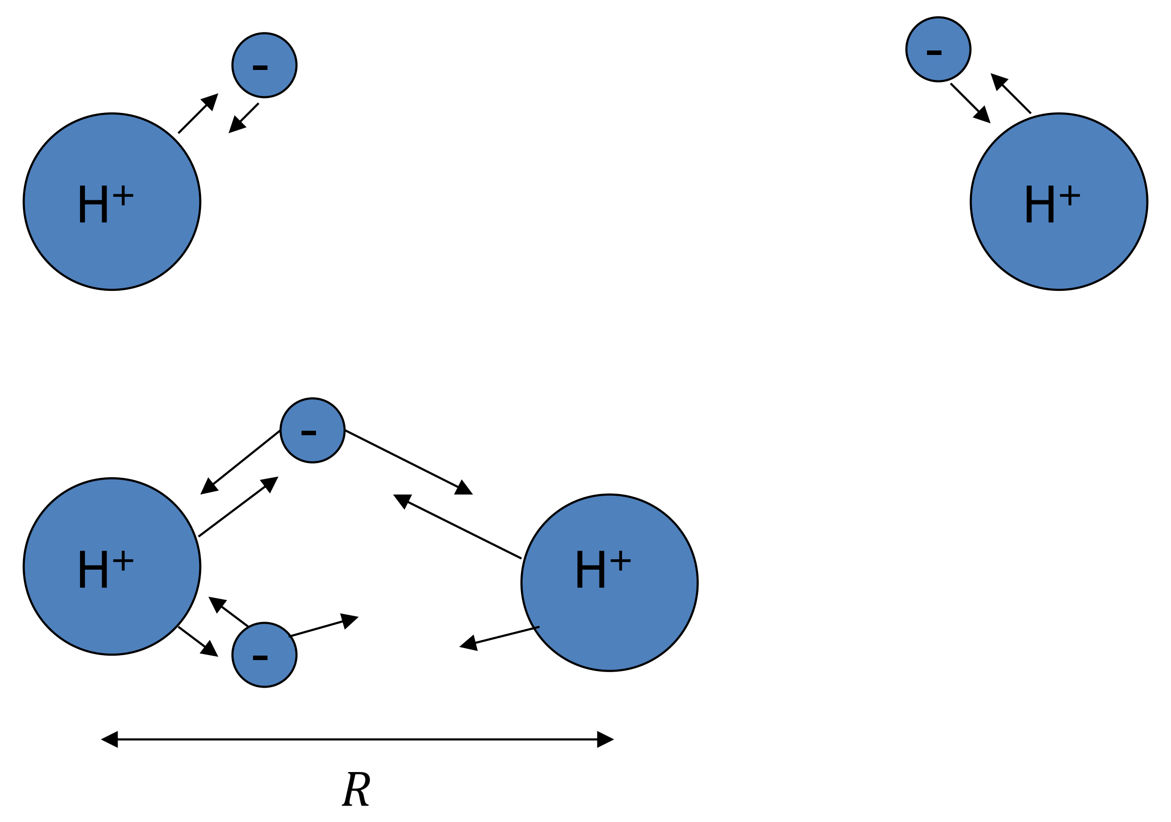
分子 Molecule



氫分子H_2包含了兩個質子原子核，兩個電子。

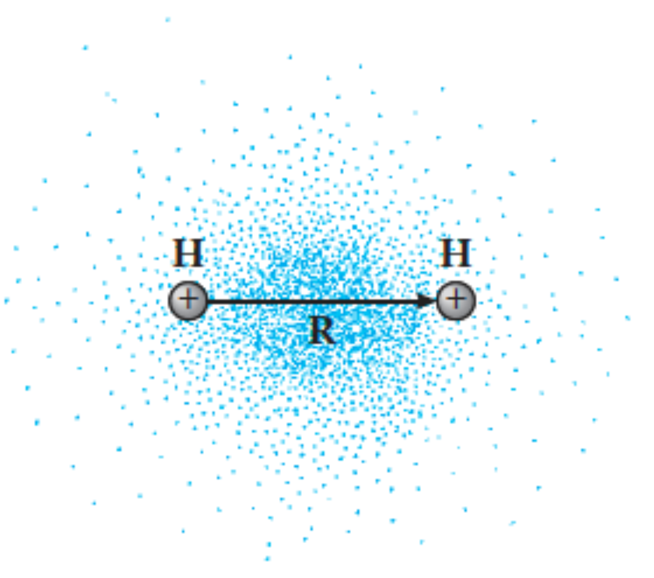
最重要的特徵是電子是由兩個分開的原子核所共享。

Born-Oppenheimer Approximation

波恩

波的機率解釋

J. Robert Oppenheimer 歐本海默



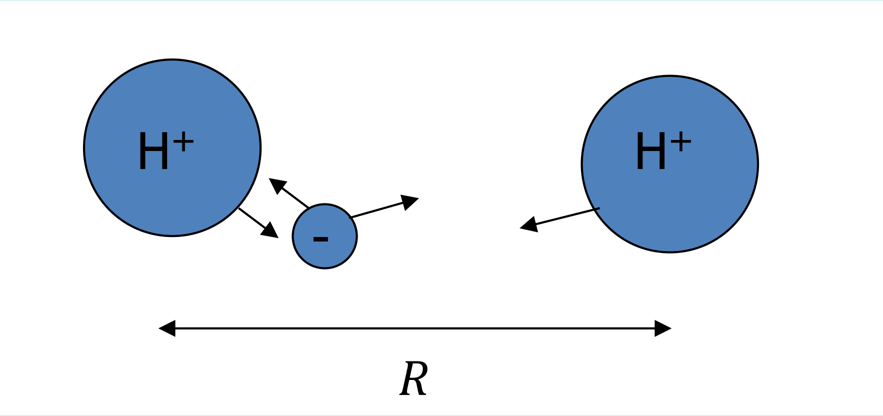
兩大近似：

原子核的運動可以看成古典粒子，而電子的運動則用量子力學波函數描述。

原子核的運動相對緩慢，計算電子的定態時，距離R近似可視為不變。

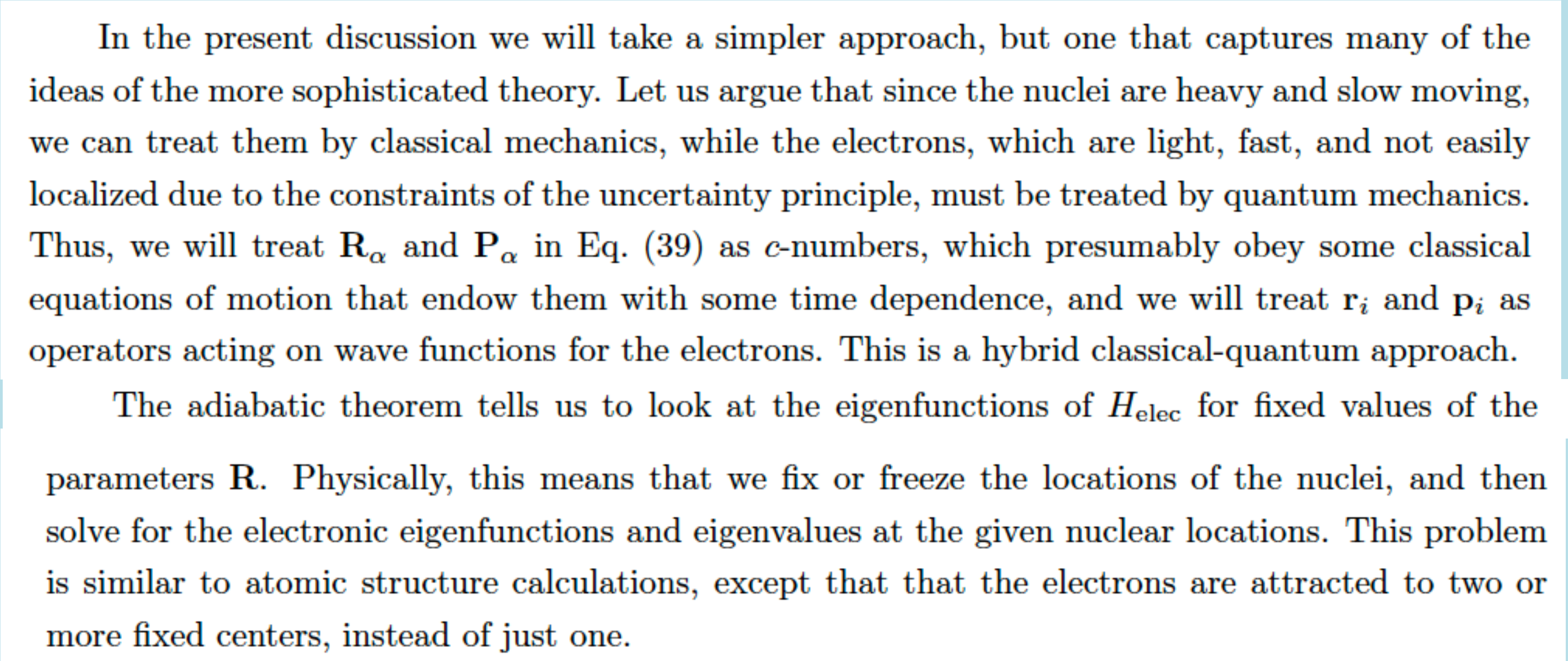
這兩個假設是植基於原子核遠比電子重約萬倍。Adiabatic Approximation

計算氫離子H_2^+的共價鍵束縛能。它包含了兩個質子原子核，一個電子。



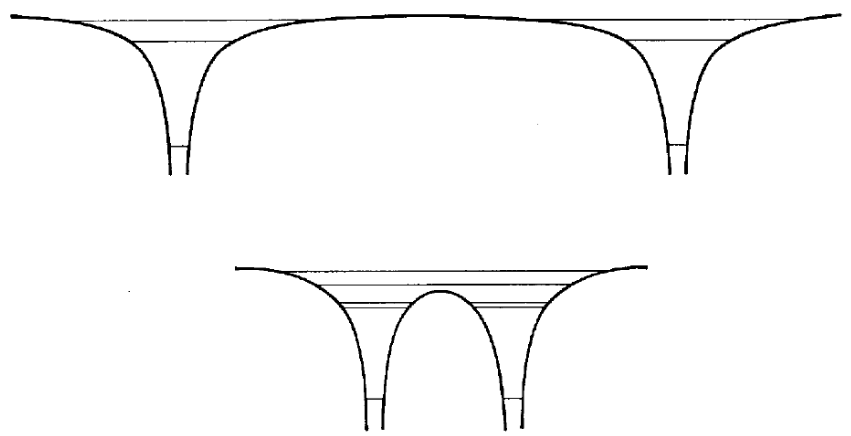
固定兩個氫原子核於距離R，計算周圍單一電子的定態與能量：

找出氫離子基態能量與距離R的關係。



In the present discussion we will take a simpler approach, but one that captures many of the ideas of the more sophisticated theory. Let us argue that since the nuclei are heavy and slow moving, we can treat them by classical mechanics, while the electrons, which are light, fast, and not easily localized due to the constraints of the uncertainty principle, must be treated by quantum mechanics. Thus, we will treat $\mathbf{R}_\alpha$ and $\mathbf{P}_\alpha$ in Eq. (39) as c-numbers, which presumably obey some classical equations of motion that endow them with some time dependence, and we will treat $\mathbf{r}_i$ and $\mathbf{p}_i$ as operators acting on wave functions for the electrons. This is a hybrid classical-quantum approach.

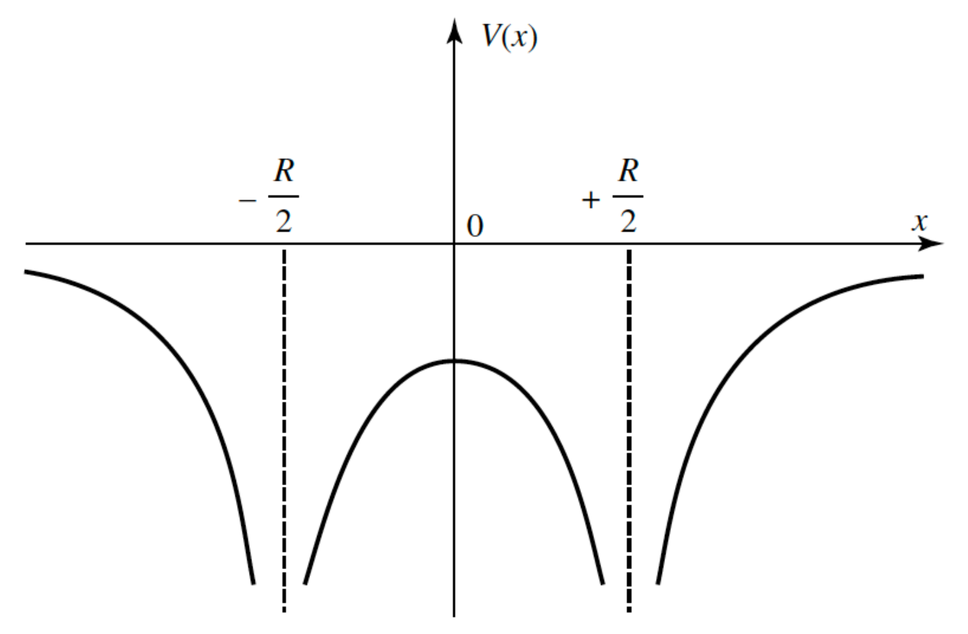
The adiabatic theorem tells us to look at the eigenfunctions of H_{elec} for fixed values of the parameters $\mathbf{R}$. Physically, this means that we fix or freeze the locations of the nuclei, and then solve for the electronic eigenfunctions and eigenvalues at the given nuclear locations. This problem is similar to atomic structure calculations, except that that the electrons are attracted to two or more fixed centers, instead of just one.

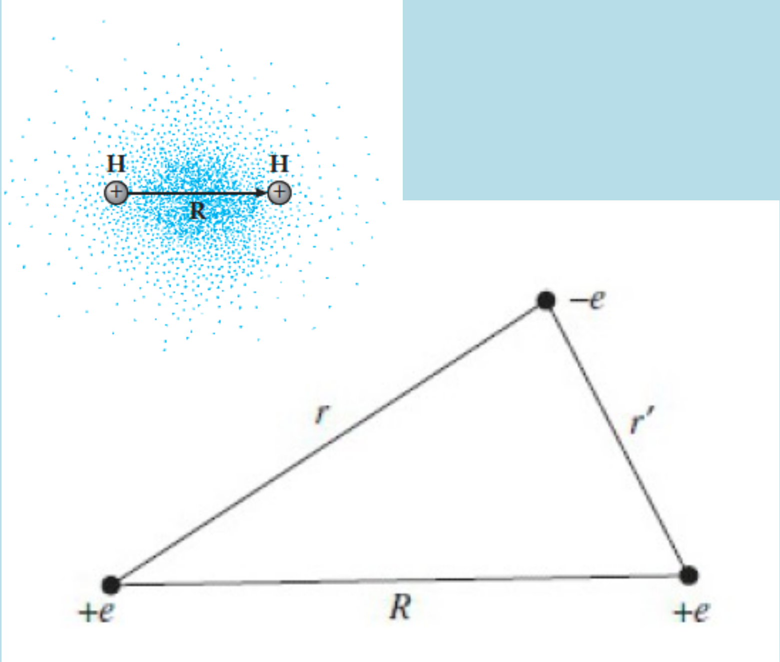


當原子核距離遙遠，原子形同獨立，

單一原子核的位能，會產生單一氫原子的基態，將兩原子基態分別標為$|1\rangle, |2\rangle$。

$R \to \infty$時，他們應該也就是氫分子內電子的基態。





$$H = K + V_1 + V_2 = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r} - \frac{e^2}{4\pi\varepsilon_0 r'}$$

$$(K + V_1)|1\rangle = E^{(0)}|1\rangle$$

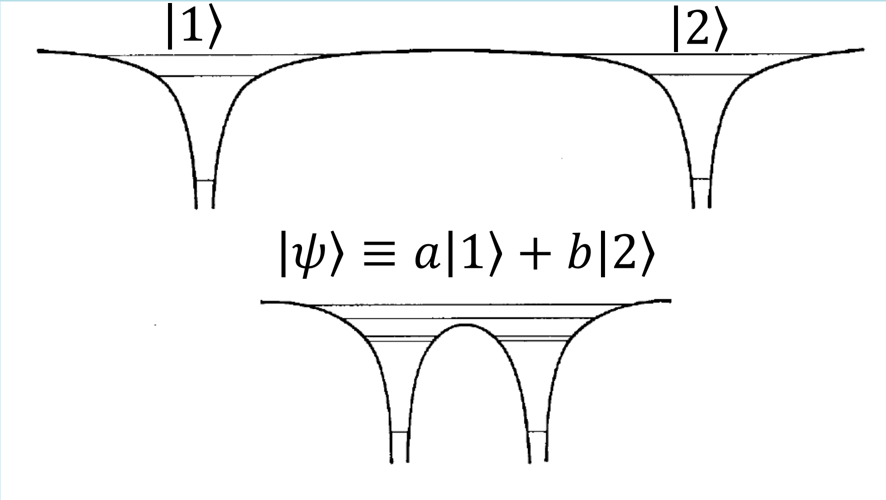
$$(K + V_2)|1\rangle = E^{(0)}|2\rangle$$

$$|1\rangle \sim \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$$

當原子漸漸靠近，一個原子中的電子會感受到旁邊另一原子的位能。

跨位$1 \to 2, 2 \to 1$的位能較小，可以視為微擾。

而$|1\rangle, |2\rangle$未微擾的本徵態，是同一能階，能量$E^{(0)}$相等，這是簡併下微擾。



大膽假設：正確的微擾零次近似解應該是$|1\rangle, |2\rangle$的線性組合。

我們要解微擾2×2矩陣的本徵問題，正確的微擾零次解即是本徵向量：

設本徵態寫成：$|\psi\rangle \equiv a|1\rangle + b|2\rangle$

在此我們把整個H一起考慮會比較方便：

$$\begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \left(E^{(0)} + E^{(1)}\right)\begin{pmatrix} a \\ b \end{pmatrix}$$

$$\langle 1|H|1\rangle = E^{(0)} + \langle 1|V_2|1\rangle = E^{(0)} + \langle 2|V_1|2\rangle = \langle 2|H|2\rangle \equiv E^{(0)} + V_{\text{cross}}$$

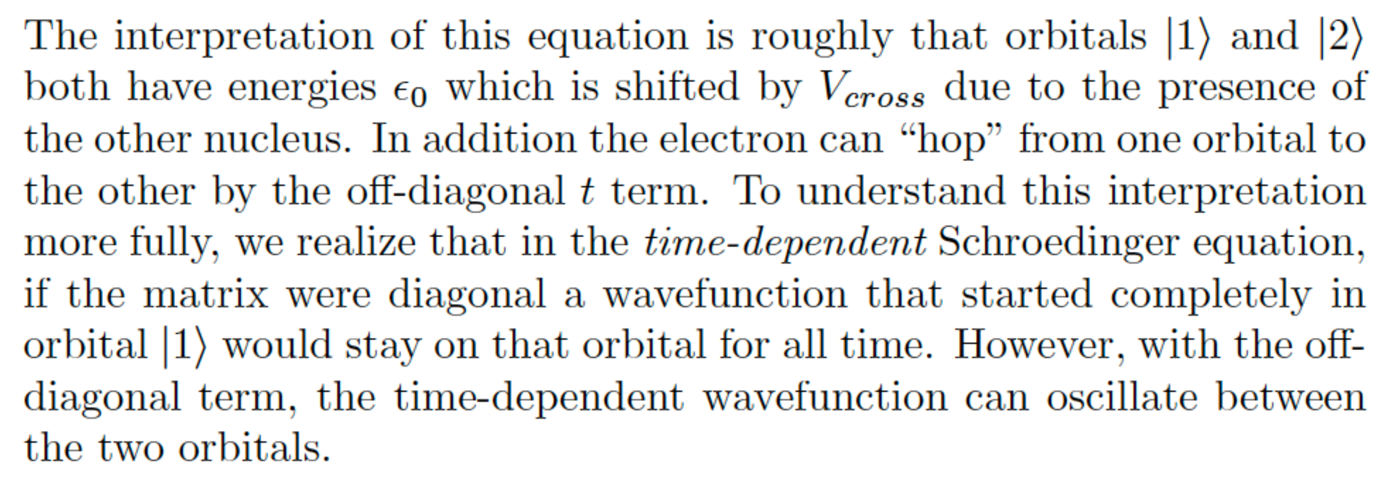
V_{cross}是臨近的位能對能量的修正。

$$\langle 2|H|1\rangle = \langle 2|V_2|1\rangle + \langle 2|K + V_1|1\rangle = \langle 2|V_2|1\rangle \equiv -t = \langle 1|V_1|2\rangle = \langle 1|H|2\rangle$$

$|1\rangle$是$K + V_1$的本徵態，$|1\rangle, |2\rangle$彼此正交。

$$\begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle \end{pmatrix} = \begin{pmatrix} E^{(0)} + V_{\text{cross}} & -t \\ -t & E^{(0)} + V_{\text{cross}} \end{pmatrix}$$

V_{cross}, t可以視為微擾。Off diagonal element t稱為hopping.



The interpretation of this equation is roughly that orbitals $|1\rangle$ and $|2\rangle$ both have energies ϵ_0 which is shifted by V_{cross} due to the presence of the other nucleus. In addition the electron can "hop" from one orbital to the other by the off-diagonal t term. To understand this interpretation more fully, we realize that in the *time-dependent* Schroedinger equation, if the matrix were diagonal a wavefunction that started completely in orbital $|1\rangle$ would stay on that orbital for all time. However, with the off-diagonal term, the time-dependent wavefunction can oscillate between the two orbitals.

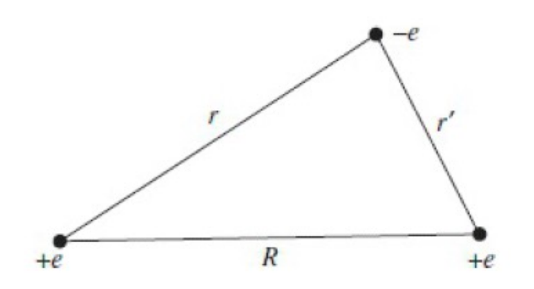
$$\begin{pmatrix} V_{\text{cross}} & -t \\ -t & V_{\text{cross}} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = (V_{\text{cross}} I - t\sigma_1) \begin{pmatrix} a \\ b \end{pmatrix} = E^{(1)} \begin{pmatrix} a \\ b \end{pmatrix}$$

σ_1的本徵態即是：$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$及$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$，本徵值為$1, -1$。

因此能量本徵值即為： $E^{(0)} + V_{\text{cross}} \mp t$

本徵態 $|\psi_{\pm}\rangle \equiv \frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle)$

$-t \equiv \langle 2|V_2|1\rangle$ 這個矩陣元非常關鍵

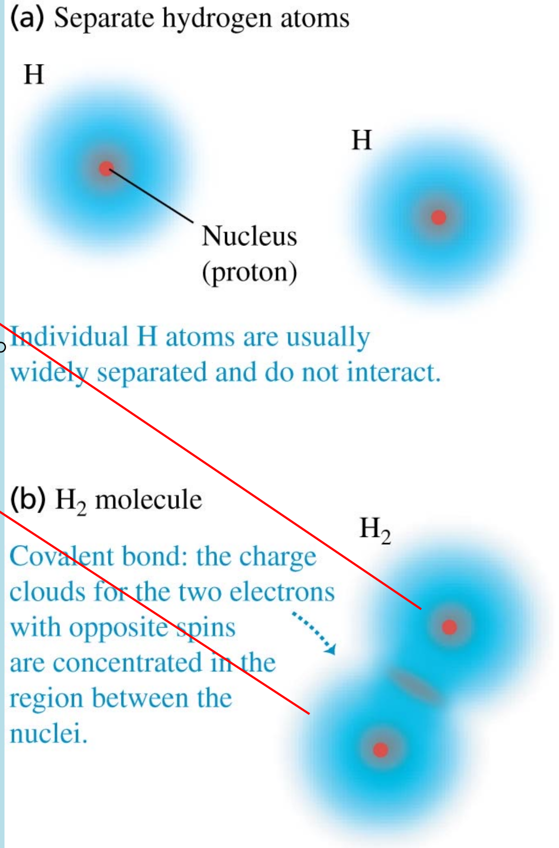


$$\sim \int d^3\vec{r}\cdot \phi_0(\vec{r}\,')\frac{e^2}{|\vec{r}-\vec{r}\,'|}\phi_0(\vec{r})$$

兩原子核越靠近，兩個波函數重疊越多。

積分就越大：$R \downarrow t \uparrow$

$$\sim\left(1+\frac{R}{a_0}\right)\cdot e^{-\frac{R}{a_0}}$$



Individual H atoms are usually widely separated and do not interact.

Covalent bond: the charge clouds for the two electrons with opposite spins are concentrated in the region between the nuclei.

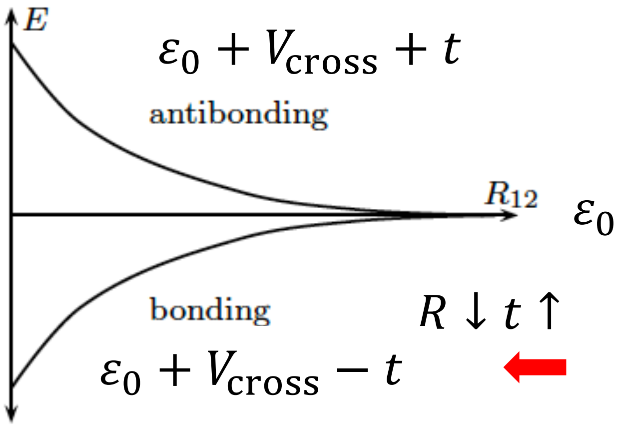


Fig. 6.5 Model tight binding energy levels as a function of distance between the nuclei of the atoms.

假設$t > 0$：

$$|\psi_-\rangle \equiv \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$$

能量較高

Anti-Bonding

$$|\psi_+\rangle \equiv \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

能量較低

Bonding

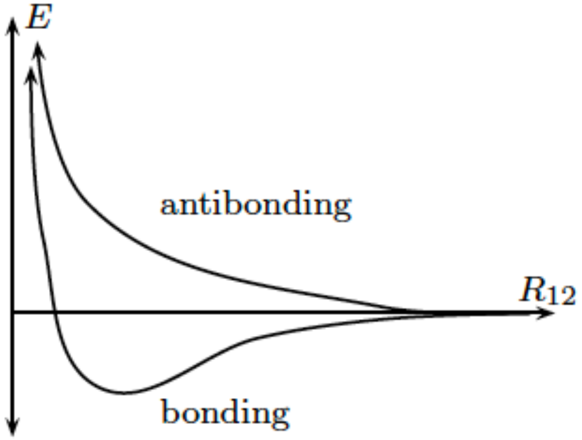


Fig. 6.6 More realistic energy levels as a function of distance between the nuclei of the atoms.

當原子核極靠近時，排斥力會拉高位能。

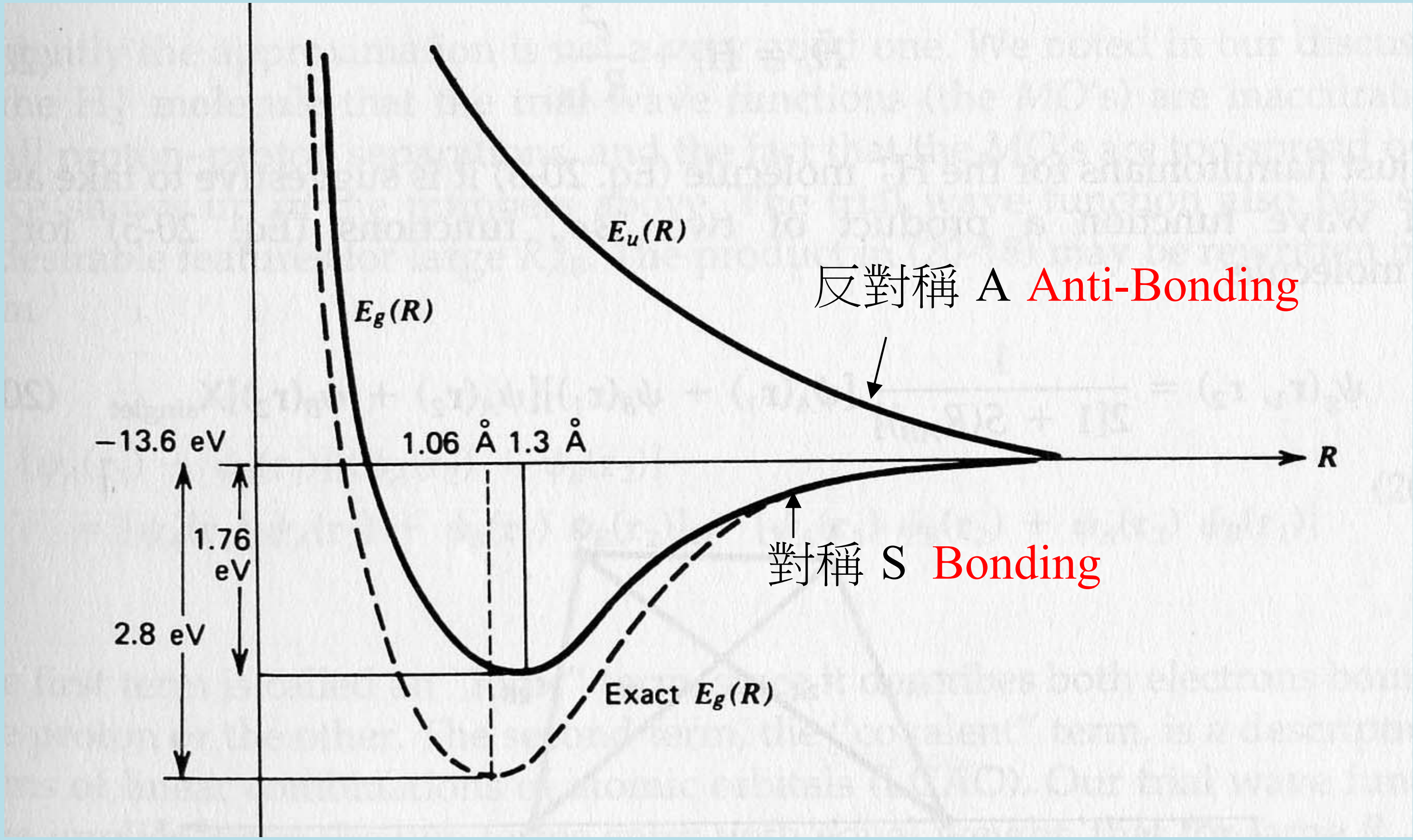
原子核的運動可以看成古典粒子。

它是近似在左圖的位能中運動。

若是bondin原子核便形成束縛態。

Textbook Gasiorowicz 在14-6用更嚴格的Variaitional Principle近似推導，得到一樣的結果，可參考。

H_2^+中電子能態的能量與距離 R 的關係：



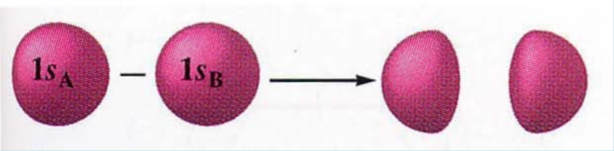
電子因為由兩個原子核共享而增加了負的庫倫位能，

使能量會因原子核距離的靠近而減少。

對稱態的確可以形成束縛態

分子軌道 Molecule Orbits σ-bond

機率密度分布



Anti-Bonding能量較高。

$$|\psi_-\rangle \equiv \frac{1}{\sqrt{2}}\left(|1\rangle - |2\rangle\right)$$

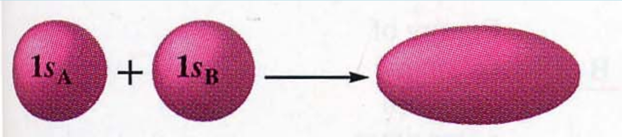
能量較高

Anti-Bonding

$$|\psi_+\rangle \equiv \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$$

能量較低

Bonding

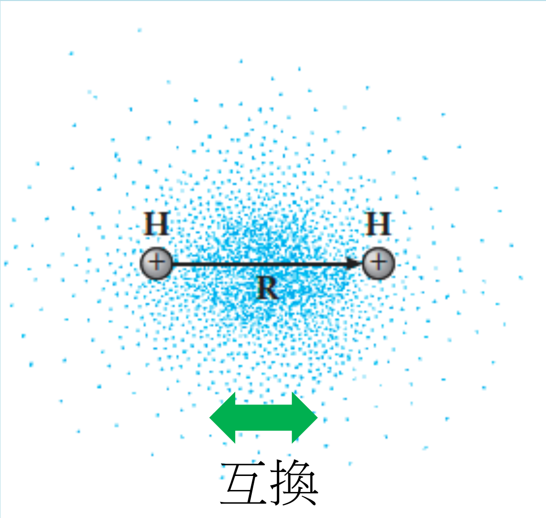


這兩個定態波函數非常特別。

注意在兩原子核互換後，$|1\rangle$及$|2\rangle$會互換，

波函數會是原來波函數乘上±1，

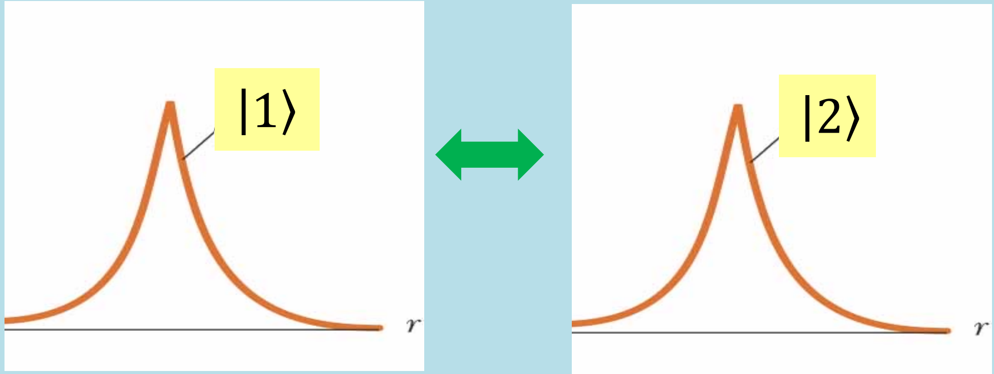
但如上圖所示，機率密度分布在兩原子核互換下都是不變的！



對任意R，兩原子核互換後，物理情境沒有任何改變，H是不變的：

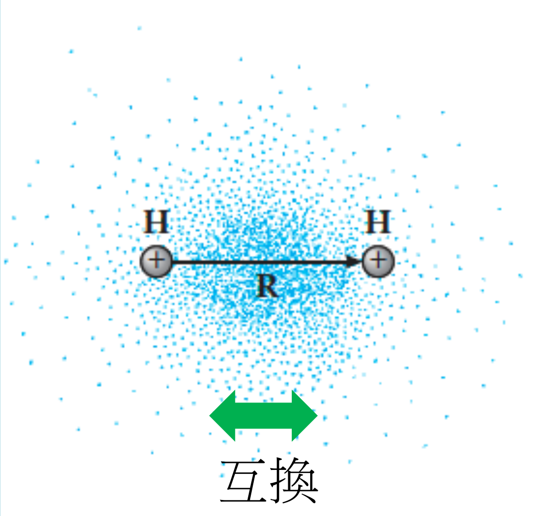
所以電子定態波函數的機率分布在兩原子核互換下也必須不變: $|\psi|^2 \leftrightarrow |\psi|^2$

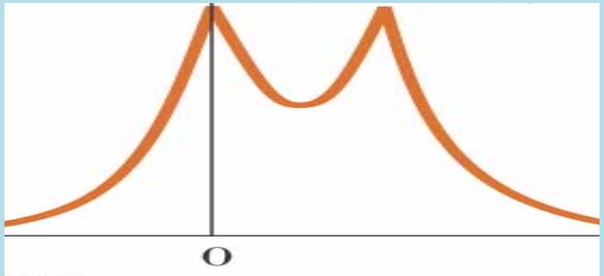
在兩原子核互換後，$|1\rangle$及$|2\rangle$很明顯互換： $|1\rangle \leftrightarrow |2\rangle$



$|\psi_1|^2 \leftrightarrow |\psi_2|^2 \neq |\psi_1|^2$

因此氫分子的電子定態不能近似於單純的$|1\rangle$及$|2\rangle$。

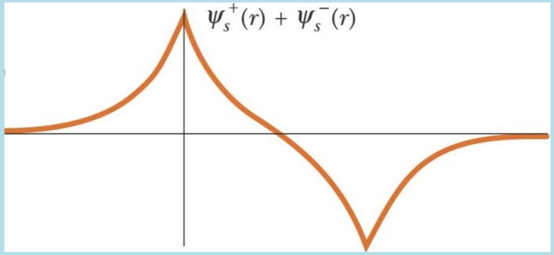




在互換下： $|1\rangle \leftrightarrow |2\rangle$

$$|\psi_+\rangle \equiv \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \rightarrow \frac{1}{\sqrt{2}}(|2\rangle + |1\rangle) = |\psi_+\rangle$$

交換對稱，或就稱對稱。

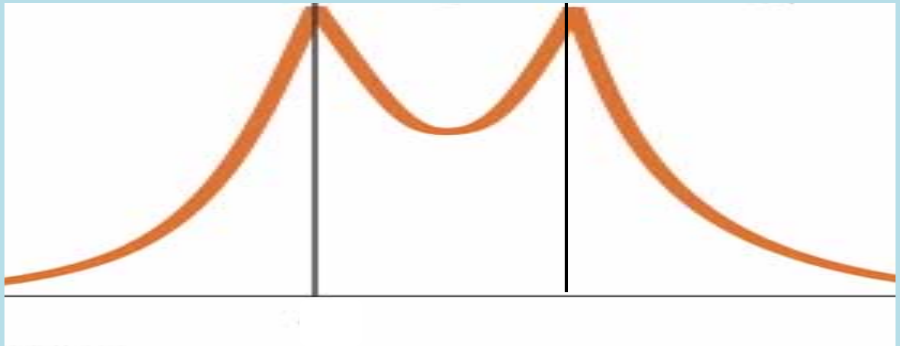


$$|\psi_-\rangle \equiv \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle) \rightarrow \frac{1}{\sqrt{2}}(|2\rangle - |1\rangle) = -|\psi_-\rangle$$

交換反對稱，或就稱反對稱。

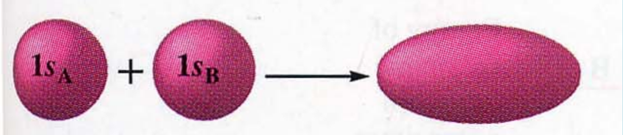
$\psi_\pm$電子能態波函數的機率分布在兩原子核互換下是不變的: $|\psi_\pm|^2 \rightarrow |\psi_\pm|^2$

因此分子的電子定態是近似於$|\psi_\pm\rangle$，而不是$|1\rangle$或$|2\rangle$。電子是共享的。

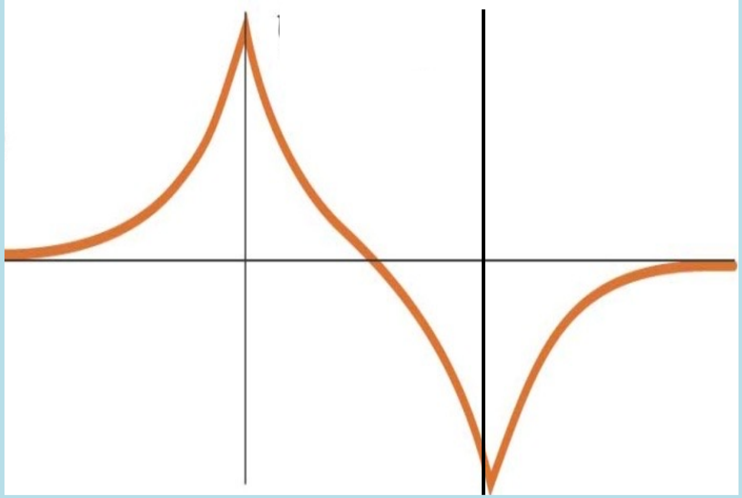


$$|\psi_+\rangle \equiv \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$$ 能量較低

對稱 S

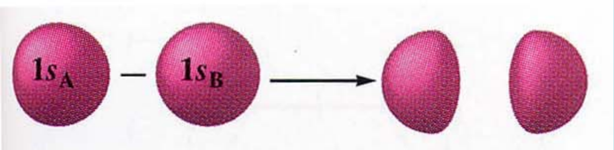


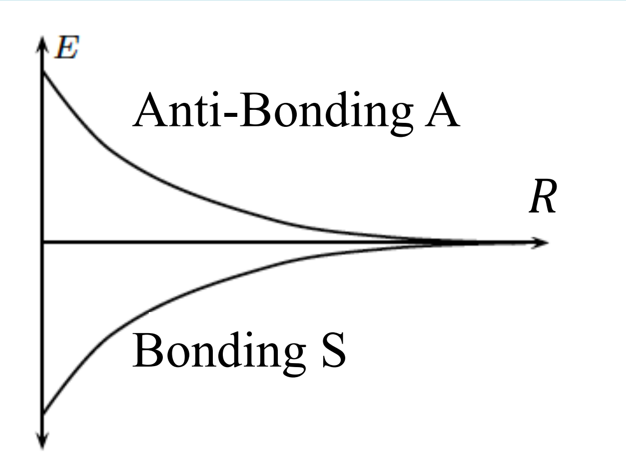
機率分布在兩原子核互換下是不變的。



$$|\psi_-\rangle \equiv \frac{1}{\sqrt{2}}\left(|1\rangle - |2\rangle\right)$$ 能量較高

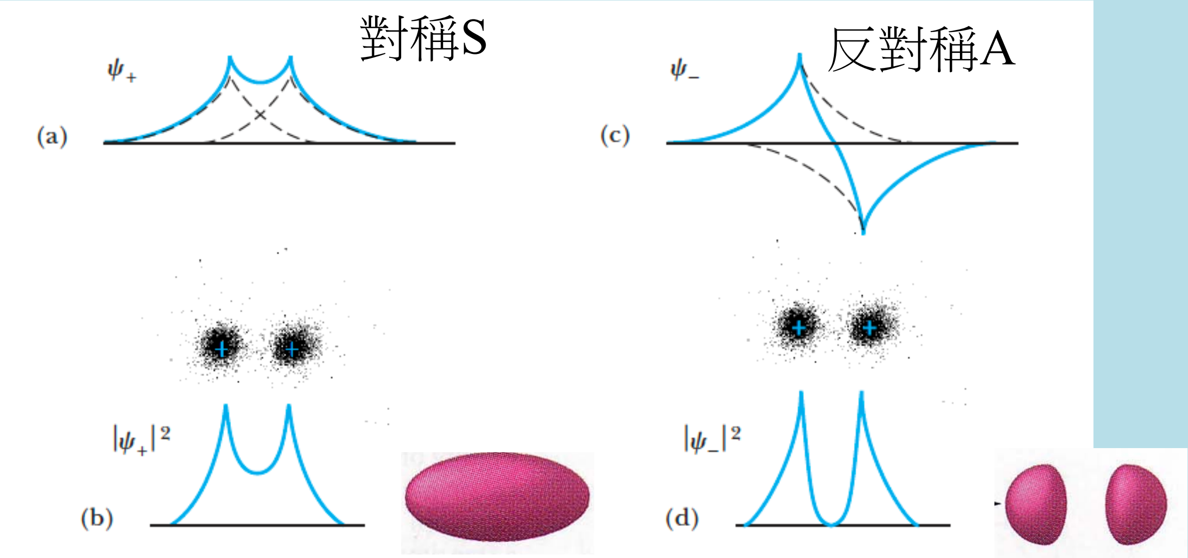
反對稱 A





這兩個能態在原子距離無限遠處，原來能量一樣，

但兩原子靠近後，能量就不一樣了：



對稱S態電子有較大機率存在於兩原子核之間，

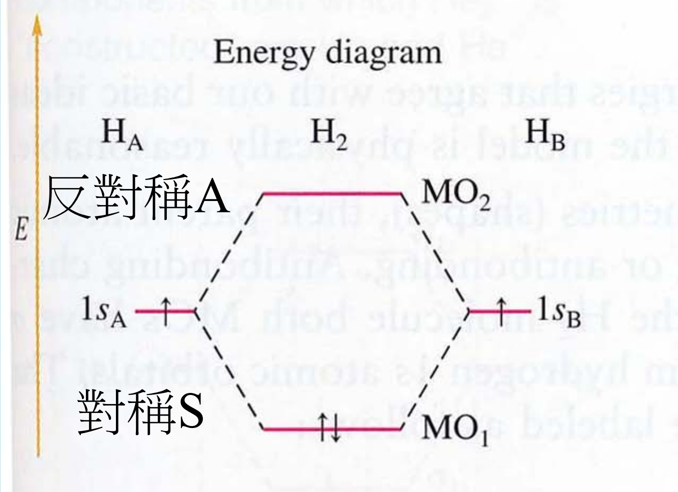
距兩帶正電的原子核較近，負的電能較大！

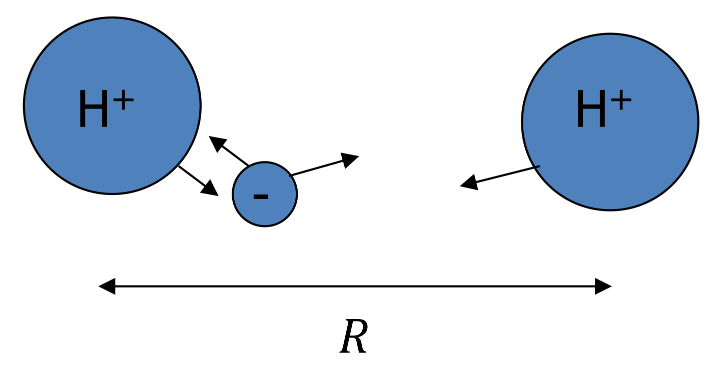
反對稱A態電子有較小機率存在於兩原子核之間，

距兩帶正電的原子核較遠，負的電能較小！

因此S態電子能量小於A態電子！

而且兩個能態的能量與原子核距離有關。





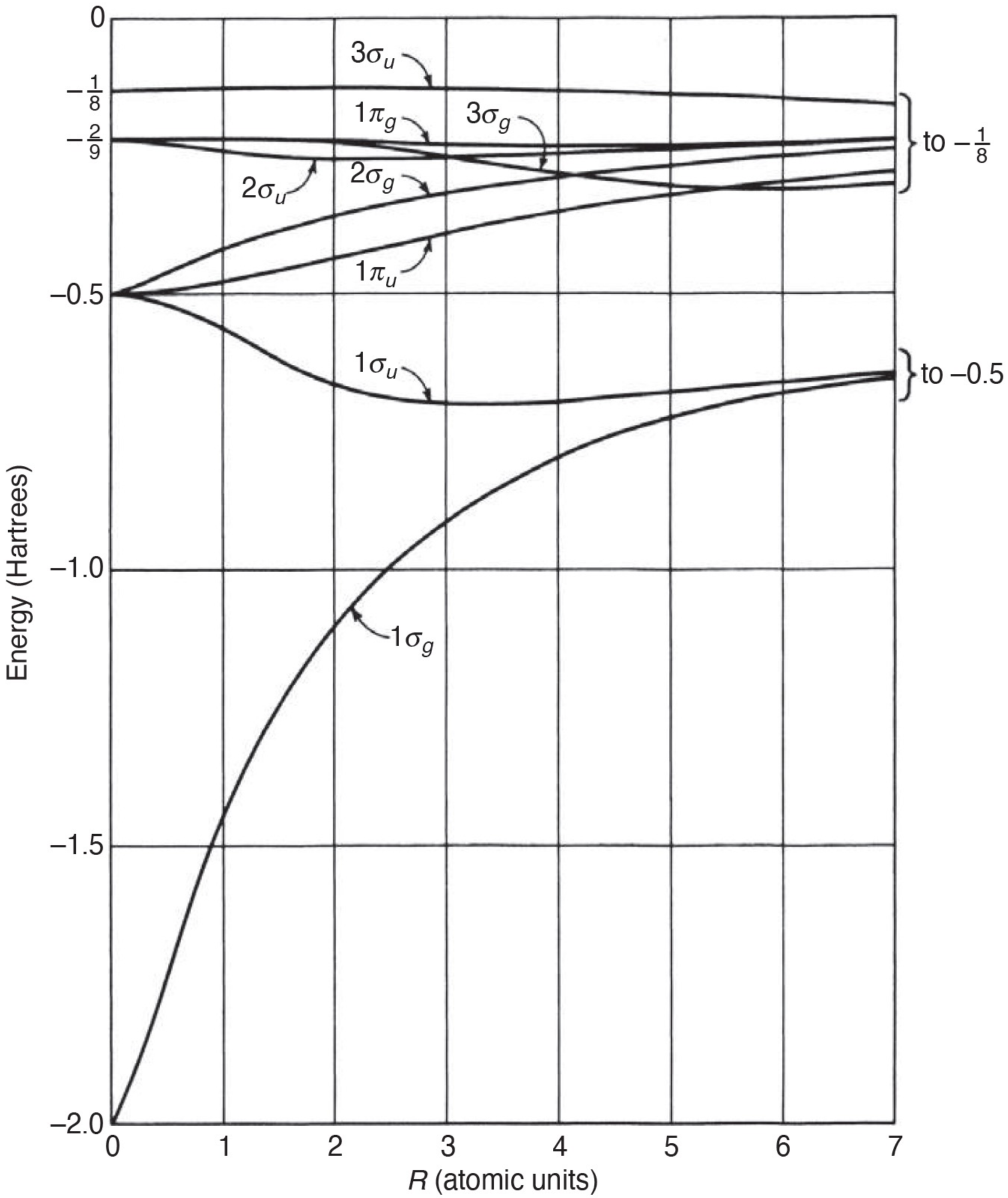
共價鍵束縛態

電子共享使能量降低，越靠近降低越多，因此形成束縛態。

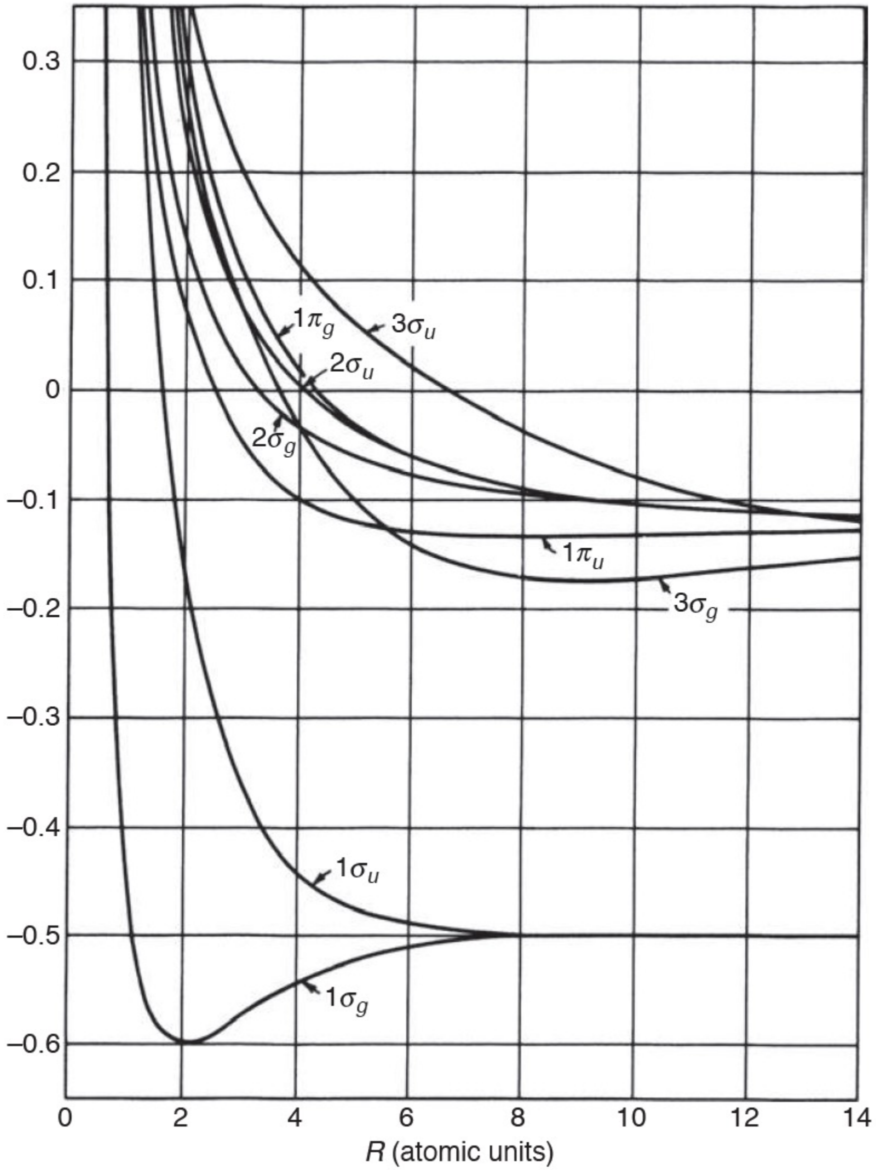
所降低的能量，來自電子的定態能量。

The notion that the electronic eigenvalue is the potential energy for the nuclear motion leads to an immediate understanding of the nature of the chemical bond. The example of the H_2 molecule will be discussed in class.

可以說，電子同時吸引兩個原子核，使得兩原子核束縛在一起。



tronic energies (in atomic units) of H_2^+ as a function of internuclear distance *R* from the exact calculation for fixed nuclei by ham, and Stewart. (Reprinted with permission from *Quantum Theory of Matter,* 2nd ed., by John C. Slater; copyright 1968, The l Companies, Inc.)



ılar potential energy curves for H_2^+ obtained by adding the nuclear repulsion energy 1/*R* to the exact solution curves of Figur

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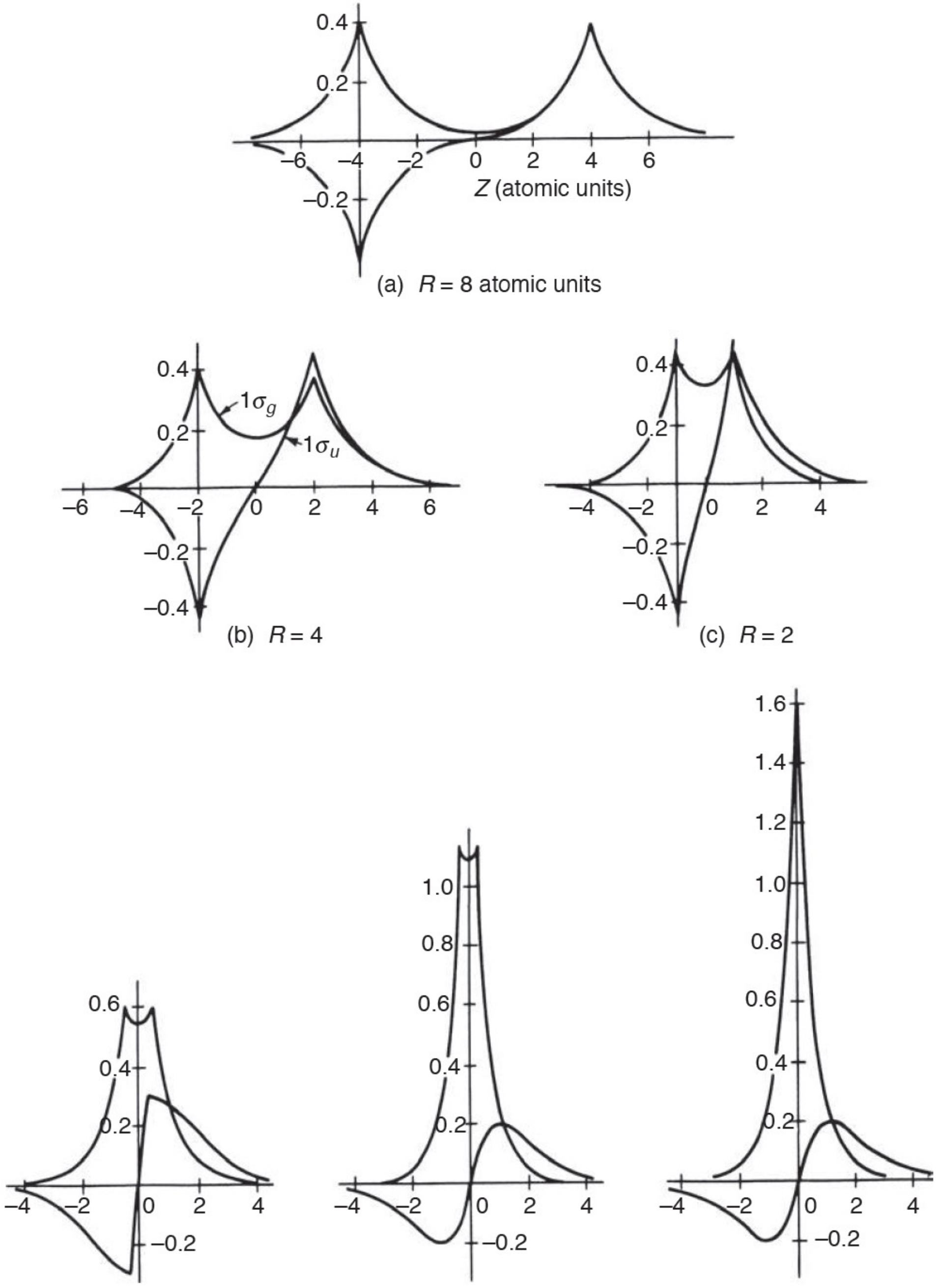

(a) $R = 8$ atomic units

(b) $R = 4$

(c) $R = 2$

(d) $R = 1$

(e) $R = 0.4$

(f) $R = 0$

and $1\sigma_u$ wave functions of H_2^+ plotted along the internuclear axis for various nuclear separations. (Reprinted with permission
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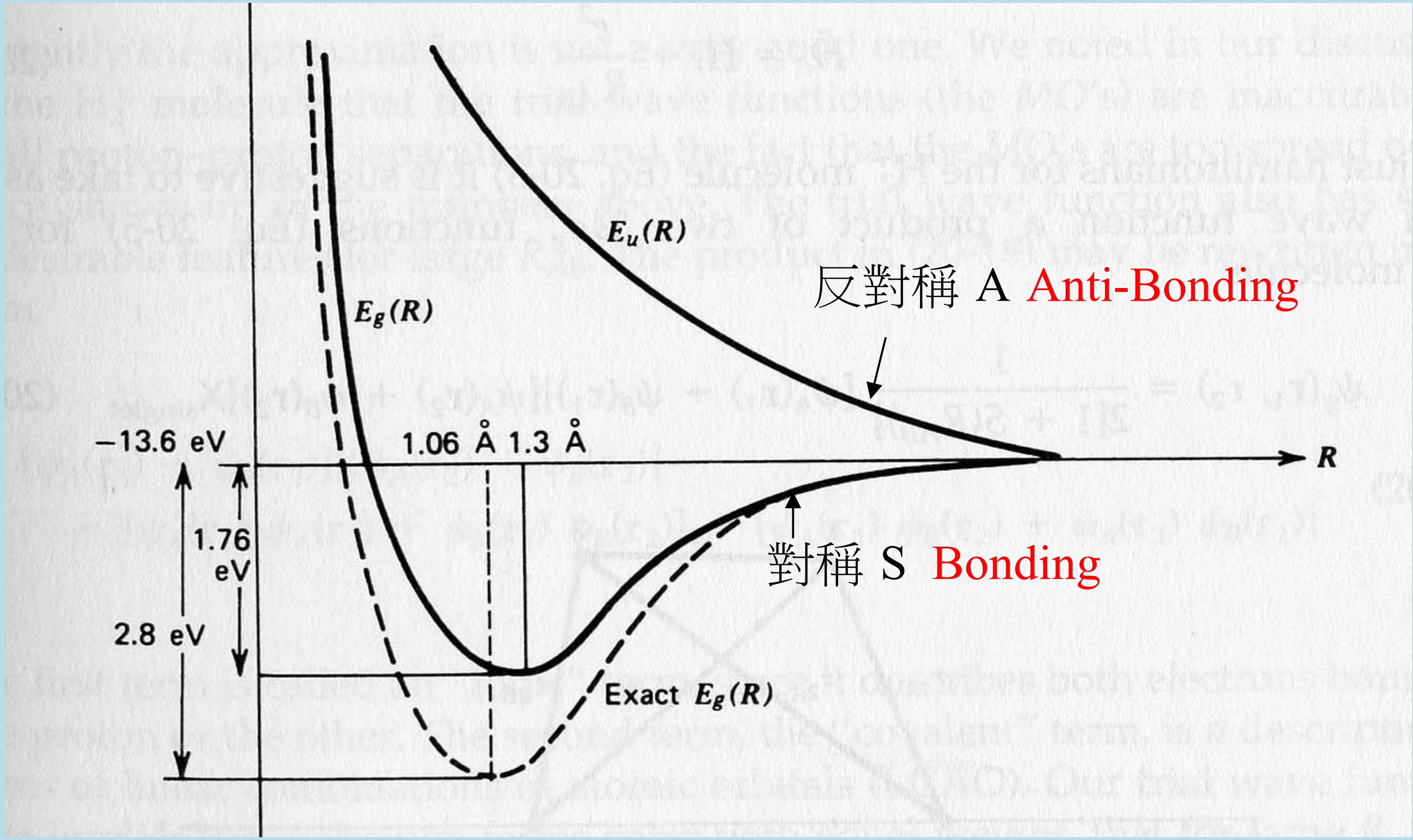
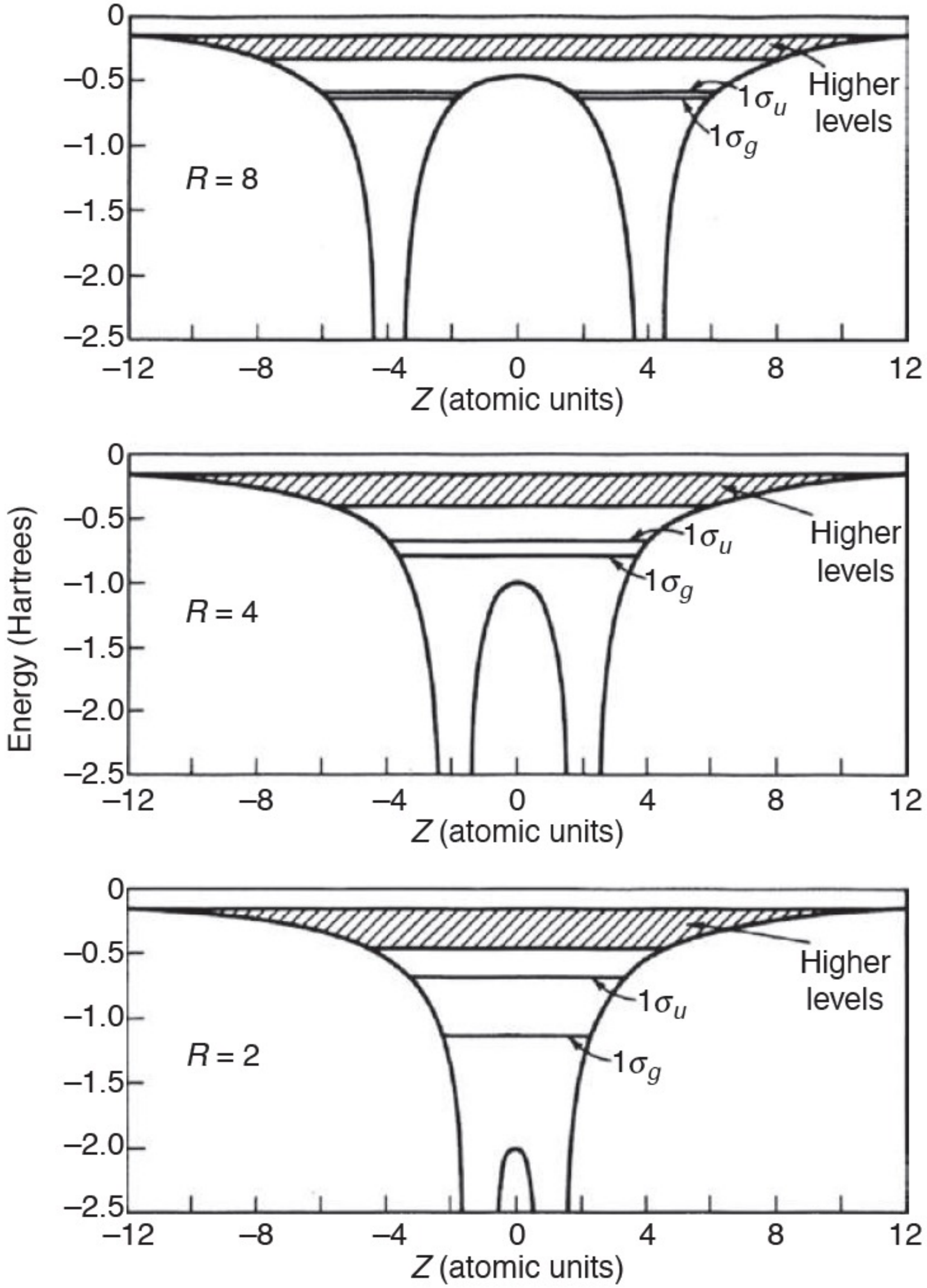
H_2^+中電子能態的能量與距離R的關係，低點~1.1Å，束縛能約是2.7 eV。

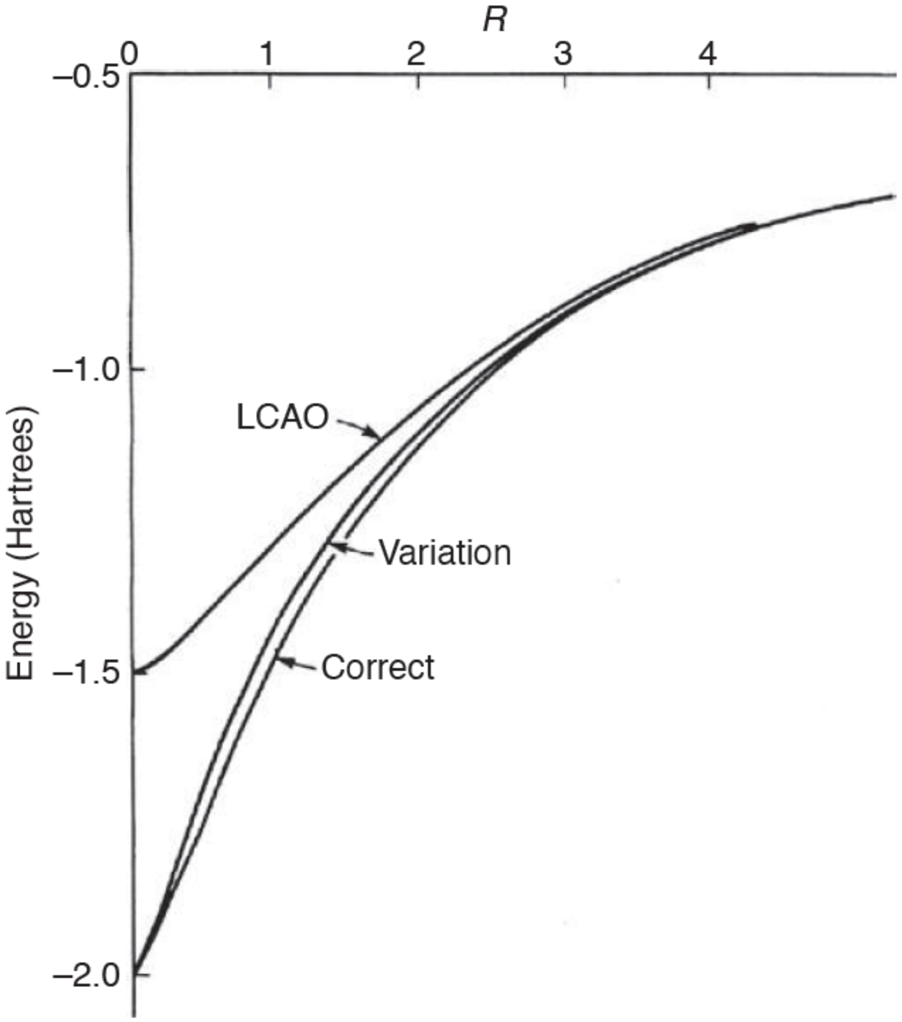


反對稱 A Anti-Bonding

對稱 S Bonding

分子軌道 Molecule Orbits σ-bond


Energy (Hartrees)
0
−0.5
−1.0
−1.5
−2.0
−2.5
R = 8
1σ_u
1σ_g
Higher levels
−12
−8
−4
0
4
8
12
Z (atomic units)
R = 4
1σ_u
1σ_g
Higher levels
R = 2
1σ_u
1σ_g
Higher levels



onal, exact, and LCAO energies for the $1\sigma_g$ state of H_2^+ . (Reprinted with permission from
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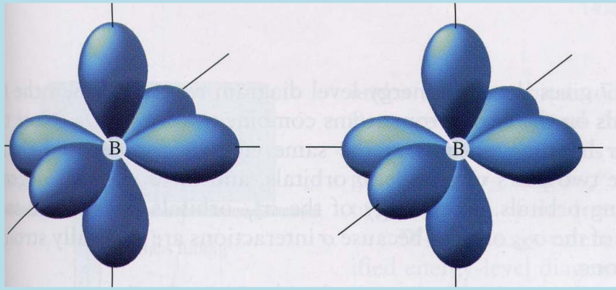
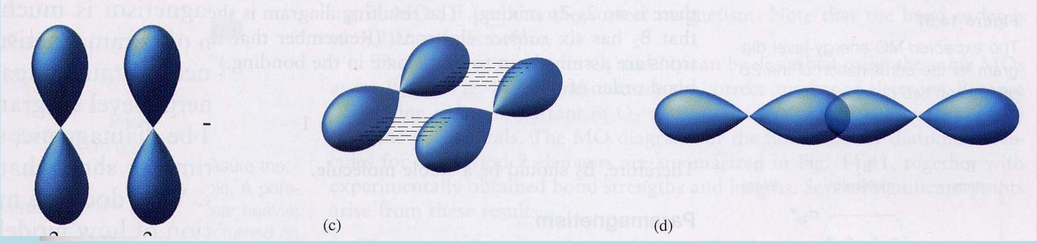
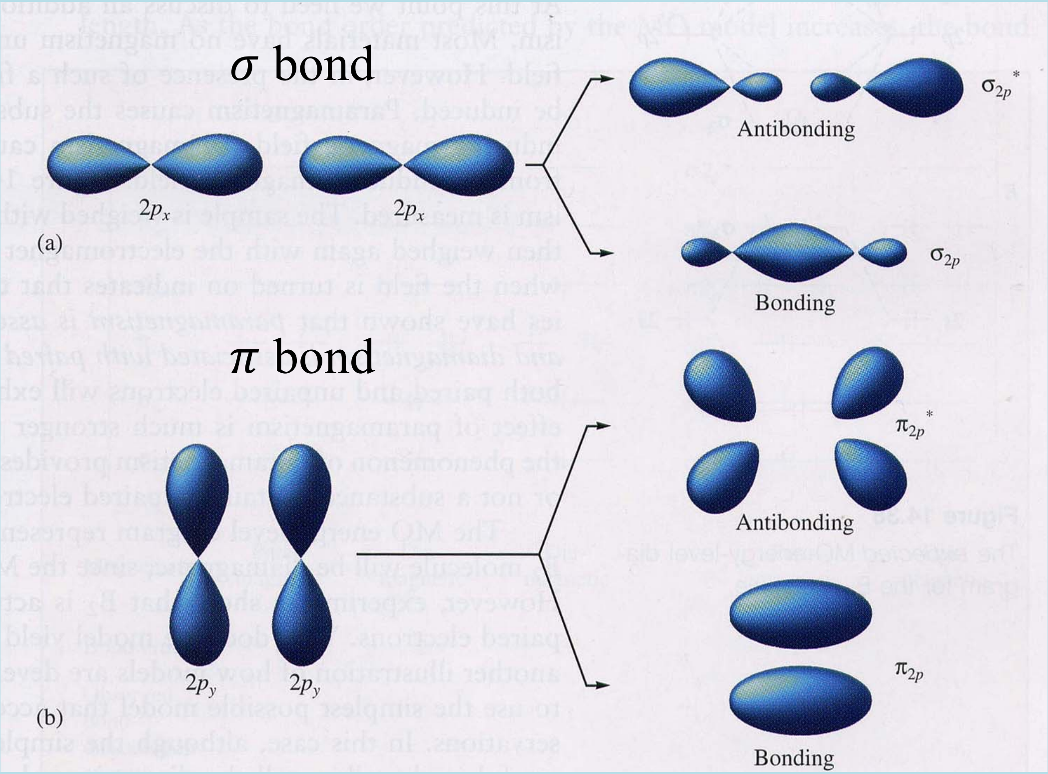


兩個原子的p態也能形成共價鍵：

σ bond and π bond





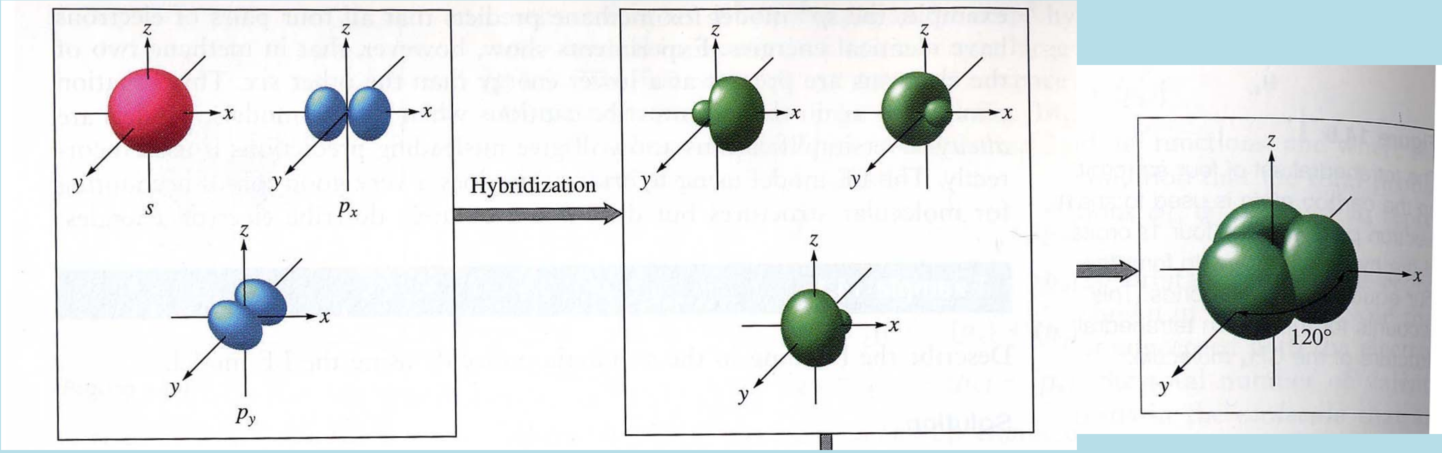
A Anti-Bonding

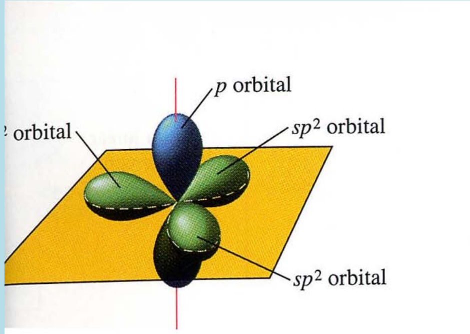
S Bonding

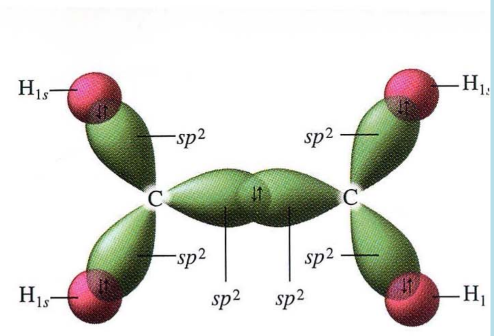
A Anti-Bonding

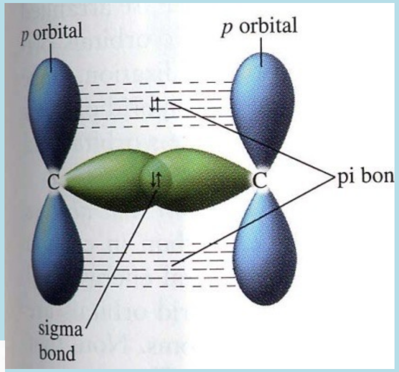
S Bonding

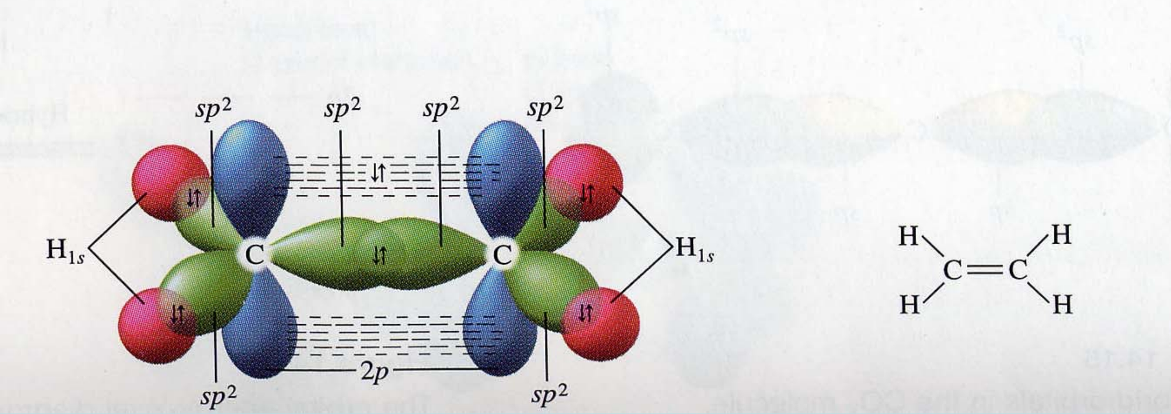
SP2

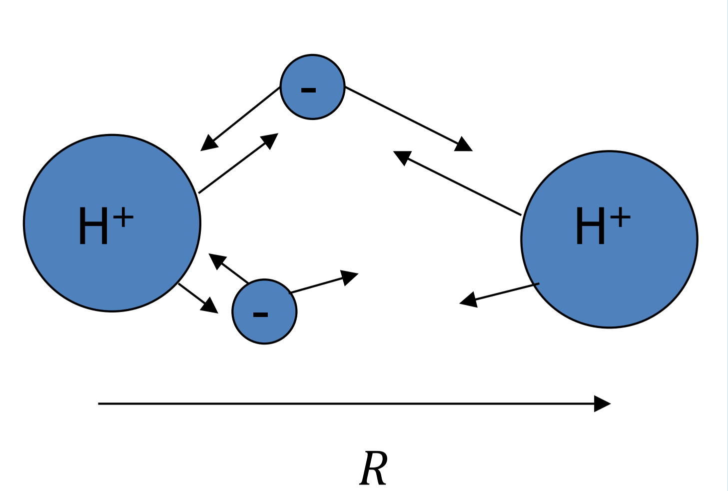

z
x
y
s
p_x
p_y
Hybridization
120°

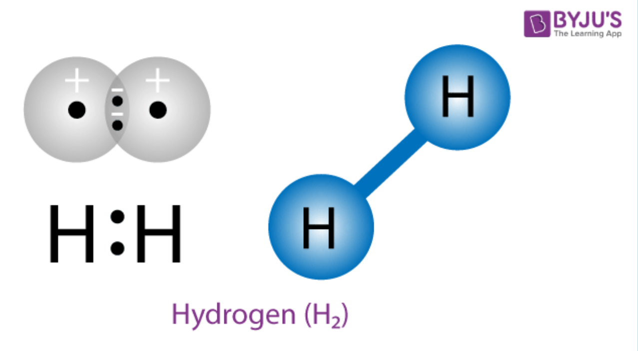

p orbital
^{2} orbital
sp^2 orbital
sp^2 orbital


H_{1s}
sp^2
sp^2
H_{1s}
C
C
sp^2
sp^2
H_{1s}
sp^2
sp^2
H_1


p orbital
p orbital
C
C
pi bon
sigma bond


sp^2
sp^2
sp^2
sp^2
H_{1s}
C
C
H_{1s}
sp^2
2p
sp^2
H
H
C
C
H
H





氫分子H_2的共價鍵束縛機制類似。

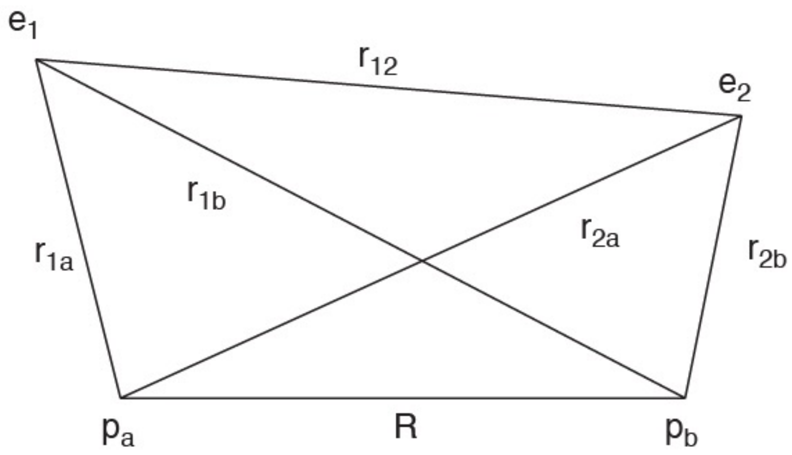
這個bonding的能態正好可以放入氫分子的兩個電子，

低點~0.7Å，束縛能約是4.7 eV。

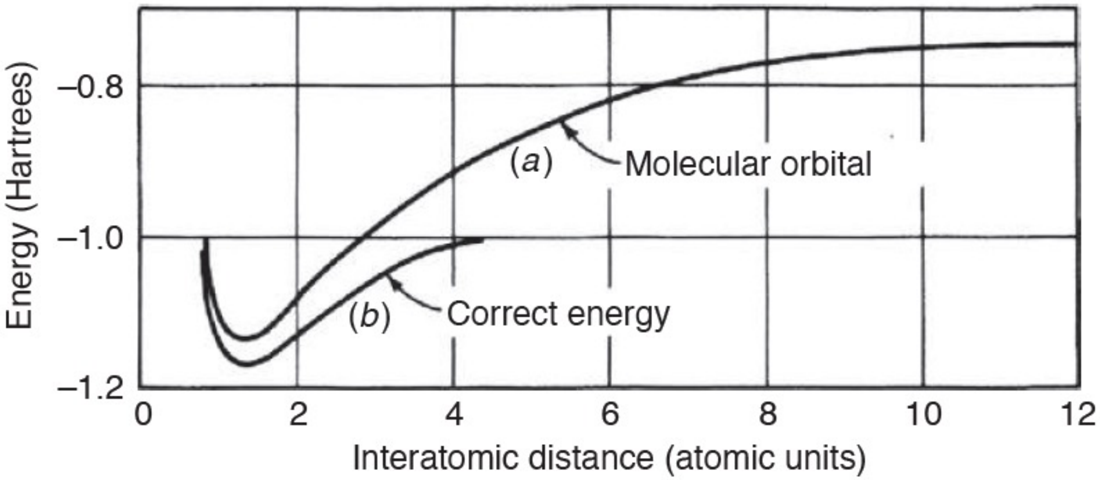
但現在電子與電子的排斥力必須考慮，電子傾向遠離彼此。

同時這兩顆電子無法彼此分辨，我們得開始學電子的社會學。

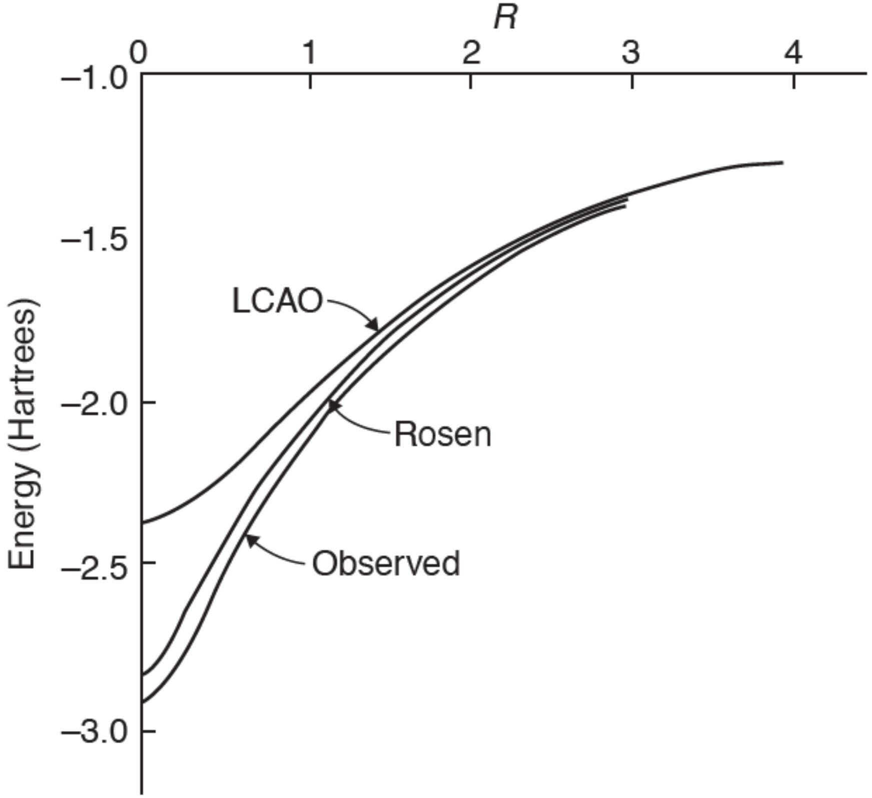
氫分子內的電子行為會很像雙電子的氦原子。



Coordinates for description of the electrons and protons in the H_2 Molecule.



Ground-state energy of H_2 as a function of R: (a) molecular orbital calculation based on (13.30); (b) experimentally determined energy curve. (Reprinted with permission from *Quantum Theory of Matter,* 2nd ed., by John C. Slater; copyright 1968, The McGraw-Hill Companies, Inc.)



Electronic energy in H_2 : Heitler-London method, as calculated for $\alpha = 1$ (LCAO), and by variational approach (Rosen). (Reprinted with permission from *Quantum Theory of Matter,* 2nd ed., by John C. Slater; copyright 1968, The McGraw-Hill Companies, Inc.)