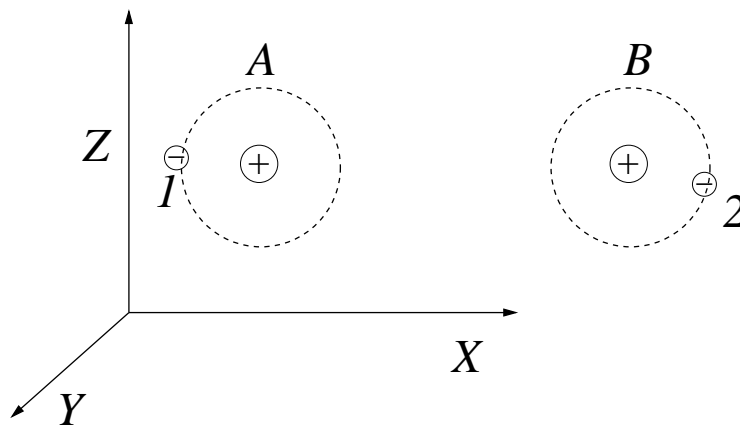


# PY4T01 Condensed Matter Theory: Lecture 2

## The H<sub>2</sub> molecules

Consider the H<sub>2</sub> molecule



The equation to solve in this case is very easy (we neglect electron-electron interaction and we consider the Born-Oppenheimer approximation)

$$H\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

$$H = \left( -\frac{\hbar^2 \nabla_1^2}{2m} - \frac{e^2}{|\vec{r}_1 - \vec{R}_A|} \right) + \left( -\frac{\hbar^2 \nabla_2^2}{2m} - \frac{e^2}{|\vec{r}_2 - \vec{R}_B|} \right) + \frac{e^2}{|\vec{r}_1 - \vec{R}_B|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_A|}$$

## How to solve this equation?

Instead of “brute force” we want to use known solutions of simpler problems and to expand the wave function of such solutions.

We should find an easy way to pass the problem to a computer. The idea is to expand  $H$  on a set of “friendly” functions.

So we have to chose the basis set.

## Dirac Notation: choosing a basis

- A quantum state can be represented as

$$|\psi\rangle$$

At each point  $\vec{r}$  in space  $\psi(\vec{r})$  is the spatial representation  $\langle\vec{r}|\psi\rangle$  of  $|\psi\rangle$

- Each state can be expanded onto a complete orthonormal basis set  $|\phi_i\rangle$

$$|\psi\rangle = \sum_i^N |\phi_i\rangle \langle\phi_i|\psi\rangle = \sum_i^N c_i |\phi_i\rangle$$

$$\langle\phi_i|\phi_j\rangle = \delta_{ij}$$

$$\langle\phi_i|\psi\rangle = c_i$$

from which it follows

$$\sum_i^N |\phi_i\rangle \langle\phi_i| = I$$

Note that it may be  $\underline{N \rightarrow \infty}$  (it depends on the Hilbert space we are working in)

- This is the case for the real-space representation

$$|\psi\rangle = \int |\vec{r}\rangle \langle \vec{r} | \psi \rangle d\vec{r} = \int |\vec{r}\rangle \psi(\vec{r}) d\vec{r}$$

$$\int |\vec{r}\rangle \langle \vec{r} | d\vec{r} = I$$

- Representation of Operator

$$\hat{L}|\psi\rangle = |\xi\rangle$$

$$\sum_j^N \hat{L}|\phi_j\rangle \langle \phi_j | \psi \rangle = \sum_j^N |\phi_j\rangle \langle \phi_j | \xi \rangle$$

$$\sum_j^N \psi_j \hat{L}|\phi_j\rangle = \sum_j^N \xi_j |\phi_j\rangle$$

now multiply by  $\langle \phi_i |$

$$\sum_j^N \langle \phi_i | \hat{L} | \phi_j \rangle \psi_j = \sum_j^N \langle \phi_i | \phi_j \rangle \xi_j$$

$$\sum_j^N L_{ij} \psi_j = \xi_i$$

This is now a matrix equation

$$\begin{pmatrix} L_{11} & L_{12} & \dots & \dots & L_{1N} \\ L_{21} & L_{22} & \dots & \dots & L_{2N} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ L_{N1} & L_{N2} & \dots & \dots & L_{NN} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \dots \\ \dots \\ \psi_N \end{pmatrix} = \begin{pmatrix} \xi_1 \\ \xi_2 \\ \dots \\ \dots \\ \xi_N \end{pmatrix}$$

You can pass this to a computer!!!

- What if my initial operator is in real space?

$$H(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$$

$$H(\vec{r})\langle\vec{r}|\psi\rangle = E\langle\vec{r}|\psi\rangle$$

I can now expand  $\langle\vec{r}|\psi\rangle$  on a set of  $M$  “friendly” functions

$$H(\vec{r}) \sum_j^M \langle\vec{r}|\phi_j\rangle \langle\phi_j|\psi\rangle = E \sum_j^M \langle\vec{r}|\phi_j\rangle \langle\phi_j|\psi\rangle$$

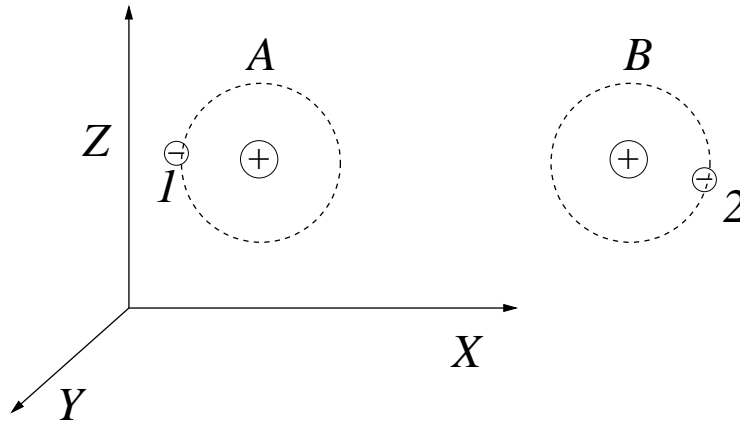
If I now multiply both side by  $\langle\phi_i|\vec{r}\rangle = \phi_i^*(\vec{r})$  and take  $\int d\vec{r}$

$$\left[ \sum_j^M \int \phi_i^*(\vec{r}) H(\vec{r}) \phi_j(\vec{r}) d\vec{r} \right] \psi_j = \sum_j^M \psi_j E \int \phi_i^*(\vec{r}) \phi_j(\vec{r}) d\vec{r}$$

$$\sum_i^M H_{ij} \psi_j = E \psi_i$$

**Note:** The relevant Hilbert space is  $\mathcal{L}^2(\mathbb{R}^{3N}) \otimes \mathbb{C}^{2s+1}$ , then  $M \rightarrow \infty$ . However, if I choose the  $|\phi_i\rangle$  in a clever way I can use a *finite*  $M$ .

## The H<sub>2</sub> molecule



$$H = \left( -\frac{\hbar^2 \nabla_1^2}{2m} - \frac{e^2}{|\vec{r}_1 - \vec{R}_A|} \right) + \left( -\frac{\hbar^2 \nabla_2^2}{2m} - \frac{e^2}{|\vec{r}_2 - \vec{R}_B|} \right) + \frac{e^2}{|\vec{r}_1 - \vec{R}_B|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_A|}$$

*In principle* we can take any set of “friendly functions” and expand the Hamiltonian. *In practice* we want to go close to the solution with the minimum effort!!

Note that this is:

$$H = H_A + H_B - \frac{e^2}{|\vec{r}_1 - \vec{R}_B|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_A|}$$

where  $H_A$  and  $H_B$  are the Hamiltonian for the isolated H atom A and B. This suggests a good set of “friendly functions”.

Consider in fact the *ground state* ( $1s$ ) wave function of the isolated H atoms

$$H_A|1\rangle = \epsilon_{1s}|1\rangle \quad \text{and} \quad H_B|2\rangle = \epsilon_{1s}|2\rangle$$

and decide these form our set of friendly wave-functions

$$|\psi\rangle = \sum_1^2 \psi_i|i\rangle = \psi_1|1\rangle + \psi_2|2\rangle$$

Note:

This way of expanding the wave function onto molecular orbitals gives the name of the theory: molecular orbital (MO) theory.

This is usually known as Linear Combination of Atomic Orbital (LCAO) Theory

Now expand the Schrödinger equation:

$$H(\psi_1|1\rangle + \psi_2|2\rangle) = E(\psi_1|1\rangle + \psi_2|2\rangle)$$



To solve this we need to project onto the basis states  $|1\rangle$  and  $|2\rangle$

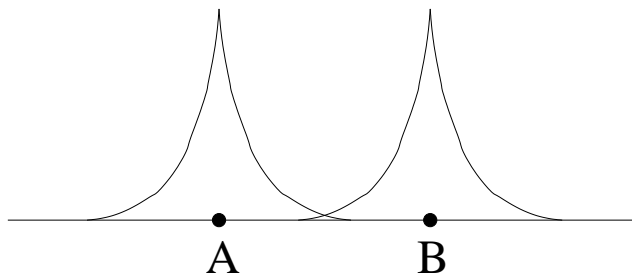
$$\begin{cases} \langle 1|H(\psi_1|1\rangle + \psi_2|2\rangle) = E\langle 1|(\psi_1|1\rangle + \psi_2|2\rangle) \\ \langle 2|H(\psi_1|1\rangle + \psi_2|2\rangle) = E\langle 2|(\psi_1|1\rangle + \psi_2|2\rangle) \end{cases}$$

Assume now that our basis set is orthonormal

$$\langle 1|2\rangle = \langle 2|1\rangle = 0 \quad \text{and} \quad \langle 1|1\rangle = \langle 2|2\rangle = 1$$

Remember that in real space:

$$\langle \vec{r}|\psi\rangle = \psi(\vec{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-r/a_0}$$



This means that our basis is orthonormal only if the H atoms are far enough from each other

We then obtain the two following equations:

$$\begin{cases} \langle 1|H|1\rangle\psi_1 + \langle 1|H|2\rangle\psi_2 = E\psi_1 \\ \langle 2|H|1\rangle\psi_1 + \langle 2|H|2\rangle\psi_2 = E\psi_2 \end{cases}$$

and these can be written as

$$\begin{cases} \epsilon_0\psi_1 + \gamma\psi_2 = E\psi_1 \\ \gamma\psi_1 + \epsilon_0\psi_2 = E\psi_2 \end{cases}$$

or

$$\begin{pmatrix} \epsilon_0 & \gamma \\ \gamma & \epsilon_0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

Note that

1. The problem is now in a matrix form:

$$\mathcal{H}\Psi = E\Psi$$

with

$$\mathcal{H} = \begin{pmatrix} \epsilon_0 & \gamma \\ \gamma & \epsilon_0 \end{pmatrix} \quad \text{and} \quad \Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

$\mathcal{H}$  is called the Hamiltonian matrix

$$2. \quad \underline{\langle 1|H|1\rangle = \langle 2|H|2\rangle = \epsilon_0}$$

$$\begin{aligned} \langle 1|H|1\rangle &= \int \psi_1(\vec{r})^* \left( H_A(\vec{r}) - \frac{e^2}{|\vec{r} - \vec{R}_B|} \right) \psi_1(\vec{r}) d\vec{r} = \\ &= \int \psi_1(\vec{r})^* H_A \psi_1(\vec{r}) d\vec{r} - \int \psi_1(\vec{r})^* \left( \frac{e^2}{|\vec{r} - \vec{R}_B|} \right) \psi_1(\vec{r}) d\vec{r} = \\ &= \epsilon_{1s} - \int \frac{\rho_1(\vec{r}) e^2}{|\vec{r} - \vec{R}_B|} d\vec{r} \end{aligned}$$

Note that ultimately

$$\epsilon_0 = \epsilon_{1s} - \int \frac{\rho_1(\vec{r}) e^2}{|\vec{r} - \vec{R}_B|} d\vec{r}$$

$\epsilon_0$  is called *on-site energy*. Integrals of this kind are called *two center integrals*.

$\epsilon_0$  is the sum of the atomic energy  $\epsilon_{1s}$  plus a (classical) electrostatic term  $\epsilon_{\text{cf}} = - \int \frac{\rho_1(\vec{r}) e^2}{|\vec{r} - \vec{R}_B|} d\vec{r}$  (the *crystal-field potential*).

3. In general  $\langle 1|H|2\rangle = \langle 2|H|1\rangle^* = \gamma$

This makes the matrix  $\mathcal{H}$  *Hermitian*. In the present case the  $|i\rangle$  are real and then  $\langle 1|H|2\rangle = \langle 2|H|1\rangle$

$$\begin{aligned}\gamma = \langle 1|H|2\rangle &= \langle 1| \left( H_A - \frac{e^2}{|\vec{r} - \vec{R}_B|} \right) |2\rangle = \\ &= -\langle 1| \frac{e^2}{|\vec{r} - \vec{R}_B|} |2\rangle\end{aligned}$$

Since  $|i\rangle$  are the  $1s$  H wave-functions (they have no nodes, therefore they are always positive)

$$\gamma < 0$$

The last result follows directly from:

$$\langle 1|H_A = \langle 1|\epsilon_{1s} \quad \longrightarrow \quad \langle 1|H_A|2\rangle = \langle 1|2\rangle\epsilon_{1s} = 0$$

$\gamma$  is called *hopping integral* or *hopping parameter*.

Now solve the eigenvalue problem

$$\begin{pmatrix} \epsilon_0 & \gamma \\ \gamma & \epsilon_0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

We have non-trivial solution only if:

$$\det \begin{pmatrix} \epsilon_0 - E & \gamma \\ \gamma & \epsilon_0 - E \end{pmatrix} = 0$$

$$(\epsilon_0 - E)^2 - \gamma^2 = 0$$

So we have two solutions:

$$E_{\text{bond}} = \epsilon_0 + \gamma$$

and

$$E_{\text{anti}} = \epsilon_0 - \gamma$$

with corresponding eigenvectors

$$\Psi_{\text{bond}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \Psi_{\text{anti}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Recalling that the vector  $\Psi$  is the vector of the expansion coefficients  $\psi_1$  and  $\psi_2$ , the final wave functions are

$$|\psi_{\text{bond}}\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \quad \text{BONDING}$$

$$|\psi_{\text{anti}}\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle) \quad \text{ANTIBONDING}$$

This is already enough to understand why the  $\text{H}_2$  forms.

