifting V_2 by $\delta V_2 = 2V_2(u/(2d))$

$$\delta\alpha_p = -V_2 V_3 \delta V_2 / (V_2^2 + V_3^2)^{3/2} = -\alpha_p (1 - \alpha_p^2) u/d .$$

could proceed by calculating the change in dipole for each bond but is easier to calculate the charge transfer from atom to atom. The change in α_p places $\delta\alpha_p$ electrons on each of the two atoms to the right of that displaced. A calculation for the bond to the left gives as large a transfer as each of those to the right. $\delta\alpha_p$ is negative so really $2|\delta\alpha_p|$ electrons have been transferred from the right neighbors to the left neighbor, a distance parallel to \vec{u} of $3d/2$. The dipole introduced by the transfer is

$$\vec{p} = 3\alpha_p (1 - \alpha_p^2) u/2$$

In contrast to the preceding two chapters, the discussion here is quite qualitative with few equations. It may be a welcome change of pace. This is one of the most active subjects in current research as is discussed here. It is nice to understand the origin of characteristic crystal shapes in terms of bond density and to learn concept of the "dangling hybrid", more commonly but less appropriately called the "dangling bond". In terms of this we can see the effect of Jahn-Teller distortions on surface reconstruction. Most workers at this point as to the nature of the 2×1 surface reconstruction on the GaAs (111) surface but not necessarily on the magnitude of the distortions. By now most also agree on the general nature of the reconstruction on polar (110) faces. However, the other reconstructions remain very controversial. As long as that is true you may skip those parts; they may become more interesting when proven right or wrong. The origin of Schottky barriers as described here is not generally accepted at present.

The prediction of valence band maxima for the study of heterojunctions and photothresholds, but because this sets the scale of the energy bands the same as that for atoms and molecules. Thus we have starting parameters for the discussion of adsorption on solid surfaces, etc. We see that the absolute values are not in accord with measured photoelectric emission, but the relative values seem to be meaningful for all systems.

LEM 10-1. Surface state energies

We need construct hybrids for Ga ($\epsilon_h = -6.52$ eV) and As (-10.27 eV) separately. These are the dangling hybrids before reconstruction. Full reconstruction raises the gallium hybrid to the same p-state energy and drops the arsenic hybrid to the same state energy (shown next page). The valence band maximum is given

$$E_v = \frac{1}{2}(\epsilon_p^{\text{Ga}} + \epsilon_p^{\text{As}}) - (v_2^2 + v_3^2)^{1/2}$$

Figure for Problem 10-1.

v_2 and v_3 can be taken from Table 4-1 or E_v from Table 10-1. States also from Table 10-1 may be added. Note that the dangling hybrid states are not even in the gap before reconstruction.

LEM 10-2. Heterojunction discontinuities

This problem is quite elementary but insures that the student everything straight. In the alloy the valence band maximum is

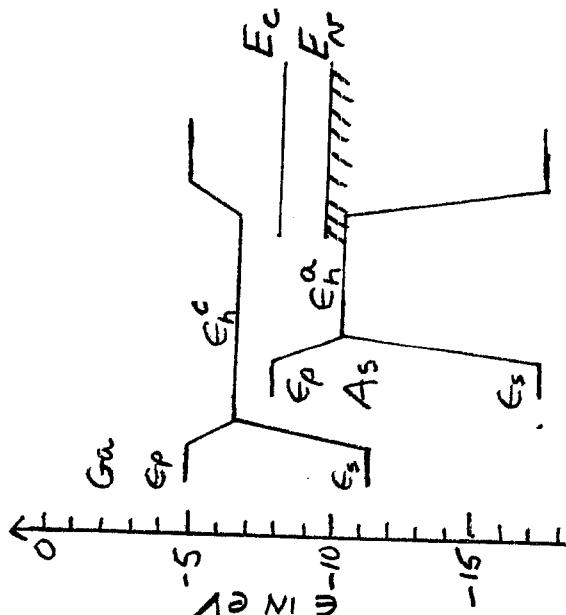
$$E_v = -9.57(x) - 9.53(1-x) \text{ eV}$$

and the conduction-band maximum is

$$E_c = E_v + 2.77x + 1.52(1-x) = -8.01 + 1.21x \text{ eV}$$

minimum is at

$$\text{which equals the ZnSe value of } -7.76 \text{ eV at } x = 0.21.$$



Systems such as SiO_2 are the most immediate next step after the discussion of simple tetrahedral solids. It does not seem appropriate to formulate it in terms of two-electron covalent bonds (this approach is very unnatural unless the bond-angle at oxygen is made 90° , and it is not close to that) and yet a bonding unit can be constructed such as a Bond Orbital Approximation can be made and much of the theory proceed just as before. The extension to polar counterparts (Al_2O_3 , or Si_2O_4 generalized to AlPO_4 , aluminum phosphate, for example) is also rather pretty. It would be possible in principle to address the materials from the ionic end, in terms of the chemical grip (Section 19F), but the covalent energy is so much larger than the ionic energy (see Table 11-1) that it is a poorly convergent process.

I like the consideration of the isoelectronic series SiO_4^{4-} , SO_4^{2-} , ClO_4^- , ArO_4 , seeing why such systems tend to be stable molecules and where the instability arises at either end of the series, if for example we tried OS_4^{2-} rather than SO_4^{2-} . We then see how a bonding unit from the SiO_2 structure, with $\text{Si}1/4\text{O}3/4$ being choice made here. After that one can select a few interesting units and move on to closed-shell systems.

At a 90° bond angle, θ becomes 45° so β_{pz} and β_{px} become identical,

$$\frac{W_3}{(W_2^2 + W_3^2)^{1/2}}$$

equal to the single-bond polarity $\beta = 0.26$.

Problem 11-1. The bonding unit

At a 90° bond angle, θ becomes 45° so β_{pz} and β_{px} become identical,

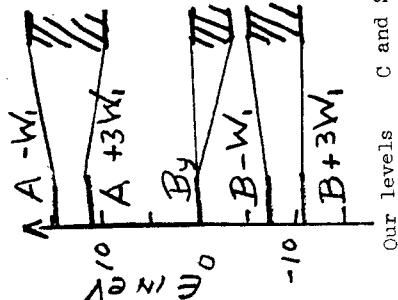
$$\frac{W_3}{(W_2^2 + W_3^2)^{1/2}}$$

We ignore the oxygen s-state energy (-29.14 eV does not fit well in the band calculation but is not so far from experiment).

The en p-state energy from the Solid State Table is -14.13 eV and this is the energy of B_y . To obtain the B_x , B_z , A_x , and A_z energies we need also the silicon hybrid energy -8.28 eV giving an average the oxygen p-state of $E = -11.20$ eV. We subtract and add

$$(W_2^2 + W_3^2)^{1/2} = 11.34 \text{ eV}$$

obtain -22.54 eV and $+0.13$ eV. These are split by the matrix element W_1 equal to $-1/2(1 - \beta)$ times the V_1 for silicon, giving 7 times 1.76 eV. This raises the triply-degenerate level by 0.65 and drops the single level by 1.95 eV. These are compared with Kikowsky and Schlüter in the diagram on the following page; this is obtained measuring all of our energies from our value for B_y .



Problem 11-2. The transverse charge

This again is little more than a thought problem but illustrates a point. We imagine displacing all oxygen atoms in the same direction \hat{u} . \hat{u} is a unit vector; let the distance be u . The component along \hat{u} of the dipole moment induced by a particular oxygen is

$$\vec{p} \cdot \hat{u} = -eu(\hat{x}e_x^* \hat{x} \cdot \hat{u} + \hat{y}e_y^* \hat{y} \cdot \hat{u} + \hat{z}e_z^* \hat{z} \cdot \hat{u}) \cdot \hat{u}$$

where \hat{x} , \hat{y} , and \hat{z} are unit vectors for the coordinate system of Fig. 11-6 for each atom. We may average this over direction of displacement (or over oxygen orientation) with each $(\hat{x} \cdot \hat{u})^2$ averaging to $1/3$ for an average effective charge of $(e_x^* + e_y^* + e_z^*)/3$. This multiplied by the oxygen atom density and $-eu$ gives the polarization density. Similarly multiplying a silicon effective charge e^* by $+eu$ and by the silicon atom density must give the same result. But the silicon atom density is half as big so

$$e^* = 2(e_x^* + e_y^* + e_z^*)/3 = 2.20$$

with the silicon positive.

neighbors is $\frac{1}{2} (-0.23\epsilon/(-\epsilon)) = 12\%$.

Problem 12-2. The Lennard-Jones binding

With this chapter we begin a totally different conceptual framework, that of the closed-shell atom or ion. We argue that for the close-packed structures a formulation in terms of the two-electron bond is not possible; we cannot go by unitary transformation from four atomic orbitals to six or eight hybrid orbitals oriented toward nearest neighbors. The idea of a "resonating bond" led many people to think that covalent bonding was related but I do not believe so. It reflects exactly the kind of unfounded thought we seek to avoid in our studies. It will turn out to be true, on the other hand, that the formulation for ionic solids can be applied back to the polar tetrahedral solids because it is not restricted as to the number of neighbors. The corresponding chemical grip will be treated in detail in Chapter 19, but does not have the conceptual simplicity of the two-electron covalent bond.

The purpose in discussing the inert gases is to lay the groundwork for understanding ionic solids. The closed-shell electronic structure is very simple and the interatomic interactions are well described by the simple two-parameter Lennard-Jones interaction, which can be obtained from first principles as an overlap interaction of the Nikulin-Cordon-Kim type. It is remarkable that this overlap interaction can be fit to the properties of the gas but then accurately describes the properties of the inert gas solid. It will be much more remarkable in the next chapter that this same overlap interaction (and same parameters) gives a good description of the overlap interaction in ionic solids.

A point worth emphasizing concerning the electronic structure of the inert gas solids is that the band gap becomes conceptually an atomic ionization rather than a transition between bonding and antibonding states. Then the very remarkable finding that that band gap varies as d^{-2} just as in covalent solids finds a quite different explanation illustrated in Fig. 12-2.

Problem 12-1. Second neighbor interactions

Both problems here are elementary and are designed to familiarize the student with the Lennard-Jones interaction which is used also for ionic solids. I think the first is better than the second.

In the face-centered cubic structure there are twelve nearest neighbors. (The 6ϵ in Table 12-3 gives the energy per atom rather than per atom pair.) The six second neighbors are in [100] directions at a spacing $2\sqrt{2}d$, where d is the nearest-neighbor distance. The Lennard-Jones interaction at this distance becomes

$$V(2\sqrt{2}d) = 4\epsilon \left[\frac{1}{2} \left(\frac{\sigma}{d} \right)^{12} - \frac{1}{2^3} \left(\frac{\sigma}{d} \right)^6 \right] = 4\epsilon \left[\frac{1}{8} - \frac{1}{2^4} \right] = -0.23\epsilon$$

comparison to the value $-\epsilon$ at d . With half as many second neighbors the ratio of the contribution of second neighbors to first

neighbors is $\frac{1}{2} (-0.23\epsilon/(-\epsilon)) = 12\%$.

Problem 12-2. The Lennard-Jones binding

The questions asked here are probably not very important but the answers should be roughly correct.

The first derivative of the Lennard-Jones potential is

$$\frac{dV_0}{dR} = 4\epsilon \left(-\frac{12\sigma^{12}}{R^{13}} + \frac{6\sigma^6}{R^7} \right)$$

We divide this by the separation R and set the first derivative of the result equal to zero:

$$4\epsilon \left(\frac{12 \times 14\sigma^{12}}{R^{15}} - \frac{6 \times 8\sigma^6}{R^9} \right) = 0$$

This is solved by multiplying through by R^9/σ^6 yielding

$$\left(\frac{\sigma}{R} \right)^6 = 0.29 \quad \text{or} \quad R = 1.23\sigma = 3.37 \text{ \AA}$$

The latter is one of the required answers. This corresponds to an attractive force between the neon atoms from the first equation above of

$$\frac{dV_0}{dR} = \frac{4\epsilon}{R} \left(-12(0.29)^2 + 6(0.29) \right) = 2.69 \times 10^{-3} \text{ eV/\text{\AA}}$$

which may be equated to $M\omega_0^2$, Thus with $M = 33.7 \times 10^{-24}$ grams

$$\begin{aligned} \omega^2 &= \frac{2.69 \times 10^{-3} (\text{eV/\text{\AA}}) \times 1.6 \times 10^{-12} (\text{erg/eV}) \times 10^{16} (\text{A}^2/\text{cm}^2)}{33.7 \times 10^{-24} (\text{grams}) \times 3.37 \text{ \AA}} \\ &= 0.038 \times 10^{25} \text{ sec}^{-2} \end{aligned}$$

$$\begin{aligned} \text{or } \omega &= 0.62 \times 10^{12} \text{ radians per second} \\ V &= 0.62/2\pi = 9.8 \times 10^{10} \text{ cycles per second.} \end{aligned}$$

Problem 13-1. Estimate of lattice distances

In this chapter we give essentially the classical description of ionic solids based upon an electronic structure for independent spherical ions. In Chapter 14 we go on to include the effects of the interatomic matrix elements which are neglected in this description.

I like to describe in class the putting together of argon atoms in a simple cubic structure, and holding the electronic structure rigid as we transfer protons between alternate nuclei making them alternately chlorine and potassium nuclei (as at the close of equation 2E). Then the electrons are allowed to relax, expanding slightly around the chlorine nucleus and shrinking around the potassium nucleus, but with the overlap interaction remaining largely unchanged. This approach provides a quantitative description of the halides and a qualitatively correct description of ionic crystals of larger ionic charge constructed from Figure 13-1.

In particular this view suggests the closely-packed NaCl and structures for AB compounds which minimize the electrostatic energy and analogous structures for compounds with more complex cations. We describe the Madelung calculation of the electrostatic energy and give an extensive table of values of reduced Madelung constants. We then can discuss the total energy by adding the overlap interaction and see that even taking the overlap interaction from the corresponding inert gas data gives a good description of the equilibrium spacing, cohesion, (and bulk modulus in the case of the solid) both the diatomic molecule and the solid. This is confirmed both by comparison with experiment and with calculations of Gordon and Kim. In particular note that the spacing is larger in the solid than in the molecule because of the greater number of overlap interactions a comparable electrostatic energy per ion. The main features illustrated nicely by Problem 13-1.

The stability of the rocksalt structure against angular distortions comes (as does the stability against transformations to less compact structures) from the electrostatic energy. This is confirmed in extensive tabulation of elastic constants and comparison with electrostatic values. There are nevertheless small corrections (deviations from the Cauchy relations) which cannot be explained in the next of radial forces used here; we return to these in Chapter 19 discussing the chemical grip.

One property which is not given by this simple theory is the structure itself; the theory does not meaningfully distinguish between the rocksalt and CsCl structures. This has been known for a time (1925) and for that reason is frequently forgotten. This has made me cautious about the extensive semiempirical correlations of structures in terms of ionic radii and Madelung energies. An approach becomes difficult to assess when it requires various corrections to the radii depending upon circumstances. It leaves me critical. We tabulate the ionic radii but perhaps have not given a large area the attention it deserves.

We calculate the energy per molecular unit or per calcium ion. From Eq. 13-3 for CaF_2 ,

$$E_{\text{es}} = -1.68 \times 3 \times 2 \times 1 e^2 / 2d = -72.53(\text{eV}\cdot\text{\AA}) / d$$

For the eight nearest-neighbor interactions per calcium ion the Lennard-Jones interaction is

$$V_0(d) = 8 \times 4 \times \epsilon ((\sigma/d)^{12} - (\sigma/d)^6)$$

With one ion from the neon row and one from the argon row ($\epsilon = 6.2 \times 10^{-3}$ eV and $\sigma = 3.00 \text{ \AA}$).

The sum of these is to be minimized. A convenient way is to write $x = \sigma/d$. Then the sum becomes

$$E_{\text{es}} + V_0 = -24.18x + 0.198(x^{12} - x^6)$$

We can set the first derivative equal to zero and solve by iteration; e.g., $x = (10.15 + x^{5/2})/11$, getting $x = 1.25$ and $d = 2.40 \text{ \AA}$. (Dropping the x^6 term gives directly $x = 1.23$ and $d = 2.43 \text{ \AA}$; good enough.) This result is to be compared with the experimental 2.36 \AA from Table 13-5. In this case it does better than the sum of ionic radii, 2.27 \AA . I don't know if such a method generally does better.

Problem 13-2. Estimate of bulk modulus

We write the change in energy per calcium ion δE due to a change in bond length δd ,

$$\delta E = \frac{1}{2} (\partial^2 E_{\text{sep}} / \partial d^2) (\delta d)^2$$

The bulk modulus B is related to that energy by

$$\frac{\delta E}{\Omega} = \frac{1}{2} B \left(\frac{\delta \Omega}{\Omega} \right)^2 = \frac{9}{2} B \left(\frac{\delta d}{d} \right)^2$$

where Ω is the volume per calcium ion or $(4d/3)^3$ in the fluorite structure. Thus

$$B = \frac{1}{64 \times 3^{1/2} d} \frac{\partial^2 E_{\text{sep}}}{\partial d^2}$$

The terms in Problem 13-1 were given in eV which would give this result

ev per Å^3 if we wrote d in Å. We convert by multiplying by $\times 10^{12}$ erg-Å³ per ev-cm³. Thus the d^{-12} term in B becomes

$$\delta B = \frac{1.6 \times 10^{12}}{64 \times 3^{1/2} \times 2.36} \cdot 32(6.2 \times 10^{-3}) \cdot 12 \times 13(3/2.36)^{12}/(2.36)^2$$

6.05×10^{11} ergs/cm³. The d^{-11} term is -0.39×10^{11} and the electrostatic term is -0.68×10^{11} for a total of 4.98×10^{11} ergs/cm³ to be compared with the experimental $(16.4 + 2 \times 4.7)/3 = 8.6 \times 10^{11}$ ergs/cm³ from Table 13-5.

The view taken here is not the standard one of independent polarizable ions which would seem consistent with the view taken in Chapter 13. That view of the dielectric properties seemed plausible and seemed to be tested in the alkali halides, but with eight adjustable parameters to fit a systematic set of 16 experimental numbers it was not a real test. We follow Pantelides in observing that the optical absorption χ_2 is dominated by the interionic transitions and that therefore the susceptibility χ_1 must be also, leading to a more accurate model with fewer parameters. The treatment of "ion softening" and effective charges follows closely the corresponding treatment of covalent solids and is another deviation from the independent-ion picture which is worth understanding. It is lowest-order perturbation theory; higher order terms and the chemical grip are postponed to Chapter 19.

Problem 14-1. Estimates of band gaps

This is a rather trivial exercise but the comparison of estimates based upon term values and upon the d^{-2} formula made in Table 14-3 is interesting. I think something is learned from going through it. The predicted band gaps in ev, with experimental values from Table 14-3 in parentheses are

Fluorites

	CaF_2	BaF_2	CdF_2
	11.58	12.50	9.92
(10.00)	(9.07)	(6.00)	

Antifluorites

	S	Se	Te
Na_2	5.14 (2.4)	4.40 (2.0)	3.46 (2.3)
K_2	6.08 (3.20)	5.34 (3.33)	4.40 (3.53)

Problem 14-2. Ion softening and $\frac{e^*}{T}$

With eight neighbors rather than six, Eq. 14-10 is replaced by

$$Z^* = 1 - 16(\frac{V_{\text{sp}}/E}{G})^2 = 1 - 16(-1.84/9.1)^2 = 0.35$$

To calculate e^* we displace the cesium ion a distance u in the [100] direction, giving changes in internuclear distance (bond length) to the right of $-u/3^{1/2}$ with corresponding increases to the

The change in $V_{\text{sp}\sigma}$ then is (by the d^{-2} dependence)

$$2\Delta V_{\text{sp}\sigma} / (3^{1/2} d) .$$

increases the electronic charge transferred from each ion (and spins) on the right to the cesium by

$$2(V_{\text{sp}\sigma}/E_g)^2 = 4(V_{\text{sp}\sigma}/E_g^2) 2\Delta V_{\text{sp}\sigma} / (3^{1/2} d) .$$

I oriented the p-state on the halogen towards the cesium. It is clearer to take three oriented along the three cubic directions, with each interatomic matrix element reduced by a factor $3^{-1/2}$. The three are added the same result is obtained. Note E_g does not change; obviously not if it was based upon term values and even bond length changes an equal number are increased and decreased. Similar reasons no angle changes enter.

With four neighbors on the right, four times this charge is transferred to the cesium and finally to the four neighbors on the left, a total distance of $2d/3^{1/2}$. This gives a total dipole moment magnitude

$$\delta P = \frac{64}{3} \text{ eu} \left(\frac{V_{\text{sp}\sigma}}{E_g} \right)^2 = 0.87 \text{ eu}$$

$Z^* \text{ eu}$ from the effective ionic charge itself. The transverse charge becomes

$$e_T^* = 0.35 + 0.87 = 1.22 .$$

CHAPTER 15. SIMPLE METALS

There is a very sharp break in moving to open-shell systems where we use plane waves rather than atomic orbitals as the basis. We describe at the outset how LCAO theory of simple metals is valid but very inconvenient for the kind of elementary calculation of properties which are central to this text. We make the detailed relation between theories of covalent and metallic systems at the end (in Chapter 18) when we apply the pseudopotential theory from simple metals to the covalent solids. In the meantime, Problems 15-1, 2, and 3 may help to tie the two parts together.

There are two parts of this chapter which should be distinguished. The first (Section B) gives the traditional free-electron theory of metals, electrons in a box, with a calculation of densities of levels and kinetic energy. This has been trimmed down to just what is needed for later discussion; it is sufficiently brief that it does not conflict with traditional solid-state physics courses which amplify the free-electron theory with thermodynamic and transport properties. We then go on to discuss electrostatic energy in the traditional way and then proceed to pseudopotentials for the discussion of equilibrium spacing, cohesion, and the bulk modulus.

We use a novel way to introduce pseudopotentials which is appropriate to the level of quantum mechanics used elsewhere in the book. We estimate the electronic kinetic energy using the results of Section B and the same local-density approximation which was used in the calculation of the overlap interaction in Chapter 7. This demonstrates the cancellation with the potential and suggests the empty-core pseudopotential which is used throughout the remainder of the text. A more complete quantum mechanical motivation for this form is given in Appendix D. There are other one-parameter models for the pseudopotential but as far as I know only this one has the remarkable feature that it gives a reasonable account of the volume-dependent properties discussed in this chapter, as well as the energy bands and the many properties describable by pseudopotential perturbation theory. Chapters 15 – 17 give an abbreviated account of the pseudopotential theory of metals in terms of this very simple model, with again all necessary parameters listed in the Solid State Table.

Problem 15-1. Two-dimensional free-electron bands

A trivial exercise designed to make contact with the earlier chapters:

$$(2A/(2\pi))^2 \pi k_F^2 = 1$$

if $A_{1/2}$ is the area per atom. The area of a hexagon in graphite is $3 \times 3^{1/2} d^2/2$ and there are two atoms per hexagon. Thus

$$k_F^2 = 8\pi / (3 \times 3^{1/2} d^2)$$

with $d = 1.42 \text{ \AA}$. Then $k_F^2 = 2.40 \text{ \AA}^{-2}$ and the energy is

$$\frac{1}{2} 7.62 \text{ eV } \text{Å}^2 \times 2.40 \text{ Å}^{-2} = 9.14 \text{ eV}$$

CHAPTER 16. ELECTRONIC STRUCTURE OF METALS

the band width estimated from the Solid State Table is $3V_{\text{pp}}\pi =$ ev or about $\frac{1}{2} \times 17 \text{ ev} = 8.5 \text{ ev}$ from the figure in Problem 3-3.

Prob. 15-2. Free-electron theory of covalent solids

This requires a bit of numerical work but is trivial if a student has a small programmable calculator. Writing Eq. 15-16 for $Z = 4$, substituting $\hbar/m = 7.62 \text{ eV-Å}^2$ and $e^2 = 14.4 \text{ eV-Å}$ we have

$$E_{\text{tot}} = 9.14 k_F^2 + 12.22 r_c^2 k_F^3 - 13.75 k_F - 37.81 \alpha k_F$$

Energy is in ev, k_F is in Å^{-1} and r_c in \AA . We set the derivative with respect to k_F equal to zero,

$$\frac{\partial E_{\text{tot}}}{\partial k_F} = 18.28 k_F + 36.66 r_c^2 k_F^2 - 13.75 - 37.81\alpha = 0$$

α is 1.67 for the diamond structure and 1.79 for the face-centered cubic structure. The results are given in the table below. I will call them semiquantitative.

r_c	Predicted		Experimental	
	k_F (fcc)	k_F (dia)	k_F (fcc)	k_F (dia)
0.37	2.59	2.50	2.76	
0.56	1.98	1.93	1.81	
0.54	2.02	1.95	1.74	
0.59	1.91	1.85	1.63	(1.51)
0.57	1.97	1.89	1.59	

Prob. 15-3. d^{-5} dependence of the bulk modulus

Even simpler than Problem 15-2 but with results of some interest. The k_F from the Solid State Table as in Problem 15-2, we obtain

	B in $10^{12} \text{ ergs/cm}^3$	B/k_F^5
Eq. 15-18	Exp.	Eq. 15-18
6.63	5.45	0.041
0.82	0.99	0.042
0.66	0.77	0.041
	0.33	0.049

ment does not follow the d^{-5} rule as well as the theory, but not exact even for theory.

The discussion of Fermi surfaces may well be contained in solid-state physics courses and could thus be eliminated here. Very likely the discussion of scattering is not, but it could be. It is essential to carry out the formulation of pseudopotential form factors and structure factors (Eq. 16-4) and see how the structure factors are evaluated in perfect crystals (Section B) and at least for a vacancy (Eq. 16-20). Problem 16-3 is excellent for clarifying this. It is also desirable to make the identification of the reduced-zone scheme with the energy bands of the Brillouin Zone which have been used in the earlier parts of the text. I believe some discussion of screening must be included since it is so essential to the electronic structure of metals. It should include in particular the simple dielectric function of Eq. 16-30. Problem 16-2 makes a nice identification with atomic physics, but part (d) is a little awkward. Note that this problem enables us to determine the pseudopotentials from numbers in the ordinary Chem.-Phys. Handbook.

Problem 16-1. Free-electron Fermi surface

If one chooses to discuss Fermi surfaces, an exercise like this should get the subject organized. The Fermi wavenumber is obtained from

$$\frac{2}{(2\pi)^3} \frac{4\pi k_F^3}{3} a^3 = 16$$

giving $k_F = 1.24 (2\pi/a)$. Then the wavenumber lattice can be constructed, spheres drawn, and squares counted to give the areas. My estimates of 1.04 and 0.16 times $(2\pi/a)^2$ are in typical accord with experiment, with larger errors for the smaller sections. (See the figure on the following page.)

(b) Similarly

	Z	E/Z^2	$2r_c$	r_c	r_c (SS Table)
Na	1	5.14	0.95	0.95	0.96
Mg	2	3.76	1.53	0.77	0.74
Al	3	3.16	2.01	0.67	0.61

The trend with valence is also well given.

(c) For SmI we read directly $r_c = 0.85$. The value 0.83 in the Solid State Table was more carefully done. For SmII we have $E/Z^2 = 2.80$ giving $2r_c$ about 2.1 or $r_c = 1.1$ in rough accord.

$$(d) \rho_c = n(n-1) + \frac{n}{\rho_c} [\rho_c - (n-1)^2]$$

$$\rho_c^2 - n^2 \rho_c + n(n-1)^2 = 0$$

$$\rho_c = \left(n^2 + \sqrt{n^4 - 4n(n-1)^2} \right) / 2$$

which is the only positive solution. For aluminum we take

$$E_n = -9e^2/(2a_0 n^2) = -28.44 \text{ eV}$$

$$\text{or } n^2 = \frac{9 \times 27.2 \text{ eV}}{2 \times 28.44} \text{ or } n = 2.07$$

$$\text{Thus } \rho_c = 3.65 \text{ and } r_c = \frac{2.07(0.529 \text{ \AA})}{2 \times 3} \times 3.65$$

$$= 0.67 \text{ \AA}, \text{ fortuitously in exact agreement with the } 0.67 \text{ obtained in part (b).}$$

Problem 16-3. Calculation of structure factors and resistivity

(a)

$$S(\vec{q}) = N_a^{-1} \sum_j e^{-iq \cdot \vec{r}_j} = S^0(\vec{q}) + N_a^{-1} (e^{-iq \cdot \vec{r}_0} - 1) e^{-iq \cdot \vec{r}_0}$$

where of course S^0 is the structure factor without distortion. The correction to it, to first order in u is

$$-N_a^{-1} iq \cdot \vec{r}_0 e^{-iq \cdot \vec{r}_0}$$

Thus $S \cdot S$ for $\vec{q} \neq 0$ different from a lattice wavenumber (i.e., where $S^0 = 0$) is $N_a^{-2} (q \cdot u)^2$ and the angular average is $q_u^2 / (3N_a)$. It is essential of course to average $S \cdot S$ and not just S . One should calculate any given property for fixed positions and then average the result over positions; resistivity depends upon $S \cdot S$. There is an equal contribution from each of the $3N_a$ degrees of freedom.

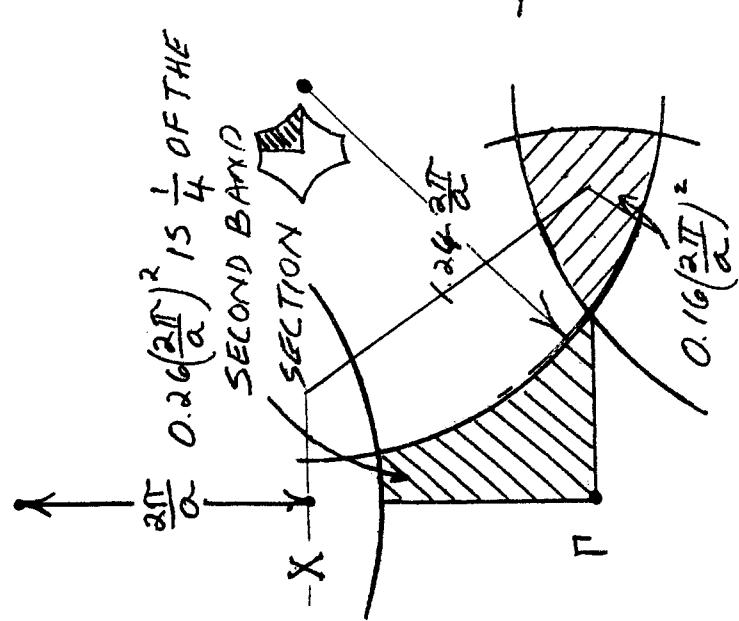


Figure for Problem 16-1

Problem 16-2. Pseudopotential core radii

These are read directly from the curve using the ϵ_g from the Solid State Table. The comparison with the r_c values from the Table is remarkably close in view of the totally different origins. I find the following r_c in \AA .

	From Curve	From Table
Li	0.85	0.92
Na	0.95	0.96
K	1.35	1.20
Rb	1.43	1.38
Cs	1.59	1.55
Fr	1.72	—

} Equating the kinetic energy of the atom to $\frac{1}{2}kT$, we have

$$\rho = \frac{CN}{K/(M\omega_E^2)} \int_0^2 \left(3N_a q^2 u^2 / 3N_a^2 \right) w_q^2 x^3 dx$$

$$= CKT k_F^2 / (M\omega_E^2) \int_0^2 x^5 w_q^2 dx$$

evaluating the integral with the form given in the problem we have 1.27 eV^2 . Then I obtain

$$\rho = \frac{233 \left(\frac{\mu\Omega \text{ cm}}{\text{eV}^2} \right)}{40} \frac{(0.73)^2 \times 10^{16} (\text{cm}^{-2})}{(39 \times 1.67 \times 10^{-24}) (8.144 \times 10^{-24} \text{ sec}^{-2})} 1.27 (\text{eV}^2)$$

$$\times 1.6 \times 10^{-12} (\text{ergs/eV}) = 6.7 \mu\Omega \text{ cm}$$

agreement is accidentally good. The fit to w_q was from an earlier calculation and not exactly what one would get from the Solid state Table.

CHAPTER 17. MECHANICAL PROPERTIES OF METALS

This takes us back to bonding properties. The simple argument encompassed in Eqs. 17-1, 17-2, and 17-4 is absolutely essential. It isolates the small structure-dependent energy and puts it in a form which can be directly evaluated in terms of the structure factors discussed in the last chapter. This should be understood in detail. On a more qualitative level one may note the equivalent representation in terms of two-body central-force interactions though this has proven less useful; one may also note that there are corrections to this lowest order theory. It should be emphasized that pseudopotential calculations of total energy are really straightforward, as illustrated in Problem 17-1, though the concept may be more difficult than for LCAO theory.

The theory of the vibration spectrum is a beautiful application if one has time to explore it. This is a real calculation in terms of the electronic structure, as was the calculation of $c_{11} - c_{12}$ for the covalent solids. It is not a force-constant model as we did for the vibration spectrum of the covalent solids. If one is short on time it is possible to describe the idea of satellites to the lattice wave-numbers, Fig. 17-3, but specialize the evaluation to the Bohm-Staver result and Table 17-1.

The dimensionless electron-phonon coupling constant λ is a very important concept with three important applications: resistivity, effective mass, and superconductivity. Ideally one would like to discuss this in detail and even make the explicit evaluation given in Problem 17-2; time is the only problem. The discussion of surfaces and liquids is less central and can be left for outside reading. One might mention that the resistivity calculation for the liquid (at the very end of the chapter) is really just as trivial as indicated there. For that reason it has been widely calculated, though it is perhaps not of high intrinsic interest.

Problem 17-1. The band structure energy.

We first evaluate the energy-wavenumber characteristic,

$$F(q) = - \frac{\Omega_0^2 \omega_0^2 q^2}{8\pi e^2} \frac{\kappa^2 \cos^2 qr_c}{q^2 + \kappa^2}$$

$$= - 0.187 \times 10^{-10} \frac{\kappa^4 \cos^2 qr_c}{q^2 (\kappa^2 + q^2)} \text{ erg}$$

where we used $\omega_0^2 = -4\pi Ze^2 / (q\Omega)$ and $\Omega_0^2 = a/4$ and $\kappa^2 = 4.23 \text{ \AA}^{-2}$. The lattice wavenumbers in the distorted lattice ($q^+ = 1.7916(2\pi/a)$ and $q^- = 1.6763(2\pi/a)$ rather than $q^0 = 1.7321(2\pi/a)$) at $\epsilon_4 = 0.1$ are then needed. The sum over nearest lattice wavenumbers gives a change of

$$4F(q^+) + 4F(q^-) - 8F(q^0) = (-27.63 - 1.51 + 21.69) \times 10^{-14}$$

$$= 7.45 \times 10^{-14} \text{ ergs/ion} .$$

ultiply by $4/(4.04 \times 10^{-8} \text{ cm})^3$ to get $4.52 \times 10^9 \text{ ergs/cm}^3$ equal contribution to the elastic $\frac{1}{2} c_{44}(0.1)^2$. Thus the contribution of $4.04 \times 10^{11} \text{ ergs/cm}^3$ in reasonable accord with the required total of $10^{11} \text{ ergs/cm}^3$.

em 17-2. The electron-phonon coupling constant.

The procedure here is rather completely laid out but if one follows it through it makes connections with many approximations which have been used in the text and the result is satisfying. Beginning Eq. 17-25 and the values suggested,

$$\lambda = \frac{1}{2kT} \left(\frac{3N}{2E_F} \right) \frac{\Omega}{4\pi k_F^2} \int | -i\mathbf{q} \cdot \mathbf{w}_q|^2 2\pi k_F^2 \sin\theta d\theta \times 2$$

last factor of two being for the two satellites. $N \Delta \omega_{\text{sat}}^2 = kT/2$ Eq. 17-17. Note that ω_q depends upon the wavenumber \mathbf{q} of the being considered. Note also $N\Omega/N_A = Z$. We have then

$$\lambda = \frac{3Z}{8ME_F} \int \frac{q^2 w_q^2}{\omega_q^2} \sin\theta d\theta$$

the Debye approximation $\omega_q = v_S q$. Using the Bohm-Staver speed of (Eq. 17-23 with $r_c = 0$)

$$\frac{2}{\omega_q} = \frac{4\pi Z e^2 q^2}{M \Omega_0 k} = \frac{Z^2 e^2 q^2}{M m \Omega_0 k_F}$$

We may also relate the volume per atom, Ω_0 , to the Fermi wavevector. Then we obtain finally

$$\lambda = \frac{9}{16} \int \left(\frac{w_q}{E_F} \right)^2 \sin\theta d\theta$$

$$= \frac{9}{16 E_F^2 k_F^2} \int w_q^2 q dq$$

$$\lambda = \frac{9}{8 A_{FS}} \int \left(\frac{w_q}{E_F} \right)^2 dA_{FS}$$

CHAPTER 18. PSEUDOPOTENTIAL THEORY OF COVALENT BONDING

To me this is the most beautiful and unfriendly subject discussed in this text, and yet it is one of the most difficult to absorb and it has little direct application; Problem 18-2 gives one of the few. It is perfectly reasonable to give the main point in class and let the interested student read what he likes of it. The central point is that one can understand the band structure of covalent solids in terms of pseudopotentials and, of course, the accurate structures we gave in Fig. 6-1 were obtained that way. If one then seeks to extract the essential features, in analogy with our LCAO theory of covalent solids, one finds a semiquantitative identification of the pseudopotential form factors with the interatomic matrix element, V_2 , and of the kinetic energy with the atomic sp-splitting. Then by comparison of the metal-covalent transition shown in Fig. 2-3 we see that in the metal it was appropriate to treat the pseudopotential as a perturbation; i.e., as small compared to E_F just as the interatomic matrix element is small compared to the sp-splitting. However, in the covalent solid it is just the reverse and the interatomic matrix element dominates. The corresponding point of view which can simplify the understanding here is the making of an expansion in the ratio of the kinetic energy to the pseudopotential. The dielectric and bonding properties are then understood even in zero order. In this context the d^2 dependence of the covalent energy and other interatomic matrix elements becomes understandable. This treatment of properties also suggests some quite different interpretations than are prevalent, such as independent physical origins of such properties as charge localization in bonds and tetrahedral stabilization. Finally, it provides an alternative approach to the calculation of the entire range of properties of covalent solids. In most cases it seems less promising than the LCAO approach, but there may be others where it is preferable. Section 18-A is a separate issue, and deserves special note.

Problem 18-1. Optical mode frequencies

(a) The pseudopotential matrix element was given for arbitrary $\vec{\tau}$ in Eq. 18-2. It is straightforward to evaluate the magnitude of $|W_{111}|$ as

$$|W_{111}| = \left(\frac{w_q^2 + w_q^2}{4} + \frac{w_q^2 \cos \vec{\tau} \cdot \vec{\tau}}{2} \right)^{1/2} \quad (\text{A})$$

where \vec{q} of course is [111] $2\pi/a$. The special case of the undistorted crystal corresponds to $\vec{q} \cdot \vec{\tau} = \pi/2$ and gives Eq. 18-3. We may square both of the Eqs. 18-5 and rewrite the above expression in terms of V_2 and V_3 , obtaining

$$|W_{111}| = \left(V_2^2 + V_3^2 + (V_2 - V_3)^2 \cos \vec{\tau} \cdot \vec{\tau} \right)^{1/2} \quad (\text{B})$$

that the next-to-last form can be written as

$\vec{q} \cdot \vec{\tau}$ becomes $\pm \frac{1}{2}\pi + \vec{q} \cdot \vec{u} + 0(\vec{u}^3)$. We may then expand the expression for W_{111} to second order in $\vec{q} \cdot \vec{u}$ and average over all; the first-order term vanishes and the second becomes

$$- |W_{111}|^{(2)} = + \frac{1}{8} \frac{(v_2^2 - v_3^2)^2}{(v_2^2 + v_3^2)^{3/2}} \frac{q_u^2}{3} \quad (\text{C})$$

is the increase in energy per electron. We multiply by eight to obtain the energy per atom pair and equate it to the kinetic energy atom pair,

$$2 \times \frac{1}{2} M \left(\frac{u}{2} \right)^2 .$$

in

$$\omega^2 = \frac{4}{3M} \frac{(v_2^2 - v_3^2)^2}{(v_2^2 + v_3^2)^{3/2}} q^2$$

in $q = 12\pi^2/a^2 = 9\pi^2/(2d^2)$. For Ge

$$\omega^2 = \frac{6\pi^2 v_2^2}{Md^2} = \frac{6\pi^2 2.76 \times 1.6 \times 10^{-12} \text{ erg}}{72.6 \times 1.67 \times 10^{-24} g(2.44)^2 \times 10^{-16} \text{ cm}^2}$$

$\omega = 0.60 \times 10^{14}$ radians per second in remarkable agreement with experimental 0.56×10^{14} radians per second. For GaAs we used $v_2 = 2.74$ eV and $v_3 = 1.51$ eV from Table 4-1 though other values are acceptable since in other factors we neglect changes in reduced mass and bond length. The v_2 above is replaced by 0.89 eV leading a frequency of 0.34×10^{14} radians per second, considerably less than the observed 0.509×10^{14} . It is interesting that the dependence upon polarity comes out quite differently in the pseudopotential approach.

) For the rocksalt structure we found $\vec{q} \cdot \vec{\tau}$ equals π so (B) above becomes

$$W_{111} = \left(v_2^2 + v_3^2 - (v_2^2 - v_3^2) \cos \vec{q} \cdot \vec{u} \right)^{\frac{1}{2}} = \left(2v_3^2 - \frac{1}{2}(v_2^2 - v_3^2)(\vec{q} \cdot \vec{u})^2 \right)^{\frac{1}{2}}$$

lowest order in u . The second-order term, analogous to Eq. (C) above, becomes

$$- |W_{111}|^{(2)} = \frac{2^{1/2}(v_3^2 - v_2^2)}{8V_3} \frac{q_u^2}{3}$$

The rocksalt structure also is stabilized by pseudopotential terms as long as $v_3 > v_2$ or $\alpha_p > 0.71$. We have not explored this further.

Problem 18-2. Metal-semiconductor contact

In Section 18G we calculated the valence-band minimum relative to a "universal" Fermi energy which we take to be the metal Fermi energy also. We then added the band width to obtain the valence band maximum relative to this energy. Finally we subtracted 7.60 eV to set the energy scale relative to the LCAO scale. We need simply add that back to obtain the required result, a rather trivial exercise. Below we compare the Fermi energy relative to the valence band maximum, and compare with $E_g/3$, all in eV.

	$E_F - E_V$	$E_g/3$
Si	3.17	0.38
Ge	1.52	0.25
Sn	-0.03	0.00
GaAs	1.48	0.51
ZnSe	2.75	0.94

The final two chapters are on huge topics, huge because of the number of systems represented and the variety of behavior; we see only the tip of the iceberg. The compounds are simpler and are fore discussed first. They are mostly insulating, corresponding to all empty bands, and it is clear that an LCAO description is appropriate. Furthermore, it seems clear that the perturbation approach including ion softening and the chemical grip is the best for the calculation of properties. The principal matrix elements which enter are sd- and pd-matrix elements and the systematics of estimating these has just recently become clear. The analysis of given in Section 20-E, is the first published account of this.

Given in Eq. 19-11 and the coefficients were obtained, as other interatomic matrix elements, by fitting known energy bands. Choice of solid state term values is not so simple nor well systematized.

We divide the compounds into systems in which the d-electrons are localized, frozen out on the ions, and those in which there are well-coupled d-bands. These require different descriptions, but both are compounds in just the sense discussed in Chapters 13 and 14.

Consist to a first approximation of spherical ions held together electrostatic forces which are balanced by an overlap interaction. Discuss the properties of the transition metal monoxides in terms of electronic structure.

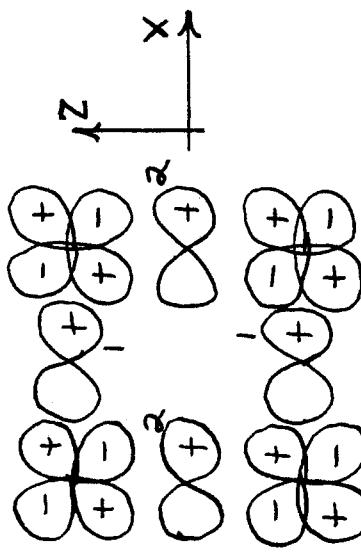
In the transition-metal compounds the deviations from the ideal independent picture are larger than for the alkali halides. We their treatment much further — here for the perovskite structures. These deviations arise from matrix elements between orbitals, which are neglected in the free-ion picture. Some of the orbitals involved are d-state orbitals which provides a variety of behavior. I believe that this approach will turn out to be better than various unformulated sd-hybrid or partially covalent concepts one occasionally hears mentioned. The concept of the chemical fourth-order in the interatomic matrix elements, and its comparison with the leading bonding term, second-order in these matrix elements, is new, easy to understand, and easy to estimate. These current effects are frequently confused as is their role in the stability of structures so that it seems to me important to discuss carefully, making contact with the corresponding effects in the ionic solids which we already understand.

Problem 19-1. Perovskite bands

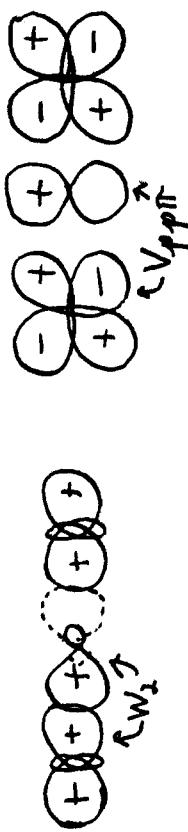
The orbital diagram is given on the following page. There are p_x -orbitals out of (and into) the plane of the figure from the states; they are numbered 3. The matrix element between states p_2 and p_3 is called V_{pp} ; that between p_2 and p_3 is taken zero. The wavenumber lies along the z-axis. Then the Hamiltonian matrix becomes:

$$H = \begin{pmatrix} d & \epsilon_d & 0 & 2iV_{pd\pi} \sin kd & 0 \\ p_1 & 0 & \epsilon_p & 4V_{pp} \cos kd & 0 \\ p_2 & -2iV_{pd\pi} \cos kd & 4V_{pp} \cos kd & \epsilon_p & 4V_{pp} \cos kd \\ p_3 & 0 & 0 & 4V_{pp} \cos kd & \epsilon_p \end{pmatrix}$$

At Γ , $kd = 0$ and the $\sin kd$ matrix element drops out so the d-state is uncoupled and its eigenvalue is ϵ_d . The secular equation for the remaining three-by-three is written down immediately, $(\epsilon_p - E)^3 - 32(\epsilon_p - E)V_{pp}^2 = 0$ giving the other values in Eq. 19-8. At X , $kd = \pi/2$ and all $\cos kd$ matrix elements vanish. Two levels with energy ϵ_p become uncoupled and the other two solutions of Eq. 19-9 are obtained by solving the remaining two-by-two.



Problem 19-2. Transverse charge in the perovskites



We begin with the σ -electrons, shown to the left above. The leftward pointing sp-hybrid on the oxygen is coupled to the d-state

W_2 . The two spin-states thus transfer $2(W_2/2W_3)^2$ electrons to the left. (Adding the corresponding transfer to the right led to the of Eq. 19-16.) Moving the oxygen ion a distance u to the right induces W_2 by $\eta W_2 u/d$ and therefore transfers $-\eta(W_2/W_3)u/d$ electrons back to the oxygen. Similarly it transfers this number of electrons to the titanium to the right, a total distance of $2d$, and thus contributes $-2\eta(W_2/W_3)^2$ to the transverse charge.

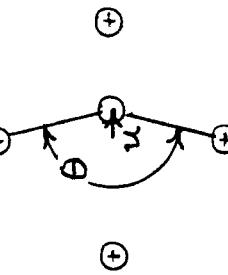
The same analysis may be applied to the π -states to the right above. Note that the sign of the matrix element is irrelevant. There are twice as many π -states as s -states, W_2 is replaced by $V_{pd\pi}$, and the energy difference $2W_3$ by $\epsilon_d - \epsilon_p$. Combining the corrections and using parameters for SrTiO_3 from Tables 19-3 and 19-4 we obtain

$$\begin{aligned} e_T^* &= Z^* - 2\eta(W_2/W_3)^2 - 16\eta V_{pd\pi}^2 / (\epsilon_d - \epsilon_p)^2 \\ &= 1.65 + 2.48 + 4.76 = 8.89 \end{aligned}$$

The chemical grip based upon s -states is of course a constant and upon the Cl p -states is proportional to the sum over angles of $\cos^2 \theta_{\alpha\beta}$ or in this case

$$\sum_{\alpha>\beta} \cos^2 \theta_{\alpha\beta}$$

$$= 2(1 - 4u^2/d^2) + 8u^2/d^2 = 2$$



We move the chlorine ions to the right by a distance u with respect to the sodium ions, as indicated above. We look at the angles θ of the three that are 180° in the undistorted crystal, two change by $\delta\theta = 2u/d$. Of the twelve that are 90° in the undistorted crystal, eight change by $\delta\theta = u/d$. To second order in u the 180° angles give $\cos^2 \theta_{\alpha\beta} = 1 - 4u^2/d^2$ and the 90° angles give $\cos^2 \theta_{\alpha\beta} = 2u^2/d^2$. The same applies to the angles at the sodium.

The chemical grip based upon s -states is of course a constant and upon the Cl p -states is proportional to the sum over angles of $\cos^2 \theta_{\alpha\beta}$ or in this case

$$\sum_{\alpha>\beta} \cos^2 \theta_{\alpha\beta} = 2(1 - 4u^2/d^2) + 8u^2/d^2 = 2$$

also independent of u to second order. Thus the grip does not contribute to the optical mode frequency in NaCl .

SUMMARY

There is some difficulty in the organization of this chapter, partly because the use of transition metal pseudopotentials as described in Section E was only developed as the book went to press. A more convenient ordering of material might be to present the transition pseudopotential theory first, giving derivations of the form and values for the interatomic matrix elements and the free-electron effective mass m_s , and then to proceed with the bands as in Section A. That would not do justice to Muffin Tin Orbital theory which had produced many of the central results earlier nor would it present at the beginning the rationale for Andersen's form of the muffin-tin potential which was essential to the use of transition metal pseudopotentials. Finally, the LCAO description of the free-electron bands, used in Section A, was necessary to the extraction of the matrix elements $V_{pd\pi}$ from pseudopotential theory. I would nevertheless suggest lecturing on the pseudopotential first if the students can accommodate to the rearrangement.

The calculation of bands in a transition metal as in Section A is quite impressive. Problem 20-1 will be quite informative if the students have the time and ability to carry it through. After describing the bands the text follows one case through with qualitative discussions of the Fermi surface (Figs. 20-5 and 20-6) and the density of states (Fig. 20-7). I think it is nice to match up the bands and the Fermi surface as in Fig. 20-5 to see the origin of the well known "jack" Fermi surface, familiar in connection with the antiferromagnetism of chromium. We note in Fig. 20-7 the familiar two-peak density of states characteristic of the bcc structure, contrasted with the more uniform density of states of the hcp structure (Fig. 20-8a).

The Friedel model, Fig. 20-8b extracts the central features of the electronic structure and the calculation of Z_s in Problem 20-3 should cement that understanding. It may be adequate to mention the central features of the Muffin Tin Orbital Theory, Atomic Sphere Approximation, and the theory of d-state resonances; a student can return to these later if he needs those formulations. The discussion makes contacts with the many treatments of transition metals currently being used and relates them to each other.

The final section on ferromagnetism and the formation of local moments is a piece of traditional solid state physics which fits well here and complements the rest of the chapter, the local moment theory depending directly on the resonance description. However, it also can be passed over if time is running out.

Problem 20-1. Band calculation for nickel

We again take the wavenumber along the z -axis. Then in each Bloch sum the states on four neighbors have phase $e^{ikz}/2$ relative to a given atom, four have phase 1, and four have phase $e^{-ikz}/2$. We begin again with the uncoupled state of symmetry zx , and using the expression $E_{zx,zx}$ we used for body-centered cubic structures (again dropping $V_{dd\delta}$)

ain for the various neighbors the $E_{zx, zx}$ shown below:

n	$E_{zx, zx}$	Phase	$E_{xy, xy}$	$E_{x^2-y^2, x^2-y^2}$
$-1/2$	$\frac{1}{2} V_{dd\pi}$	$e^{ika/2}$	$\frac{1}{2} V_{dd\pi}$	$\frac{3}{16} V_{dd\sigma} + \frac{1}{4} V_{dd\pi}$
0	$\frac{3}{4} V_{dd\sigma}$	$e^{ika/2}$	$\frac{1}{2} V_{dd\pi}$	$\frac{3}{16} V_{dd\sigma} + \frac{1}{4} V_{dd\pi}$
$-1/2$	$\frac{1}{2} V_{dd\pi}$	1	$\frac{3}{4} V_{dd\sigma}$	$V_{dd\pi}$
$-1/2$	$\frac{1}{2} V_{dd\pi}$	$e^{-ika/2}$	$\frac{1}{2} V_{dd\pi}$	$\frac{3}{16} V_{dd\sigma} + \frac{1}{4} V_{dd\pi}$
0	$\frac{3}{4} V_{dd\sigma}$	$e^{ika/2}$	$\frac{1}{2} V_{dd\pi}$	$\frac{3}{16} V_{dd\sigma} + \frac{1}{4} V_{dd\pi}$
$-2^{-1/2}$	$\frac{1}{2} V_{dd\pi}$	1	$\frac{3}{4} V_{dd\sigma}$	$V_{dd\pi}$

Other six neighbors with all direction cosines of opposite sign have the same $E_{zx, zx}$, but the phase factors are the complex conjugates of these. Summing the contributions to $H_{\alpha\alpha}$ for the twelve neighbors (and the central atom itself) gives

$$E_k^S = \epsilon_d + 3V_{dd\sigma} \cos \frac{ka}{2} + 2V_{dd\pi} \left(1 + \cos \frac{ka}{2} \right)$$

Energy for yz is identical. For the d-state of symmetry xy we listed above and sum them to obtain in the $E_{xy, xy}$

$$E_k^2 = \epsilon_d + 3V_{dd\sigma} \cos \frac{ka}{2} + 4V_{dd\pi} \cos \frac{ka}{2}$$

Similarly for the $x^2 - y^2$ form we obtain

$$E_k^2 = \epsilon_d + \frac{3}{2} V_{dd\sigma} \cos \frac{ka}{2} + 2V_{dd\pi} \left(2 + \cos \frac{ka}{2} \right)$$

For the coupled states, s and $3z^2 - r^2$ we obtain in the same (requiring three more columns in a table as above)

$$E_k^d = \epsilon_d + V_{dd\sigma} \left(1 + \frac{1}{2} \cos \frac{ka}{2} \right) + 2V_{dd\pi} \cos \frac{ka}{2}$$

$$E_k^s = \epsilon_s + 4V_{ss} \left(2 \cos \frac{ka}{2} + 1 \right) \quad (\text{and we take } \epsilon_s = \epsilon_d)$$

$$E_k^{sd} = 2V_{sdd} \left(\cos \frac{ka}{2} - 1 \right)$$

The same solution of the quadratic equation given in the text obtains with these new values of E_k^s , E_k^d , and E_k^{sd} . Note the value at $\Gamma(1=0)$ are $\Gamma_1 = \epsilon_d - 12 V_{ss}$, $\Gamma_{25} = \epsilon_d + 3V_{dd\sigma} + 4V_{dd\pi}$, and $\Gamma_{12} = \epsilon_d + 3/2 V_{dd\sigma} + 6V_{dd\pi}$.

For nickel we obtain from the Solid State Table $r_o = 1.38\text{\AA}$, $r_d = 0.71$, and $k_d = 1.22$. For an fcc structure the unit (of edge a) contains four atoms so $4\pi r_o^3 / 3 = a^3/4$ or $a = 3.53$ and $d = a/\sqrt{2} = 2.50\text{\AA}$. Thus $h_{rd}/md^5 = 0.0281 \text{ eV}^{so}$, $V_{dd\sigma} = -0.46 \text{ eV}$, $V_{dd\pi} = 0.25 \text{ eV}$, $V_{sdd} = -0.59 \text{ eV}$ (from $h^2 r_d^7 / 2 \text{ md}^7 / 2 = 0.1856 \text{ eV}^{so}$). Finally,

$$E_d = \frac{\hbar^2}{2m} k_d^2 \left(1 + \frac{5r_d^3}{4\pi r_o^3} \right) = 6.90 \text{ eV} \quad \text{or} \quad V_{ss} = -0.56 \text{ eV} .$$

The plot in Fig. 20-4 was based on a slightly different set of matrix elements ($V_{dd\pi} = 0.24 \text{ eV}$, $V_{dd\sigma} = -0.48 \text{ eV}$, $V_{sdd} = -0.53 \text{ eV}$, $V_{ss} = -0.56 \text{ eV}$) and gave $\Gamma_1 = -6.81$, $\Gamma_{25} = 0.72$, $X_1 = -2.60$, $X_3 = -2.40$, $X_2 = 1.20$, $X_5 = 1.44$ and X_1 (corresponding to the X_4 p-like state of Fig. 20-4) = 3.19, all in eV relative to ϵ_d . The difference in the two sets of values is of the order of the line thicknesses in the figure.

Problem 20-2. Equilibrium density of rare earths

Summing Eq. 15-16 with respect to k_F we obtain

$$\frac{\partial E_{\text{tot}}}{\partial k_F} = \frac{3Z \hbar^2 k_F}{5m} + \frac{2Zr_c^2 k_F^2 e}{\pi} - \frac{3ze^2}{4\pi} - \frac{Z^2 \alpha e^2}{(18\pi Z)^{1/3}} = 0$$

With $Z = 3$, $r_c = 0.83\text{\AA}$ and $\alpha = 1.79$ we have in eV:

$$18.95 k_F^2 + 13.72 k_F - 52.27 = 0$$

or $k_F = 1.34 \text{ \AA}^{-1}$. Thus $r_o = (9\pi Z/4)^{1/3}/k_F$ (from the Solid State Table) = 2.07\AA , in reasonable agreement with the observed $r_o = 2.02\text{\AA}$ from the Solid State Table.

Problem 20-3. Number of free electrons in transition metals

$$Z_S = \int_0^{E_F} n_s(E) dE = \frac{4}{9\pi} \left(\frac{2m r_o^2}{\hbar^2} \right)^{3/2} E_F^{3/2} \quad (1)$$

The d bands contain 10 electrons per atom and are filled to E_F with the bottom of the d bands at $E_d - W_d/2$. (See Fig. 20-14.) Thus

$$E_d = 10(E_F - E_d + W_d/2)/W_d \quad (2)$$

than -1 at the crossing ($n^+ = n^- = 5/2$) , as in part a of the figure, no moment will form. If it is less than -1, the curves cross in such a way as to give three solutions. (Even without identifying the curves we can see that $dn^+/dn^- = -1$ is the critical value.)

Taking a derivative of the above equation with respect to n^- ,

$$-\frac{1}{\sin^2(m/5)} \frac{\pi}{5} \frac{dn^+}{dn^-} = \frac{2U_x}{\Gamma}$$

$$Z_d = 6 - Z_s \quad (4)$$

To iterate we start with $Z_s = 1$, then obtain (Cr is D6)

$$E_F = E_d - \frac{W_d}{2} + \frac{Z_d W_d}{10} \quad (3)$$

Substitute in (3) , then substitute this E_F in (1) to obtain $Z_s = 36$. Continued iteration gives: 0.760, 0.758, 0.758. The answer is 0.758.

The needed parameters were obtained in terms of $r_d = 0.90\text{\AA}$, $= 1.22 \text{\AA}^{-1}$, and $r_o = 1.42\text{\AA}$ and

$$\frac{m_s}{m} = \left(1 + \frac{5r_d^3}{\pi r_o^3} \right)^{-1} = 0.71$$

$$W_d = 6.83 \frac{\hbar^2 r_d^3 / (mr_o^5)}{2m_s} = 6.57$$

$$E_d = \frac{\hbar^2}{2m_s} k_d^2 = 7.97$$

$$\frac{4}{9\pi} \left(\frac{2m_s r_o^2}{\hbar^2} \right)^{3/2} = 0.0327$$

If U_x is larger, a moment forms. Tables 20-4 and 20-5 give $U_x/\Gamma = (0.64/1.82) = 0.35$ for chromium, greater than the critical ratio of 0.314. It does predict the local moment.

Problem 20-4. Criterion for formation of local moments

$$\text{Setting } E_d^0 + 5U_x/2 = E_F \text{ in Eq. 20-59 gives} \\ \tan \left(\frac{\pi m^+}{5} \right) = \frac{\Gamma}{2U_x(n^- - 5/2)}$$

Reciprocals give

$$\cot \left(\frac{\pi m^+}{5} \right) = \frac{2U_x(n^- - 5/2)}{\Gamma}$$

or $n^+ = n^- = 5/2$, both sides are zero, for a solution.

From Fig. 20-20 we may identify the curve going to finite n^+ as goes to zero with the above equation. If dn^+/dn^- is greater