Lecture 1

Atoms and molecules

What will we learn in this course?

Please read the syllabus first. Solid state physics deals with materials that consist of enormous quantity of electrons and ions. In solid state physics, we learn the collective behaviors of electrons and ions. For instance, a solid is … solid: it has a certain form, is resilient (elastic), and hurts you when you kick it. These are some examples of collective properties: properties that are not inherent to one electron/ion, but arise only due to many interacting electrons/ions. Other more exotic collective properties include magnetism and superconductivity. We will learn about these properties of solids.

Starting from this angle of approach, it might seem almost miraculous that sometimes we can think of solids as consisting of free electrons. Surprising as this may be, this approach has been proven to be quite effective. Indeed, the success of the free electron theory of solids has formed the fundamental basis for the solid state physics. In fact, many things that we will learn in this course will use a so-called "independent particle" theory, be it the free electron theory or the free phonon theory, as our very useful starting point.

Note that you will often hear the term "condensed matter physics" when it seems to mean "solid state physics." Condensed matter physics is a more comprehensive term, since it includes not only solids but also liquids. In fact, the study of liquid He has been critical in developing the "free electron theory" or Landau Fermi liquid theory applicable to many metals. Also, soft matters such as polymers and bio matters are also included in condensed matter physics. In this course, we will deal with solid state physics, but keep in mind that a more general name of this field is condensed matter physics.

Hydrogen-like atom

Before we learn about solids, it is helpful to remind ourselves about some basic facts about atoms and molecules. Study of atoms and molecules is an active field of physics by itself. Here, let us focus on very basic facts about atoms and molecules.

Let us consider a hydrogen-like atom with the potential

$$V(r) = -\frac{Ze^2}{r} \tag{1.1}$$

Note: I will be preferring the cgs unit for this course. In the SI unit, $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$.

The energy levels of the bound states for this problem are given by

$$E_n = -\frac{Z^2}{n^2}R, \quad R = 13.6 \text{ eV} \tag{1.2}$$

where $= 1, 2, 3, \ldots$. In the atomic unit, R is referred to as 1 Rydberg. It is a fundamental energy scale in atomic physics. The size of the radius for the atomic orbitals can be estimated by the following formula

$$\langle\frac{1}{r}\rangle = \frac{Z}{n^2 a_B} \tag{1.3}$$

where $\langle\rangle$ means the expectation value (for a stationary state in the present case) and

$$a_B = \frac{\hbar^2}{me^2} = 0.529 \text{ Å} \;\; \text{(Bohr radius)} \tag{1.4}$$

where m is the electron mass. One easy way to remember R is that

$$R = \frac{1}{2}\frac{e^2}{a_B} \tag{1.5}$$

In considering the interaction of light and electron, the following constant is immensely important

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \;\; \text{(fine structure constant)} \tag{1.6}$$

For instance, it is easy to derive that the atomic energy scale (R) and the atomic length scale (a_B) can be expressed as follows

$$R = \frac{mc^2\alpha^2}{2} \tag{1.7}$$

$$a_B = \frac{\lambda_e}{\alpha} \text{ where } \lambda_e = \frac{\hbar}{mc} \text{ is the (reduced) Compton length} \tag{1.8}$$

where $mc^2 = 0.511$ MeV. The hierarchy of energy scales in atomic physics governed by α in fine structure and hyperfine structure is well-known in quantum mechanics (see Griffiths, p. 267, e.g.).

Of course, it is not the purpose of this short note to derive the above results. Nevertheless, my favorite way to recall the above results is to do it like Bohr, using the Bohr-Sommerfeld semi-classical quantization rule[1] $\oint p\, dq = nh$ where p is the momentum corresponding to the (generalized) coordinate q (and the integral is over a closed path corresponding to a classical mechanical motion for one period), on top of what we know about the classical mechanics of a circular motion. The two starting equations are then $mvr = n\hbar$ and $2T = -V$, where $T = \frac{mv^2}{2}$ (kinetic energy) and $V = -\frac{Ze^2}{r}$ (potential energy)[2]. The steps are summarized in the following.

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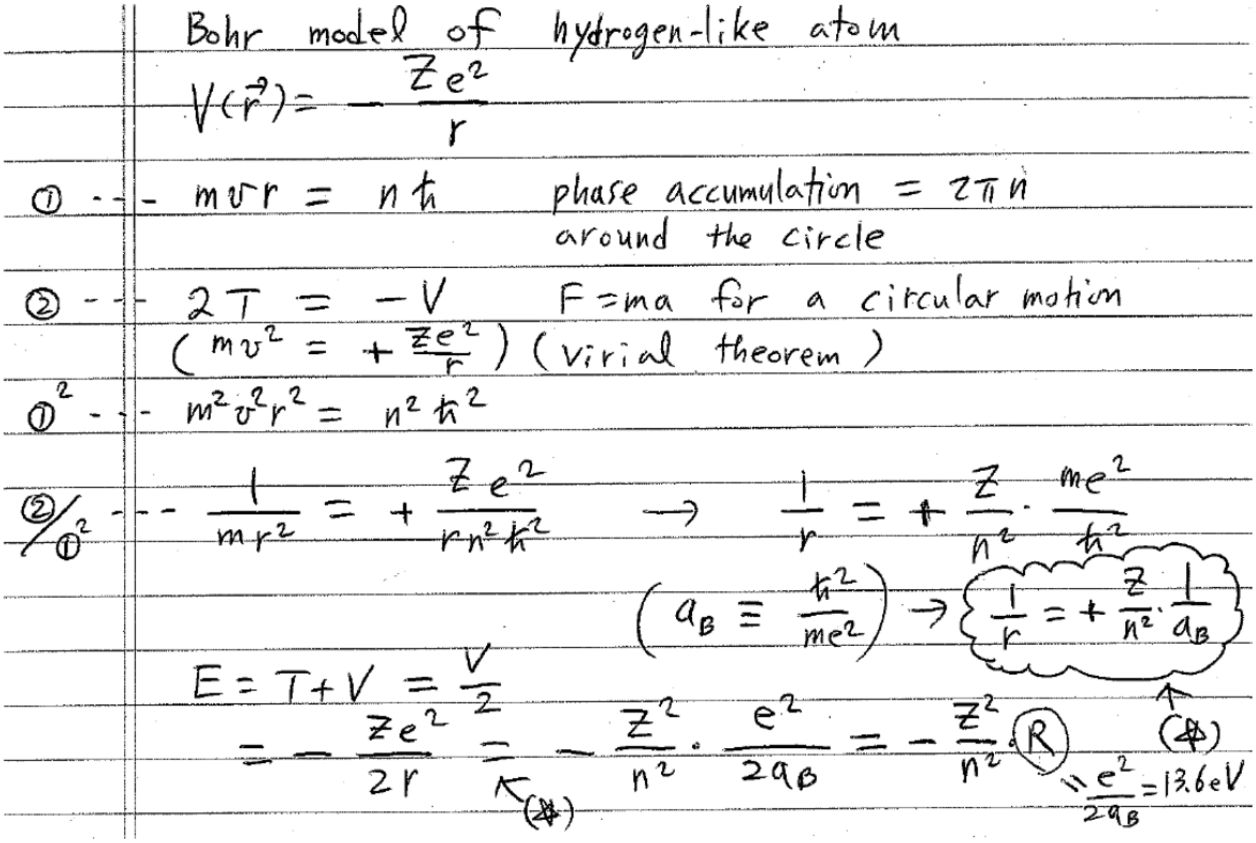
[1] The general form of this rule uses $n + \gamma$ in place of n where γ is a problem dependent constant.

[2] The relation $2\langle T\rangle = -\langle V\rangle$ is strictly valid for bound states of this problem in classical mechanics (in which case the bracket means the time-average) and also in quantum mechanics (in which case the bracket means the expectation value for a stationary state), and is the consequence of the so-called "virial theorem" (see Griffiths, p. 190, e.g.).



Bohr model of hydrogen-like atom

$$V(\vec{r}) = -\frac{Ze^2}{r}$$

① --- $mvr = n\hbar$ phase accumulation $= 2\pi n$ around the circle

② --- $2T = -V$ F=ma for a circular motion

$$\left(mv^2 = +\frac{Ze^2}{r} \right) \text{ (virial theorem)}$$

①^2 --- $m^2 v^2 r^2 = n^2 \hbar^2$

②/①^2 --- $$\frac{1}{mr^2} = +\frac{Ze^2}{rn^2\hbar^2} \rightarrow \frac{1}{r} = +\frac{Z}{n^2} \cdot \frac{me^2}{\hbar^2}$$

$$\left(a_B \equiv \frac{\hbar^2}{me^2} \right) \rightarrow \frac{1}{r} = +\frac{Z}{n^2} \cdot \frac{1}{a_B}$$

$$E = T + V = \frac{V}{2}$$

$$= -\frac{Ze^2}{2r} \underset{(*)}{=} -\frac{Z^2}{n^2} \cdot \frac{e^2}{2a_B} = -\frac{Z^2}{n^2} \cdot \text{Ⓡ}$$

(*)

$$\text{Ⓡ} \equiv \frac{e^2}{2a_B} = 13.6\,\text{eV}$$

Core electrons and valence electrons

In general, atomic orbitals are designated by quantum numbers[3] n, l, m_l, m_s where $n = 1, 2, 3, \ldots$ as introduced above already, is the principal quantum number, and $l = 0, 1, \ldots n-1$ is called the azimuthal quantum number for the orbital angular momentum and $m_l = -l, -l+1, \ldots, l-1, l$ is the magnetic quantum number for the orbital angular momentum. $m_s = \frac{1}{2}, -\frac{1}{2}$ is the magnetic quantum number for the spin angular momentum, $s = \frac{1}{2}$ for the electron. $m_s = \frac{1}{2}$ is often referred to as spin "up" and $m_s = -\frac{1}{2}$ as spin "down." The atomic orbital is often referred to as using symbols such as 1s, 2s, 2p, etc. Here, the number is n, and the alphabet letter s, p, d, f … corresponds to $l = 0, 1, 2, 3 \ldots$ respectively.

In hydrogen model of the previous section, the energy level depends only on n. This simple result is not valid in real atoms with many electrons. The main reason is the electron-electron interaction.

Consider the electronic configuration for a Li atom. There are three electrons in this atom. What would be the ground state? If we ignore for now, the electron-electron interaction, then one can use the results of the previous section to obtain this simple answer: place two electrons (spin up and down) in the lowest energy orbital, i.e. 1s orbital, and then placing the remaining one electron in 2s or 2p orbital. The ambiguity as to where to put the last electron comes from the fact that the energy level (1.2) depends only on n. In reality, this ambiguity does not exist, and the remaining electron always goes to the 2s orbital.

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[3] Here the fine structure and the hyperfine structure of atomic energy levels are ignored for simplicity. For instance, with the spin orbit interaction (fine structure), the m_l and m_s are no longer good quantum numbers.

Why? The 2p orbital extends out more than the 2s orbital in the radial direction, since the angular momentum is higher. For this reason, the 1s electrons tend to *screen out* the nucleus charge better for 2p electrons. In other words, 2s electrons are more strongly bound, due to the electron-electron interaction.

The effect of this screening can be also seen in the first ionization energy of Li, which is[4] 5.39 eV. If Z = 3 applies, then this value should be $\frac{3^2}{2^2} \times 13.6$ = 30.6 eV, whereas if $Z = 1$ applies, then this value should be $\frac{13.6}{2^2} = 3.4$ eV. Notice that the actual value is much closer to the latter value, meaning that $Z \approx 1$ is indeed valid. In reality, we would expect that Z to be somewhat greater than 1, since there is a probability that the 2s electron is closer to the nucleus than 1s electrons, which is the reason why the actual value 5.39 eV lies between 30.6 eV and 3.4 eV.

For a given atom, the ionization energy of the electron is then a function of n and l. The so-called valence "shell" corresponds to the quantum number n corresponding to the highest orbital, while different l values denote "sub-shells." For instance, for Li, 2s is the valence shell. Inner shells are called "core." In the case of Li, the electronic structure is often written as [He]2s, where [He] means the core electrons forming He like configuration $1s^2$. Continuing like this, the following electronic structure is obtained: Be: [He]$2s^2$, B: [He]$2s^2 2p^1$ and C: [He]$2s^2 2p^2$, etc. Here the electrons in 1s orbital are called "**core electrons**" while those in 2s,2p orbital are called "**valence electrons**." This definition can be generalized to other rows of the periodic table, so that the electrons in the outermost sp orbitals define valence electrons and other orbitals define core electrons. Exceptions are transition metal elements and rare earth and actinides. For transition metal elements d orbitals are included in the valence electrons, and for rare earth and actinides, f and d orbitals are included. The physical and chemical meaning is that valence electrons determine how an atom interacts with other atoms, while core electrons are inert and do not participate in bonding at all. From this point of view, valence electrons are those electrons whose binding energy is on the order of, or less than, ~ 20 eV. Core electrons have much higher binding energy and they do not participate in the chemical interaction.

[*Please read the contents from here to the end of this lecture note. We will come back to them when necessary – when we do magnetism or band theory*.]

Multiplet, term symbol, exchange interaction, and Hund's rules

Often, the ground state, or any Hamiltonian eigenstate in fact, of an atom or an ion is characterized by the total S, L, J values to a good approximation[5], and said to form a multiplet. Thus, each multiplet is defined by the so-called term symbol, defined accordingly as ${}^{2S+1}L_J$. Here, S is the total spin quantum number, while J is the total angular momentum quantum number. L on the other hand is not a number here, but symbols S,P,D,F,G,H, … corresponding to the total orbital angular momentum values 0,1,2,3,4,5,… respectively.

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[4] http://science.jrank.org/pages/3677/Ion-Ionization-Ionization-energy.html

[5] Here, we are assuming that the spin-orbit interaction is small, compared to Coulomb and exchange interactions. If this assumption is valid, then we are in the "LS coupling regime." However, this assumption may break for heavy elements, and if it does S, L are no longer good quantum numbers, while J remains a good quantum number. In such a case, one goes into the "jj coupling regime."

For instance, the ground state of C atom ([He]$2s^2 2p^2$) is given by $^3P_0$. As another example, the ground state of Fe ([Ar] $4s^2 3d^6$) is given by $^5D_4$. Other examples can be found in Kittel pages 306 and 308.

In getting a sense of why these multiplets are ground states, we first consider the **exchange interaction**. Let us consider the two electrons in the p shell as those in the C atom. In principle, the total spin quantum number can be 1 (corresponding to spin triplet) and 0 (corresponding to spin singlet). The term $^3P_0$ means that the spin triplet is the ground state. Why? Note that in the case of spin triplet, the spin wave function is symmetric, and thus the orbital wave function must be anti-symmetric. Compared to the symmetric wave function, the anti-symmetric wave function arranges the two electrons farther apart. For instance, the probably that the two electrons are found at the same point in space is zero for an anti-symmetric wave function, while it is not zero for the symmetric wave function. This means that the electron-electron repulsion will be less for an anti-symmetric wave function. This is the reason why the anti-symmetric wave function is more stable. This spin dependent energy lowering arises from Coulomb interaction and Pauli exclusion principle, and is called the **exchange interaction**, and is usually written as an interaction term in the Hamiltonian as

$$J\vec{S}_1 \cdot \vec{S}_2 \tag{1.9}$$

where $\vec{S}_1$ and $\vec{S}_2$ are the two spins that interact. We just argued that the sign of J is negative for the exchange interaction between two electrons in a given sub-shell.

The Hund's rules are empirical rules formulated to give a guide line as to what the ground state multiplet term of an atom or an ion may be. They work very well for lone atoms and ions in the ground state. They work less well for the excited states or for ions in solids, but they are nevertheless often quite useful. Here are the rules:

1. The maximum value of the total spin S allowed by the exclusion principle.
2. The maximum value of the total orbital angular momentum L consistent with this value of S.
3. The value of the total angular momentum J is equal to $|L - S|$, if the shell is less then half full, and $L + S$, if the shell is more than half full. When the shell is just half full, $J = S$, since $L = 0$ by rule 2.

The physical origin of the first two Hund's rules is an often debated topic, but the first rule is attributed to the afore-mentioned exchange interaction. The third rule is attributed to the spin orbit interaction.

Application of these rules does give the correct ground state configuration for C and Fe, mentioned above.

Molecules – H$_2$ molecule

Common molecular bonding is a covalent bonding or an ionic bonding. Other type of bonding includes a hydrogen bonding.

Here, we consider a very simplified model of a H_2 molecule, a primary example of a covalently bonded molecule. The goal here is not to present a quantitative model that is suitable for calculating molecular energy levels, but to present a qualitative model to point out some salient features that are very important in solid state physics, as we consider energy bands and magnetism later.

Consider the potential energy that an electron feels in H_2. We can write $V\,(\vec{r}) = V_1(\vec{r}) + V_2(\vec{r})$ where V_1 is the potential energy due to proton 1, and V_1 is the potential energy due to proton 2. In the actual H_2 molecule, the distance between proton 1 and proton 2 is 0.74 Å, but here we treat this distance a theoretical parameter.

The so-called linear combination of atomic orbitals (LCAO) method is a general approach in quantum chemistry. In this approach, one may guess that the ground state wave function for $V\,(\vec{r})$ should, in the first approximation, consist of the two 1s orbitals centered at each proton. This is a good approximation, as long as the bond length is not so small. Then, the ground state is, in the Dirac notation, $|G\rangle = C_1|1\rangle + C_2|2\rangle$ where $|G\rangle$ is the ground state, $|1\rangle$ is the 1s state centered on proton 1, $|2\rangle$ is the 1s state centered on proton 2, and C_1, C_2 are complex numbers. Notice that the Hamiltonian of this problem has symmetry w.r.t. the exchange of proton 1 and proton 2. What this means is that the ground state is either the symmetric combination $|S\rangle = N_s(|1\rangle + |2\rangle)$ or the anti-symmetric combination $|A\rangle = N_A(|1\rangle - |2\rangle)$, where N_s, N_A are normalization constants. Which one is the ground state? It is $|S\rangle$, which is often called the **bonding** orbital. Why? For $|S\rangle$, there is an enhanced probability that the electron will be found in between protons. This excess negative charge in between protons is obviously a cause for the two protons to come closer to each other, i.e. bond. On the other hand, for $|A\rangle$, electrons are depleted from the space between the two protons. Such orbital is called the **anti-bonding** orbital.

It is rather straightforward to calculate the energy levels of $|S\rangle$ and $|A\rangle$. We will do it at two levels.

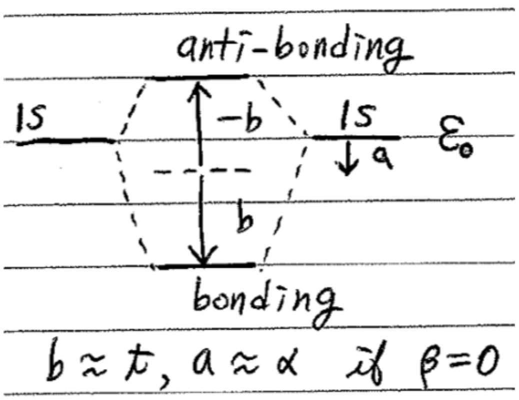
At the first level, let us assume that $\langle 1|2\rangle = 0$, for simplicity. The Hamiltonian is given by $H = T + V_1 + V_2 = H_1 + V_2 = H_2 + V_1$, where $H_1 = T + V_1$ and $H_2 = T + V_2$. By definition, $H_1|1\rangle = \varepsilon_0|1\rangle$ and $H_2|2\rangle = \varepsilon_0|2\rangle$. Also, let us define $\langle 2|V_2|1\rangle = \langle 1|V_1|2\rangle = t$ and $\langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle = \alpha$. Both $\alpha, t < 0$, because the (conventional) 1s wave function is positive, and the potential energy is negative, at any position in space. Since we assumed that $\langle 1|2\rangle = 0$ the Hamiltonian is a 2x2 matrix in the $|1\rangle, |2\rangle$ basis:

$$H = \begin{bmatrix} \varepsilon_0 + \alpha & t \\ t & \varepsilon_0 + \alpha \end{bmatrix} \tag{3.1}$$

This immediately leads to the solution $H|S\rangle = (\varepsilon_0 + \alpha + t)|S\rangle$ and $H|A\rangle = (\varepsilon_0 + \alpha - t)|A\rangle$, proving that the bonding state indeed has a lower energy.

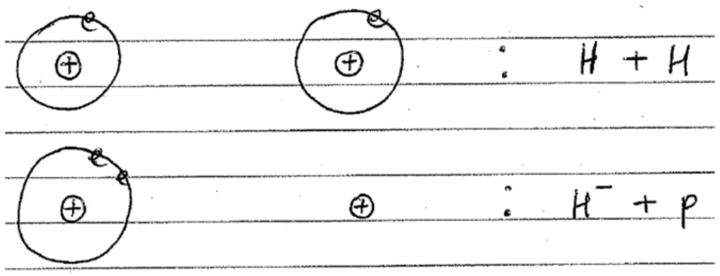
At the second, fuller, level, let us put $\langle 1|2\rangle = \beta$, which is a number less than 1, unless the two protons are at the same position. In this case, we are working with non-orthogonal states, and the problem is slightly more complicated, but by putting $H|S\rangle = E_s|S\rangle$, one can calculate E_s. With a little calculation, one gets $V_2|1\rangle = a|1\rangle + b|2\rangle$ and $V_1|2\rangle = a|2\rangle + b|1\rangle$, where $a = \frac{\alpha - t\beta}{1-\beta^2}$ and $b = \frac{t - \alpha\beta}{1-\beta^2}$. Then, it is easy to see that $H|S\rangle = (\varepsilon_0 + a + b)|S\rangle$ and $H|A\rangle = (\varepsilon_0 + a - b)|A\rangle$. Since, generally $b < 0$, $|S\rangle$ is a lower energy state.

One can see that the second calculation is more correct, but the qualitative essence is still preserved in the first calculation. To summarize, two atomic energy levels interact to produce one bonding orbital and an anti-bonding orbital, as shown in the following figure.



So, in the ground state of H_2, the two electrons It corresponds to putting two electrons in the symmetric wave function. In this case, the spin is anti-parallel, i.e. the total spin quantum number is 0, giving a singlet ground state. If one puts two electrons in the same orbital state, the orbital wave function necessarily has to be symmetric, and the spin wave function therefore have to be anti-symmetric (i.e. spin 0).

The above description follows the prescription of the **molecular orbital theory**. However, that it would not be applicable for all situations is quite evident from the following consideration.



Let us for a moment consider stretching the H_2 molecule so that the proton-proton distance becomes very large. Does the above picture remain valid? No … but partially yes. The spatial wave function does not remain valid, while the spin singlet nature of the ground state wave function remains valid. What is the problem of the above spatial wave function? According to that, each of the two electrons occupy the same molecular orbital $|S\rangle$. Each electron spends half of the time around one proton and the other half of the time around the other proton. While this sounds plausible, it does mean the following – the two electrons spend half of the time in the H+H configuration (“covalent”), and the other time in the H^-+p configuration (“ionic”). Common sense would tell us that the latter configuration is very unlikely when two atoms are far apart, and this is the reason why the molecular orbital approach above is incorrect at large separation. What is the reason for this? It is the **electron-electron interaction energy**. Indeed the original Heitler-London calculation (1927), which formed the starting point for the **valence bond theory**, explicitly disallowed the H^-+p configuration. When two electrons coexist in the same orbital, there is a strong electron-electron repulsion energy, which is typically a few eV. Let us call this energy U. We have been ignoring this in the above model of hydrogen molecule. Even in that case, U cannot be ignored if one is looking for quantitatively accurate results. When atoms are far apart, things become even worse. The reason is that U is basically independent of, or weakly dependent on, the inter-atomic separation, while t decreases very rapidly as the atomic separation increases. So a regime where where $U > t$ can be quickly reached. In this case, thinking in terms of molecular orbitals above is not even a good starting point. Instead, the good unperturbed wave function is putting one electron each at each proton site. It turns out that this wave function can be perturbed to give a lower energy only for a spin singlet state. This is the “yes” part. The spin remains singlet. This is the origin of **anti-ferromagetism** for many transitional metal compounds.

One could characterize the molecular orbital theory as an independent electron theory and the valence bond theory as a correlated electron theory. They are often contrasting and contentious views. In practice, each theory learns from the other and makes appropriate modifications for improvements of results.