Part II: Bonding in solids

Since we are now familiar with the elements and their properties, we can start to discuss how they can be put together to create bigger structures – ultimately, we're interested in crystalline solids.

1 Van der Waals bonds

Let's start with the noble elements, from group 8, and consider what are the possible interactions between two such atoms, for example two Ne atoms. At first sight, it would be tempting to say that they don't interact at all with one another. As we've seen, because they have completely filled shells, they have very large ionization energies (it's very hard to remove an electron away from them) and vanishing electron affinity (they don't want an extra electron). So each Ne keeps its electrons in a filled spherical atomic shell, and what we have are two charge-neutral objects and no interactions (apart from gravitational attraction which is so weak that we can safely ignore it).

This is not true, though. First, if we force the atoms close together by making the distance r between them smaller and smaller, it is clear that at some point the electronic clouds will start to overlap and at that point we should have very strong repulsion between them. This is because, according to Pauli's principle, we can't have electrons in the same place with the same spin, and that's exactly what overlap of the electronic clouds would do if the electrons stay undisturbed in their inner shells. So when we bring the atoms close together, some of the electrons have to go into higher energy states and rearrange themselves to stay out of each other's way, and this costs a lot of energy, leading to strong repulsion at very short distances.

Interestingly, even if r is much larger than the atomic radius, there are some interactions between these atoms. This is due to the fact that while the positive charge is localized in the nucleus, the negative charge is more spread out, in the electronic cloud that surrounds it. Suppose now that there is a small fluctuation which pushes the center of negative charge a bit away from the nucleus, for atom 1, thus creating a small electric dipole of magnitude p_1. This dipole will create an electric field whose magnitude at a large distance r is $E(r) \sim \frac{p_1}{r^3}$. This electric field will polarize the other atom – it acts with opposite forces on its positive vs negative charges and pushes them apart – creating a dipole $\vec{p}_2 = \alpha \vec{E}(r)$. The constant α is known as polarizability; the previous equation simply says that the larger the electric field at the location of atom 2, the larger the induced electric dipole p_2. Because we now have a dipole in an electric field, the energy is lowered by $-\vec{p}_2 \cdot \vec{E}(r) = -\alpha |E(r)|^2 < 0$. So, by this process of induced dipole-dipole interactions, there is an attractive potential between atoms, proportional to $-1/r^6$. This is known as the **van der Waals attraction.** If you found this argument a bit too handwaving, let me assure you that one can derive this long-range, attractive $1/r^6$ potential from quantum mechanical considerations – maybe I will give that to you as a homework problem; if not, you're sure to see it in a more advanced course.

Taken together, we find that the total potential between two inert atoms placed at a distance r from each other is:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

This is known as the **Lennard-Jones potential**. σ is a distance typical of the atomic radius, since you can see that $V(\sigma) = 0$, i.e. for $r < \sigma$ the potential becomes very repulsive, whereas it is weakly attractive for $r > \sigma$ (see sketch on next page). The second term is the van der Waals attraction, while the first is a convenient way to model the repulsion (this is not derived from a calculation, is a

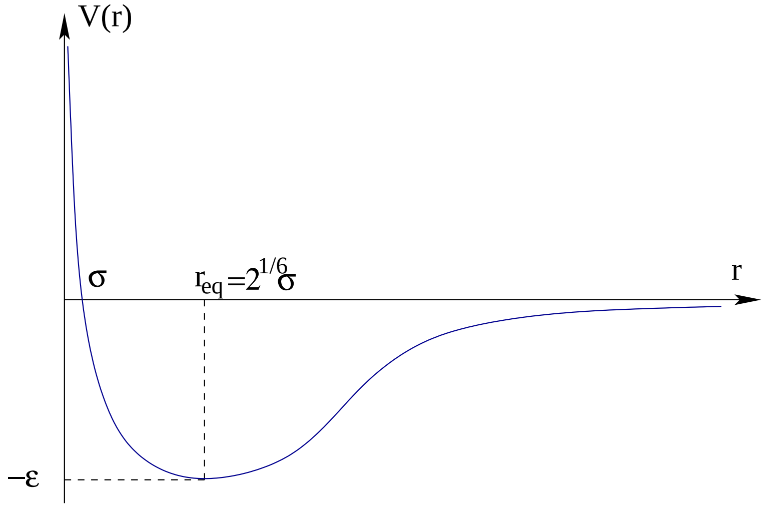


Figure 1: The Lennard-Jones potential describing interactions between two noble elements

simple form that was found to fit measurements well). ϵ is the maximum attractive energy between the two atoms, reached when they are at rest at the distance $r_{eq} = \sigma 2^{\frac{1}{6}} \approx 1.12\sigma$ from each other.

The parameters ϵ and σ can be measured experimentally. For example, at high temperatures in the gas phase, these interactions lead to some changes in the equation of state, from that of a perfect gas $pV = Nk_BT$, to a so-called van der Waals equation of state:

$$(p + n^2b)(V - Na) = Nk_BT$$

where $n = N/V$ is the concentration of the gas. When you take a stat mech course, I hope you'll have the pleasure of deriving this equation of state starting from the Lennard-Jones potential, and showing that $b = \epsilon v/2$ and $a = v/2$, where $v = 4\pi\sigma^3/3$ is known as the "exclusion volume" (this is the volume within which no other atom can come because the repulsion becomes too great). In any event, one can measure a and b, and therefore ϵ, σ, from how pressure, temperature and volume vary with one another. This is a neat example of how microscopic interactions determine the macroscopic behaviour of a system, and very much the sort of thing we'd like to understand for solids.

Back to our 2 inert atoms: clearly, at low temperatures where they don't have much kinetic energy, they could become bound in a molecule. The most stable state would have them at r_{eq} from each other, with energy $-\epsilon$. If we have many atoms at very low temperatures, so they don't move much, their most stable arrangement (the lowest energy states possible) will be when each atom is surrounded by as many as possible other atoms, roughly close to r_{eq} away from each other. But since all atoms are identical, each should be in a similar environment like any other one – hence the perfect crystal order that develops here.

But can we predict what crystal will be created? The answer is "yes", and let me show you how with a simpler 2D example (of course, the real crystal will be 3D, because you can bring more atoms closer together in that case). But suppose that, for instance, we have inert atoms trapped on the surface of a material, so they can only order in 2D. They could make a simple square lattice with a distance R between neighbours (this distance is known as the lattice constant); or they could make a triangular lattice, or whatever other options there are in 2D (we will discuss all these options in about a week from now).

Let's assume they make a square lattice. The total energy, if the atoms are frozen in their places, is:

$$U_{tot}(R) = \frac{1}{2}\sum_i \sum_{j\neq i} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

where r_{ij} is the distance between atoms i and j, and all I've done is sum over all Lennard-Jones potentials for all pairs of atoms in the lattice. But $r_{ij} = Rp_{ij}$, where p_{ij} are simple numbers. For instance, each atom has $z_1 = 4$ nearest-neighbour atoms at distance R, so for these $p = 1$; there are $z_2 = 4$ second-nearest neighbour atoms at distance $r = R\sqrt{2}$, so for these $p = \sqrt{2}$, and so on an so forth, we can keep counting (by the way, z is called the **coordination number**). Since each atom contributes equally to the total energy (because they are in identical environments), we can write the total energy per atom as:

$$\frac{U_{tot}(R)}{N} = 2\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} \sum_j \frac{1}{p_{ij}^{12}} - \left(\frac{\sigma}{R}\right)^{6} \sum_j \frac{1}{p_{ij}^{6}}\right]$$

where the sum is over all the neighbours and will simply give some numbers. For instance, for our square lattice example:

$$a_{12} = \sum_j \frac{1}{p_{ij}^{12}} = \frac{4}{1^{12}} + \frac{4}{\sqrt{2}^{12}} + \frac{4}{2^{12}} + ... \approx 4.063$$

(the sum converges very fast). One can calculate $a_6 = \sum_j \frac{1}{p_{ij}^6}$ similarly, to find:

$$\frac{U_{tot}(R)}{N} = 2\epsilon \left[a_{12}\left(\frac{\sigma}{R}\right)^{12} - a_6\left(\frac{\sigma}{R}\right)^{6}\right]$$

We can now find the value of R_0 for which this energy is minimized, and then its corresponding value, i.e. $\frac{U_{tot}(R_0)}{N}$ for the square lattice.

We then repeat the calculation for the triangular lattice. Clearly, this will lead to different values for a_6 and a_{12}, since the number of neighbours and where they are located is different. As a result, we will find a different value R_0 which minimizes the total energy per atom, and therefore a different minimum $\frac{U_{tot}(R_0)}{N}$ than we found for the square lattice.

We then repeat this for all other possible 2D lattices, and whichever lattice has the lowest overall energy per atom is clearly the most stable, so it must be the one that will occur in nature. Note that this gives us not only the lattice structure (square, triangular, ...) but also the expected value for the **lattice constant** R_0 and the **cohesion energy** $\frac{U_{tot}(R_0)}{N}$, i.e. the energy needed to remove one atom from the crystal. These can be compared against experimental measurements.

How does it work, in practice? Well, for a 3D crystal, it turns out that the winning structure is the so-called FCC (face centered cubic) lattice, because it has high-packing with as many atoms as close together as possible (we will discuss these lattices next, so don't worry if you don't know what FCC looks like). For this lattice, $a_{12} = 12.13188$ and $a_6 = 14.45392$, and for these numbers, the minimum in the energy is reached when $R_0 \approx 1.09\sigma$. Experimentally, it is found that indeed, the noble elements form FCC crystals at low-enough temperatures. Independent measurements of their R_0 and σ give the experimental values $R_0/\sigma = 1.14; 1.11; 1.10; 1.09$ in Ne, Ar, Kr and Xe (these values are taken from Kittel's book). In other words, the heavier the atom, the better our prediction – but all are pretty good, considering what a simple calculation this is.

Why is the prediction worse for the lighter atoms? Well, simply because the lighter they are, the more important is their kinetic energy $p^2/(2m)$. These are quantum objects, so they can't possibly be at rest at known locations, this would violate Heisenberg's uncertainty principle $\Delta x \Delta p_x \geq \hbar/2$. The uncertainty in the location of the particle is some fraction of R_0 (else we cannot speak of any crystalline order), so its momentum is of order $p \sim \hbar/R_0$, and its resulting kinetic energy is $\propto \frac{\hbar^2}{2mR_0^2}$. For heavy atoms this is negligible, but for lighter ones it is not, and we should add it into the total energy and use this total to find the equilibrium value R_0 which minimizes the total energy. This additional term will change where the minimum is – clearly it prefers to keep atoms a bit farther apart, to lower their kinetic energy. This is why we find larger values of R_0 for the lighter atoms. In case you're wondering, yes, one can do honest quantum-mechanical calculations for this, and the agreement indeed improves. We will discuss this motion of the atoms in the lattice (lattice vibrations) towards the end of the course.

This completes the discussion of the inert elements. As we've seen, we get molecules and crystals forming, but the physics is not so exciting, we can understand this at a (semi)classical level. What happens for elements from the other groups? Is there anything more interesting to be learned?

2 The simplest example of a "quantum" molecule: H_2^+

We will use this simple example, with two protons (H nuclei) and a single electron, to learn many useful ideas. We expect that a stable state is possible, with the electron somehow serving as the "glue" that keeps all three objects bound together. Let's see how this happens.

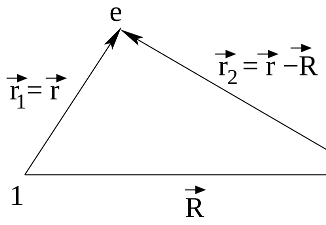


Figure 2: Geometry of the H_2^+ problem.

This problem can be solved exactly. If the distance between nuclei is $\vec{R}$ and the distance from the electron to nucleus 1 is $\vec{r}$, then the distance to nucleus 2 is $\vec{r} - \vec{R}$ and Schrödinger's equation reads:

$$\hat{H}\phi(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{ke^2}{r} - \frac{ke^2}{|\vec{r}-\vec{R}|} + \frac{ke^2}{R}\right]\phi(\vec{r}) = E(R)\phi(\vec{r})$$

where the first term is the kinetic energy of the electron, the next two are its Coulomb attraction to the two nuclei, and the last is the repulsion between nuclei. On the right, I wrote $E(R)$ for the energy to suggest that the eigenenergies will depend on the value R we choose between the nuclei (the nuclei are assumed to be at rest – which is reasonable, since they are much heavier than the electron). The true ground-state will correspond to the equilibrium distance R_{eq} which minimizes the lowest eigenenergy.

While this can be solved exactly to find the true molecular eigenstates, we will be happy to get a good approximation (and to learn, in the process, how to go about finding such approximations). Here's the idea: if the electron is close to the 1st nucleus, the lowest energy configuration must be like the $1s$ orbital bound to this nucleus, i.e. $\phi_1(\vec{r}) \propto \exp(-r/a_B)$. Similarly, if it is close to the 2nd nucleus, it would occupy its $1s$ orbital, $\phi_2(\vec{r}) \propto \exp(-|\vec{r} - \vec{R}|/a_B)$. Higher orbitals are much more expensive energetically, so it is a reasonable approximation to guess (this is called a **variational**

approximation) that the ground-state we're looking is not too far from:

$$\phi(\vec{r}) = \alpha\phi_1(\vec{r}) + \beta\phi_2(\vec{r})$$

(we could add in $2s$, $2p$ etc orbitals to make this more accurate, but since those states are much more expensive, we expect the probabilities for them to be occupied in the ground-state to be very small. There is some subtlety about this basis being overcomplete, but we won't even go there).

How to find what the coefficients α and β are? Well, if you're used to thinking of symmetries, you can just see that we must have $|\alpha|^2 = |\beta|^2$, since the two nuclei are identical. So surely we must have $\alpha = \pm\beta$. Which is true, but it still doesn't tell us what the energy is.

The way to do it is to calculate the expectation value of the energy:

$$E = \frac{\int d\vec{r}\phi^*(\vec{r})\hat{H}\phi(\vec{r})}{\int d\vec{r}\phi^*(\vec{r})\phi(\vec{r})}$$

and find the values of α and β which minimize this. It is now a matter of going through calculations, and I will probably give this as a homework, to show that we can rewrite:

$$E = \frac{\alpha^2 E_{11} + \beta^2 E_{22} + \alpha\beta E_{12} + \alpha\beta E_{21}}{\alpha^2 + \beta^2 + 2\alpha\beta S}$$

Note that I assumed α, β to be real numbers. If you wish, repeat the calculation with complex numbers and show that there is no way to choose them so as to lower the energy more than we can with real numbers. In this expression:

$$E_{11} = \int d\vec{r}\phi_1^*(\vec{r})\hat{H}\phi_1(\vec{r}) = E_{H,GS} + \frac{ke^2}{R} - \Delta E = E_{22}$$

where I used the fact that $\phi_1(\vec{r})$ is an eigenstate for the ground-state of a single H:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{ke^2}{r}\right]\phi_1(\vec{r}) = E_{H,GS}\phi_1(\vec{r})$$

where $E_{H,GS} = -13.6eV$. The second term is just the repulsion between the nuclei, and the third one is the average attraction between the electron and nucleus 2, when the electron is in the 1s state of nucleus 1 (or viceversa):

$$\Delta E = \int d\vec{r}\phi_1^*(\vec{r})\frac{ke^2}{|\vec{r} - \vec{R}|}\phi_1(\vec{r}) \to \frac{ke^2}{R} \text{ as } R \to \infty.$$

The exact formula can be calculated with a bit of goodwill.

Similarly, we find:

$$E_{12} = \int d\vec{r}\phi_1^*(\vec{r})\hat{H}\phi_2(\vec{r}) = \left(E_{H,GS} + \frac{ke^2}{R}\right)S - T = E_{21},$$

where

$$S = \int d\vec{r}\phi_1^*(\vec{r})\phi_2(\vec{r})$$

is called the overlap between the two orbitals, and

$$T = \int d\vec{r}\phi_1^*(\vec{r})\frac{ke^2}{|\vec{r} - \vec{R}|}\phi_2(\vec{r})$$

is the **hopping matrix** (we'll see soon why it has this name). Both S and T can also be calculated analytically, with some good will. Note that since both ϕ_1 and ϕ_2 are positive, it follows that $S > 0, T > 0$. Also, since they involve the product of $\phi_1 \cdot \phi_2$, and these functions decrease exponentially with the distance, we expect both S and T to decrease exponentially with the distance R, i.e. be proportional to $\exp(-R/a_B)$ at the very least.

With all this, we can rewrite:

$$E = E_{H,GS} + \frac{ke^2}{R} - \Delta E - (T - S\Delta E)\frac{2\alpha\beta}{\alpha^2 + \beta^2 + 2\alpha\beta S}$$

Now we request that $\frac{\partial E}{\partial \alpha} = 0, \frac{\partial E}{\partial \beta} = 0$. Both lead to the equation $\alpha^2 = \beta^2$, which has two solutions (surprise surprise!) $\alpha = \pm\beta$. Let's consider them separately:

- the symmetric combination $\alpha = \beta \rightarrow \phi_B(\vec{r}) \propto \phi_1(\vec{r}) + \phi_2(\vec{r})$, and the corresponding energy is:

$$E_B = E_{H,GS} + \frac{ke^2}{R} - \Delta E - \frac{T - S\Delta E}{1 + S}$$

- the antisymmetric combination $\alpha = -\beta \rightarrow \phi_{AB}(\vec{r}) \propto \phi_1(\vec{r}) - \phi_2(\vec{r})$, and the corresponding energy is:

$$E_{AB} = E_{H,GS} + \frac{ke^2}{R} - \Delta E + \frac{T - S\Delta E}{1 - S}$$

A sketch of these energies as a function of R (remember that $\Delta E, T, S$ are also functions of R) looks like below. We see that for all R, the symmetric combination has the lower energy, and in particular that there is a value R_{eq} which minimizes it. That shows that indeed, a stable molecule exists. But this is all math; what we'd really like to understand is what is the physical explanation for this stable state, and why is the other one not stable? Well, this is easy to see if we plot the wavefunctions of the electron in the two cases, as shown on the next page.

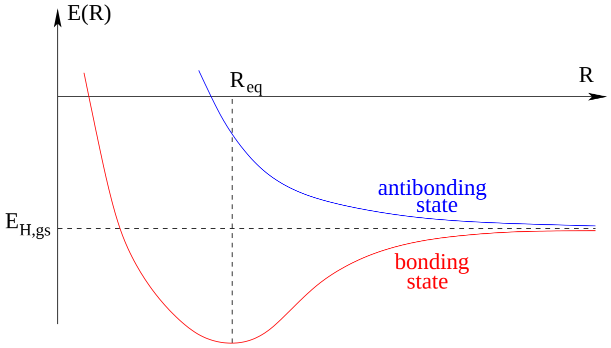


Figure 3: Energies of the bonding and anti-bonding molecular orbitals as a function of R.

In the symmetric case, since we add two positive functions, we get an increase in the probability to find the electron in between the two nuclei (shown in a rather exaggerated fashion in my sketch). And this is what bonds the system together, since now both nuclei are attracted towards the electron, but are also as far from each other as possible to minimize their direct repulsion. This is known as the **bonding molecular orbital**, for obvious reasons. In the other case, for the so-called **anti-bonding molecular orbital**, the two contributions nearly cancel each other in the middle, so the probability to find the electron between the two nuclei vanishes – in this case, the electron is found with most probability on the "outside" of the nuclei, so the direct repulsion between the nuclei is dominant and

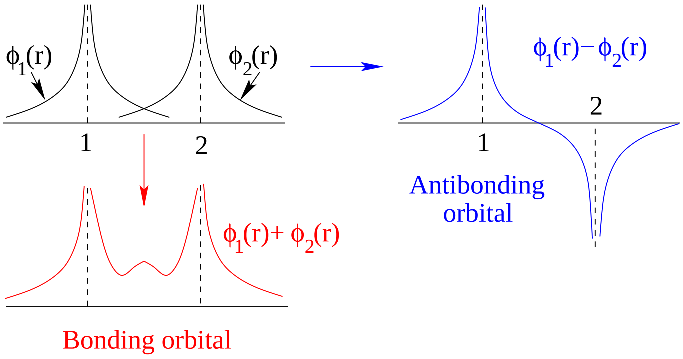


Figure 4: Bonding and anti-bonding molecular orbitals.

makes this an unstable state (it is energetically more favourable for the nuclei to be at $R \to \infty$, with one getting the electron, than in this state).

As already mentioned, here $T > 0$ because we used two s-orbitals (turns out that S is by far the smallest number if $R \gg a_B$, so we can ignore its contribution). If we had, instead, $T < 0$, then the situation would be reversed. You might want to think how could that happen (even if you don't want to, I might force you to do so in the homework).

In principle we could move on, but let me show you how we can solve this much more easily if we introduce better notation to simplify our lives. We'll use this simpler notation later on, and you will certainly get introduced to it, probably in a much more formal manner, in a more advanced QM course; so this is also good preparation towards that.

One problem with using wavefunctions, like $\phi_1(\vec{r})$, is that we actually mix two kinds of information here. One is what is the state of the electron (answer, in this case, is $1s$ orbital centered at nucleus 1), and the second is where are we looking for the electron to be when in this state, i.e. what's the value of $\vec{r}$. The important information is what is the state. Once we know that, we could figure out what is the probability to find the electron in different positions, or with different momenta, or any other question we have about it. So let me introduce the notation $|\phi\rangle$ to show the state. For example, $|\vec{r}\rangle$ is the usual notation for the state where the electron is certainly at $\vec{r}$; $|\vec{p}\rangle$ is the usual notation for the state where the electron certainly has momentum $\vec{p}$; etc.

If we have two states $|A\rangle$ and $B\rangle$, whatever they may be, then $\langle A|B\rangle$ is the amplitude of probability that if the particle was in state B, I would also find it in state A. For example, $\langle\vec{r}|\phi\rangle$ is the amplitude of probability that if the particle is in state ϕ, we find it at $\vec{r}$. But this is just the wavefunction, so $\langle\vec{r}|\phi\rangle = \phi(\vec{r})$. As one example, $\langle\vec{r}|\vec{p}\rangle \sim e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}$. As another one, for a $1s$ orbital centered at the origin, $|1s\rangle$, we have $\langle\vec{r}|1s\rangle \propto \exp(-r/a_B)$. Of course, for any normalized state, $\langle\phi|\phi\rangle = 1$, whereas for two orthogonal states $\langle\phi|\psi\rangle = 0$.

Ok, so let's go back to our H_2^+ molecule. We want an approximation for the low-energy eigenstates (ground state, in particular), and we've already decided that it must be built of the $|1\rangle$ and $|2\rangle$ states, which describe the electron in the $1s$ orbital of nucleus 1 and 2, respectively.

These states are normalized, $\langle 1|1\rangle = \langle 2|2\rangle = 1$. For simplicity, let me assume that they are orthogonal, i.e. we set $\langle 1|2\rangle = S \to 0$. As I said, the overlap S is very small unless R becomes comparable to a_B or less, so this is a reasonable approximation. All it says is that the 1s orbitals are reasonably well separated spatially, so that if the electron is in $|1\rangle$ (i.e., in orbital centered at nucleus 1), the probability to see it close to 2 and to mistake it as being in state $|2\rangle$ is basically zero.

Ok, so we have a space with two possible states, so any eigenstates will be of the general form $|\phi\rangle = \alpha|1\rangle + \beta|2\rangle$. What sort of operators can we have in this space? (because we need to build the

Hamiltonian). We only have 4 possible operators, namely:

$$\hat{P}_{i\to j} = |j\rangle\langle i|$$

where $i = 1, 2$ and $j = 1, 2$. What is the action of such an operator when acting on a state? Let's check:

$$\hat{P}_{1\to 1}|\phi\rangle = |1\rangle\langle 1| \left(\alpha|1\rangle + \beta|2\rangle\right) = \alpha|1\rangle$$
$$\hat{P}_{1\to 2}|\phi\rangle = |2\rangle\langle 1| \left(\alpha|1\rangle + \beta|2\rangle\right) = \alpha|2\rangle$$

etc. In other words, $\hat{P}_{i\to j}$ selects the part of where the particle is in state i, discards the rest, and then moves the particle to state j.

So what is the Hamiltonian in this notation? The answer is:

$$\hat{H} = \epsilon\left(|1\rangle\langle 1| + |2\rangle\langle 2|\right) - t\left(|1\rangle\langle 2| + |2\rangle\langle 1|\right)$$

The first part doesn't really change anything (if the particle was in 1 it stays in 1, if it was in 2 it stays in 2), but its adds ϵ to the total energy. This is because whether the electron is in $|1\rangle$ or in $|2\rangle$, it does have energy $E_{H,GS}$ from interacting with its own nucleus, plus the other two corrections we've discussed, namely ke^2/R and ΔE.

The second part is called **the hopping Hamiltonian**, because if the particle was at $|1\rangle$ it moves it to $|2\rangle$, and viceversa. Physically, this describes the fact that attraction from the other nucleus could pull the electron close to it and change its state. The parameter t, which has units of energy, is called **the hopping integral**, and is essentially equal to T (you could worry about small corrections from S, if you really wanted to, but people usually do not).

So now let's find the eigenvalues of this Hamiltonian, i.e. what values of α, β, E satisfy the eigenequation:

$$\hat{H}|\phi\rangle = E|\phi\rangle \to \hat{H}\left(\alpha|1\rangle + \beta|2\rangle\right) = E\left(\alpha|1\rangle + \beta|2\rangle\right) \to \alpha\left(\epsilon|1\rangle - t|2\rangle\right) + \beta\left(\epsilon|2\rangle - t|1\rangle\right) = E\left(\alpha|1\rangle + \beta|2\rangle\right)$$

Bracket this with a $\langle 1|$ from the left, and we find:

$$\alpha\epsilon - \beta t = E\alpha$$

while doing the same with $\langle 2|$ gives:

$$-\alpha t + \beta\epsilon = \beta E$$

This can be rewritten as:

$$\begin{cases} (E-\epsilon)\alpha + t\beta &= 0 \\ t\alpha + (E-\epsilon)\beta &= 0 \end{cases}$$

A nontrivial solution exists if the determinant vanishes, i.e. $(E-\epsilon)^2 - t^2 = 0 \to E_\pm = \epsilon \mp t$. You can now go back and check that the $E_+ = \epsilon - t$ solution, with the lower energy if $t > 0$, corresponds to $\alpha = \beta \to |\phi_+\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$ is indeed the bonding orbital. The second solution is the anti-bonding one. Not surprisingly, we arrived at the same solution, but the calculation is much simpler. We will see more examples like this and you'll become more comfortable with this sort of notation, too.

To conclude, in this case we have a stable molecule, but the mechanism for it is quite different than for noble elements. Here, the electron occupies the bonding molecular orbital which is a superposition of the atomic orbitals, i.e. quantum mechanics is involved non-trivially.

3 The H_2 molecule and the covalent bond

Now we are ready to discuss what happens if we bring two H atoms together: can they bind into a molecule, and if yes, why and how?

If we can ignore electron-electron interactions the answer is definitely yes, since we can place the two electrons, with opposite spins, into the bonding orbital. As a result, the energy of the molecule is $2(\epsilon - t) < 2\epsilon$, i.e. it is more stable than having each electron belonging to its own nucleus, only.

The way we sketch this is shown below. The outsides show what levels are available to the electrons from each individual atom (here, a level $1s$ for each, with the same energy ϵ); in the middle we show the eigenstates of the molecule, the bonding one with energy lower by t, and the anti-bonding one with energy higher by t. The ground state is shown by the placement of the two electrons with opposite spins into the bonding orbital.

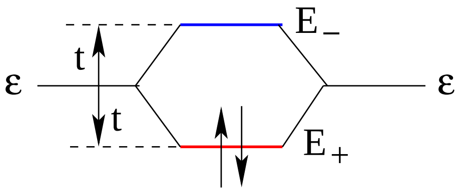


Figure 5: Energy levels for the H_2 molecule.

Now you might wonder why is this stable at a finite R_{eq}? After all, the closer we bring the nuclei, the bigger t is because the overlap between wavefunctions increases (have another look at the definition of $t = T$), so the energy becomes more negative. However, if we bring them too close together, the direct repulsion between the nuclei, ke^2/R, starts to increase fast and makes this unfavourable, so there is an optimum at a finite distance which can be calculated and compared (favourably) with the experimental value.

If you wish to know what the wavefunction is, here we go:

$$\psi_{GS}(\vec{r}_1, \vec{r}_2) = \phi_B(\vec{r}_1)\phi_B(\vec{r}_2)\frac{\chi_{1\uparrow}\chi_{2\downarrow} - \chi_{1\downarrow}\chi_{2\uparrow}}{\sqrt{2}}$$

where the last bit is just the singlet for the spins, and $\phi_B(\vec{r}) = \frac{1}{\sqrt{2}}(\phi_1(\vec{r}) + \phi_2(\vec{r}))$ is the bonding orbital, with the correct normalization if we take $S = 0$.

If you expand the spatial part, we find $\psi_{GS}(\vec{r}_1, \vec{r}_2) \propto \phi_1(\vec{r}_1)\phi_1(\vec{r}_2) + \phi_2(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)$. The first term has both electrons at nucleus 1, the second has both at nucleus 2, and the last 2 terms have one electron at each nucleus. So, in this state, it is 50% probable that both electrons are at the same nucleus (equally shared, 25% with one and 25% with the other), and 50% that each nucleus has one electron.

This is a rather troublesome, actually, because it says that no matter how far the nuclei are, this state is more favourable than having one electron per nucleus with 100% probability. This is because no matter how small t becomes, we still have $2(\epsilon - t) < 2\epsilon$, so this state is more stable. On the other hand, it is very improbable that if we have two H very far apart, 50% of the time both electrons will be with one nucleus. That's just wrong.

The reason for this is that we ignored the interactions between the electrons. Maybe I will show you how we can add those in, in a simple way, in a bonus problem – if not, you're sure to do this in a more advanced course. Let me just state here that if we add the interactions in the model even very simply, we find that the farther away the nuclei are, the closer to 100% is the probability for each to have its own electron. Put it another way, a more correct description for the spatial part of the wavefunction is:

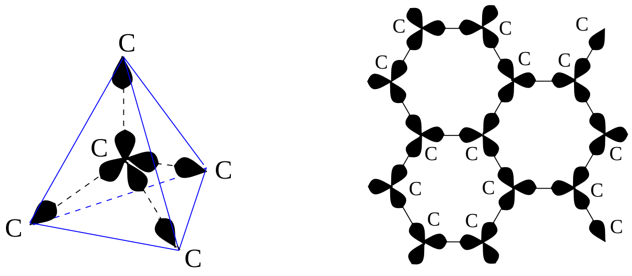
$$\psi_{GS}(\vec{r}_1,\vec{r}_2) \propto a\left[\phi_1(\vec{r}_1)\phi_1(\vec{r}_2)+\phi_2(\vec{r}_1)\phi_2(\vec{r}_2)\right]+b\left[\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)+\phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\right].$$

For large R, $a \propto t/U$, where t is the hopping and U is the average repulsion energy when both electrons are in the same orbital. Since $t \to 0$ as $R \to \infty$, while U is a constant, we can see that in this limit $a \to 0, b \to 1$, as expected. This is a good lesson to always remember what approximations we are making, and correct them if the answer is wrong.

Going back to our solution: this type of bond is known as a **covalent bond**. In this covalent bond, both electrons occupy the bonding orbital and have high probability to be found in between the two nuclei, thus helping to "glue" them together. Another way to think of this, is that ideally each H would like to have a full $1s$ shell to become noble-like, but there are only 2 electrons between the two of them. In this covalent bond, for 25% of the time each nucleus has both electrons (and the other has none), and in average this turns out to better than each nucleus having only its own electron all the time.

Before continuing, let's see why we don't have covalent bonds for two He atoms (or any other noble elements). We could again make the bonding and the antibonding orbitals and fully occupy them with the 4 electrons. However, the total energy now is back to 4ϵ, so there is nothing stable about this – whatever energy gain there is from the bonding orbitals, it is lost because of how expensive the antibonding ones are. In fact, if you look at the more accurate solution we discussed first (with S kept in it), you'll see that the antibonding orbital is a bit more expensive, so in fact the total energy would go up. If we also add the electron-electron repulsion, it makes it even more so. This is why for 2 He, it is energetically more favourable if each keeps its 2 electrons all the time (then we have the weak Lennard-Jones attraction to bind them, but that is a very different mechanism).

We can now generalize, and deduce that if we have atoms with at least half-filled shells, there is a way to create enough covalent bonds to be able to put all these electrons in bonding-like levels and lower the energy. One famous example is diamond, which is made of C. Of course, C has 4 electrons in the $2s+2p$ orbitals, so half-way to being full. In diamond, the C arrange themselves on a certain lattice (we will discuss the particulars next) so that each one is at the center of a regular tetragon, with 4 other C in the corners. There is a bonding orbital between each pair of C, occupied by an electron each from each C. The sketch below tries to suggest what this looks like. This way, all the electrons can be placed in covalent bonds and the structure is very stable. Technically, these orbitals are called sp^3 orbitals, because each one is a linear combination of the one $2s$ and the three $2p$ orbitals of the C.



sp^3bonds in a tetragonal cage: diamond structure

sp^2bonds in a graphite plane

Figure 6: Diamond structure (left) and graphite structure (right).

Because each of these valence electrons is localized in between two C atoms and is not free to move away from there, we can infer that this material will be an insulator. Another way to see this is that all the states for all the bonding orbitals are filled, so that band is completely filled, while the next one with anti-bonding states is completely empty (we'll come back to this, so don't worry if this sentence is not making any sense, yet).

C can also crystallize as graphite (the stuff we use in our pens, to write with). In this case, it creates planar sp^2 bonds, which lie at 120^o degrees from one another, and mix together the $2s, 2p_x$ and $2p_y$ orbitals. This leads to a honeycomb lattice, as shown above. Each C forms strong covalent bonds with its 3 neighbours, by creating bonding orbitals out of their corresponding sp^2 and filling them with two electrons, one from each C. This leaves one electron per C in the $2p_z$ orbital. What precisely happens to these we will learn a bit later on – they form so-called metallic bonding, which among other things helps link the layers together, but rather weakly. This is why graphite is not structurally as strong as C. In fact, as we write, we break bonds between successive planes – so the trace that we leave on the paper are these thin layers of C. Isn't that neat?

It turns out that graphite is more stable than diamond, so the rumour that somewhere there is a mine where diamonds turn to graphite is not impossible. These are not the only forms of crystalline C, though. Very recently, people have figured out how to get graphene, which is a single layer of graphite – a Nobel prize was given out for this very recently, and graphene is believed by many to have a very bright future for applications (it is very strong but as thin as can be, one-atom thick). There are also nanotubes, which you get by slicing a piece out of a graphene sheet, rolling it up and gluing the sides. There are also buckyballs, C_{60}, which are molecules that look like soccer balls, and which order into crystals, as well. And who knows what other surprises are in store.

We can make such insulators/semiconductors not only with elements from group 4, but also by combining an element from group III with one from group V (eg. GaAs), or one from II with one from VI (eg ZnSe). We still have an average of 4 electrons per atom, which can be placed in bonding orbitals to stabilize the lattice. What happens here, however, is that because the atoms are not identical, one of them will attract the electrons a bit more than the other, so the electrons are not equally shared between the two, as is the case when all atoms are identical. As a result, these bonds start to acquire more and more of an ionic character. We discuss ionic bonds next.

4 Ionic bonds

Let's consider the typical example of what happens if we have one Na (structure $1s^2 2s^2 2p^6 3s^1$, i.e. like Ne plus one extra electron in the $3s$ shell) and one F (structure $1s^2 2s^2 2p^5$, i.e. like a Ne missing one electron from its $n = 2$ shell). In other words, we go all the way to the extreme of a group 1 + a group 7 combo. There's no way they'll share the 8 electrons equally to average 4 each and make covalent bonds. In fact, only 1 electron really matters here, namely the extra one that Na has and that F would dearly like to steal away.

Let's make a model for this. For the Na, I will only keep the $3s$ level (the other ones are either already full, or are empty and cost too much energy to occupy), and only the $2p_z$ for F, for the same reasons (here, I assume that Na and F are lying along the z axis. Can you think of any reason why p_z might be more interesting to keep than p_x or p_y?). We have one electron (the one that initially belongs to Na), and this could be either in the $3s$ shell of Na – let me call this state as $|1\rangle$, or fill up the $2p_z$ shell of F – let me call this state $|2\rangle$.

So let's write a low-energy Hamiltonian for these two states. Just like in the case we considered before, we must have some hopping between the two states, let's call the hopping integral $t = -|t| < 0$

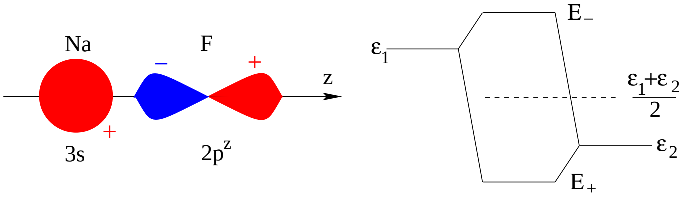


Figure 7: Level structure for the ionic bond. Now there is only 1 electron to be placed in the "bonding" orbital. The lower ϵ_2 is compared to ϵ_1, the higher the probability to find this electron in state $|2\rangle$.

(look at the figure above to understand why t as a different sign than it did for H atoms). It will depend on the distance R between nuclei and can be calculated from the overlap of their orbitals.

The main difference is that the electron has different energies in $|1\rangle$ vs $|2\rangle$, because these are no longer equivalent states. So, we now have:

$$\hat{H} = \epsilon_1|1\rangle\langle 1| + \epsilon_2|2\rangle\langle 2| + |t|\left(|1\rangle\langle 2| + |2\rangle\langle 1|\right)$$

We can actually also evaluate ϵ_1, ϵ_2. The ionization energy of Na is $-5.14eV$, so this must be the energy of the electron if it stayed there all the time. Plus, actually, we must add some short-range repulsion between the filled electronic clouds of the two atoms, if we bring them too close together and they start to overlap. The later could be modeled either as a power law (like we did in the Lennard-Jones potential), or like a fast-decaying exponential. Let's do the latter:

$$\epsilon_1 = -5.14eV + \lambda e^{\frac{-R}{\rho}}$$

For F, the electron affinity is $-3.61eV$, so this must be the energy if we give it the extra electron – plus, again, the short-range repulsion with the Na filled shells, PLUS, now, also attraction between the two atoms. Because if we give the electron to the F it will have an effective charge $-e$, while the Na has $+e$ after loosing the electron. So:

$$\epsilon_2 = -3.61eV + \lambda e^{\frac{-R}{\rho}} - \frac{ke^2}{R}$$

At first sight you might worry that $\epsilon_1 < \epsilon_2$ and the electron might prefer to stay at the Na and nothing much happens. But in fact, the last term in ϵ_2 can be substantial: if R is a few A that energy is $\sim 10eV$, making $\epsilon_2 < \epsilon_1$. Thus, having the electron at 2 is more convenient.

It turns out that this is precisely what happens. We can find the eigenstates and eigenvalues just as before:

$$\hat{H}|\phi\rangle = E|\phi\rangle \rightarrow \hat{H}\left(\alpha|1\rangle + \beta|2\rangle\right) = E\left(\alpha|1\rangle + \beta|2\rangle\right) \rightarrow$$
$$\alpha\left(\epsilon_1|1\rangle + |t||2\rangle\right) + \beta\left(\epsilon_2|2\rangle + |t||1\rangle\right) = E\left(\alpha|1\rangle + \beta|2\rangle\right)$$

so now:

$$\begin{cases} (E-\epsilon_1)\alpha - |t|\beta & = 0 \\ -|t|\alpha + (E-\epsilon_2)\beta & = 0 \end{cases}$$

A nontrivial solution exists if the determinant vanishes, i.e. $(E-\epsilon_1)(E-\epsilon_2) - t^2 = 0 \rightarrow$

$$E_\pm = \frac{\epsilon_1+\epsilon_2}{2} \pm \sqrt{\left(\frac{\epsilon_1-\epsilon_2}{2}\right)^2 + t^2}$$

Of course, this agrees with what we had before when $\epsilon_1 = \epsilon_2 = \epsilon$. What we see (sketched above) is that again we obtain a bonding and an anti-bonding level, but now the situation is no longer symmetric. The wavefunctions are no longer symmetric either, clearly $|\alpha|^2 \neq |\beta|^2$ now. You can evaluate these exactly, but let's do this assuming that $|t| \ll \epsilon_1 - \epsilon_2 = \Delta\epsilon$, so that we can Taylor-expand the square root. We then find, for the binding state, that

$$E_B \approx \epsilon_2 - \frac{t^2}{\Delta\epsilon}$$

and

$$|\Phi_B\rangle \sim |2\rangle - \frac{t}{\Delta\epsilon}|1\rangle$$

In other words, the electron spends most of its time at $|2\rangle$ since this is energetically more favourable, but with small probability $\propto t^2/(\Delta\epsilon)^2$ it "visits" 1 and this allows it to lower its energy even more, by $\frac{t^2}{\Delta\epsilon}$. As I said, you could calculate the exact α and β to check that they evolve towards being equal if we make $\epsilon_1 \to \epsilon_2$, so all is well.

The conclusion here is that again we have a bonding orbital, but unlike for the covalent bond this is now occupied by a single electron. Also, it is very unequally distributed, with much higher probability for the electron to be at F than at Na – and it is this that stabilizes the molecule, since when the electron is at F, the two ions strongly attract each other and lock into a stable molecule. I could, in fact, assign a charge $-q = -|\beta|^2 e$ to the F ion, since that is its average charge, and of course, $+q$ to Na ion. In a perfectly ionic bond, we would have $q = e$, while in a perfectly covalent bond, $q = 0$. Most bonds lie somewhere in between, having mixed character.

Can we make a crystal, based on ionic bonds, and if yes what would be its structure? Well, of course we can, because we have charged objects with some effective interactions between them:

$$V_{ij} = \frac{kq_iq_j}{|\vec{R}_i - \vec{R}_j|} + \lambda e^{-\frac{|\vec{R}_i - \vec{R}_j|}{\rho}}$$

where q_i, q_j are the effective charges of the ions placed at positions $\vec{R}_i, \vec{R}_j$. Just like we did for the van der Walls bonds, we should now sum over all energies for a given crystal structure, and figure which structure and which lattice constant minimize the cohesion energy.

The only difference is that we must decide where to place the positive and where the negative ions (for van der Waals, all atoms were identical). After some reflection, you should agree that it's best to make sure that each Na is surrounded by as many F as possible, and viceversa. Looking again at our 2D example, this is easy to realize for a square lattice (see panel (a) in the sketch on next page), but can't be done for a triangular lattice (panel (b)). This is because for a triangle, if we place a positive ion in a corner and a negative one in the next (so that they are close together), it is not clear what we should do with the 3rd corner. Whether we put a positive or a negative ion there, one of its neighbours is "unhappy", there's no simple winning arrangement. This sort of thing is known as **frustration**, and should convince you that the best structure in this case is certainly not triangular. It could be the honey-comb lattice, though (panel (c)), for which we do not have trouble making sure that each positive ion only has negative ions as nearest neighbours, and viceversa.

As we'll see in a bit, in 3D the correct structure for NaCl and NaF looks like a 3D analog of the square lattice. The results agree well with experiments, for instance the cohesion energy (in kcal/mol) is calculated to be 242.3; 198.9; 189.9 for LiF, LiCl, LiBr. Measurements put these at 242.2; 192.9; 181.0 (these values are again taken from Kittel's book). The agreement is reasonable.

Two more things. First, for an ionic lattice, the cohesion energy is also known as the Madelung energy, because he's the first to have calculated it. I think. Second, you can again see that these crystals must be insulators, because these electrons are tightly bound to their F (negative ion, in general), so they can't move around freely.

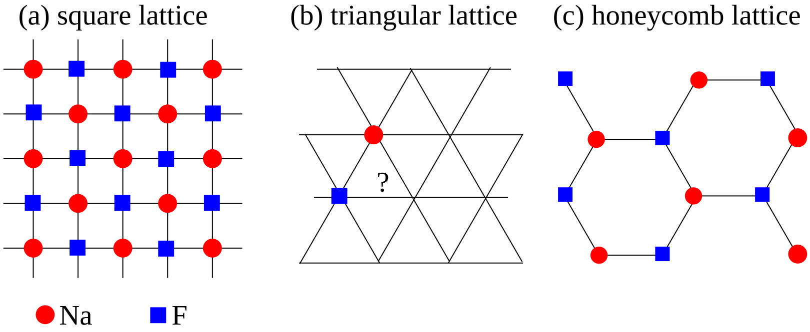


Figure 8: Positive and negative ions arranged on a 2D square (left), triangular (middle) and honey-comb (right) lattice. In the triangular case there is "frustration" and we can't make a stable lattice.

To summarize, so far we've seen three routes to getting insulators: (a) from van der Waals interactions for noble elements. Here each atom holds on to its electrons; (b) with covalent bonds from atoms with more than half-filled shells. The covalent bonds insure that at least for some fraction of the time, each atom has a filled shell. The bond is stabilized by having these electrons "piled up" predominantly in between the two atoms; (c) with ionic bonds, which appear if we put together different elements, one with a few extra and one with a few missing electrons. In this case, the electrons are moved from the atom with a nearly empty shell to the one with a nearly full shell, so that both resulting ions have completely filled shells (most of the time). The bond is stabilized by the Coulomb attraction arising between the resulting ions.

The next question is: what happens if we put together similar elements which all have just a few electrons in the last shell (i.e., nearly empty shells)? Clearly, none of the above strategies works here. Instead, what we get is the so-called "metallic bonding", and finally we'll have candidates for metals, too. Let's see how this works.

5 Metallic bonding

For simplicity, let's assume that we put together many Li ions, each with a $1s^22s^1$ structure, in a crystal. What keeps them together, now? Clearly it is neither ionic nor covalent bonds, since we don't have enough electrons to make covalent bonds between all atoms, and we can't make differently charged ions out of identical atoms.

What happens here is that none of the atoms is particularly fond of its lone 2s electron. As a result, it is energetically favourable to release these electrons to be free to move anywhere in the system, leaving Li^+ ions behind, at the lattice sites. The system is still neutral (in average each ion has one electron in its vicinity), however the electrons lower their kinetic energy by moving around the crystal and this is what stabilizes the structure.

To show you how can this be, let me consider the simplest 1D model, where we have a chain of such ions, placed equidistantly from each other. We can label these with an index $n = 1, ..., N$, where I will let $N \to \infty$, in the end. Let's make a model for this. When isolated, each Li has a $2s^1$ electron as a valence electron, so we need to figure out what happens to them when we bring the Li close together. Let's keep only these states in our model, so that our basis consists of the states $|1\rangle, |2\rangle, ..., |N\rangle$ showing that the electron is in the $2s$ orbital centered at nucleus $1, 2, ..., N$. This is a direct generalization of what we did for the covalent bond, and just like there we will first find the eigenstates for a single electron, and then fill them up with all the electrons available, to see what the ground-state is. Also like there, this is a reasonable approximation if the distance between neighbour ions is much smaller than the "size" of the $2s$ orbital, so that there is no confusion to which orbital an electron belongs. This is sketched below to the left, and is known as a "tight-binding" limit. One could also consider the "nearly-free electron limit", which would be valid if the atomic orbitals spread over many lattice sites, so that you couldn't be sure to which orbital an electron which is close to ion n, let's say, belongs in reality. This is sketched to the right. We will discuss this second case in detail in a few weeks.

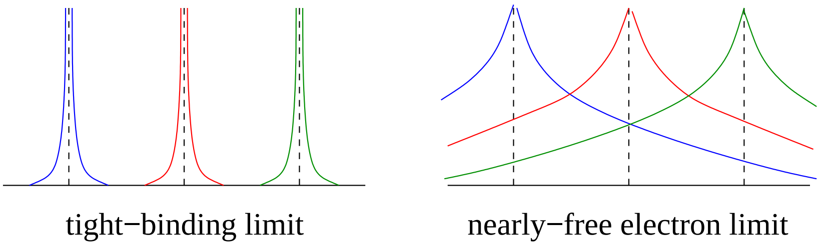


Figure 9: Contrast between a tightly-bound model, with orbitals small compared to the lattice constant (left) and a nearly-free model, with orbitals spread over many lattice constants.

For our tight-binding model, we can assume $\langle n|m\rangle = \delta_{nm}$, i.e. 1 if $n = m$ (these states are normalized) and 0 otherwise (meaning, if the electron is in $|m\rangle$, i.e. the orbital centered at m, there is very little probability of finding it close to another ion n and confusing it as being in state $|n\rangle$).

The simplest Hamiltonian to describe this system is:

$$\hat{H} = \epsilon \sum_{n=1}^{N} |n\rangle\langle n| - t \sum_{n=1}^{N-1} \left(|n\rangle\langle n+1| + |n+1\rangle\langle n|\right)$$

The first term is just the energy to have the electron at any given site (equal to the ionization energy for a Li, basically, although we should add repulsion between inner shells if we bring the ions too close together). If each atom keeps its electron 100% of the time, the energy would be $N\epsilon$.

The second term describes hopping: if the electron is at site n, attraction from the neighbouring ions can make it move either to $n+1$ or to $n-1$. This is known as **nearest-neighbour hopping**. In reality, the electron will feel attraction from ions $n+2$ and $n-2$ and ions further away, as well, and could hop directly two or more lattice sites, to one of those. However, remember that the hopping matrix decreases exponentially with the distance between the sites, so nearest-neighbour hopping is by far the largest term. In many cases it is a good approximation to ignore longer-range hopping, and we will do so. It can be easily included and you should know how to do that and be able to figure out precisely what its effects are.

One issue is what happens at the ends of the chain. I will use the so-called **periodic boundary conditions** (PBC), which state that if the electron is at site 1, it can hop either to 2 or to N, and if the electron is at site N, it can hop either to N-1 or to 1. In other words, it's as if the chain is actually closed into a circle, and 1 and N are nearest neighbours.

The reason we prefer to do this is because it makes the calculations simpler, as we'll see soon. The logic is that for a macroscopic crystal, with $N \sim 10^{23} \gg 1$, it should not matter how we "end" the crystal, because the vast majority of the contributions comes from the bulk sites and small contributions from the surface must be negligible by comparison. So we can choose whichever situation makes calculations easiest, and PBC do. If you are ambitious you might want to have fun and try to prove this statement, by repeating the calculation we do next for a chain with open ends, i.e. where an electron at site 1 can only hop to 2, and one at N can only hop to N-1.

We're finally ready to find the eigenfunctions $|\phi\rangle = \sum_{n=1}^{N} c_n|n\rangle$ and eigenenergies $\hat{H}|\phi\rangle = E|\psi\rangle$. Repeating the steps from the H_2^+ example, we now find that the coefficients must satisfy the equations:

$$Ec_n = \epsilon c_n - t(c_{n-1} - c_{n+1}), \qquad n = 1, 2, ..., N$$

where PBC means that we take $c_0 \equiv c_N$, and similarly $c_{N+1} \equiv c_1$. These are simple recurrence relations, and there are straightforward ways to solve these mathematically. Maybe I'll give this as a problem at some point, although it's mostly math, not physics. But it is a nice solution.

As physicists, we are allowed (and indeed, encouraged) to use our intuition to guess what the solutions might look like. In this particular case, since all ions are identical, the probability for the electron to be at a site must be the same for all sites. The most general functions that have this property are known as plane-waves (you should be familiar with them from considering electrons in free space). So let's guess that:

$$c_n(k) = \frac{1}{\sqrt{N}} e^{ikna}$$

where now the solution depends on a parameter k, which at this point could be anything. Does this guess work? Yes, if you plug it into the recurrence relation, you'll find that this works provided that we choose $E(k) = \epsilon - 2t\cos(ka)$. In other words, to the wavefunction:

$$|\phi_k\rangle = \sum_{n=1}^{N} \frac{e^{ikna}}{\sqrt{N}} |n\rangle$$

corresponds the eigenenergy

$$E(k) = \epsilon - 2t\cos(ka).$$

Can the parameter k be anything, or do we have some restrictions? Well, our planewave must satisfy the PBC conditions, which can be written more generally as $c_{n+N} = c_n$ for any n. If we put this into our plane-wave, we find that we must have

$$e^{ikNa} = 1 \rightarrow k = \frac{2\pi m}{Na}, m = 0, \pm 1, \pm 2, ...$$

So it seems that we have an infinite (but countable) number of eigenstates, one for each integer.

More careful thinking shows that this is not true, in fact we have distinct values only for N consecutive values of m, and then we repeat the same eigenfunctions and eigenvalues. Because we don't find something new, we can't pretend those to be distinct eigenfunctions, so we throw them out. To see this, consider $m = 0$ and $m = N$. The first corresponds to $k = 0$, the second to $k = 2\pi$. It is easy to see that $c_n(k = 0) = c_n(k = 2\pi) = c_n(k = 4\pi) = ... = 1$. This should not be surprising, since plane waves are linear combinations of sin and cosine functions, and these are periodic functions.

So we actually only get N distinct eigenstates. We could choose these as being $m = 0, 1, 2, ..., N-1$ or any other choice of N consecutive integers. Because we like symmetry, the traditional choice is $m = -\frac{N}{2} + 1, ..., -1, 0, 1, ... \frac{N}{2}$, i.e. values symmetrically placed about the origin. In other words, we only consider values such that $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$. This interval is the **Brillouin zone**. The allowed values for k and the corresponding eigenenergies in a chain with $N = 21$ sites are sketched on next page.

Sanity check: is it reasonable that we have N eigenstates? Maybe we didn't find all of them – we always have to worry about this when we guess. The answer is: all is good. As I hope you remember from linear algebra, an N-dimensional space has a basis with N states. The eigenstates form a basis, so there must be precisely N of them. We found N, so we have all of them (by the way, I forgot to mention that these eigenstates must be orthonormal. You can check by direct calculation that this is indeed the case).

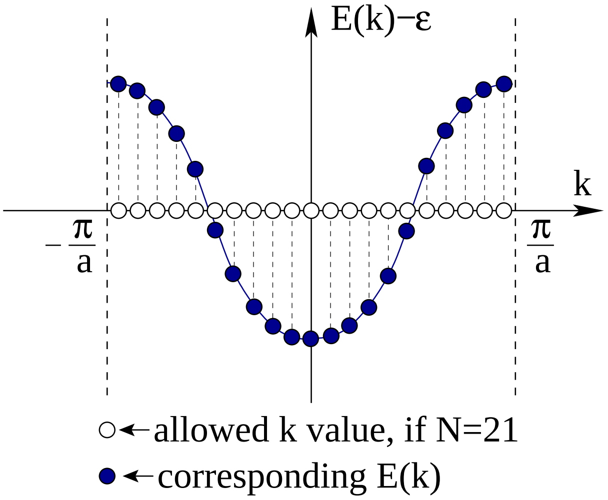


Figure 10: Allowed momenta k and corresponding eigenenergies $E(k)$ (white and blue circles, respectively) inside the first Brillouin zone $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$. For a chain with N sites there are precisely N allowed values, equidistantly placed.

So now we're basically done. We know that we have these N eigenstates with their energies $E(k)$. We have to place N electrons in these, one from each atom, and in the ground-state they must occupy the lowest available levels. At this point, it is essential to remember that electrons have spin, so we can actually put two electrons in each of these states. That means that we will occupy with electrons the half of the states with energies $E(k) < \epsilon$ (these are the states with momenta $-\frac{\pi}{2a} < k \leq \frac{\pi}{2a}$), and we will leave empty all the other states, with energy $E(k) > \epsilon$. So clearly the total energy is lower than the $N\epsilon$ we would have if each Li kept its electron. In fact, the ground-state energy is now:

$$E_{GS} = 2 \sum_{occupied} E(k) = N\epsilon - 4t \sum_{\frac{-\pi}{2a}<\epsilon<\frac{\pi}{2a}} \cos(ka)$$

In the limit $N \to \infty$, the sum can be turned into an integral. This should not be too surprising, since now the allowed values of k come closer and closer together. Maybe I'll ask you to prove this in a homework, but just for general reference, one can show that:

$$\sum_{k=k_{min}}^{k_{max}} f(k) = \frac{Na}{2\pi} \int_{k_{min}}^{k_{max}} dk f(k)$$

where k_{min} and k_{max} are the limiting values for the allowed k, in our case $\pm\pi/2a$. If you do the integral, you'll find that:

$$\frac{E_{GS}}{N} = \epsilon - \frac{4}{\pi} t < \epsilon$$

So there is a gain of $4t/\pi$ per atom in cohesion energy. Again, this is increased if we bring the atoms closer and t becomes larger, but then we start to pay the price due to repulsion between the electronic clouds (this is included in ϵ) – so there is some equilibrium distance between ions where the total energy is minimized. For other types of lattices (especially in higher dimension), the expression of $E(k)$ will be different, and as a result the prefactor multiplying t changes, so different lattices lead to different cohesion energies. The best one will be the preferred structure.

In any event, in all cases only half of the states are filled so we expect a metallic state. There is an important caveat to this statement, which is that we have ignored electron-electron interactions.

We will discuss later in more detail why this is a good approximation in some metals, in which case what I just said is fine. However, as we will see, in other materials the electron-electron interactions cannot be ignored. In those cases, it may happen that a gap is opened between the empty and the occupied states because of these interactions, so what ought to be a metal (if we could ignore the interactions) turns out to still be an insulator. Studying such systems with strong interactions (aka **strongly correlated systems**) is a very hard problem and a lot of research is being dedicated to it right now. Hopefully we'll have time to discuss a bit more about this at the end of the class, but now we will move on to the last type of bonding we consider, namely:

6 Hydrogen bonds

As an example of what hydrogen bonds are, let's consider what happens if we bring two water molecules close together. Each molecule is, of course, H_2O. Each hydrogen brings in 1e, while the O has 6 valence electrons. Two covalent bonds are created where each H shares its electron with one from the O. These two bonds make an angle of around 110^o between them. However, because of the very different Z, the oxygen attracts the electrons a lot more strongly than the H (the bond has a partially ionic character), so the H are positively charged and the O is negatively charged. I think the partial charges are somewhere around $0.4e$ for each H, and so of course, the O is at $\approx -0.8e$.

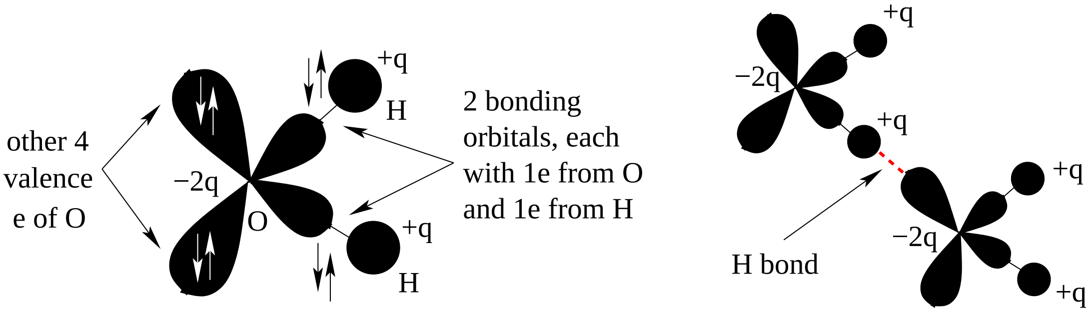


Figure 11: Left: Water molecule, with electrons roughly sketched. 2 go into two covalent bond with the two H, and the remaining 4 occupy two other orbitals which point in different directions, so that the electrons avoid each other. Right: The H bond is established by Coulomb attraction between a H from another molecule and one of these doubly occupied O orbitals.

This happens to the H not only in water, but in nearly all molecules (except H_2) – any other atom is likely to attract the electrons more than the tiny H, and so H has some partial positive charge. Because of this, it can interact with other charged objects and establish a (weaker) bond with them, based on Coulomb attraction, which is known as a hydrogen bond.

Going back to our water molecules, you can now see that one of the positive H of one of the water molecules can establish such a bond with the negatively charged O of the other molecule. The way this is usually indicated is something like H-O-H. . .OH−2. The dots are supposed to indicate the weaker H bond between one H and the other O, but the notation is a bit cumbersome.

In practice, what happens is this. The O has 6 valence electrons (it has 8 in all, but the 2 in the 1s shell are happy and don't do anything). Two of them go into the two covalent bonds with the two H, so they are occupying the respective bonding states located in between the O and each H. This leaves 4 other electrons. These want to stay out of the way of the bonds, to avoid overlap with those electrons, so they orient into two orbitals pointing in two other directions. It's somewhat analogous with the C in a diamond, with its 4 orbitals pointing towards the corners of a tetrahedron, except here the tetrahedron is distorted because it has 2 H in two corners and nothing in the other two.

So once you picture this, it is easy to see that the H bond is most easily established when the H of the other molecule points towards one of these other two orbitals which have 2e in them and no other positively charged H anywhere nearby. The previous sketch tried to indicate this.

The H bond is weaker than the one between the H and its own O, so the distance is a bit longer. This is actually the reason why ice has a lower density than water (I'm sure you all know that ice floats on/in water, which can only happen if it has lower density than it. Archimedes and all that, yes?). Ice is a crystal made of water molecules, and what fixes them in place are precisely these H bonds which, however, push the water molecules a bit further away than they would stay if there were no H bonds. The lattice structure of ice is that of distorted planes with honey-comb order, layered on top of each other. Each O has 4 neighbours, 3 from its honeycomb plane and one from the layer either above, or below it (distortions push each O closer to the layer above and further from the one below, or viceversa. The O will make a bond with the one in the closer layer). Each molecule has its two H pointed towards two neighbour molecules, creating H-bonds with them. Its other two neighbours have one of their H pointed towards it, also creating H-bonds. Unfortunately, my attempts to sketch this deformed structure were spectacularly unsuccessful; I suggest you google “ice crystal structure” to see some decent pictures of it.

We will not discuss H bonds any more than this in this course, but before concluding I would like to say that they are extremely important in many aspects of condensed matter systems, including us and all living beings. For example, it is H bonds that are responsible for linking together the two strands of the double helix in the DNA. In their absence life, as we know it, would be impossible.