Chapter 1: Chemical Bonding

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Contents

Periodic Table

Group	Element	Atomic No.	Name	Atomic Weight
1	H	1	Hydrogen	1.008
18	He	2	Helium	4.003
1	Li	3	Lithium	6.941
2	Be	4	Beryllium	9.012
13	B	5	Boron	10.811
14	C	6	Carbon	12.011
15	N	7	Nitrogen	14.007
16	O	8	Oxygen	15.999
17	F	9	Fluorine	18.998
18	Ne	10	Neon	20.180
1	Na	11	Sodium	22.990
2	Mg	12	Magnesium	24.305
13	Al	13	Aluminum	26.982
14	Si	14	Silicon	28.086
15	P	15	Phosphorous	30.974
16	S	16	Sulfur	32.066
17	Cl	17	Chlorine	35.453
18	Ar	18	Argon	39.948
1	K	19	Potassium	39.098
2	Ca	20	Calcium	40.078
3	Sc	21	Scandium	44.956
4	Ti	22	Titanium	47.88
5	V	23	Vanadium	50.942
6	Cr	24	Chromium	51.996
7	Mn	25	Manganese	54.938
8	Fe	26	Iron	55.847
9	Co	27	Cobalt	58.933
10	Ni	28	Nickel	58.69
11	Cu	29	Copper	63.546
12	Zn	30	Zinc	65.39
13	Ga	31	Gallium	69.723
14	Ge	32	Germanium	72.61
15	As	33	Arsenic	74.922
16	Se	34	Selenium	78.96
17	Br	35	Bromine	79.904
18	Kr	36	Krypton	83.80
1	Rb	37	Rubidium	85.468
2	Sr	38	Strontium	87.62
3	Y	39	Yttrium	88.906
4	Zr	40	Zirconium	91.224
5	Nb	41	Niobium	92.906
6	Mo	42	Molybdenum	95.94
7	Tc	43	Technetium	(98)
8	Ru	44	Ruthenium	101.07
9	Rh	45	Rhodium	102.906
10	Pd	46	Palladium	106.42
11	Ag	47	Silver	107.868
12	Cd	48	Cadmium	112.411
13	In	49	Indium	114.82
14	Sn	50	Tin	118.71
15	Sb	51	Antimony	121.75
16	Te	52	Tellurium	127.60
17	I	53	Iodine	126.905
18	Xe	54	Xenon	131.29
1	Cs	55	Caesium	132.905
2	Ba	56	Barium	137.327
3	Lu	71	Lutetium	174.967
4	Hf	72	Halfnium	178.49
5	Ta	73	Tantalum	180.948
6	W	74	Tungsten	183.85
7	Re	75	Rhenium	186.207
8	Os	76	Osmium	190.2
9	Ir	77	Iridium	192.22
10	Pt	78	Platinum	195.08
11	Au	79	Gold	196.967
12	Hg	80	Mercury	200.59
13	Tl	81	Thallium	204.383
14	Pb	82	Lead	207.2
15	Bi	83	Bismuth	208.980
16	Po	84	Polonium	(209)
17	At	85	Astatine	(210)
18	Rn	86	Radon	(222)
1	Fr	87	Francium	(223)
2	Ra	88	Radium	226.025
3	Lr	103	Lawrencium	(260)

Lanthanides

Element	Atomic No.	Name	Atomic Weight
La	57	Lanthanum	138.906
Ce	58	Cerium	140.115
Pr	59	Praseodymium	140.908
Nd	60	Neodymium	144.24
Pm	61	Promethium	(145)
Sm	62	Samarium	150.36
Eu	63	Europium	151.965
Gd	64	Gadolinium	157.25
Tb	65	Terbium	158.925
Dy	66	Dysprosium	162.50
Ho	67	Holmium	164.93
Er	68	Erbium	167.26
Tm	69	Thulium	168.934
Yb	70	Ytterbium	173.04

Actinides

Element	Atomic No.	Name	Atomic Weight
Ac	89	Actinium	227.028
Th	90	Thorium	232.038
Pa	91	Protactinium	231.036
U	92	Uranium	238.029
Np	93	Neptunium	237.048
Pu	94	Plutonium	(244)
Am	95	Americium	(243)
Cm	96	Curium	(247)
Bk	97	Berkelium	(247)
Cf	98	Californium	(251)
Es	99	Einsteinium	(252)
Fm	100	Fermium	(257)
Md	101	Mendelevium	(258)
No	102	Nobelium	(259)

Solid state physics is the study of mainly periodic systems (or things that are close to periodic) in the thermodynamic limit $\approx 10^{21}$ atoms/cm^3. At first this would appear to be a hopeless task, to solve such a large system.
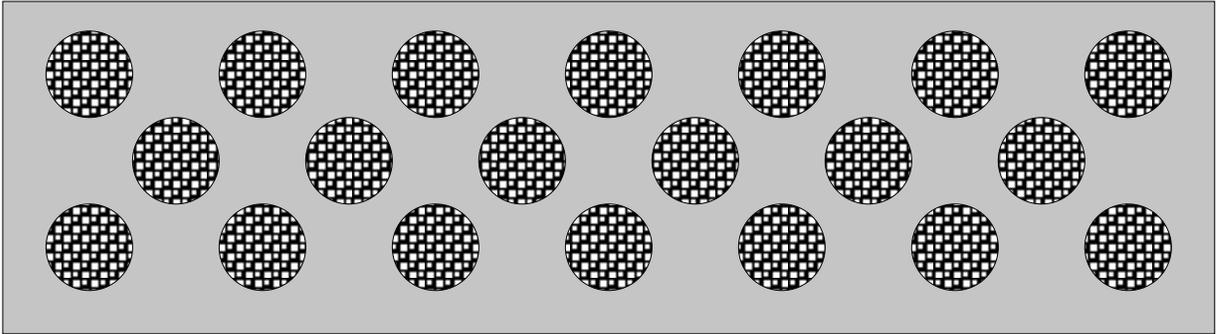
Figure 1: *The simplest model of a solid is a periodic array of valance orbitals embedded in a matrix of atomic cores.*

However, the self-similar, translationally invariant nature of the periodic solid and the fact that the core electrons are *very* tightly bound at each site (so we may ignore their dynamics) makes approximate solutions possible. Thus, the simplest model of a solid is a periodic array of valance orbitals embedded in a matrix of atomic cores. Solving the problem in one of the irreducible elements of the periodic solid (cf. one of the spheres in Fig. 1), is often equivalent to solving the whole system. For this reason we must study the periodicity and the mechanism (chemical bonding) which binds the lattice into a periodic structure. The latter is the emphasis of this chapter.

1 The development of Bands and their filling

nl	elemental solid
1s	H,He
2s	Li,Be
2p	B→Ne
3s	Na,Mg
3p	Al→Ar
4s	K,Ca
3d	transition metals Sc→Zn
4p	Ga→Kr
5s	Rb,Sr
4d	transition metals Y→Cd
5p	In-Xe
6s	Cs,Ba
4f	Rare Earths (Lanthanides) Ce→Lu
5d	Transition metals La→Hg
6p	Tl→Rn

Table 1: *Orbital filling scheme for the first few atomic orbitals*

We will imagine that each atom (cf. one of the spheres in Fig. 1) is composed of Hydrogenic orbitals which we describe by a screened

Coulomb potential

$$V(r) = \frac{-Z_{nl}e^2}{r} \tag{1}$$

where Z_{nl} describes the effective charge seen by each electron (in principle, it will then be a function of n and l). As electrons are added to the solid, they then fill up the one-electron states 1s 2s 3s 3p 3d 4s 4p 4d 4f$\cdots$, where the correspondence between spdf and l is $s \rightarrow l = 0$, $p \rightarrow l = 1$, etc. The elemental solids are then made up by filling these orbitals systematically (as shown in Table 1) starting with the lowest energy states (where $E_{nl} = \frac{me^4 Z_{nl}^2}{2\hbar^2 n^2}$

Note that for large n, the orbitals do not fill up simply as a function of n as we would expect from a simple Hydrogenic model with $E_n = \frac{mZ^2 e^4}{2\hbar^2 n^2}$ (with all electrons seeing the same nuclear charge Z). For example, the 5s orbitals fill *before* the 4d! This is because the situation is complicated by atomic screening. I.e. s-electrons can sample the core and so are not very well screened whereas d and f states face the angular momentum barrier which keeps them away from the atomic core so that they feel a potential that is screened by the electrons of smaller n and l. To put is another way, the effective Z_{5s} is larger than Z_{4d}. A schematic atomic level structure, accounting for screening, is shown in Fig. 2.

Now let's consider the process of constructing a periodic solid. The simplest model of a solid is a periodic array of valence orbitals embedded in a matrix of atomic cores (Fig. 1). As a simple model of how
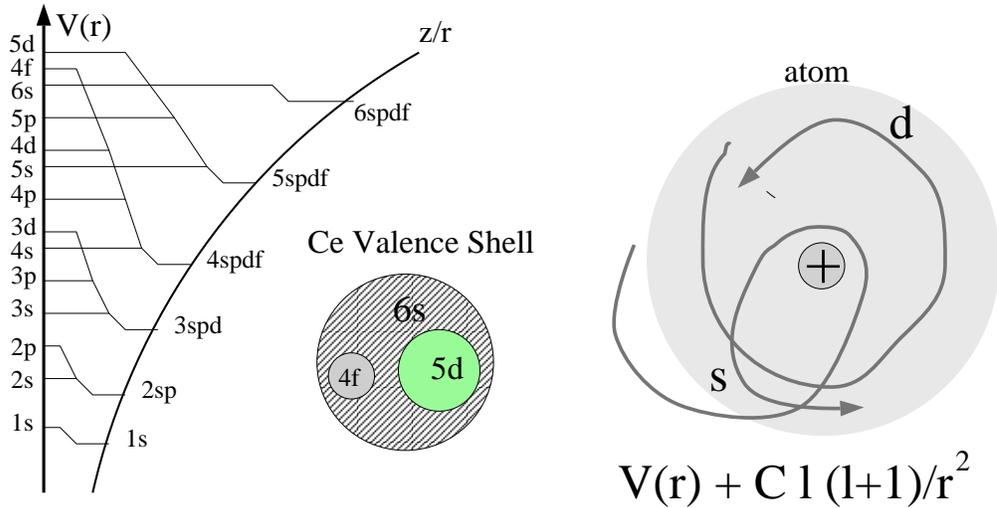
Figure 2: *Level crossings due to atomic screening. The potential felt by states with large l are screened since they cannot access the nucleus. Thus, orbitals of different principle quantum numbers can be close in energy. I.e., in elemental Ce, $(4f^1 5d^1 6s^2)$ both the 5d and 4f orbitals may be considered to be in the valence shell, and form metallic bands. However, the 5d orbitals are much larger and of higher symmetry than the 4f ones. Thus, electrons tend to hybridize (move on or off) with the 5d orbitals more effectively. The Coulomb repulsion between electrons on the same 4f orbital will be strong, so these electrons on these orbitals tend to form magnetic moments.*

the eigenstates of the individual atoms are modified when brought together to form a solid, consider a pair of isolated orbitals. If they are far apart, each orbital has a Hamiltonian $H_0 = \epsilon n$, where n is the orbital occupancy and we have ignored the effects of electronic correlations (which would contribute terms proportional to $n_\uparrow n_\downarrow$). If we bring them together so that they can exchange electrons, i.e. hybridize, then the degeneracy of the two orbitals is lifted. Suppose the system can gain

Figure 3: *Two isolated orbitals. If they are far apart, each has a Hamiltonian $H_0 = \epsilon n$, where n is the orbital occupancy.*
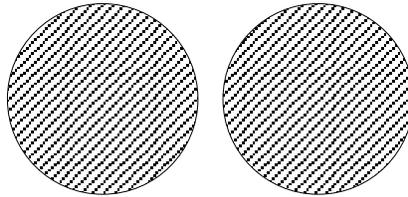
Figure 4: *Two orbitals close enough to gain energy by hybridization. The hybridization lifts the degeneracy of the orbitals, creating bonding and antibonding states.*

an amount of energy t by moving the electrons from site to site (Our conclusions will not depend upon the sign of t. We will see that t is proportional to the overlap of the atomic orbitals). Then

$$H = \epsilon(n_1 + n_2) - t(c_1^\dagger c_2 + c_2^\dagger c_1).\qquad(2)$$

where c_1 ($c_1^\dagger$) destroys (creates) an electron on orbital 1. If we rewrite this in matrix form

$$H = \left(c_1^\dagger, c_2^\dagger\right) \begin{bmatrix} \epsilon & -t \\ -t & \epsilon \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}\qquad(3)$$

then it is apparent that system has eigenenergies $\epsilon \pm t$. Thus the two states split their degeneracy, the splitting is proportional to $|t|$, and they remain centered at ϵ

If we continue this process of bringing in more isolated orbitals into the region where they can hybridize with the others, then a band of states is formed, again with width proportional to t, and centered around ϵ (cf. Fig. 5). This, of course, is an oversimplification. Real
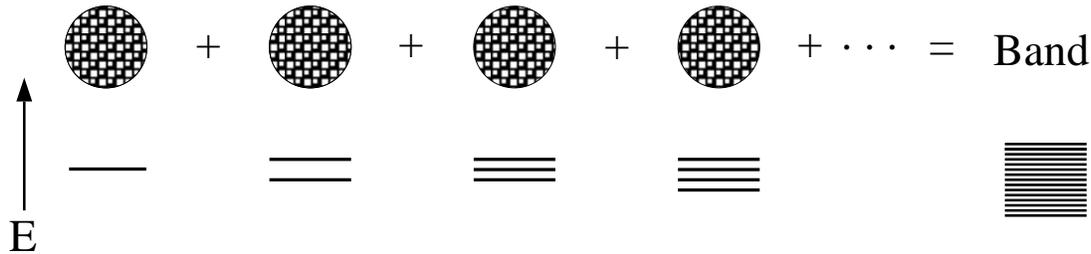
Figure 5: *If we bring many orbitals into proximity so that they may exchange electrons (hybridize), then a band is formed centered around the location of the isolated orbital, and with width proportional to the strength of the hybridization*

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solids are composed of elements with multiple orbitals that produce multiple bonds. Now imagine what happens if we have several orbitals on each site (ie s,p, etc.), as we reduce the separation between the orbitals and increase their overlap, these bonds increase in width and may eventually overlap, forming bands.

The valance orbitals, which generally have a greater spatial extent, will overlap more so their bands will broaden more. Of course, eventually we will stop gaining energy ($\tilde{t}$) from bringing the atoms closer together, due to overlap of the cores. Once we have reached the optimal

point we fill the states 2 particles per, until we run out of electrons. Electronic correlations complicate this simple picture of band formation since they tend to try to keep the orbitals from being multiply occupied.

2   Different Types of Bonds

These complications aside, the overlap of the orbitals is bonding. The type of bonding is determined to a large degree by the amount of overlap. Three different general categories of bonds form in solids (cf. Table 2).

Bond	Overlap	Lattice	constituents
Ionic	very small ($< a$)	closest unfrustrated packing	dissimilar
Covalent	small ($\sim a$)	determined by the structure of the orbitals	similar
Metallic	very large ($\gg a$)	closest packed	unfilled valence orbitals

Table 2: *The type of bond that forms between two orbitals is dictated largely by the amount that these orbitals overlap relative to their separation a.*

2.1 Covalent Bonding

Covalent bonding is distinguished as being orientationally sensitive. It is also short ranged so that the interaction between nearest neighbors is of prime importance and that between more distant neighbors is often neglected. It is therefore possible to describe many of its properties using the chemistry of the constituent molecules.

Consider a simple diatomic molecule O_2 with a single electron and

$$H = -\frac{\nabla^2}{2m} - \frac{Ze^2}{r_a} - \frac{Ze^2}{r_b} + \frac{Z^2e^2}{R} \tag{4}$$

We will search for a variational solution to the the problem of the molecule ($H\Psi_{mol} = E\Psi_{mol}$), by constructing a variational wavefunction from the atomic orbitals ψ_a and ψ_b. Consider the variational molecular wavefunction

$$\Psi' = c_a\psi_a + c_b\psi_b \tag{5}$$

$$E' = \frac{\int \Psi'^* H \Psi'}{\int \Psi'^* \Psi'} \geq E \tag{6}$$

The best Ψ' is that which minimizes E'. We now define the quantum integrals

$$S = \int \psi_a^* \psi_b \quad H_{aa} = H_{bb} = \int \psi_a^* H \psi_a \quad H_{ab} = \int \psi_a^* H \psi_b . \tag{7}$$

Note that $1 > S_r > 0$, and that $H_{abr} < 0$ since ψ_a and ψ_b are bound states [where $S_r = \mathrm{Re} S$ and $H_{abr} = \mathrm{Re} H_{ab}$]b. With these definitions,

$$E' = \frac{(c_a^2 + c_b^2)H_{aa} + 2c_a c_b H_{abr}}{c_a^2 + c_b^2 + 2c_a c_b S_r} \tag{8}$$

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and we search for an extremum $\frac{\partial E'}{\partial c_a} = \frac{\partial E'}{\partial c_b} = 0$. From the first condition, $\frac{\partial E'}{\partial c_a} = 0$ and after some simplification, and re-substitution of E' into the above equation, we get the condition

$$c_a(H_{aa} - E') + c_b(H_{abr} - E'S_r) = 0 \qquad (9)$$

The second condition, $\frac{\partial E'}{\partial c_b} = 0$, gives

$$c_a(H_{abr} - E'S) + c_b(H_{aa} - E') = 0 \,. \qquad (10)$$

Together, these form a set of secular equations, with eigenvalues

$$E' = \frac{H_{aa} \pm H_{abr}}{1 \pm S_r} \,. \qquad (11)$$

Remember, $H_{abr} < 0$, so the lowest energy state is the $+$ state. If we substitute Eq. 10 into Eqs. 8 and 9, we find that the $+$ state corresponds to the eigenvector $c_a = c_b = 1/\sqrt{2}$; i.e. it is the bonding state.

$$\Psi'_{bonding} = \frac{1}{\sqrt{2}} (\psi_a + \psi_b) \quad E'_{bonding} = \frac{H_{aa} + H_{abr}}{1 + S_r} \,. \qquad (12)$$

For the $-$, or antibonding state, $c_a = -c_b = 1/\sqrt{2}$. Thus, in the bonding state, the wavefunctions add between the atoms, which corresponds to a build-up of charge between the oxygen molecules (cf. Fig. 6). In the antibonding state, there is a deficiency of charge between the molecules.

Energetically the bonding state is lower and if there are two electrons, both will occupy the lower state (ie., the molecule gains energy by bonding in a singlet spin configuration!). Energy is lost if there are more electrons which must fill the antibonding states. Thus the covalent
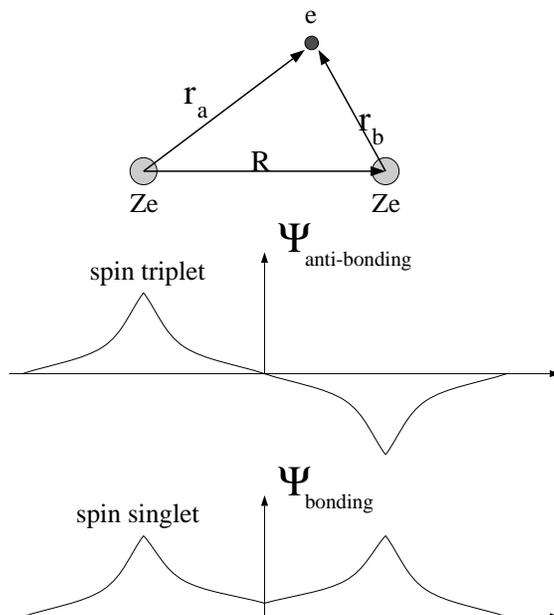
Figure 6: *Two oxygen ions, each with charge Ze, bind and electron with charge e. The electron, which is bound in the oxygen valence orbitals will form a covalent bond between the oxygens*

bond is only effective with partially occupied single-atomic orbitals. If the orbitals are full, then the energy loss of occupying the antibonding states would counteract the gain of the occupying the bonding state and no bond (conventional) would occur. Of course, in reality it is much worse than this since electronic correlation energies would also increase.

The pile-up of charge which is inherent to the covalent bond is important for the lattice symmetry. The reason is that the covalent bond is sensitive to the orientation of the orbitals. For example, as shown in Fig. 7 an S and a P_σ orbital can bond if both are in the same plane;

whereas an S and a P_π orbital cannot. I.e., covalent bonds are directional! An excellent example of this is diamond (C) in which the
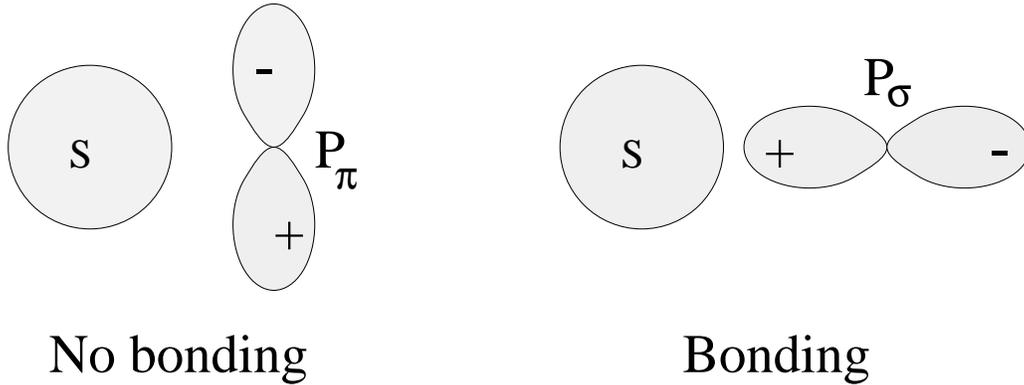
Figure 7: *A bond between an S and a P orbital can only happen if the P-orbital is oriented with either its plus or minus lobe closer to the S-orbital. I.e., covalent bonds are directional!*

(tetragonal) lattice structure is dictated by bond symmetry. However at first sight one might assume that C with a $1s^2 2s^2 2p^2$ configuration could form only 2-bonds with the two electrons in the partially filled p-shell. However, significant energy is gained from bonding, and 2s and 2p are close in energy (cf. Fig. 2) so that sufficient energy is gained from the bond to promote one of the 2s electrons. A linear combination of the 2s $2p_x$, $2p_y$ and $2p_z$ orbitals form a sp^3 hybridized state, and C often forms structures (diamond) with tetragonal symmetry.

Another example occurs most often in transition metals where the d-orbitals try to form covalent bonds (the larger s-orbitals usually form metallic bonds as described later in this chapter). For example, consider a set of d-orbitals in a metal with a face-centered cubic (fcc) structure,

as shown in Fig. 8. The xy, xz, and yz orbitals all face towards a neighboring site, and can thus form bonds with these sites; however, the $x^2 - y^2$ and $3z^2 - r^2$ orbitals do not point towards neighboring sites and therefore do not participate in bonding. If the metal had a simple cubic structure, the situation would be reversed and the $x^2 - y^2$ and $3z^2 - r^2$ orbitals, but not the xy, xz, and yz orbitals, would participate much in the bonding. Since energy is gained from bonding, this energetically favors an fcc lattice in the transition metals (although this may not be the dominant factor determining lattice structure).
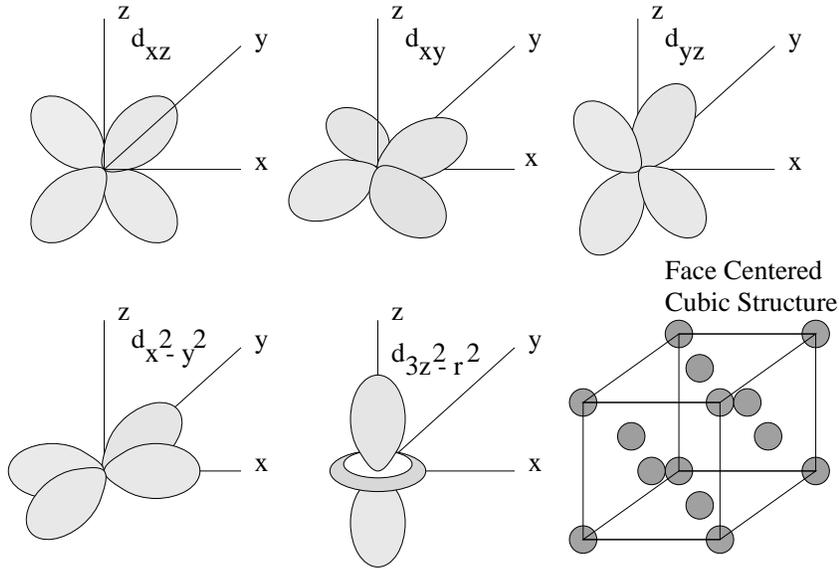
Figure 8: *In the fcc structure, the xy, xz, and yz orbitals all face towards a neighboring site, and can thus form bonds with these sites; however, the $x^2 - y^2$ and $3z^2 - r^2$ orbitals do not point towards neighboring sites and therefore do not participate in bonding*

One can also form covalent bonds from dissimilar atoms, but these will also have some ionic character, since the bonding electron will no

longer be shared equally by the bonding atoms.

2.2   Ionic Bonding

The ionic bond occurs by charge transfer between dissimilar atoms which initially have open electronic shells and closed shells afterwards. Bonding then occurs by Coulombic attraction between the ions. The energy of this attraction is called the cohesive energy. This, when added to the ionization energies yields the energy released when the solid is formed from separated neutral atoms (cf. Fig. 9). The cohesive energy is determined roughly by the ionic radii of the elements. For example, for NaCl

$$E_{cohesive} = \frac{e^2}{a_o} \frac{a_o}{r_{Na} + r_{Cl}} = 5.19 eV \ . \tag{13}$$

Note that this does not agree with the experimental figure given in the caption of Fig. 9. This is due to uncertainties in the definitions of the ionic radii, and to oversimplification of the model. However, such calculations are often sufficient to determine the energy of the ionic structure (see below). Clearly, ionic solids are insulators since such a large amount of energy $\sim$ 10eV is required for an electron to move freely.

The crystal structure in ionic crystals is determined by balancing the needs of keeping the unlike charges close while keeping like charges apart. For systems with like ionic radii (i.e. CsCl, $r_{Cs} \approx 1.60$ Å, $r_{Cl} \approx$ 1.81 Å) this means the crystal structure will be the closest unfrustrated
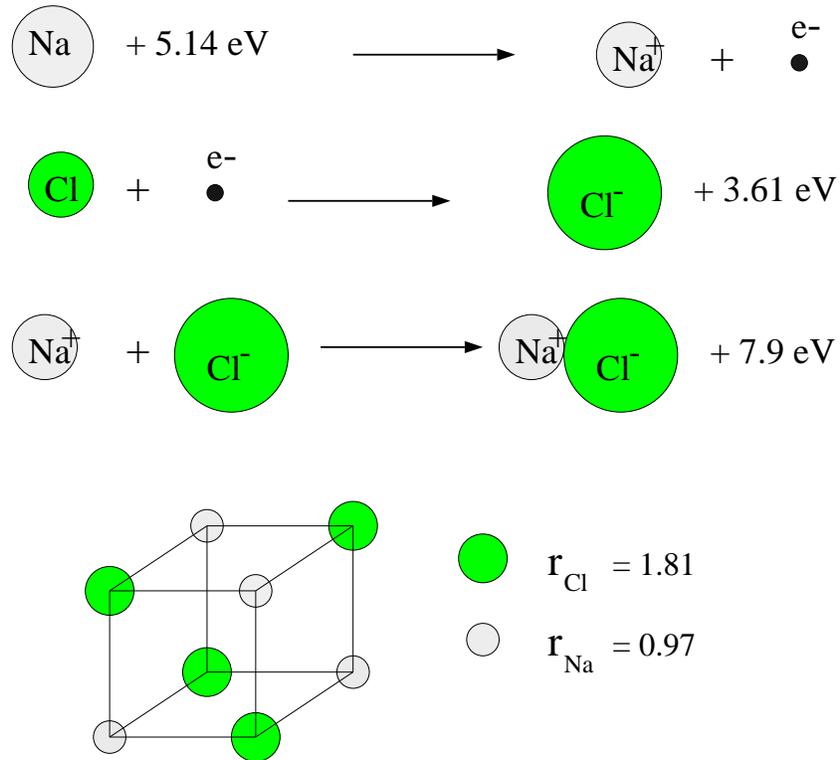
Figure 9: *The energy per molecule of a crystal of sodium chloride is (7.9-5.1+3.6) eV=6.4eV lower than the energy of the separated neutral atoms. The cohesive energy with respect to separated ions is 7.9eV per molecular unit. All values on the figure are experimental. This figure is from Kittel.*

packing. Since the face-centered cubic (fcc) structure is frustrated (like charges would be nearest neighbors), this means a body-centered cubic (bcc) structure is favored for systems with like ionic radii (see Fig. 10). For systems with dissimilar radii like NaCl (cf. Fig. 9), a simple cubic structure is favored. This is because the larger Cl atoms requires more room. If the cores approach closer than their ionic radii, then since they are filled cores, a covalent bond including both bonding and anti-

bonding states would form. As discussed before, Coulomb repulsion makes this energetically unfavorable.
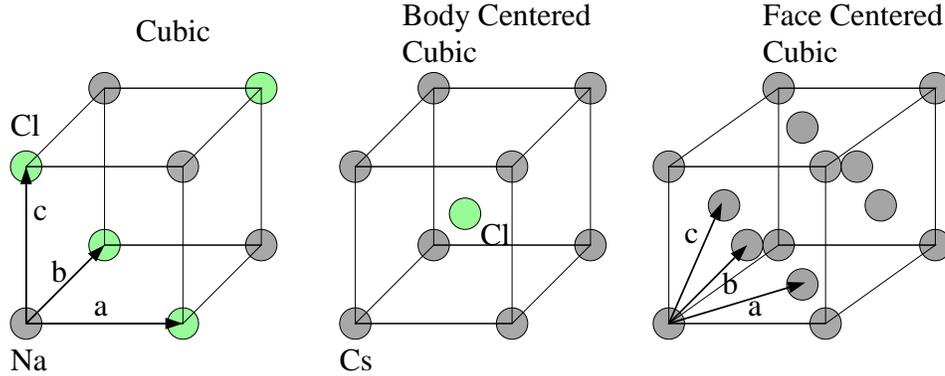
Figure 10: *Possible salt lattice structures. In the simple cubic and bcc lattices all the nearest neighbors are of a different species than the element on the site. These ionic lattices are unfrustrated. However, it not possible to make an unfrustrated fcc lattice using like amounts of each element.*

2.2.1 Madelung Sums

This repulsive contribution to the total energy requires a fully-quantum calculation. However, the attractive Coulombic contribution may be easily calculated, and the repulsive potential modeled by a power-law. Thus, the potential between any two sites i and j, is approximated by

$$\phi_{ij} = \pm\frac{e^2}{r_{ij}} + \frac{B}{r_{ij}^n} \tag{14}$$

where the first term describes the Coulombic interaction and the plus (minus) sign is for the potential between similar (dissimilar) elements. The second term heuristically describes the repulsion due to the over-

lap of the electronic clouds, and contains two free parameters n and B (Kittel, pp. 66–71, approximates this heuristic term with an exponential, $B\exp(-r_{ij}/\rho)$, also with two free parameters). These are usually determined from fits to experiment. If a is the separation of nearest neighbors, $r_{ij} = ap_{ij}$, and their are N sites in the system, then the total potential energy may be written as

$$\Phi = N\Phi_i = N\left[-\frac{e^2}{a}\sum_{i\neq j}\frac{\pm}{p_{ij}} + \frac{B}{a^n}\sum_{i\neq j}\frac{1}{p_{ij}^n}\right] . \qquad (15)$$

The quantity $A = \sum_{i\neq j}\frac{\pm}{p_{ij}}$, is known as the Madelung constant. A depends upon the type of lattice only (not its size). For example $A_{NaCl} = 1.748$, and $A_{CsCl} = 1.763$. Due to the short range of the potential $1/p^n$, the second term may be approximated by its nearest neighbor sum.

2.3 Metallic Bonding

Metallic bonding is characterized by at least some long ranged and non-directional bonds (typically between s orbitals), closest packed lattice structures and partially filled valence bands. From the first characteristic, we expect some of the valance orbitals to encompass many other lattice sites, as discussed in Fig. 11. Thus, metallic bonds lack the directional sensitivity of the covalent bonds and form non-directional bonds and closest packed lattice structures determined by an optimal filling of space. In addition, since the bands are composed of partially
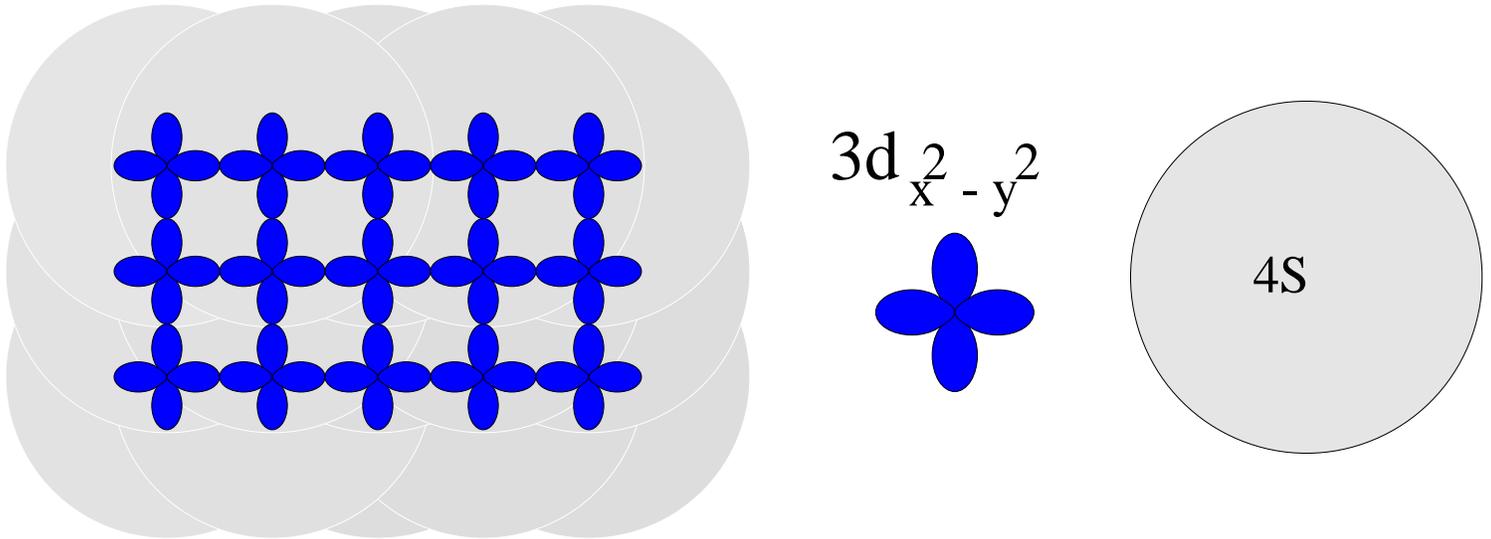
Figure 11: *In metallic Ni (fcc, $3d^8 4s^2$), the 4s and 3d bands (orbitals) are almost degenerate (cf. Fig. 2) and thus, both participate in the bonding. However, the 4s orbitals are so large compared to the 3d orbitals that they encompass many other lattice sites, forming non-directional bonds. In addition, they hybridize weakly with the d-orbitals (the different symmetries of the orbitals causes their overlap to almost cancel) which in turn hybridize weakly with each other. Thus, whereas the s orbitals form a broad metallic band, the d orbitals form a narrow one.*

filled orbitals, it is always possible to supply a small external electric field and move the valence electrons through the lattice. Thus, metallic bonding leads to a relatively high electronic conductivity. In the transition metals (Ca, Sr, Ba) the d-band is narrow, but the s and p bonds are extensive and result in conduction. Partially filled bands can occur by bond overlap too; ie., in Be and Mg since here the full S bonds overlap with the empty p-bands.

2.4   Van der Waals Bonds

As a final subject involving bonds, consider solids formed of Noble gases
or composed of molecules with saturated orbitals. Here, of course, there
is neither an ionic nor covalent bonding possibility. Furthermore, if the
charge distributions on the atoms were rigid, then the interaction be-
tween atoms would be zero, because the electrostatic potential of a
spherical distribution of electronic charge is canceled outside a neutral
atom by the electrostatic potential of the charge on the nucleus. Bond-
ing can result from small quantum fluctuations in the charge which
induce electric dipole moments.
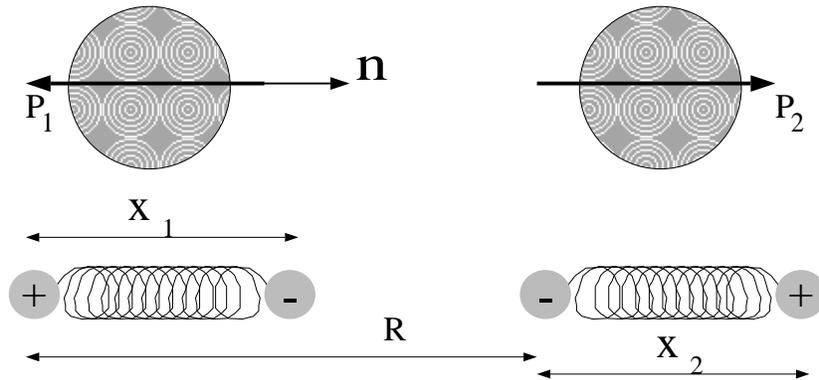
Figure 12: *Noble gasses and molecules with saturated orbitals can form short ranged
van der Waals bonds by inducing fluctuating electric dipole moments in each other.
This may be modeled by two harmonic oscillators binding a positive and negative
charge each.*

As shown in Fig. 12 we can model the constituents as either induced
dipoles, or more correctly, dipoles formed of harmonic oscillators. Sup-

pose a quantum fluctuation on 1 induces a dipole moment $\mathbf{p}_1$. Then dipole 1 exerts a field

$$\mathbf{E}_1 = \frac{3\mathbf{n}(\mathbf{p}_1 \cdot \mathbf{n}) - \mathbf{p}_1}{r^3} \tag{16}$$

which is felt by 2, which in turn induces a dipole moment $\mathbf{p}_2 \propto E_1 \propto 1/r^3$. This in turn, generates a dipole field E_2 felt by $1 \propto \mathbf{p}_2/r^3 \propto 1/r^6$. Thus, the energy of the interaction is very small and short ranged.

$$W = -\mathbf{p}_1 \cdot \mathbf{E}_2 \propto 1/r^6 \tag{17}$$

2.4.1 Van der Waals-London Interaction

Of course, a more proper treatment of the van der Waals interaction should account for quantum effects in induced dipoles modeled as harmonic oscillators (here we follow Kittel).

As a model we consider two identical linear harmonic oscillators 1 and 2 separated by R. Each oscillator bears charges $\pm e$ with separations x_1 and x_2, as shown in Fig. 12. The particles oscillate along the x axis with frequency ω_0 (the strongest optical absorption line of the atom), and momenta $\mathbf{P}_1$ and $\mathbf{P}_2$. If we ignore the interaction between the charges (other than the self-interaction between the dipole's charges which is accounted for in the harmonic oscillator potentials), then the Hamiltonian of the system is

$$H_0 = \frac{P_1^2 + P_2^2}{2m} + \frac{1}{2}m\omega_0^2(x_1^2 + x_2^2) \,. \tag{18}$$

If we approximate each pair of charges as point dipoles, then they interact with a Hamiltonian

$$H_1 \approx \frac{-3(\mathbf{p}_2 \cdot \mathbf{n})(\mathbf{p}_1 \cdot \mathbf{n}) + \mathbf{p}_1 \cdot \mathbf{p}_2}{|\mathbf{x}_1 + \mathbf{R} - \mathbf{x}_2|^3} = -\frac{-2p_1 p_2}{R^3} = -\frac{2e^2 x_1 x_2}{R^3}. \quad (19)$$

The total Hamiltonian $H_0 + H_1$ can be diagonalized a normal mode transformation that isolates the the symmetric mode (where both oscillators move together) from the antisymmetric one where they move in opposition

$$x_s = (x_1 + x_2)/\sqrt{2} \quad x_a = (x_1 - x_2)/\sqrt{2} \quad (20)$$

$$P_s = (P_1 + P_2)/\sqrt{2} \quad P_a = (P_1 - P_2)/\sqrt{2} \quad (21)$$

After these substitutions, the total Hamiltonian becomes

$$H = \frac{P_s^2 + P_a^2}{2m} + \frac{1}{2}\left(m\omega_0^2 - \frac{2e^2}{R^3}\right)x_s^2 + \frac{1}{2}\left(m\omega_0^2 + \frac{2e^2}{R^3}\right)x_a^2 \quad (22)$$

The new eigenfrequencies of these two modes are then

$$\omega_s = \left(\omega_0^2 - \frac{2e^2}{mR^3}\right)^{1/2} \quad \omega_a = \left(\omega_0^2 + \frac{2e^2}{mR^3}\right)^{1/2} \quad (23)$$

The zero point energy of the system is now

$$E_0 = \frac{1}{2}\hbar(\omega_s + \omega_a) \approx \hbar\omega_0\left(1 - \frac{1}{4}\left(\frac{2e^2}{m\omega_0^2 R^3}\right)^2 + \cdots\right) \quad (24)$$

or, the zero point energy is lowered by the dipole interaction by an amount

$$\Delta U \approx \frac{\hbar\omega_0}{4}\left(\frac{2e^2}{m\omega_0^2 R^3}\right)^2 \quad (25)$$

which is typically a small fraction of an electron volt.

This is called the Van der Waals interaction, known also as the London interaction or the induced dipole-dipole interaction. It is the principal attractive interaction in crystals of inert gases and also in crystals of many organic molecules. The interaction is a quantum effect, in the sense that $\Delta U \to 0$ as $\hbar \to 0$.