

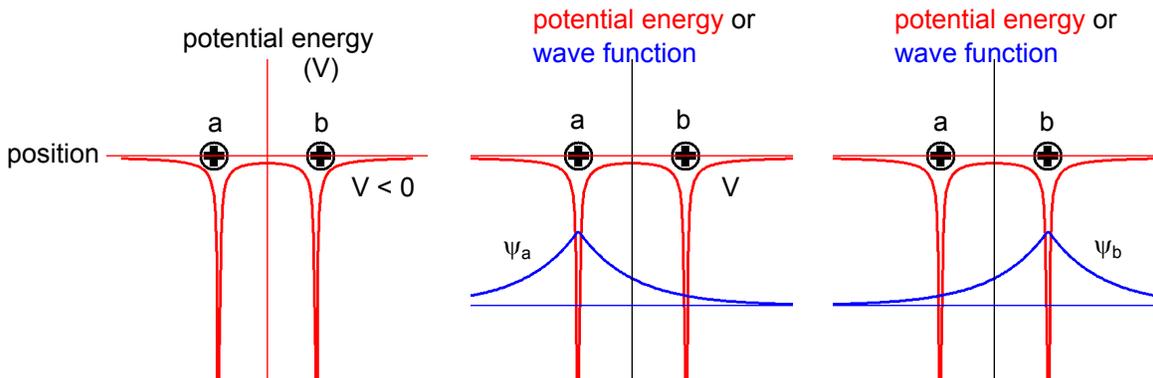
Notes for Lecture 4

Molecule, Energy Band

4.1 Hydrogen Molecule, cont.

4.1.1 H_2^+ – overview

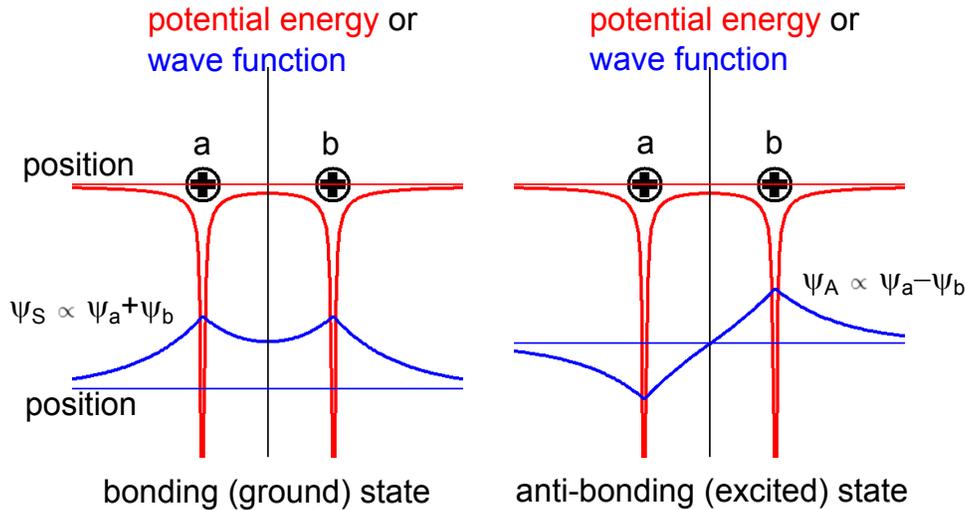
Two protons. One at position a and the other at position b . One electron with charge $-e$. When a and b are far away from each other. The electron belongs in one proton, say one at a . The ground state orbital is ψ_a , by which we mean the $1s$ orbital of the Hydrogen atom problem. This electron is in the “Coulombic potential well.” We call that it is in a bound state. Just as we are bound to the Earth, and as the Earth is bound to the Sun.



As the two protons are brought together, the electron can tunnel to the proton b , and starts to oscillate back and forth. The question is what is the ground state that the electron will settle in?

4.1. HYDROGEN MOLECULE, CONT.

From all the drumbeats that we played so far, we “know” that the ground state is “something like” (more about this later) $\psi_a + \psi_b$, i.e. a symmetric state. Here, ψ_b is just like ψ_a , but centered at b .



4.1.2 Details of an essential bare bone model

But, here we prove it.

To prove it, we make the following assumption, which is something of an oversimplification. But this does not affect the physics, which is why we make this assumption. Indeed, in a solid, this condition is strictly true in some special sense, which we will get to later in this lecture.

$$\int d^3\vec{r} \psi_a^* \psi_b = 0 \quad (4.1)$$

Here, $\int d^3\vec{r}$ is the volume integral in the entire space¹ The functions ψ_a and ψ_b are now the functions of the vector position \vec{r} , and so they should be written as $\psi_a(\vec{r})$ and so on – but we omit the (\vec{r}) part for simplicity. Quantum mechanically, Eq. ?? means that the state ψ_a and the state ψ_b are *orthogonal* to each other. But it would be fine for this course if you don't pick up this word.

¹The notation dV is avoided in this note, to avoid confusion with the potential energy V . The volume element can be written in many forms, and the following are some examples: dV , $d\vec{r}$, $d^3\vec{r}$, and $dx dy dz$.

Note the following two normalization conditions (see the last lecture, page 4).

$$\int d^3\vec{r} \psi_a^* \psi_a = 1 \tag{4.2}$$

$$\int d^3\vec{r} \psi_b^* \psi_b = 1 \tag{4.3}$$

This must hold for *any* wave function.

From ψ_a and ψ_b , we can form $\psi_a + \psi_b$ (symmetric wave function) and $\psi_a - \psi_b$ (anti-symmetric wave function). What we will show is that the energy of the symmetric wave function E_S is lower than the energy of the antisymmetric wave function E_A .

But, the first thing first. We write

$$\psi_S = N_S(\psi_a + \psi_b) \tag{4.4}$$

$$\psi_A = N_A(\psi_a - \psi_b) \tag{4.5}$$

N_S and N_A are normalization constants. Why do we need them? Because any wave function must satisfy the normalization condition. So,

$$\begin{aligned} 1 &= \int d^3\vec{r} \psi_S^* \psi_S \\ &= \int d^3\vec{r} N_S^2 (\psi_a^* + \psi_b^*) (\psi_a + \psi_b) && \text{Eq. 4.4} \\ &= N_S^2 \int d^3\vec{r} (\psi_a^* \psi_a + \psi_a^* \psi_b + \psi_b^* \psi_a + \psi_b^* \psi_b) \\ &= N_S^2 \left(1 + \int d^3\vec{r} \psi_a^* \psi_b + \int d^3\vec{r} \psi_b^* \psi_a + 1 \right) && \text{Eqs. 4.2, 4.3} \\ &= N_S^2 (1 + 0 + 0 + 1) && \text{Eq. 4.1 and its complex conjugate} \end{aligned}$$

Thus, $N_S = 1/\sqrt{2}$. Similarly, $N_A = 1/\sqrt{2}$, also. Therefore, the wave functions ψ_S and ψ_A are

$$\psi_S = \frac{1}{\sqrt{2}}(\psi_a + \psi_b) \tag{4.6}$$

$$\psi_A = \frac{1}{\sqrt{2}}(\psi_a - \psi_b) \tag{4.7}$$

Now, let us get down to the business of the energy, which is really what we want to do.

We assume the following²

$$H\psi_S = E_S\psi_S \quad \text{This means that } \psi_S \text{ is an eigenfunction of } H. \quad (4.8)$$

$$H\psi_A = E_A\psi_A \quad \text{This means that } \psi_A \text{ is an eigenfunction of } H. \quad (4.9)$$

$$H = T + V = -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r}) \quad H \text{ is the Hamiltonian (or energy) operator.} \quad (4.10)$$

Here, H is the total Hamiltonian for the H_2^+ problem. It is different from the Hamiltonian of the hydrogen atom problem, only in that there is one more proton. I.e., the Coulomb potential energy comes from two protons, not one.

$$V(\vec{r}) = V_a(\vec{r}) + V_b(\vec{r}) \quad (4.11)$$

$V_a(\vec{r})$ is the Coulomb potential energy due to proton a , i.e. $-e^2/|\vec{r} - \vec{r}_a|$, where \vec{r}_a is the position for proton a . Similarly, $V_b(\vec{r}) = -e^2/|\vec{r} - \vec{r}_b|$. The details of these mathematical forms are not terribly important for our discussion. We just have to know that V_a and V_b are negative potential well functions centered at proton a and proton b respectively.

What is cute to notice is that

$$H_a\psi_a = (T + V_a)\psi_a = -R\psi_a \quad \psi_a \text{ is the 1s orbital for the hydrogen atom at } a \quad (4.12)$$

$$H_b\psi_b = (T + V_b)\psi_b = -R\psi_b \quad \psi_b \text{ is the 1s orbital for the hydrogen atom at } b \quad (4.13)$$

$$H = T + V_a + V_b \quad (4.14)$$

$$= H_a + V_b \quad (4.15)$$

$$= H_b + V_a \quad (4.16)$$

$$R = 13.6 \text{ eV} \quad (4.17)$$

Recall from the last lecture that Eqs. 4.8, 4.9 lead to the following (if we apply $\int d^3\vec{r} \psi_S^*$ and $\int d^3\vec{r} \psi_A^*$ from the left, respectively, to those two equations):

$$E_S = \int d^3\vec{r} \psi_S^* H \psi_S \quad (4.18)$$

$$E_A = \int d^3\vec{r} \psi_A^* H \psi_A \quad (4.19)$$

²Without the full QM theory, we will have to *assume* this. In the full QM theory, it can be proven that ψ_S and ψ_A are indeed eigenstates. The intuitive reason is “because Nature selects a nice wave function like a symmetric wave function or an antisymmetric wave function as an Hamiltonian eigenstate.”

Here, we work on E_S , while leaving E_A for readers' work.

$$E_S = \int d^3\vec{r} \psi_S^* H \psi_S \quad (4.20)$$

$$= \frac{1}{\sqrt{2}} \int d^3\vec{r} \psi_S^* H (\psi_a + \psi_b) \quad \text{Eq. 4.6} \quad (4.21)$$

$$= \frac{1}{\sqrt{2}} \int d^3\vec{r} \psi_S^* (H\psi_a + H\psi_b) \quad (4.22)$$

$$= \frac{1}{\sqrt{2}} \int d^3\vec{r} \psi_S^* [(H_a + V_b)\psi_a + (H_b + V_a)\psi_b] \quad \text{Eqs. 4.15, 4.16} \quad (4.23)$$

$$= \frac{1}{\sqrt{2}} \int d^3\vec{r} \psi_S^* [(-R + V_b)\psi_a + (-R + V_a)\psi_b] \quad \text{Eqs. 4.12, 4.13} \quad (4.24)$$

$$= \frac{1}{2} \int d^3\vec{r} (\psi_a^* + \psi_b^*) [(-R + V_b)\psi_a + (-R + V_a)\psi_b] \quad \text{Eq. 4.6} \quad (4.25)$$

$$= \frac{1}{2} \int d^3\vec{r} [-R(|\psi_a|^2 + \psi_b^* \psi_a) + V_b(|\psi_a|^2 + \psi_b^* \psi_a) + (a \leftrightarrow b)] \quad (4.26)$$

In the last step, $(a \leftrightarrow b)$ means the same as the previous four terms except that the indices a and b are swapped: i.e. $-R(\psi_b^* \psi_b + \psi_a^* \psi_b) + V_a(\psi_b^* \psi_b + \psi_a^* \psi_b)$. When integrated over, each of these four terms is equal to the corresponding term in the first part of Eq. 4.26. This follows from the following two facts: (1) ψ_a and ψ_b are normalized *real* wave functions ($\psi_a(\vec{r}) = \frac{1}{\sqrt{\pi a_B^3}} \exp(-|\vec{r} - \vec{r}_a|/a_B)$ and $\psi_b(\vec{r}) = \frac{1}{\sqrt{\pi a_B^3}} \exp(-|\vec{r} - \vec{r}_b|/a_B)$) and (2) the ‘‘symmetry’’ ($\int d^3\vec{r} V_a \psi_a^* \psi_b = \int d^3\vec{r} V_b \psi_b^* \psi_a$). Both these facts can be noted in the first figure of this lecture note. For instance, the 2nd term $\int d^3\vec{r} (-R \psi_a^* \psi_b) = \int dv (-R \psi_a \psi_b^*) = \int dv (-R \psi_b^* \psi_a)$ due to the reality of ψ_a and ψ_b .

Therefore,

$$E_S = \int d^3\vec{r} [-R(\psi_a^* \psi_a + \psi_b^* \psi_a) + V_b(\psi_a^* \psi_a + \psi_b^* \psi_a)] \quad (4.27)$$

$$= -R + 0 + \int d^3\vec{r} V_b(\psi_a^* \psi_a + \psi_b^* \psi_a) \quad \text{Eqs. 4.2, 4.1} \quad (4.28)$$

Let us define

$$t = - \int d^3\vec{r} V_b \psi_b^* \psi_a = - \int d^3\vec{r} V_a \psi_a^* \psi_b \quad (4.29)$$

$$\alpha = - \int d^3\vec{r} V_b \psi_a^* \psi_a = - \int d^3\vec{r} V_a \psi_b^* \psi_b \quad (4.30)$$

4.1. HYDROGEN MOLECULE, CONT.

As $V_a, V_b < 0$ (see the first figure of this note), and $\psi_a, \psi_b > 0$, we see that $t > 0$ and $\alpha > 0$. Notice both these parameters arise due to the potential energy.

t is the so-called **hopping amplitude**. It is a very important parameter. This is the parameter that is responsible mainly for the tunneling of the electron between the two Coulombic potential wells. Consider “hopping” as synonymous to “tunneling.”

In terms of α and t , we get, from Eq. 4.28,

$$E_S = -R - \alpha - t \quad (4.31)$$

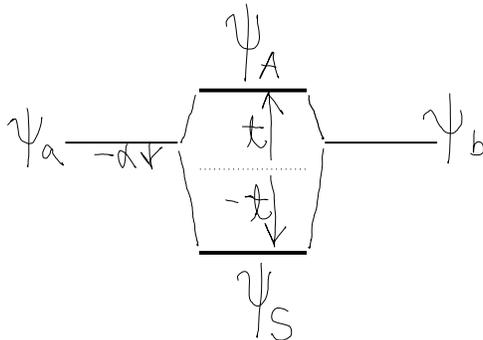
Note that compared to $-R$, E_S is lowered by $-\alpha - t$. That is, it is always an energy lowering process if the electron is shared by the two protons!

It is left for readers to show that

$$E_A = -R - \alpha + t \quad (4.32)$$

In this case, the energy is actually higher than $-R$, since $t > \alpha$.

This situation is summarized in the following **molecular orbital energy diagram**, which is a common way to visualize the formation of molecular orbitals from atomic orbitals.



Typically, on the left and the right of the diagram, atomic energy levels are drawn. Then, at the center the energy levels of molecular orbitals are drawn. Our wave functions ψ_S and ψ_A are examples of molecular orbitals. These are often called **hybrid(ized) orbitals**. It means atomic orbitals from different atoms are mixed up in ψ_S or ψ_A . So, the above diagram can be called a hybridization diagram. The energy difference between them arises due to the hopping amplitude t , whose microscopic origin is the potential energy.

4.1.3 Beyond the essential bare bone model

The model presented in the previous section provides an excellent summary of the essential physics. However, it is far from enough to give a quantitative agreement.

One might complain that the assumption of Eq. 4.1 makes no sense. The reason becomes obvious if one considers the fact that the proton-proton distance, i.e. the “bond length”, of H_2^+ is 1.06 Å. What does this mean? As the $1s$ wave function has the “ $1/e$ decay length”³ of 0.53 Å, one sees that ψ_a and ψ_b have a lot of overlap! In fact, the first figure of this note depicts this situation quite truthfully. You can clearly infer from it that ψ_a and ψ_b will have a large overlap integral $\int \psi_a^* \psi_b$ is in fact ≈ 0.6 , which is not close to 0 at all. However, as I explained early on, we ignored this overlap integral, not because it is small, but because it is not qualitatively important for physics. For quantitative work, it must be included.

For an advanced student, here is a challenge. Prove all of the following, with $S \equiv \int d^3\vec{r} \psi_a^* \psi_b = \int d^3\vec{r} \psi_b^* \psi_a$.

$$N_S = \sqrt{\frac{1}{2(1+S)}} \quad (4.33)$$

$$N_A = \sqrt{\frac{1}{2(1-S)}} \quad (4.34)$$

$$E_S = -R - \frac{t + \alpha}{1 + S} \quad (4.35)$$

$$E_A = -R + \frac{t - \alpha}{1 - S} \quad (4.36)$$

$$E_S < -R < E_A \quad (4.37)$$

A second point is that the assumption that ψ_a and ψ_b is the $1s$ orbital is in fact an unnecessary one. We made that assumption just to make the calculation simple. In a quantitative calculation, the result will become more and more accurate if ψ_a (and ψ_b by the same token) is considered as a linear combination of more and more orbitals, $1s, 2s, 2p, \dots$. This is the general scheme of the “**linear combination of atomic orbitals (LCAO)**” method. This is a very useful and popular method in quantum chemistry. Technically, even if ψ_a and ψ_b are assumed to be $1s$ orbitals, we have the LCAO method. However, in a real quantitative LCAO method, this is hardly enough, as a substantial error (several tens of %) can result in comparison to

³This is the length at which function is $1/e$ of its maximum value. This concept is used for exponentially decaying function, just like the $1s$ orbital $\propto \exp(-r/a_B)$, which has the decay length of a_B , the Bohr radius.

experiment. For a quantitatively more correct calculation, E_A becomes lower than $-R$ due to being “pushed down” by interaction with higher energy level orbitals.

A third point is that in the above consideration, we’ve been ignoring the proton-proton repulsion. This is important in bringing the equilibrium. By inspecting the result that we got for E_S , it is seen that t will increase monotonically as the bond-length decreases. So, from the consideration of E_S alone, the zero bond length would be the best choice. However, the two protons will repel each other as they become close to each other, and the balance between the attraction through bonding and the Coulomb repulsion determines the equilibrium bond length.

The bonding energy of H_2^+ , i.e. the difference in energy between H_2^+ and $H + p$ is given by $R - E_S$ minus the proton-proton Coulomb repulsion. This value is 2.65 eV. This is true energy gain by sharing one electron between two protons.

4.1.4 H_2

Now consider the hydrogen molecule. The only difference is that we have two electrons, not one. Naively, we put two electrons in the bonding orbitals that we discussed in previous sections, and that is the end of the story. We know that two electrons with one with spin up and the other with spin down would just do. It satisfies the Pauli exclusion principle, since the spin quantum numbers are different, although the two electrons occupy the same spatial quantum number ($n = 1$ of the Bohr theory).

This is OK for a crude qualitative discussion, but, the following points must be kept in mind.

Now, with two electrons, the bonding energy gain through E_S is doubled. So, the bond length will decrease. This gain in energy is balanced both by the proton-proton repulsion and the electron-electron repulsion. The actual bond length for H_2 is 0.74 Å, much shorter than 1.06 Å of H_2^+ .

One would expect that if the electron-electron repulsion is absent, then the total bonding energy would be greater than twice that of H_2^+ (greater since the bonding energy will be already twice that of H_2^+ for the same bond length). This expectation is not met, since the electron-electron repulsion is large. The actual binding energy of the hydrogen molecule is actually 4.7 eV, smaller than 2 times $2.65 = 5.3$ eV.

4.2 Energy band – H crystal in one dimension

A formal theory of the electron band is beyond the scope for this course. Here, we consider a hypothetical one dimensional crystal consisting of hydrogens. Using the insights gained from the study of the hydrogen molecule problem, we can gain a significant qualitatively correct insight into the formation of the energy band.

We shall deal with the essential bare bone picture for the molecular orbitals only.

I have already mentioned that the orthogonality relation Eq. 4.1 is justified in the theory of solid. This is because the formal theory of the electron band does not use the hydrogen $1s$ orbital, but a much more complicated, but well-defined, orbital called a “Wannier orbital.” A Wannier orbital in a one dimensional crystal is like the $1s$ orbital in the sense that it is localized around each hydrogen atom, and it consists *mostly* of $1s$ orbital for the lowest lying band. But, they contain much more than just $1s$ orbital. A special way⁴ that it is defined guarantees that the two Wannier orbitals centered at different atoms. So, Eq. 4.1 is *exact* if ψ_a and ψ_b are interpreted as Wannier orbitals!

Now, consider two H atoms in a crystal, and forget about all other H atoms. We can calculate the bonding and the anti-bonding orbitals, just as we did in Section 4.1.2, and we would simply get $E_S = -R - (t + \alpha)$ (for $\psi_S = (\psi_a + \psi_b)/\sqrt{2}$) and $E_A = -R + (t - \alpha)$ (for $\psi_S = (\psi_a - \psi_b)/\sqrt{2}$).

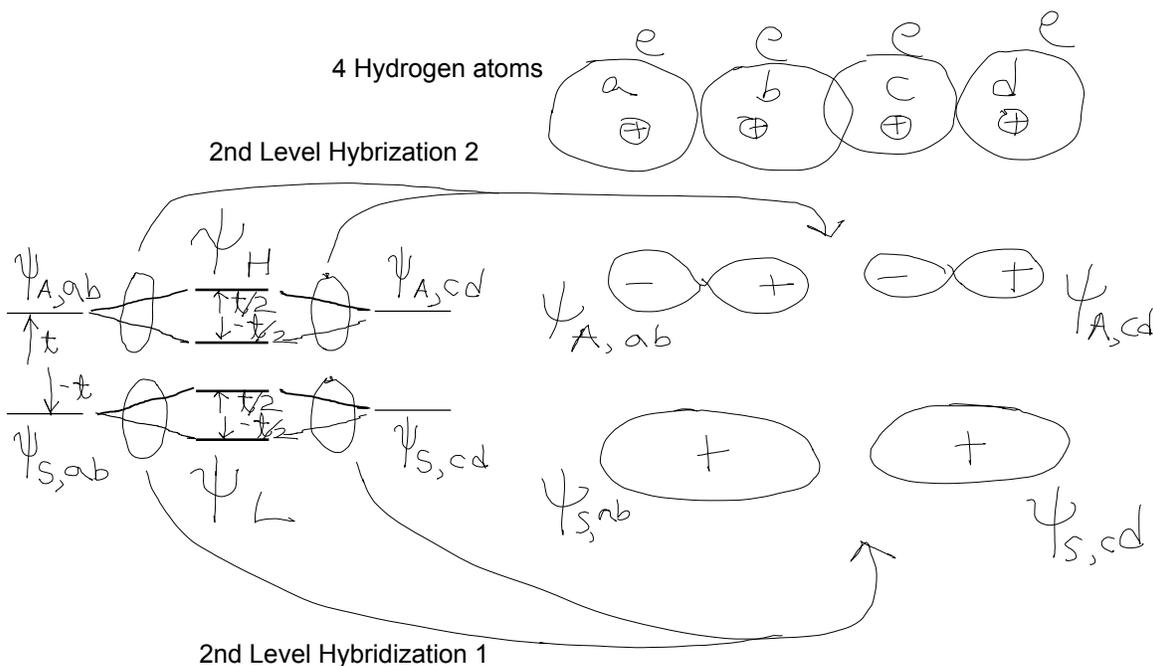
The next step is to consider four atoms, a, b and c, d . We consider that we have already solved the problem for a, b and c, d , as we just described (for the c, d pair, simply change $a, b \rightarrow c, d$ in the last paragraph).

Now, we ask the question. How would the four orbitals $\psi_{S,ab}$, $\psi_{A,ab}$, $\psi_{S,cd}$, and $\psi_{A,cd}$ “hybridize with each other”? In considering this mixing, it helps to note that the electron tunneling is the greatest between nearest neighbor atoms. There is a probability that the electron will skip the nearest neighbor atom and go right to the next nearest neighbor. However, such a probability is low and can be ignored. By the same token the probability that the electron will tunnel into the next nearest neighbor due to the potential at farther neighbor atoms is also small. Thus, we can ignore integrals such as $\int dx \psi_a \psi_c V_c$ or $\int dx \psi_a \psi_b V_c$ and so on. It can be shown then (as I did on the board in class – this math not terribly important) that the tunneling can occur between the orbitals $\psi_{S,ab}$ and $\psi_{S,cd}$ occur with the tunneling amplitude $t/2$, a half-reduced amplitude. The cause of this reduction is the normalization constant $1/\sqrt{2}$ in the wave functions $\psi_{S,ab}$ and $\psi_{A,ab}$ etc. Due to the symmetry reason, no

⁴To know how it is defined is beyond the scope of this course. The Kittel reference book can be read, if you are interested, though.

4.2. ENERGY BAND – H CRYSTAL IN ONE DIMENSION

hybridization occurs between symmetric states to anti-symmetric states. The uniform shift parameter α is also reduced by half. Since this parameter gives a uniform shift to all states, it is actually not important. So, ignoring α , we get the following “molecular orbital energy diagram.”



In this diagram, I am calling the further hybridization of molecular orbitals of H_2 at this level a “2nd level hybridization.” Notice that $\psi_{S,ab}$ and $\psi_{S,cd}$ have the same sign when they overlap. So, the bonding state arising from this “2nd level hybridization 1” is (qualitatively this is much like hybridizing 1s orbitals; see the “activity slides” for more info)

$$\begin{aligned}\psi_L &= \frac{1}{\sqrt{2}}(\psi_{S,ab} + \psi_{S,cd}) \\ &= \frac{1}{2}(\psi_a + \psi_b + \psi_c + \psi_d)\end{aligned}\quad (4.38)$$

On the other hand, the “2nd level hybridization 2” is different, since when $\psi_{A,ab}$ and $\psi_{A,cd}$ meet at the center, they have opposite signs. Thus, the bonding orbital is the *anti-symmetric* sum, while the anti-bonding orbital is the *symmetric* sum. (For more info, see the “activity slides.”) We are interested in the latter, which we call the ψ_H , for the highest energy orbital.

$$\begin{aligned}\psi_H &= \frac{1}{\sqrt{2}}(\psi_{A,ab} + \psi_{A,cd}) \\ &= \frac{1}{2}(\psi_a - \psi_b + \psi_c - \psi_d)\end{aligned}\quad (4.39)$$

We also ask – what is the maximum energy separation between different eigenstates? The answer, plain from the diagram, is $2(t + t/2) = 3t$.

This much result is excellent! Going beyond 4 atoms becomes increasingly complicated. In fact, there are other ways to calculate the band structure, which you will learn later in QM or solid state physics. After all, here we are trying to see the plausibility of the emergence of the energy band. So, we make the following table, with some “educated guess.” N_H and N_L are normalization constants.

# of H atoms	# of eigenstates	ψ_L/N_L ($1/N_L = \sqrt{N}$)	ψ_H/N_H ($1/N_H = \sqrt{N}$)	Band Width
$N = 2$	2	$\psi_a + \psi_b$	$\psi_a - \psi_b$	$2t$
$N = 4$	4	$\psi_a + \psi_b + \psi_c + \psi_d$	$\psi_a - \psi_b + \psi_c - \psi_d$	$2t(1 + \frac{1}{2})$
...
$N = 2^n$	2^n	$\psi_1 + \psi_2 + \dots + \psi_N$	$\psi_1 - \psi_2 \dots + \psi_{N-1} - \psi_N$	$2t(1 + \frac{1}{2} + \dots + \frac{1}{2^{n-1}})$

In this table, the index of atoms changed from a, b, c, d to $1, 2, 3, \dots, N$ as N increases. Also, we introduce a new terminology **band width** – this is simply the total energy range, i.e. the energy difference between ψ_H and ψ_L .

The band width, in the limit of $N \rightarrow \infty$, is then $4t$.

Notice that ψ_L has the periodicity of a , if a is the lattice constant of the crystal, i.e. the distance between two adjacent H atoms. On the other hand, the periodicity of ψ_H is $2a$.

Let us calculate the wave vectors. $k = 2\pi/a$ for ψ_L and $k = 2\pi/(2a) = \pi/a$ for ψ_H .

These results provide a glimpse of the so-called “tight-binding band theory,” which is basically the crystal version of the LCAO method.

In the tight binding theory, not only the two end states ψ_L and ψ_H are obtained, but also all intermediate states. The correct function for the eigenvalues turn out to be

$$\varepsilon(k) = -2\alpha - 2t \cos(ka) \tag{4.40}$$

This is an example of the so-called **energy band**! Please verify yourself that this function $\varepsilon(k)$ does have the minimum energy when $k = 2\pi/a$ and that it has the maximum energy when $k = \pi/a$, as we expect from our discussion above. Also, please verify yourself that the band width is $4t$.

The number of eigenstates above is equal to the unique k values in any single band, i.e. any k - ε dispersion relation like the one just given. This is an important result to remember.

For your benefit, whenever you consider a crystal, consider a real crystal where N is large, but not infinite. Then, there must be N eigenstates in a band. (This is true, in general, even if $N \neq 2^n$. The choice of $N = 2^n$ above is for pedagogy only.) Each of these eigenstates correspond to a unique k value!

So, even if a function $\varepsilon(k)$, like the one given above, might suggest that it is a continuous function, consider it as **a discontinuous function, defined at, equally spaced (as it turns out), discrete numbers of k values!** This is the most physical way to think about an energy band!