

## Part 3. Molecules and Chemical Bonding

Okay, we've "done" **atoms**. But for important chemical applications, such as bonding, we need to apply Schrödinger's equation to **molecules**.

You might say "Doesn't everyone know that atoms bond together to form molecules?"

*Not according to classical mechanics!* Even for the hydrogen H<sub>2</sub> molecule, or the simpler yet H<sub>2</sub><sup>+</sup> molecule ion, it is impossible to account for chemical bonding using classical physics.

*The formation of chemical bonds is a quantum mechanical effect.*

One of the great early achievements of quantum mechanics is an explanation of chemical bonding, starting with the work of Heitler and London on H<sub>2</sub> in 1927, laying the foundation for a branch of science called "chemical physics".

### The Hydrogen Molecule Ion H<sub>2</sub><sup>+</sup> → Why do Atoms Bond?

With two nuclei and only one electron, H<sub>2</sub><sup>+</sup> is the *simplest molecule* (even simpler than H<sub>2</sub>). This is a good place to start with the quantum mechanical treatment of bonding.

We'll see that chemical bonding can be interpreted in terms of a **coulomb integral**, an **exchange integral**, and an **overlap integral**. This example will also illustrate that atomic orbitals for hydrogen-like single-electron atoms can be extended to reasonably describe the electronic structure of molecules.

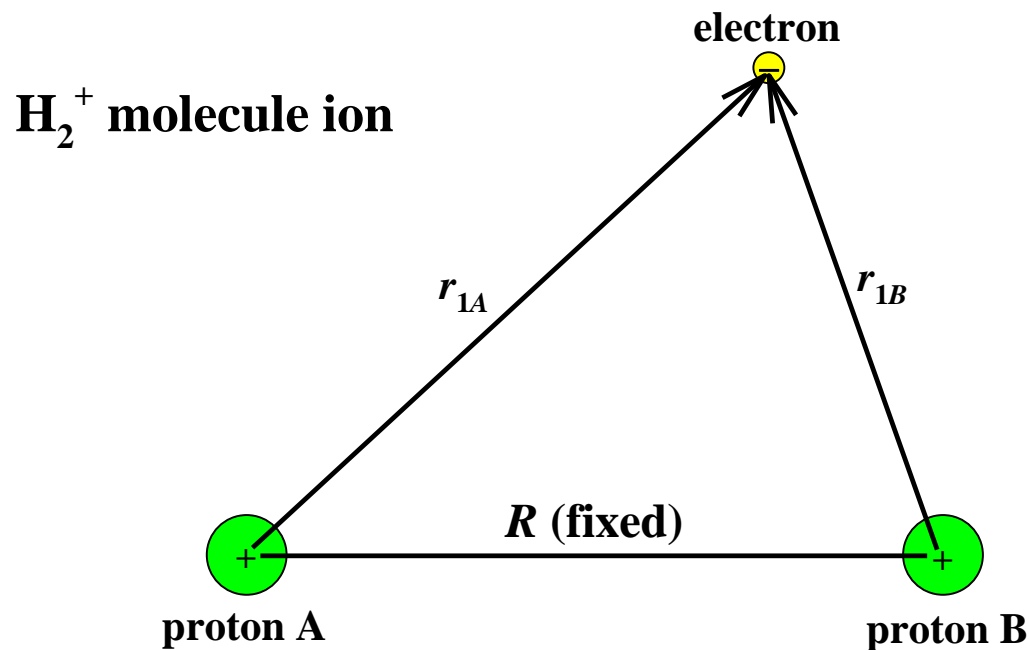
### Schrödinger's Equation and the Hamiltonian Operator for H<sub>2</sub><sup>+</sup>

$$\hat{H}\psi(\vec{r}_1, \vec{R}_A, \vec{R}_B) = E\psi(\vec{r}_1, \vec{R}_A, \vec{R}_B)$$

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} + \frac{e^2}{4\pi\epsilon_0 R}$$

$M$  is the mass of each nucleus (equal to the proton mass in this case),  $m_e$  is the electron mass,  $r_{1A}$  is the distance between the electron and nucleus  $A$ ,  $r_{1B}$  is the distance between the electron and nucleus  $B$ , and  $R$  is the distance between the two nuclei.

It's impossible to solve Schrödinger's equation for the hydrogen molecule ion (a three-body problem). But because the nuclei are thousands of times heavier than the electron, the electron moves much more rapidly than the nuclei. So it's an excellent approximation to apply the Schrödinger equation to  $H_2^+$  ions at **fixed internuclear distance  $R$** . This is called the **Born Oppenheimer Approximation**.



The Born Oppenheimer approximation allows the total wave function for  $\text{H}_2^+$  to be factored into nuclear and electronic contributions:

$$\hat{H}\psi(\vec{r}_1, \vec{R}_A, \vec{R}_B) = \psi_e(\vec{r}_1, R)\psi_n(\vec{R}_A, \vec{R}_B)$$

The **Schrödinger equation for the electron motion** we're interested in is

$$\hat{H}_e\psi(\vec{r}_1, R) = E_e(R)\psi_e(\vec{r}_1, R)$$

with the **electronic Hamiltonian operator for the  $\text{H}_2^+$  molecule ion** (nuclei “frozen”)

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} + \frac{e^2}{4\pi\epsilon_0 R}$$

The first term represents the electron kinetic energy. The remaining terms account for the electron-nucleus  $A$  potential energy, electron-nucleus  $B$  potential energy, and the nucleus-nucleus potential energy (repulsive).  $R$  is assumed to be constant. This application of the Born Oppenheimer approximation allows the electronic Schrödinger equation to be solved exactly, giving the electronic energy as a function of the **internuclear distance  $R$** .

[If we were interested in the translational, vibrational, and rotational motion of the nuclei (not here, but later) we would solve the **Schrödinger equation for the nuclei**

$$\left[ -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) + E_e(R) \right] \psi_n(\vec{R}_A, \vec{R}_B) = E_n \psi_n(\vec{R}_A, \vec{R}_B)$$

The nuclear wave function is a product of translational, vibrational, and rotational wave functions, which are important for statistical thermodynamics and spectroscopy.]

The Schrödinger equation for the electron  $\hat{H}_e \psi(\vec{r}_1, R) = E_e(R) \psi(\vec{r}_1, R)$  at fixed nuclear separation can be solved exactly, but the solutions are complicated and it is not easy to grasp their meaning.

A much more informative approach, though only qualitatively accurate, is to solve the electronic Schrödinger equation by using the variational method with trial wave functions made up of hydrogen-like atomic orbitals centered on each nucleus. This will illustrate **molecular orbital theory**. Our analysis will only be approximate. By including more functions in the trial wave functions, however, the treatment can be improved to any degree of accuracy.

### **Trial Wave Function for the H<sub>2</sub><sup>+</sup> Molecule Ion**

As the trial wave function for the one-electron hydrogen molecule ion, we will use linear combinations of 1s atomic orbitals

$$\psi = c_1 1s_A + c_2 1s_B$$

centered on protons *A* and *B*. This kind of wave function is called a “**linear combination of atomic orbitals**” (**LCAO**).

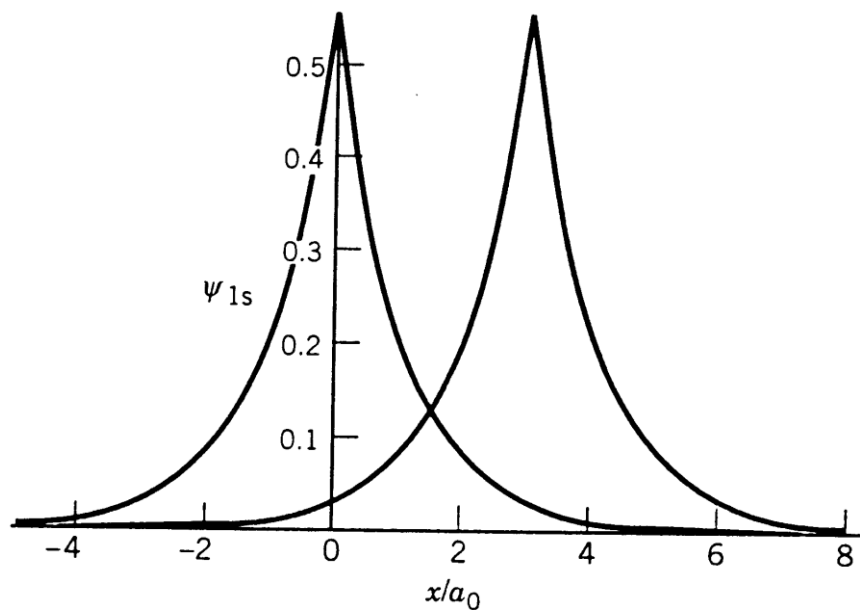
Because the nuclei are identical and indistinguishable, we must use wave functions that are linear combinations of 1s<sub>A</sub> and 1s<sub>B</sub> with  $c_1 = c_2 = c$  or  $c_1 = -c_2$

$$\psi_+(r_{1A}, r_{1B}) = c_1 1s_A(r_{1A}) + c_1 1s_B(r_{1B}) \quad (\text{symmetrical})$$

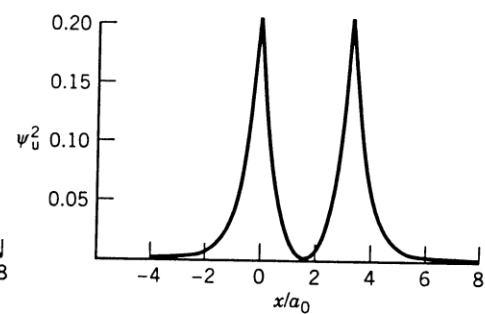
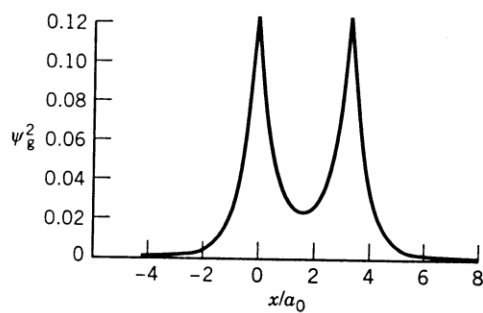
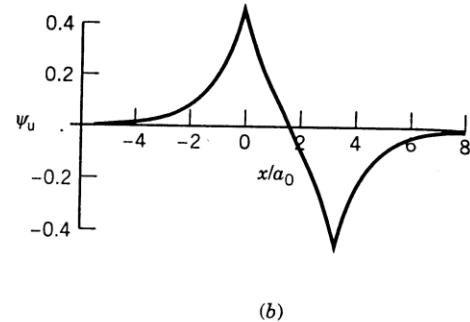
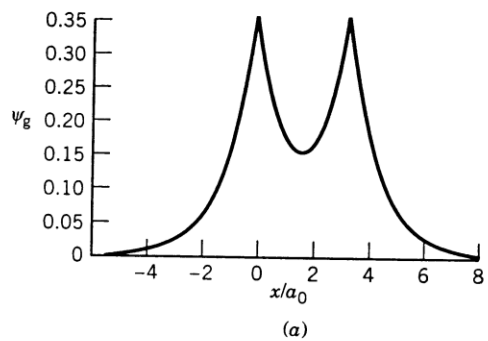
$$\psi_-(r_{1A}, r_{1B}) = c_1 1s_A(r_{1A}) - c_1 1s_B(r_{1B}) \quad (\text{unsymmetrical})$$

(Recall that we had to do something like this before to get acceptable wave functions for the helium atom.)

## Atomic orbitals used to approximate the wave function for $\text{H}_2^+$



**Symmetrical and  
Unsymmetrical  
Wave Functions  
for  $\text{H}_2^+$**



Which wave function leads to stronger bonding?

Notice that  $\psi_+(x_{1A}, x_{1B})$  is **symmetric** about the midway point between the nuclei. Stated more precisely:

$$\psi_+(x_{1A}, x_{1B}) = \psi_+(-x_{1A}, -x_{1B}) = \psi_g(x_{1A}, x_{1B})$$

In the jargon used by spectroscopists,  $\psi_+(x_{1A}, x_{1B})$  is said to be “**gerade**” (even parity in German), and is labeled  $\psi_g(x_{1A}, x_{1B})$ .

$\psi_-(x_{1A}, x_{1B})$  is **antisymmetric**, on the other hand, and called “**ungerade**” (odd parity)

$$\psi_-(x_{1A}, x_{1B}) = -\psi_-(-x_{1A}, -x_{1B}) = \psi_u(x_{1A}, x_{1B})$$

and is labeled  $\psi_u(x_{1A}, x_{1B})$ .

To normalize the even wave function  $\psi_g$  we require

$$1 = \int \psi_g^* \psi_g \, d\tau$$

and therefore

$$\begin{aligned} 1 &= \int (c1s_A + c1s_B)^*(c1s_A + c1s_B) \, d\tau \\ &= c^2 \int 1s_A^* 1s_A \, d\tau + c^2 \int 1s_A^* 1s_B \, d\tau + c^2 \int 1s_B^* 1s_A \, d\tau + c^2 \int 1s_B^* 1s_B \, d\tau \end{aligned}$$

Because the 1s orbitals are normalized, the first and last of the four integrals are unity. The second and third integrals are identical.

$$\int 1s_A^* 1s_B \, d\tau = \int 1s_B^* 1s_A \, d\tau = S \quad \text{overlap integrals } S$$

They are called **overlap integrals S** and increase in magnitude as the internuclear separation decreases and  $1s_A$  and  $1s_B$  overlap more completely.

The overlap integral  $S$  for the  $\text{H}_2^+$  ion can be evaluated analytically as a function of the internuclear distance (*Tutorial #3*)

$$S = e^{-R} \left( 1 + R + \frac{R^2}{3} \right)$$

Notice that when  $R = 0$ , the  $1s_A$  and  $1s_B$  orbitals overlap perfectly and  $S = 1$ . In the limit  $R \rightarrow \infty$  (corresponding to an H atom and an  $\text{H}^+$  ion), there is no overlap and  $S = 0$ .

The normalization requirement for  $\psi_+$  becomes

$$1 = c^2(2 + 2S)$$

which gives

$$\psi_g = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B)$$

Similarly, the normalization constant for  $\psi_u$  is  $[2(1-S)]^{-1/2}$  and

$$\psi_u = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B)$$

We can now use our trial wave function and the variational principle

$$E' = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

to estimate the trial energy  $E'$  of the  $\text{H}_2^+$  molecule ion.

Letting  $\psi = c_1 1s_A + c_2 1s_B$  [with  $c_1 = c_2 = c$  for the even (gerade) wave function  $\psi_g$  and  $c_1 = c = -c_2$  for the odd (ungerade) wave function  $\psi_u$ ], the estimated energy is

$$E' = \frac{\int (c_1 1s_A + c_2 1s_B)^* \hat{H} (c_1 1s_A + c_2 1s_B) d\tau}{\int (c_1 1s_A + c_2 1s_B)^* (c_1 1s_A + c_2 1s_B) d\tau}$$

Using the following abbreviations

$$H_{AA} = \int 1s_A \hat{H} 1s_A d\tau = \int 1s_B \hat{H} 1s_B d\tau = H_{BB}$$

$$H_{AB} = \int 1s_A \hat{H} 1s_B d\tau = \int 1s_B \hat{H} 1s_A d\tau = H_{BA}$$

$$S_{AA} = \int 1s_A 1s_A d\tau = \int 1s_B 1s_B d\tau = S_{BB} = 1$$

$$S_{AB} = \int 1s_A 1s_B d\tau = \int 1s_B 1s_A d\tau = S_{BA}$$

the expression for the energy becomes

$$\begin{aligned} E' &= \frac{c_1^2 H_{AA} + 2c_1 c_2 H_{AB} + c_2^2 H_{BB}}{c_1^2 S_{AA} + 2c_1 c_2 S_{AB} + c_2^2 S_{BB}} \\ &= \frac{c_1^2 H_{AA} + 2c_1 c_2 H_{AB} + c_2^2 H_{BB}}{c_1^2 + 2c_1 c_2 S + c_2^2} \end{aligned}$$

$H_{AB}$  and  $H_{BA}$  are called **exchange integrals**, a measure of energy contributed by possible interactions of the orbitals centered on different nuclei.

Because the 1s wave functions are normalized, the integrals  $S_{AA}$  and  $S_{BB}$  are unity.  $S_{AB} = S_{BA} = S$  are the **overlap integrals**.



To find the minimum energy, it is convenient to clear out the denominator in the equation for  $E'$

$$E'(c_1^2 + 2c_1c_2S + c_2^2) = c_1^2H_{AA} + 2c_1c_2H_{AB} + c_2^2H_{BB}$$

and differentiate with respect to  $c_1$  and  $c_2$

$$E'(2c_1 + 2c_2S) + \frac{\partial E'}{\partial c_1}(c_1^2 + 2c_1c_2S + c_2^2) = 2c_1H_{AA} + 2c_2H_{AB}$$

$$E'(2c_1S + 2c_2) + \frac{\partial E'}{\partial c_2}(c_1^2 + 2c_1c_2S + c_2^2) = 2c_1H_{AB} + 2c_2H_{BB}$$

The derivatives  $\partial E'/\partial c_1$  and  $\partial E'/\partial c_2$  are zero for the minimum energy, so we get

$$c_1(H_{AA} - E) + c_2(H_{AB} - SE) = 0$$

$$c_1(H_{AB} - SE) + c_2(H_{BB} - E) = 0$$

In general, a nontrivial solution to these equations exists if the determinant

$$\begin{vmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{BB} - E \end{vmatrix} = 0$$

is zero which provides the quadratic equation for the energy

$$\boxed{(H_{AA} - E)(H_{BB} - E) - (H_{AB} - SE)^2 = 0}$$

and therefore two values of the energy  $E$ . The lower value of  $E$  is our variational estimate of the ground state energy of the  $\text{H}_2^+$  molecule ion.

The  $S$ ,  $H_{AA}$ ,  $H_{BB}$ , and  $H_{AB}$  terms are a bit difficult to evaluate. The result is

$$H_{AA} = H_{BB} = E_{1s} + J_1$$

$$H_{AB} = H_{BA} = SE_{1s} + K_1$$

The overlap integral has already been evaluated:

$$S = \int 1s_A 1s_B d\tau = e^{-R} \left( 1 + R + \frac{R^2}{3} \right)$$

**$J_1$  is the Coulomb integral** measuring the potential energy for the electron-nuclei attraction ( $< 0$ ) and the nucleus-nucleus repulsion ( $> 0$ ):

$$J_1 = -2E_{1s} e^{-2R} \left( 1 + \frac{1}{R} \right) \quad (E_{1s} = -13.60 \text{ eV})$$

$$= \frac{e^2}{4\pi\epsilon_0} \int 1s_A \left( -\frac{1}{r_{1B}} + \frac{1}{R} \right) 1s_A d\tau$$

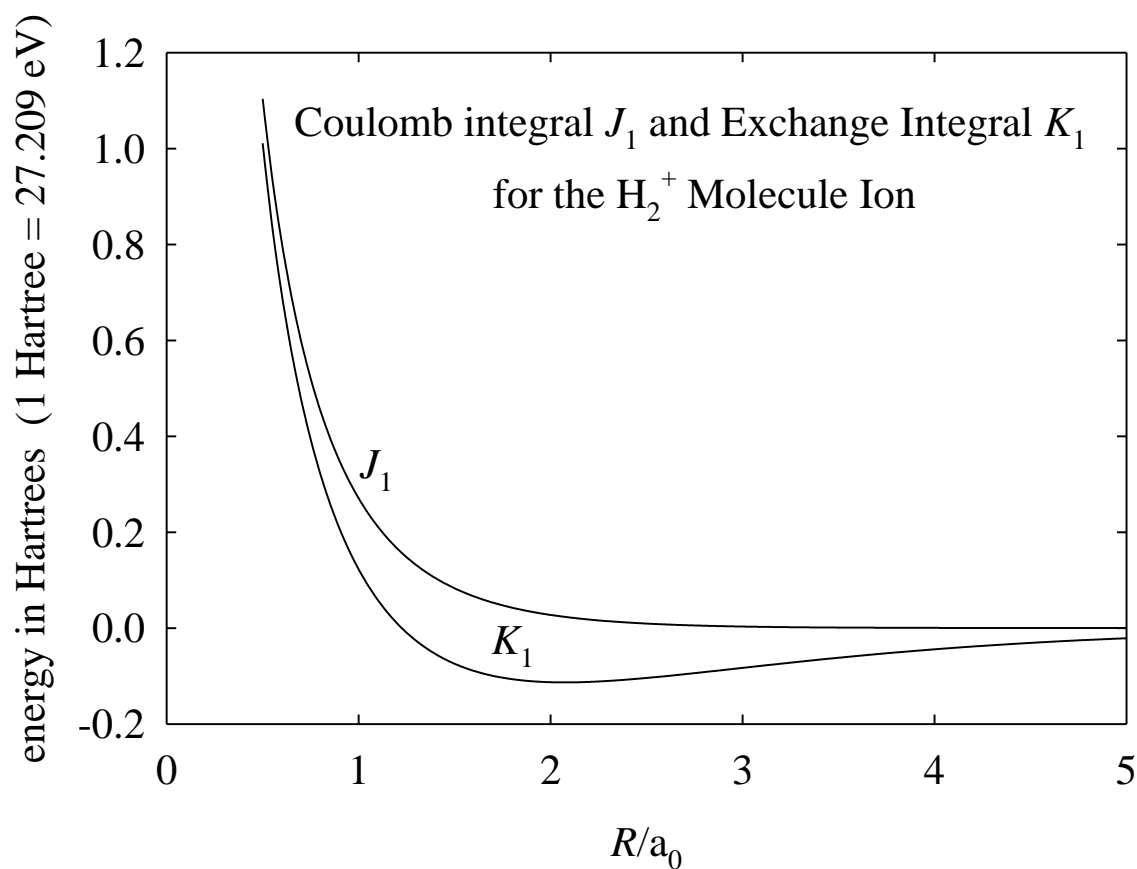
**$K_1$  is the exchange integral:**

$$K_1 = -2E_{1s} \left[ \frac{S}{R} - e^{-2R} (1 + R) \right]$$

$$= \frac{e^2}{4\pi\epsilon_0} \int 1s_A \left( -\frac{1}{r_{1B}} + \frac{1}{R} \right) 1s_B d\tau$$

Notice that the Coulomb integral is positive. *Classically, the  $H_2^+$  molecule ion is unstable and should not exist!*

**The exchange integral  $K_1$  has no classical physical interpretation.** It arises because the electron can simultaneously be in the  $1s_A$  or  $1s_B$  orbital centered on different nuclei! We will see that the exchange integral is responsible for the stability of the chemical bond in the  $H_2^+$  molecule ion.



## Energies of the H<sub>2</sub><sup>+</sup> Molecule Ion

Solving the quadratic in  $E$ , the predicted energies of the H<sub>2</sub><sup>+</sup> molecule ion are:

**Even Parity  $\psi_g$  Wave Function (find  $c_1 = c_2$ )**

$$E_g = \frac{H_{AA} + H_{AB}}{1 + S} = E_{1s} + \frac{J_1 + K_1}{1 + S}$$

Relative to the energy of a 1s electron in a hydrogen atom, the energy of the H<sub>2</sub><sup>+</sup> molecule ion is

$$E_g - E_{1s} = \frac{J_1 + K_1}{1 + S}$$

**Odd Parity  $\psi_u$  Wave Function (find  $c_1 = -c_2$ )**

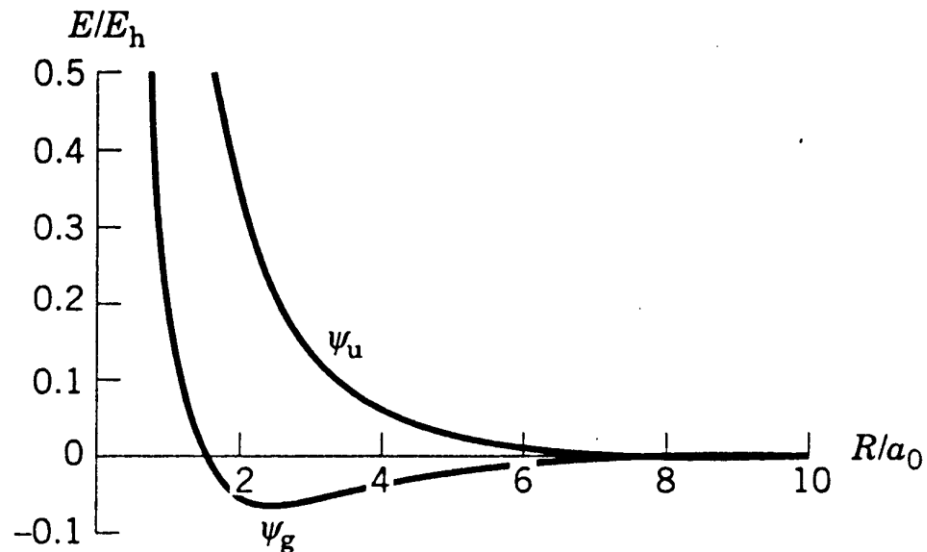
$$E_u = \frac{H_{AA} - H_{AB}}{1 - S} = E_{1s} + \frac{J_1 - K_1}{1 - S}$$

Relative to a 1s electron in a hydrogen atom:

$$E_u - E_{1s} = \frac{J_1 - K_1}{1 - S}$$

Notice that  $E_g - E_u$  is approximately equal to  $2K_1$ . This means that the exchange integral is crucial to the energies for the different states.

The energies  $E_g - E_{1s}$  and  $E_u - E_{1s}$  calculated for the even parity and odd parity wave functions plotted as a function of  $R$ :



The plot employs “atomic units”: the Bohr radius ( $a_0 = h^2 \epsilon_0 / \pi m_e e^2$ ) for length, and the Hartree ( $e^2 / 2\pi \epsilon_0 a_0 = 2 \times 13.60$  eV, twice the ionization energy of the hydrogen atom) for energy.

**Key result:** a negative energy minimum and therefore a bound state are predicted for the even-parity state of  $\text{H}_2^+$ .

This is our first quantum mechanical chemical bond! It results from the exchange integral, a non-classical effect.

In the limit  $R \rightarrow \infty$  (*i.e.*, the nuclei are infinitely far apart), the exchange integral is zero and  $E_g = E_u = E_{1s}$ . We have a proton and a hydrogen atom in its ground state.

Notice that two atomic orbitals produce two molecular orbitals,  $\psi_g$  and  $\psi_u$ .

For the even-parity wave function  $\psi_g$ , the calculated energy passes through a minimum at  $2.50a_0 = 0.132$  nm, in qualitative agreement with the  $2.00a_0 = 0.106$  nm experimental bond length of the  $\text{H}_2^+$  ion.

The calculated minimum energy is  $-0.0648$  Hartrees ( $-170$  kJ mol $^{-1}$ ), compared to the experimental value  $-0.102$  Hartrees ( $-258$  kJ mol $^{-1}$ ).

Because  $\psi_g$  describes a bound molecule, it is called a **bonding orbital**.

$\psi_g$  is symmetrical about the midway point of the bond in the  $\text{H}_2^+$  molecule ion. For this reason, it is called a sigma ( $\sigma$ ) orbital. Because it is formed from two 1s orbitals, its designation is  $\sigma_g 1s$ .

If we try to push the two nuclei too close together, notice that the energy of the bonding orbital increases sharply and becomes repulsive. Steric hindrance!

The molecular wave function  $\psi_u$  leads to repulsion at all internuclear separations. For this reason, it is called **antibonding orbital**. It can be interpreted as an excited molecular state. Its designation is  $\sigma_g^* 1s$ . The asterisk indicates “excited” (not conjugate in this case).

The simple model we have used gives only qualitative numerical results, but nevertheless provides insight into the main factors governing the strength of chemical bonds.

Quantitative agreement with experiment can be obtained by using a larger number of functions in the variational calculations.

## The Hydrogen Molecule

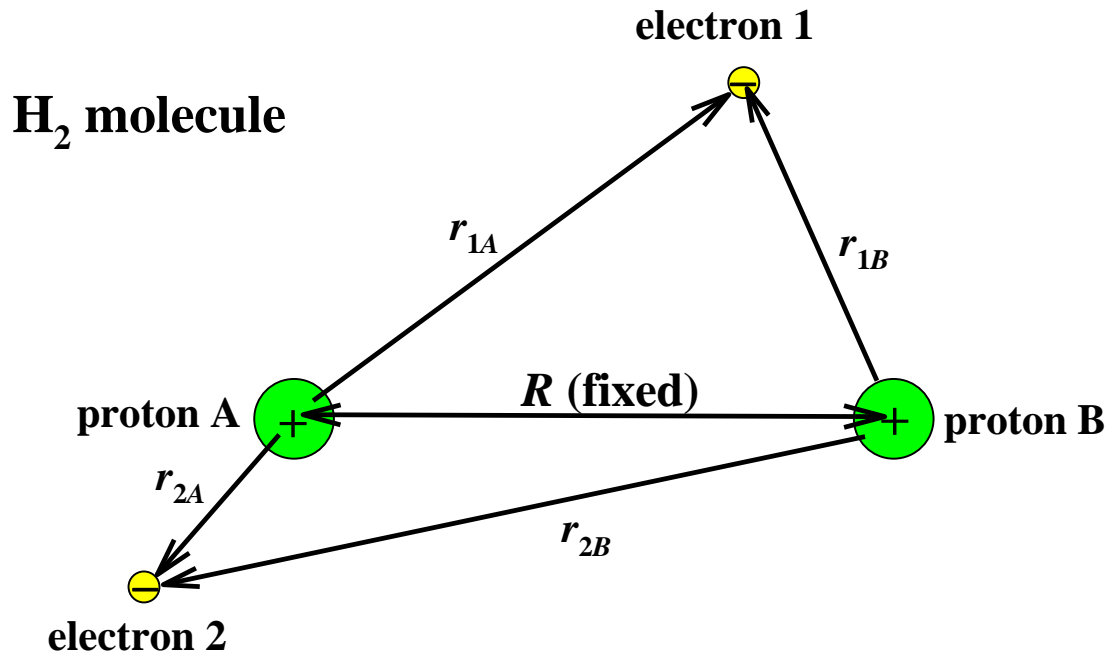
After  $\text{H}_2^+$ , the next simplest molecule is  $\text{H}_2$ .

Again, we will see that chemical bonding can be interpreted in terms of a coulomb integral, an exchange integral, and an overlap integral

### Schrödinger's Equation and the Hamiltonian Operator for $\text{H}_2$

$$\hat{H}\psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) = E\psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B)$$

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e2}^2 - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R}$$



Using the Born Oppenheimer approximation (fixed nuclei), we factor the total wave function for H<sub>2</sub> into nuclear and electronic contributions:

$$\hat{H}\psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) = \psi_e(\vec{r}_1, \vec{r}_2, R)\psi_n(\vec{R}_A, \vec{R}_B)$$

The **Schrödinger equation for the electron motion** we are interested in is

$$\hat{H}_e\psi(\vec{r}_1, \vec{r}_2, R) = E_e(R)\psi_e(\vec{r}_1, \vec{r}_2, R)$$

with the electronic Hamiltonian operator

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e2}^2 - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R}$$



Unfortunately, even with the Born Oppenheimer approximation, the Schrödinger equation for the H<sub>2</sub> molecule *cannot be solved exactly* as a result of the electron-electron repulsion term  $e^2/4\pi\epsilon_0r_{12}$ . This makes the analysis of bonding in the H<sub>2</sub> molecule considerably more complicated than the analysis of the H<sub>2</sub><sup>+</sup> molecule ion.

We could try using the approximate wave function

$$\psi_1 = 1s_A(1)1s_B(2)$$

for electron 1 in a 1s orbital centered on nucleus A and electron 2 in a 1s orbital centered on nucleus 2. The wave function

$$\psi_2 = 1s_B(1)1s_A(2)$$

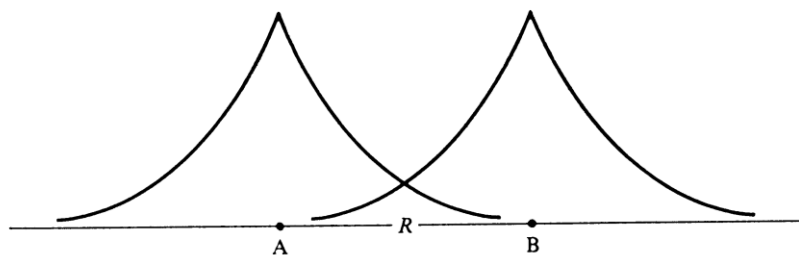
could also be used. But as we should know by now,  $\psi_1$  and  $\psi_2$ , individually, are unacceptable because their construction assumes, incorrectly, that electrons 1 and 2 are distinguishable.

To obtain valid trial wave functions, we take linear combinations of  $\psi_1$  and  $\psi_2$

$$\psi = c_1\psi_1 + c_2\psi_2 = c_11s_A(1)1s_B(2) + c_21s_B(1)1s_A(2)$$

and treat the constants  $c_1$ ,  $c_2$  as variational parameters.

### 1s<sub>A</sub>(1) and 1s<sub>B</sub>(2) Wave Functions

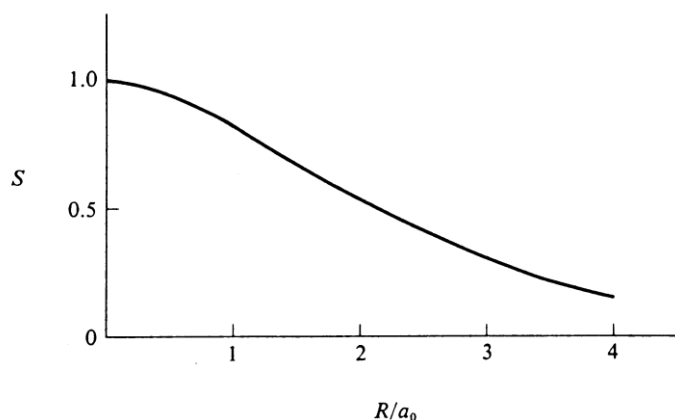


The **overlap integral** is a bit tricky to evaluate. The result, however, is simple. Once

again  $S = 1$  in the limit  $R \rightarrow 0$ . In the limit  $R \rightarrow \infty$  (two isolated H atoms),  $S = 0$ .

$$S = \int 1s_A(1)1s_B(1) d\tau_1 \int 1s_A(2)1s_B(2) d\tau_2$$

$$S = e^{-R} \left( 1 + R + \frac{R^2}{3} \right)$$



The **Coulomb integral** is

$$J_{12} = -\frac{e^2}{4\pi\epsilon_0} \int \frac{[1s_A(1)]^2}{r_{1B}} d\tau_1 - \frac{e^2}{4\pi\epsilon_0} \int \frac{[1s_B(2)]^2}{r_{2A}} d\tau_2 + \frac{e^2}{4\pi\epsilon_0} \iint \frac{[1s_A(1)]^2 [1s_B(2)]^2}{r_{12}} d\tau_1 d\tau_2 + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R}$$

$$= -2E_{1s} e^{-2R} \left( \frac{5}{8} - \frac{3}{4}R - \frac{R^2}{6} + \frac{1}{R} \right)$$

The first Coulombic term can be classically interpreted as the charge density of electron 1 around nucleus  $A$  interacting with nucleus  $B$ . The second term represents the charge density of electron 2 around nucleus  $B$  interacting with nucleus  $A$ . The last two terms (notice they are positive) are the repulsive energy due to electron-electron and nucleus-nucleus electrostatic interactions. (Recall that the nuclei are a fixed distance  $R$  apart.)

What about the kinetic energy of the electrons, the interaction of electron 1 with nucleus  $A$ , and the interaction of electron 2 with nucleus  $B$ ? These energies will be

included in the term  $2E_{1s}$  in the final expression for the energy of the  $H_2$  molecule.

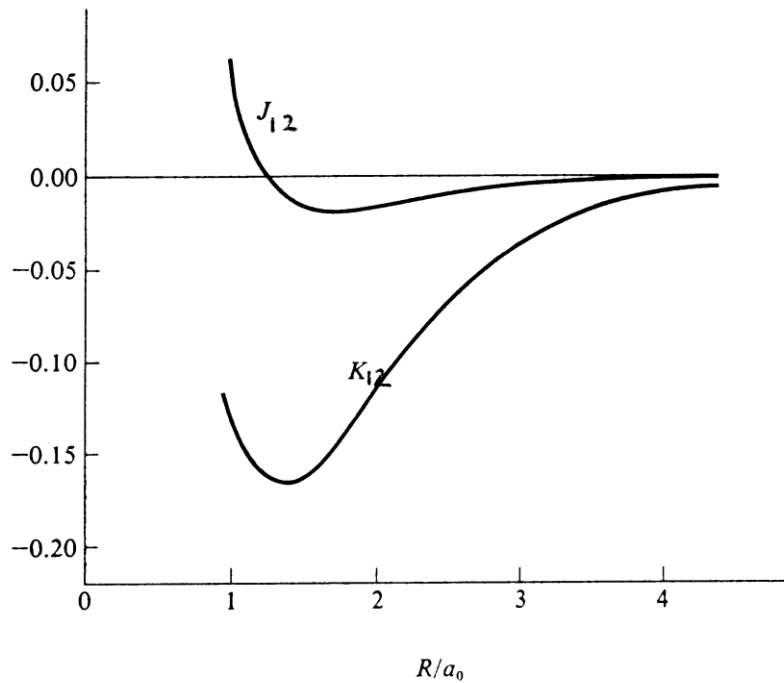
The **exchange integral**

$$K_{12} = \frac{e^2}{4\pi\epsilon_0} \int 1s_A(1)1s_B(2) \left( -\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R} \right) 1s_A(2)1s_B(1) d\tau_1 d\tau_2$$

is not easy to evaluate! But it has been done. More interestingly,  $K_{12}$  does not lend itself to a classical interpretation! The exchange integral is a direct consequence of the indistinguishability of the electrons. If we use  $c_1\psi_1$  or  $c_2\psi_2$  as our wave function (instead of  $c_1\psi_1 + c_2\psi_2$ ), the exchange integral vanishes.

### Coulomb $J_{12}$ and Exchange $K_{12}$ Integrals for the $H_2$ Molecule as a Function of Bond Length $R$

[in atomic units, the Bohr radius for  $R$  and the Hartree (23.60 eV) for  $J_{12}$ ,  $K_{12}$ ]



The nonclassical exchange integral makes a negative contribution to the calculated energy of  $H_2$ , thereby stabilizing the molecule.

Solving the secular equation gives two wave functions and two corresponding energies for the  $H_2$  molecule:

**Symmetric Wave Function  $\psi_+ = c_1\psi_1 + c_1\psi_2$**

$$c_1 = c_2 = \frac{1}{\sqrt{2(1+S^2)}}$$

$$\psi_+ = \frac{\psi_1 + \psi_2}{\sqrt{2(1+S^2)}} = \frac{1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)}{\sqrt{2(1+S^2)}}$$

$$E_+ = 2E_{1s} + \frac{J + K}{1 + S^2}$$

### Antisymmetric Wave Function $\psi_- = c_1\psi_1 - c_1\psi_2$

$$c_1 = -c_2 = \frac{1}{\sqrt{2(1-S^2)}}$$

$$\psi_- = \frac{\psi_1 - \psi_2}{\sqrt{2(1-S^2)}} = \frac{1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)}{\sqrt{2(1-S^2)}}$$

$$E_- = 2E_{1s} + \frac{J - K}{1 - S^2}$$

Heitler and London (1929) were the first to carry out these calculations. Notice that the symmetric wave function  $\psi_+$  they used is *not an acceptable wave function* according to the general statement of the Pauli exclusion principle. We can fix this later!

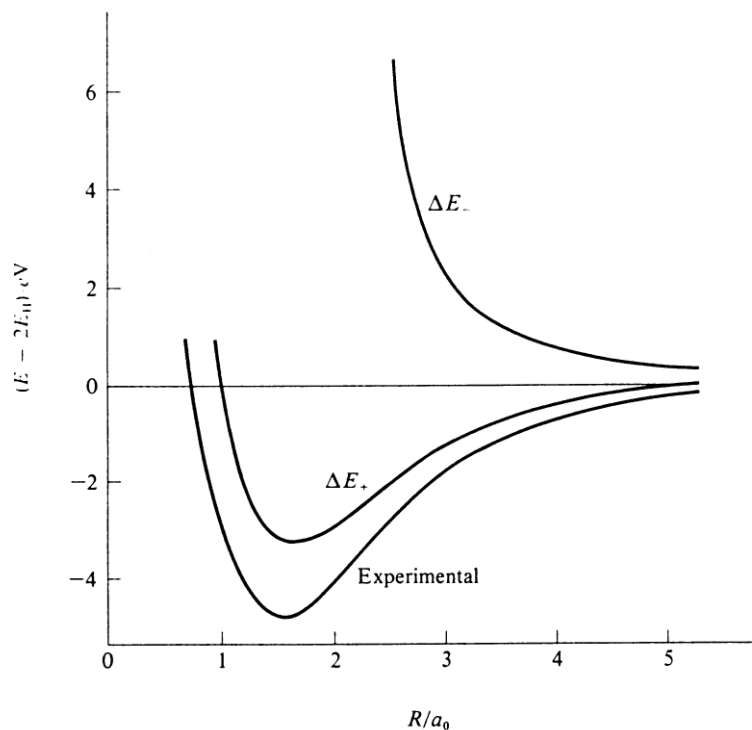
*The suspense mounts!*

*Does quantum mechanics predict a stable bond for the H<sub>2</sub> molecule?*

### Calculated Energy of the H<sub>2</sub> Molecule Relative to the Energy of Two Isolated H Atoms as a Function of Bond Length

$$\Delta E_- = E_- - 2E_{1s}$$

$$\Delta E_+ = E_+ - 2E_{1s} \quad (\text{lower energy, "+" means symmetric})$$



## Results:

- The symmetric wave function  $\psi_+$  describes a stable  $H_2$  molecule.** The two H atoms attract each other and as they approach, and the energy  $E_+$  passes through a minimum value that is lower (more negative) than the energy of two isolated H atoms. Bonding is a result of the exchange integral.
- The **minimum in the energy** curve (where  $dE/dR = 0$ ) represents a stable equilibrium. The  $R$  value at the minimum is therefore the predicted bond length. Heitler and London's calculations gave 0.087 nm compared to the experimental value of 0.074 nm.
- The minimum in the energy gives the predicted bond **dissociation energy**, 3.15 eV or 305 kJ per mole. The experimental dissociation energy is 4.75 eV, somewhat higher.

4. We can even get the **force constant** for the  $H_2$  bond and therefore the fundamental vibrational frequency! Taking the derivative to evaluate the force constant and using the reduced mass to calculate the **fundamental frequency** gives 4080 wavenumbers ( $cm^{-1}$ ), compared to the experimental value  $4400\ cm^{-1}$ . Not bad!
5. The energy rises steeply if the atoms move too close together. **Steric hindrance!** In the other limit,  $R \rightarrow \infty$ ,  $\Delta E_+ = E_+ - 2E_{1s} = 0$ ,  $\Delta E_- = E_- - 2E_{1s} = 0$ , and therefore  $E_+ = E_- = 2E_{1s}$  (we have two ground-state H atoms infinitely far apart).
6. We have only used two atomic 1s orbitals to form our trial wave function for the hydrogen molecule. **Molecular Orbital Theory!** The accuracy of the calculations can be improved to experimental accuracy by using more elaborate sets of functions.
7. The higher energy state of the  $H_2$  molecule is an excited **triplet state** ....

**The Two States of the Hydrogen Molecule Predicted by Heitler-London Theory**  
**are a Single State and and Triplet State**

The Heitler-London original treatment of the  $H_2$  molecule did not include spin explicitly. There are no spin terms in the Hamiltonian operator for the total energy, so it might appear that spin has no effect on the energy. *Not true!*

As mentioned earlier, the symmetric wave function used by Heitler and London that gave the bonding state is unacceptable in the sense that it violates the general statement of the Pauli exclusion principle that electronic wave functions must be antisymmetric with respect to interchanging any two electrons.

We can easily “fix” the spatially symmetric wave function by multiplying it by an antisymmetric spin function. Similarly, the spatially antisymmetric wave function can be multiplied by a symmetric spin function:

**symmetric  $\psi_+$  X antisymmetric spin function = antisymmetric function**

**antisymmetric  $\psi_-$  X symmetric spin function = antisymmetric function.**

As a bonus, including spin also provides a nice interpretation of the two energy states predicted for the H<sub>2</sub> molecule.

At first glance, the four possible spin functions for the two-electron H<sub>2</sub> system (two electrons, each with two possible spin states) are:

$$\begin{aligned} &\alpha(1) \alpha(2) \\ &\beta(1) \beta(2) \\ &\alpha(1) \beta(2) \\ &\alpha(2) \beta(1) \end{aligned}$$

But the last two spin functions are unacceptable because they distinguish electron 1 from electron 2.  $\alpha(1) \beta(2)$  and  $\alpha(2) \beta(1)$  can however be transformed into acceptable spin functions by taking linear combinations, as we have done before.

**The four acceptable spin functions are:**

1.  $\alpha(1) \alpha(2)$  (symmetric,  $M_s = 1$ )
2.  $\beta(1) \beta(2)$  (symmetric,  $M_s = -1$ )
3.  $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$  (symmetric,  $M_s = 0$ )
4.  $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$  (antisymmetric,  $M_s = 0$ )

**The four complete wave functions are:**

1.  $\psi-\alpha(1) \alpha(2)$  (antisymmetric,  $M_s = 1$ )
2.  $\psi-\beta(1) \beta(2)$  (antisymmetric,  $M_s = -1$ )



$$3. \quad \frac{\psi_-}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (\text{antisymmetric, } M_s = 0)$$

$$4. \quad \frac{\psi_+}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (\text{antisymmetric, } M_s = 0)$$

Wave functions 1, 2, 3, and 4 are *complete* because they include spatial and spin factors. In addition, the wave functions are *acceptable* because they are antisymmetric and therefore consistent with the Pauli exclusion principle.

The three spin functions associated with  $\psi_-$  have values of  $M_s$  equal to  $-1$ ,  $0$  and  $+1$ , corresponding to total spin angular momentum  $S = 1$  with its three possible  $z$ -projections  $-1$ ,  $0$  and  $+1$ . This is a **triplet state**.

The single wave function associated with  $\psi_+$  has  $M_s = 0$ , corresponding to  $S = 0$  and a **singlet state**.

We can therefore identify the two states of the  $\text{H}_2$  molecule as

Excited nonbonding (all repulsive) triplet state with  $E = 2E_{1s} + E_-$

Ground bonding singlet state with  $E = 2E_{1s} + E_+$