

# Variational Method and Molecular Structure

## Molecular Hamiltonian

Write down the Hamiltonian for the  $He - H$  molecule.

## Variation Method

1. For a particle in a box of length  $L$ , use the wavefunction  $\psi(x) = x(L-x)$  to calculate the energy. Then use this energy to calculate the energy of a particle in a 3-dimensional box with side-length  $L$ . By comparing these results with the exact ground-state energy of a particle in a 1 and 3 dimensional box, calculate the error in each case.
2. If the wavefunction  $\psi(x) = x$  is used to estimate the energy of the particle in a box, one finds that the variational energy is *less* than the true ground state energy. What is wrong?  
**hint** Draw a picture of this wavefunction in the box.

### 3. Huckel Theory

In order to study  $\pi$  bonding in ethylene, a  $2 \times 2$  Huckel matrix was constructed,

$$H = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

Find the two eigenvalues and eigenvectors of this Hamiltonian matrix by solving the eigenvalue equation,

$$HC = EC$$

where  $C$  is a column vector,

$$C = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Use the eigenvectors  $C$  to draw a rough sketch of the two molecular orbitals, indicating the presence of any nodes.

What is the binding energy of the  $\pi$  bonding molecular orbital, ie how much lower is the energy of the bonding molecular orbital than the atomic orbital energy?

## Pauli Exclusion Principle

1. Does the following wavefunction obey the Pauli Exclusion Principle?

$$\Psi(1, 2) = p_x(1)p_y(2)\alpha(1)\beta(2)$$

Explain your answer. If the wavefunction does not obey the exclusion principle, can you ‘fix it up’ so that it does obey the exclusion principle?

2. Consider a spatial molecular orbital  $\phi(r)$  containing two  $\alpha$ -spin electrons,

$$\Psi(1, 2) = \phi(1)\phi(2)\alpha(1)\alpha(2)$$

Clearly this wavefunction violates the Exclusion Principle. Antisymmetrize this wavefunction (to give a total of 2 terms), and show that the antisymmetrized wavefunction is zero.

3. Consider a spatial molecular orbital  $\phi(r)$  containing two  $\alpha$ -spin electrons and one  $\beta$ -spin electron,

$$\Psi(1, 2, 3) = \phi(1)\phi(2)\phi(3)\alpha(1)\beta(2)\alpha(3)$$

Clearly this wavefunction violates the Exclusion Principle. Antisymmetrize this wavefunction (to give a total of 6 terms), and show that the antisymmetrized wavefunction is zero.

4. Consider two electrons in a 1-dimensional box. For simplicity assume that the electrons are neutral (zero charge). Write down the wavefunctions, including spin, for states that have one electron with  $n = 1$  and one electron with  $n = 2$ . Make sure that the wavefunctions obey the exclusion principle.

## $\mathbf{H}_2^+$

1. Plot the bonding and antibonding molecular orbitals for  $H_2^+$  along the internuclear axis without worrying about normalization. Then plot the probability densities, again neglecting normalization.
2. The wavefunction for the ground state of  $H_2^+$  may be approximated as a linear combination of atomic orbitals  $1s_A$  and  $1s_B$ ,

$$\phi = 1s_A + 1s_B$$

(a) Express the electron density for  $H_2^+$  in terms of the atomic orbitals, without worrying about normalization. (b) Express the electron density as a sum of the atomic densities and an additional ‘molecular’ density, again without worrying about normalization.

**H<sub>2</sub>** Starting from the Hartree-Fock wavefunction for  $H_2$ ,

$$\Psi(1, 2) = \phi(1)\phi(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

Expand the molecular orbital  $\phi$  as a L.C.A.O. of atomic orbitals  $1s_A$  and  $1s_B$ ,

$$\phi = 1s_A + 1s_B$$

By expressing  $\Psi$  in terms of the atomic orbitals show that the Hartree-Fock wavefunction gives unphysical behaviour at long bond-lengths.

### Many-electron molecules

An approximate description of the  $\pi$  electrons in conjugated polyene,  $CH_2=CH(-CH=CH-)_nCH=CH_2$ , is the free electron molecular orbital model. In this model, the  $\pi$  electrons are assumed to be non-interacting and to be in a one-dimensional box of length equal to one less than the number of carbon atoms multiplied by the  $C-C$  distance of  $150\text{ pm}$ . [ $\text{pm} = 10^{-12}\text{ m}$ ]. For butadiene and hexatriene, what are the electron configurations of the ground and first excited states in terms of particle-in-a-box eigenfunctions? What is the excitation energy from the ground to the first excited state? What is the wavelength of this transition?

### General Problems True or False?

1. Two electrons with the same spin have zero probability of being at the same point in space.
2. If sufficient basis functions are used in the LCAO expansion of the molecular orbitals, the Hartree-Fock wavefunction (determinant of the product of molecular orbitals) of a many-electron molecule will reach the true wavefunction.
3. The maximum electron probability density in the ground electronic state of  $H_2^+$  occurs at each nucleus.
4. The  $H_2^+$  ground electronic state has spin quantum number  $S = 0$ .

5. The  $H_2$  ground electronic state has spin quantum number  $S = 0$ .

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# Solutions

## Molecular Hamiltonian

Write down the Hamiltonian for the  $He - H$  molecule.

**Answer:**

$$\begin{aligned}
 H &= T_e + V_{nn} + V_{ne} + V_{ee} \\
 &= -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\hbar^2}{2m_e} \nabla_3^2 \\
 &\quad + \frac{2e^2}{4\pi\epsilon_o R_{HeH}} \\
 &\quad - \frac{2e^2}{4\pi\epsilon_o r_{1He}} - \frac{2e^2}{4\pi\epsilon_o r_{2He}} - \frac{2e^2}{4\pi\epsilon_o r_{3He}} \\
 &\quad - \frac{4\pi\epsilon_o r_{1H}}{e^2} - \frac{4\pi\epsilon_o r_{2H}}{e^2} - \frac{4\pi\epsilon_o r_{3H}}{e^2} \\
 &\quad + \frac{4\pi\epsilon_o r_{12}}{e^2} + \frac{4\pi\epsilon_o r_{13}}{e^2} + \frac{4\pi\epsilon_o r_{23}}{e^2}
 \end{aligned}$$

## Variation Method

- For a particle in a box of length  $L$ , use the wavefunction  $\psi(x) = x(L-x)$  to calculate the energy. Then use this energy to calculate the energy of a particle in a 3-dimensional box with side-length  $L$ . By comparing these results with the exact ground-state energy of a particle in a 1 and 3 dimensional box, calculate the error in each case.

**Answer**

$$\begin{aligned}
 \langle H \rangle &= \frac{\int \psi^* H \psi}{\int \psi^* \psi} \\
 &= \frac{\int_0^L x(L-x) \frac{-\hbar^2}{2m} (-2)}{\int_0^L (x(L-x))^2} \\
 &= \frac{2\hbar^2}{2m} \frac{[Lx^2/2 - x^3/3]_0^L}{[L^2 x^3/3 - 2Lx^4/4 + x^5/5]_0^L} \\
 &= \frac{2\hbar^2}{2m} \frac{L^3/2 - L^3/3}{L^5/3 - 2L^5/4 + L^5/5}
 \end{aligned}$$

$$\begin{aligned}
&= \frac{2\hbar^2 L^3/6}{2m L^5/30} \\
&= \frac{2\hbar^2 5}{2m L^2} \\
&= \frac{10\hbar^2}{2mL^2}
\end{aligned}$$

The exact energy in a 1-D box is  $E = \frac{\hbar^2\pi^2}{2mL^2} \approx \frac{9.86\hbar^2}{2mL^2}$ , so the approximate energy is about 1% above the true energy.

The energy of a particle in a three-dimensional box is just three times the energy of a particle in a one-dimensional box. So the error in the 3-D case is three times the error in the 1-D case, though the percentage error remains the same.

2. If the wavefunction  $\psi(x) = x$  is used to estimate the energy of the particle in a box, one finds that the variational energy is *less* than the true ground state energy. What is wrong?

**hint** Draw a picture of this wavefunction in the box.

**Answer**

Drawing a picture of the approximate wavefunction, it is clear that it does not go to zero at the right hand end of the box as required.

### 3. Huckel Theory

In order to study  $\pi$  bonding in ethylene, a  $2 \times 2$  Huckel matrix was constructed,

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Find the two eigenvalues and eigenvectors of this Hamiltonian matrix by solving the eigenvalue equation,

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where  $C$  is a column vector,

$$C = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Use the eigenvectors  $C$  to draw a rough sketch of the two molecular orbitals, indicating the presence of any nodes.

What is the binding energy of the  $\pi$  bonding molecular orbital, ie how much lower is the energy of the bonding molecular orbital than the atomic orbital energy?

**Answer**

The bonding orbital is  $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ , with binding energy  $-1$ . The anti-bonding orbital is  $\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ .

A very crude picture of the orbitals is obtained by plotting the sign of the coefficients. For the bonding orbital this gives  $++$ , and for the antibonding orbital  $+ -$ . There are no sign-changes in the bonding orbital, and hence no nodes. There is one sign change, and hence one node, in the antibonding orbital.

### Pauli Exclusion Principle

1. Does the following wavefunction obey the Pauli Exclusion Principle?

$$\Psi(1, 2) = p_x(1)p_y(2)\alpha(1)\beta(2)$$

Explain your answer. If the wavefunction does not obey the exclusion principle, can you 'fix it up' so that it does obey the exclusion principle?

**Answer**

The Exclusion Principle says that the wavefunction must change sign when two electrons are interchanged. Swapping particles one and two in the wavefunction gives,

$$p_y(1)p_x(2)\beta(1)\alpha(2)$$

Clearly the wavefunction does not simply change sign, so the wavefunction violates the Exclusion Principle.

The wavefunction is an orbital product, and we can force it to obey the Exclusion Principle by taking the determinant of the orbital product:

$$\text{Det} \begin{pmatrix} p_x\alpha & p_y\beta \end{pmatrix}$$

The only thing that could go wrong here is that the determinant could be zero - so one should really expand the determinant and check this.

2. Consider a spatial molecular orbital  $\phi(r)$  containing two  $\alpha$ -spin electrons,

$$\Psi(1, 2) = \phi(1)\phi(2)\alpha(1)\alpha(2)$$

Clearly this wavefunction violates the Exclusion Principle. Antisymmetrize this wavefunction (to give a total of 2 terms), and show that the antisymmetrized wavefunction is zero.

**Answer**

$$\begin{aligned} \text{Det} \begin{pmatrix} \phi\alpha & \phi\alpha \end{pmatrix} &= \text{Det} \begin{pmatrix} \phi\alpha(1) & \phi\alpha(1) \\ \phi\alpha(2) & \phi\alpha(2) \end{pmatrix} \\ &= \phi\alpha(1)\phi\alpha(2) - \phi\alpha(1)\phi\alpha(2) \\ &= 0 \end{aligned}$$

3. Consider a spatial molecular orbital  $\phi(r)$  containing two  $\alpha$ -spin electrons and one  $\beta$ -spin electron,

$$\Psi(1, 2, 3) = \phi(1)\phi(2)\phi(3)\alpha(1)\beta(2)\alpha(3)$$

Clearly this wavefunction violates the Exclusion Principle. Antisymmetrize this wavefunction (to give a total of 6 terms), and show that the antisymmetrized wavefunction is zero.

**Answer**

$$\begin{aligned} \text{Det} \begin{pmatrix} \phi\alpha & \phi\beta & \phi\alpha \end{pmatrix} &= \text{Det} \begin{pmatrix} \phi\alpha(1) & \phi\beta(1) & \phi\alpha(1) \\ \phi\alpha(2) & \phi\beta(2) & \phi\alpha(2) \\ \phi\alpha(3) & \phi\beta(3) & \phi\alpha(3) \end{pmatrix} \\ &= \phi\alpha(1)\text{Det} \begin{pmatrix} \phi\beta(2) & \phi\alpha(2) \\ \phi\beta(3) & \phi\alpha(3) \end{pmatrix} \\ &\quad - \phi\beta(1)\text{Det} \begin{pmatrix} \phi\alpha(2) & \phi\alpha(2) \\ \phi\alpha(3) & \phi\alpha(3) \end{pmatrix} \\ &\quad + \phi\alpha(1)\text{Det} \begin{pmatrix} \phi\alpha(2) & \phi\beta(2) \\ \phi\alpha(3) & \phi\beta(3) \end{pmatrix} \\ &= \phi\alpha(1) (\phi\beta(2)\phi\alpha(3) - \phi\alpha(2)\phi\beta(3)) \\ &\quad - \phi\beta(1) (\phi\alpha(2)\phi\alpha(3) - \phi\alpha(2)\phi\alpha(3)) \\ &\quad + \phi\alpha(1) (\phi\alpha(2)\phi\beta(3) - \phi\beta(2)\phi\alpha(3)) \\ &= 0 \quad \text{since all terms cancel} \end{aligned}$$

4. Consider two electrons in a 1-dimensional box. For simplicity assume that the electrons are neutral (zero charge). Write down the wavefunctions, including spin, for states that have one electron with  $n = 1$  and one electron with  $n = 2$ . Make sure that the wavefunctions obey the exclusion principle.

**Answer**

This question asks for the spin of the wavefunctions. This means that the wavefunctions must be eigenfunctions of the spin-angular momentum operator  $S^2$ . Determinants of orbital products are not always eigenfunctions of  $S^2$ , so in this problem it's best not to use determinants.

The three triplet wavefunctions (with spin  $S = 1$  and multiplicity  $2S + 1 = 3$ ) are:

$$\begin{aligned}\psi_A(1, 2) &= (\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) (\alpha(1)\alpha(2)) \\ \psi_B(1, 2) &= (\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) (\beta(1)\beta(2)) \\ \psi_C(1, 2) &= (\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) (\alpha(1)\beta(2) + \beta(1)\alpha(2))\end{aligned}$$

The singlet wavefunction (with spin  $S = 0$  and multiplicity  $2S + 1 = 1$ ) are:

$$\psi_D(1, 2) = (\phi_1(1)\phi_2(2) + \phi_2(1)\phi_1(2)) (\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

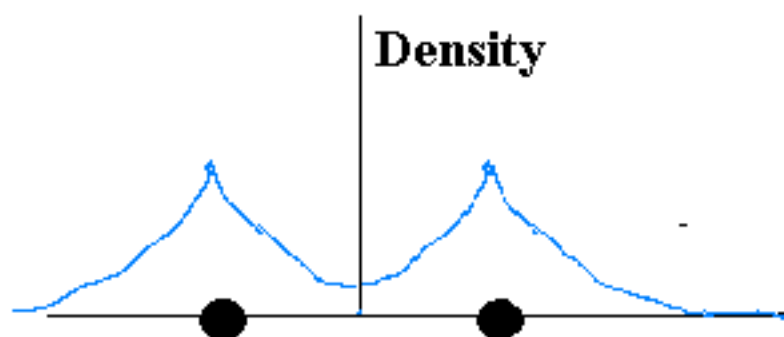
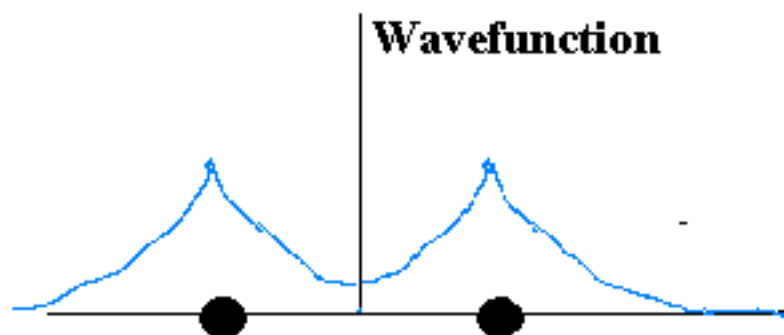
Note that in the triplet wavefunctions the spin-part of the wavefunction is symmetric and the space-part is anti-symmetric, whereas in the singlet wavefunction it's the other way around.

**H<sub>2</sub><sup>+</sup>**

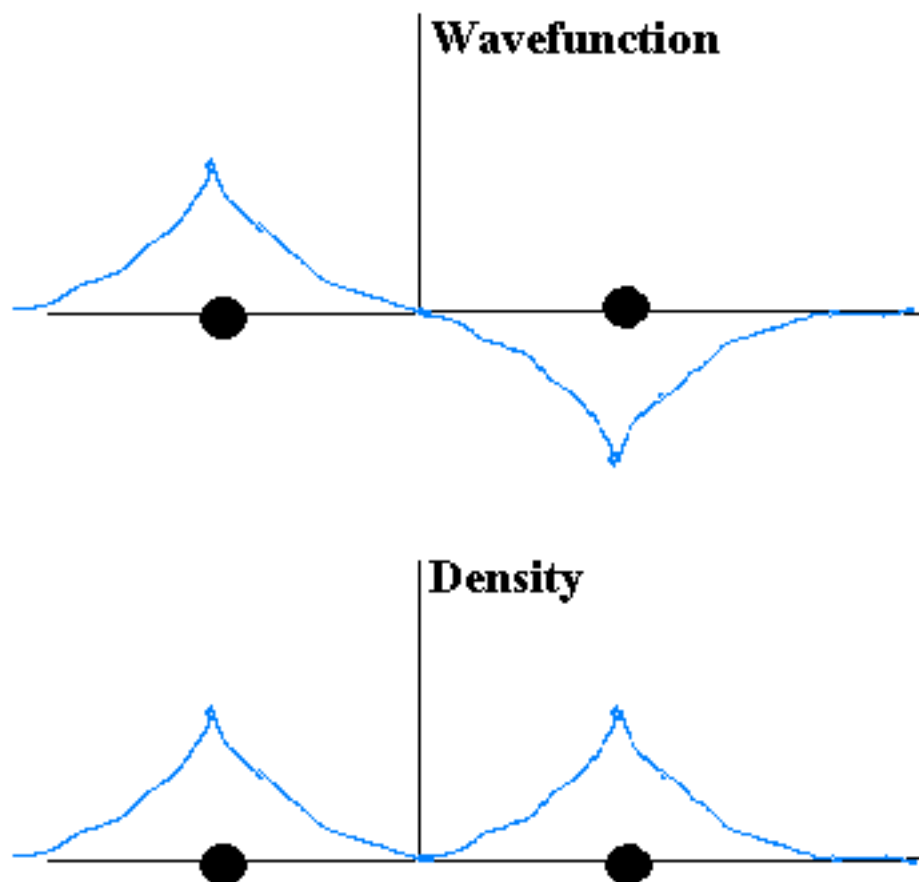
1. Plot the bonding and antibonding molecular orbitals for  $H_2^+$  along the internuclear axis without worrying about normalization. Then plot the probability densities, again neglecting normalization.

**Answer**

The bonding orbital and density are:



The antibonding orbital and density are:



2. The wavefunction for the ground state of  $H_2^+$  may be approximated as a linear combination of atomic orbitals  $1s_A$  and  $1s_B$ ,

$$\phi = 1s_A + 1s_B$$

- (a) Express the electron density for  $H_2^+$  in terms of the atomic orbitals, without worrying about normalization. (b) Express the electron density as a sum of the atomic densities and an additional 'molecular' density, again without worrying about normalization.

**Answer**

$$\begin{aligned}
\rho(r) &= \phi^*(r)\phi(r) \\
&= (1s_A(r) + 1s_B(r))^*(1s_A(r) + 1s_B(r)) \\
&= 1s_A^*(r)1s_A(r) + 1s_B^*(r)1s_B(r) + \\
&\quad 1s_A^*(r)1s_B(r) + 1s_B^*(r)1s_A(r) + \\
&= \rho(\text{atom A}) + \rho(\text{atom B}) + \\
&\quad 1s_A^*(r)1s_B(r) + 1s_B^*(r)1s_A(r)
\end{aligned}$$

**H<sub>2</sub>** Starting from the Hartree-Fock wavefunction for  $H_2$ ,

$$\Psi(1, 2) = \phi(1)\phi(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

Expand the molecular orbital  $\phi$  as a L.C.A.O. of atomic orbitals  $1s_A$  and  $1s_B$ ,

$$\phi = 1s_A + 1s_B$$

By expressing  $\Psi$  in terms of the atomic orbitals show that the Hartree-Fock wavefunction gives unphysical behaviour at long bond-lengths.

**Answer**

The unphysical behaviour lies in the spatial part of the wavefunction, so for brevity I'll ignore the spin part of the wavefunction:

$$\begin{aligned}
\phi(1)\phi(2) &= (1s_A(1) + 1s_B(1))(1s_A(2) + 1s_B(2)) \\
&= 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) \quad \text{ionic terms} \\
&\quad + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) \quad \text{covalent terms}
\end{aligned}$$

The two ionic terms correspond to  $H_A^- H_B^+$  and  $H_A^+ H_B^-$ . These electron configurations are unphysical at long bond-lengths, because the molecule dissociates to the neutral atoms,  $H_A \dots H_B$ .

### Many-electron molecules

An approximate description of the  $\pi$  electrons in conjugated polyene,  $CH_2=CH(-CH=CH-)_n CH=CH_2$ , is the free electron molecular orbital model. In this model, the  $\pi$  electrons are assumed to be non-interacting and to be in a one-dimensional box of length equal to one less than the number of carbon atoms multiplied by the  $C-C$  distance of  $150 \text{ pm}$ . [ $\text{pm} = 10^{-12} \text{ m}$ ]. For butadiene and

hexatriene, what are the electron configurations of the ground and first excited states in terms of particle-in-a-box eigenfunctions? What is the excitation energy from the ground to the first excited state? What is the wavelength of this transition?

**Answer**

1. The energy levels for a particle in a box are  $E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$ , where  $n = 1, 2, 3, \dots$ . The corresponding eigenfunctions are denoted by  $\phi_n$ .
2. According to the Exclusion Principle there can be at most two electrons per orbital.
3. So the ground state electron configuration for butadiene is  $\phi_1^2 \phi_2^2$ , while the first excited state is  $\phi_1^2 \phi_2^1 \phi_3^1$ . The excitation energy is  $\Delta_E = E_3 - E_2 = \dots$ . This can be converted to a wavelength using  $E = h\nu = hc/\lambda$ .
4. Similarly for hexatriene the ground state electron configuration for butadiene is  $\phi_1^2 \phi_2^2 \phi_3^2$ , while the first excited state is  $\phi_1^2 \phi_2^2 \phi_3^1 \phi_4^1$ . The excitation energy is  $\Delta_E = E_4 - E_3 = \dots$

### General Problems True or False?

1. Two electrons with the same spin have zero probability of being at the same point in space.

**Answer**

Always True, for any number of electrons and for any wavefunction that obeys the Exclusion Principle. That's why it's called the Exclusion Principle!

Eg examine a simple 2-electron case,

$$\Psi(1, 2) = (\phi_a(r_1)\phi_b(r_2) - \phi_b(r_1)\phi_a(r_2))\alpha(1)\alpha(2)$$

Setting  $r_1 = r_2$  the space part of the wavefunction goes to zero.

2. If sufficient basis functions are used in the LCAO expansion of the molecular orbitals, the Hartree-Fock wavefunction (determinant of the product of molecular orbitals) of a many-electron molecule will reach the true wavefunction.

**Answer**

False. The (determinantal) orbital-product wavefunction would

only be exact if the Hamiltonian were separable, ie if the  $e^2/r_{ij}$  electron-electron repulsion terms didn't exist.

3. The maximum electron probability density in the ground electronic state of  $H_2^+$  occurs at each nucleus.

**Answer**

True.

4. The  $H_2^+$  ground electronic state has spin quantum number  $S = 0$ .

**False**

A single electron has spin  $S = 1/2$ .

5. The  $H_2$  ground electronic state has spin quantum number  $S = 0$ .

**True**

Doubly occupied orbitals have  $S = 0$ .