

Lecture 23: Introduction to Valence Bond Theory

The material in this lecture covers the following in Atkins.

- 14 Molecular structure**
 - Valence-bond theory**
 - 14.1 The hydrogen molecule**
 - (a) The spatial wavefunction**
 - (b) The role of the electron spin**

Lecture on-line

Introduction to Valence Bond Theory (PowerPoint)

Introduction to Valence Bond Theory (PDF)

Handout for this lecture

Valence Bond Theory

Basic Theory

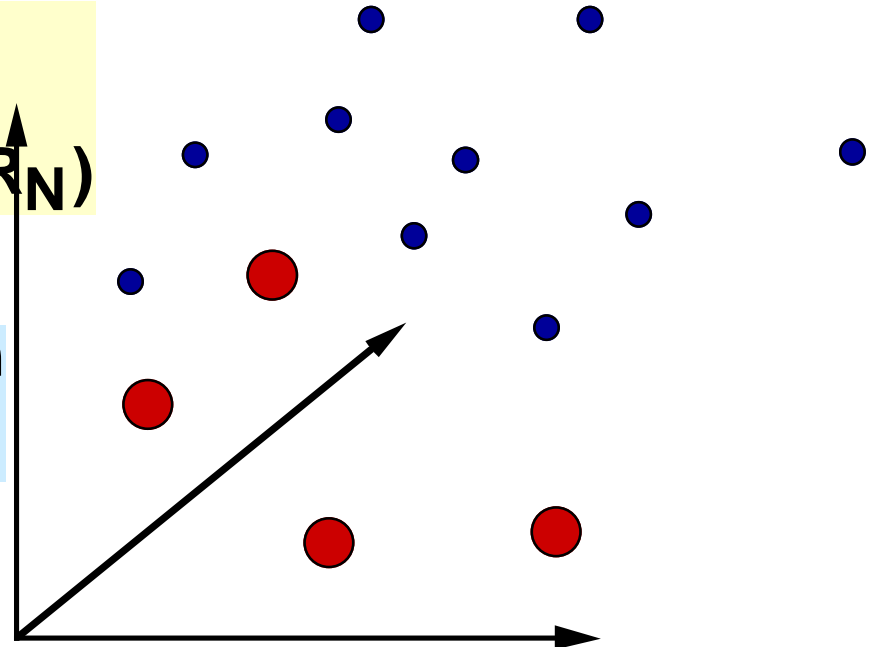
We shall now discuss ways to approximately solve :

$$H_e(r_e, R_N)\psi(r_e, R_N) = E_e(R_N)\psi(r_e, R_N)$$

and represent the many - electron wave - function $\psi(r_e, R_N)$

Here

$$\hat{H}_e = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \tilde{V}_{NN}$$



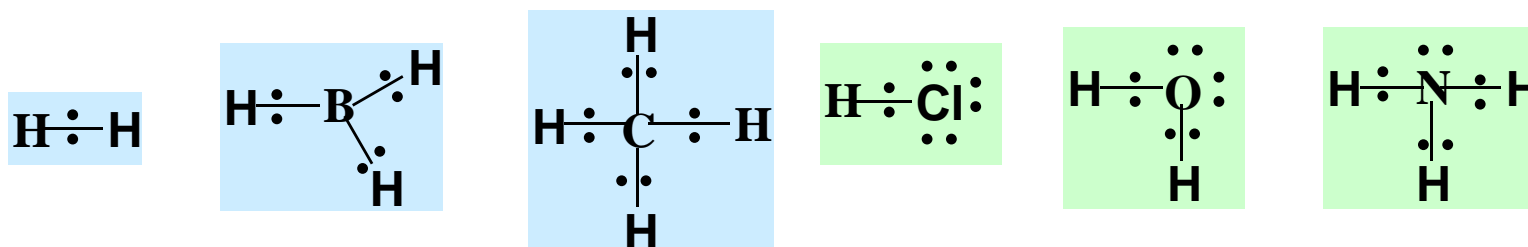
We shall start with the :

Valence-bond Theory

Valence Bond Theory

Basic Theory

In valence bond theory we start by writing down the Lewis structure of our molecule



Subsequently we write $\psi(r_e, R_N)$ as the product of electron pair functions $\omega_i(r_{2i-1}, r_{2i})$ as

$$\psi(r_e, R_N) = \omega_1(r_1, r_2) \times \omega_2(r_3, r_4) \times \dots \times \omega_i(r_{2i-1}, r_{2i}) \times \omega_j(r_{2j-1}, r_{2j}) \dots \times \omega_n(r_{2n-1}, r_{2n})$$

Pair i

Pair j

Pair n

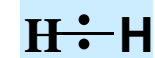
Pair 1

Pair 2

Valence Bond Theory

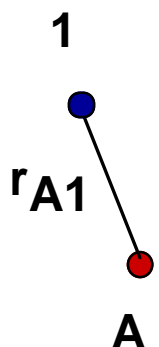
Basic Theory

We shall now illustrate this simple theory for H_2



We have two well separated hydrogen atoms A and B

each with one electron



We can describe hydrogen A by $1s_{HA}(r_{A1})\alpha(1); 1s_{HA}(r_{A1})\beta(1)$

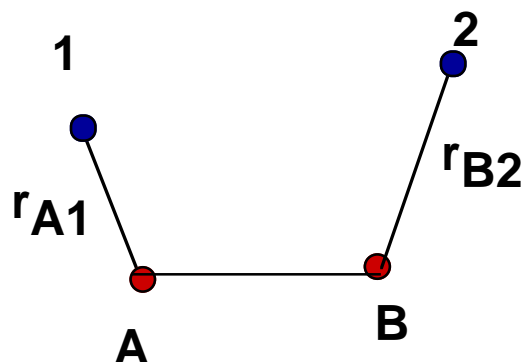
We can describe hydrogen B by $1s_{HB}(r_{B2})\alpha(2); 1s_{HB}(r_{B2})\beta(2)$

$A(1)\alpha(1); A(1)\beta(1)$

Or in short

$B(2)\alpha(2); B(2)\beta(2)$

We now bring the two hydrogens together to form H_2



Valence Bond Theory

The hamiltonian of the H_2 molecule is :

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}}$$

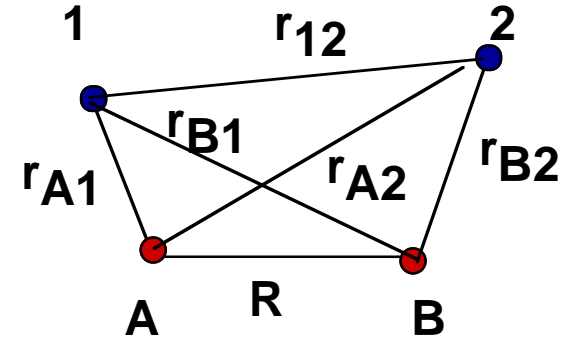
$$-\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{B2}}$$

$$-\frac{e^2}{4\pi\epsilon_0 r_{B1}} - \frac{e^2}{4\pi\epsilon_0 r_{A2}}$$

$$+\frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$+\frac{e^2}{4\pi\epsilon_0 R}$$

Basic Theory



Hamiltonian of H_A

Hamiltonian of H_B

Attraction between el. 1 and H-atom B

Attraction between el. 2 and H-atom A

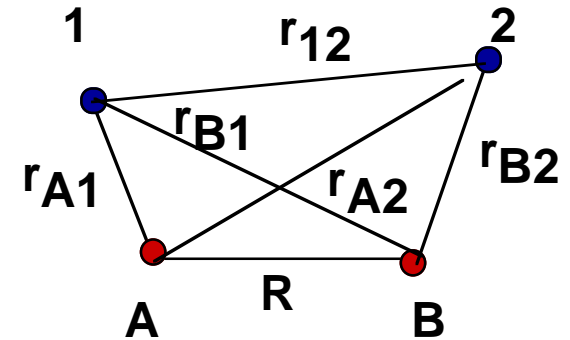
Repulsion between el. 2 and el. 1

Repulsion between A and B

Valence Bond Theory

We can thus write the Hamiltonian as

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + \frac{e^2}{4\pi\epsilon_0 R} + V$$



where

$$V = -\frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Subsequently we write $\psi(r_e, R_N)$ as the product of electron pair functions $\omega_i(r_{2i-1}, r_{2i})$ as

$$\psi(r_1, r_2, R) = \omega_1(r_1, r_2)$$

We shall further write $\omega_1(r_1, r_2)$ as linear combinations of product between functions on A and B

$$A(1)\alpha(1); A(1)\beta(1)$$

$$B(2)\alpha(2); B(2)\beta(2)$$

Valence Bond Theory

From the functions

$$A(1)\alpha(1); A(1)\beta(1)$$

$$B(2)\alpha(2); B(2)\beta(2)$$

We can construct the products :

$$A(1)\alpha(1)B(2)\alpha(2)$$

$$A(1)\alpha(1)B(2)\beta(2)$$

$$A(1)\beta(1)B(2)\alpha(2)$$

$$A(1)\beta(1)B(2)\beta(2)$$

Allowing for interchange of the two affords :

$$A(2)\alpha(2)B(1)\alpha(1)$$

$$A(2)\alpha(2)B(1)\beta(1)$$

$$A(2)\beta(2)B(1)\alpha(1)$$

$$A(2)\beta(2)B(1)\beta(1)$$

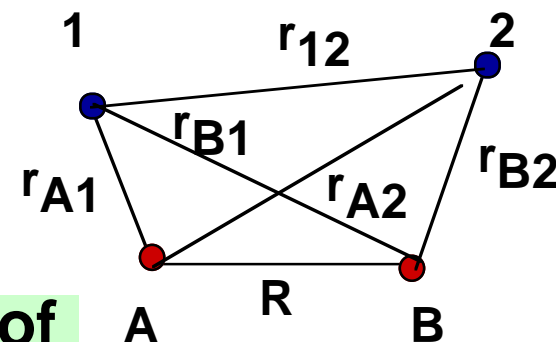
We have further that

$$\psi(r_1, r_2, R) = \omega_1(r_1, r_2)$$

Must be anti symmetric

$$\psi(r_1, r_2, R) = \omega_1(r_1, r_2) = -\psi(r_2, r_1, R) = -\omega_1(r_2, r_1)$$

Basic Theory



Valence Bond Theory

From the product functions

$A(1)\alpha(1)B(2)\alpha(2)$	$A(2)\alpha(2)B(1)\alpha(1)$
$A(1)\alpha(1)B(2)\beta(2)$	$A(2)\alpha(2)B(1)\beta(1)$
$A(1)\beta(1)B(2)\alpha(2)$	$A(2)\beta(2)B(1)\alpha(1)$
$A(1)\beta(1)B(2)\beta(2)$	$A(2)\beta(2)B(1)\beta(1)$

We can construct the anti-symmetric linear combinations :

$$\xi_1 = [A(1)B(2) + A(1)B(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\xi_2 = [A(1)B(2) - A(1)B(2)] \times [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\xi_3 = [A(1)B(2) - A(1)B(2)]\alpha(1)\alpha(2)$$

$$\xi_4 = [A(1)B(2) - A(1)B(2)]\beta(1)\beta(2)$$

Basic Theory

- Symmetric in space
- anti-symmetric in spin
 $\langle S^2 \rangle = 0$: singlet

- Anti-symmetric in space
- symmetric in spin
 $\langle S^2 \rangle = 2\hbar^2$: triplet

$$m_s = 0$$

$$m_s = 1$$

$$m_s = -1$$

Valence Bond Theory

Singlet

$$\xi_1 = C_1[A(1)B(2) + A(1)B(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

triplet

$$\xi_2 = C_2[A(1)B(2) - A(1)B(2)] \times [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\xi_4 = C_4[A(1)B(2) - A(1)B(2)]\beta(1)\beta(2)$$

$$\xi_3 = C_3[A(1)B(2) - A(1)B(2)]\alpha(1)\alpha(2)$$

C_i insures normalization

Electron density :

$$\rho(r_1) = \int \psi^*(1, 2, \dots, n) \psi(1, 2, \dots, n) \times$$

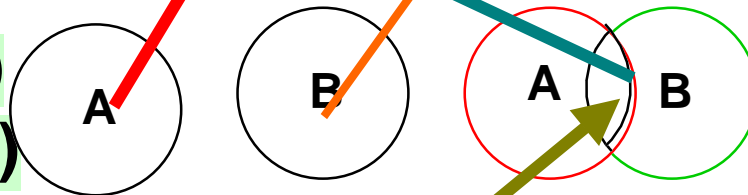
$dr_2 dr_3 \dots dr_n d\text{spin}$

probability of finding el.
no matter where other el.
are

Basic Theory

Singlet density :

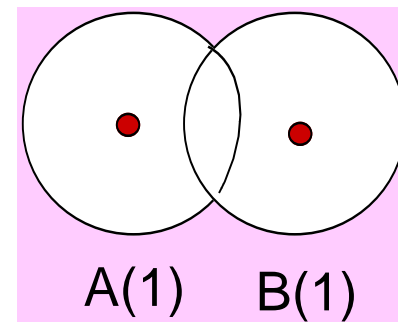
$$\rho_{\text{sing}}(1) = \frac{\rho_{\text{HA}}(1)}{1 - S^2} + \frac{\rho_{\text{HB}}(1)}{1 + S^2} + \frac{2A(1)B(1)}{1 + S^2}$$



positive overlap density

Density build up between nuclei

$$S = \int 1s_A(1)1s_B(1)d\tau$$



Overlap between
1s orbitals on A and B

Valence Bond Theory

Singlet

$$\xi_1 = C_1[A(1)B(2) + A(1)B(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

triplet

$$\xi_2 = C_2[A(1)B(2) - A(1)B(2)] \times [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

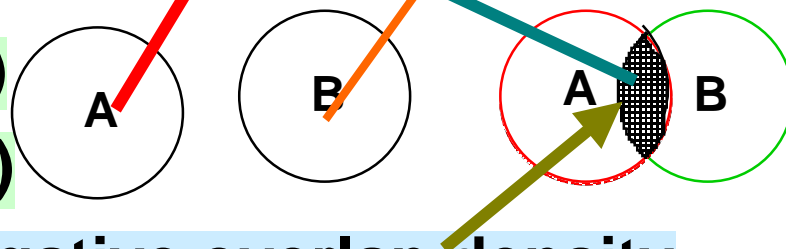
$$\xi_4 = C_4[A(1)B(2) - A(1)B(2)]\beta(1)\beta(2)$$

$$\xi_3 = C_3[A(1)B(2) - A(1)B(2)]\alpha(1)\alpha(2)$$

Basic Theory

Triplet density :

$$\rho_{\text{sing}}(1) = \frac{\rho_{\text{HA}}(1)}{1 - S^2} + \frac{\rho_{\text{HB}}(1)}{1 - S^2} - \frac{2A(1)B(1)}{1 - S^2}$$



negative overlap density

Density reduced between nuclei

Valence Bond Theory

Singlet :

$$\xi_1 = C_1[A(1)B(2) + A(1)B(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Triplet :

$$\xi_2 = C_2[A(1)B(2) - A(1)B(2)] \times [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\xi_3 = C_3[A(1)B(2) - A(1)B(2)]\alpha(1)\alpha(2)$$

$$\xi_4 = C_4[A(1)B(2) - A(1)B(2)]\beta(1)\beta(2)$$

Basic Theory

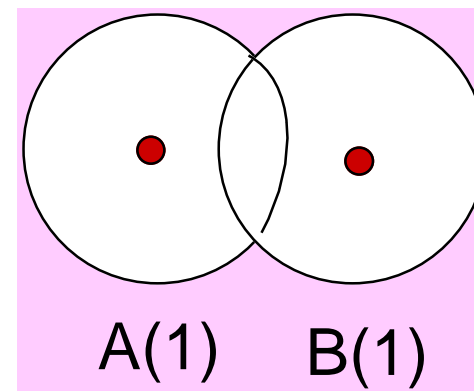
$$E = 2E_H + \frac{J+K}{1+S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$

$$E = 2E_H + \frac{J-K}{1-S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$

Energy hydrogen atom

$$S = \int 1s_A(1)1s_B(1)d\tau$$

Overlap between
1s orbitals on A and B



Valence Bond Theory

Singlet :

$$E = 2E_H + \frac{J+K}{1+S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$

Triplet :

$$E = 2E_H + \frac{J-K}{1-S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$

$$J = -\frac{e^2}{4\pi\epsilon_0} \int A(1)A(1) \frac{1}{r_{1B}} dv_1$$

Int. el.1 with Nuc. B

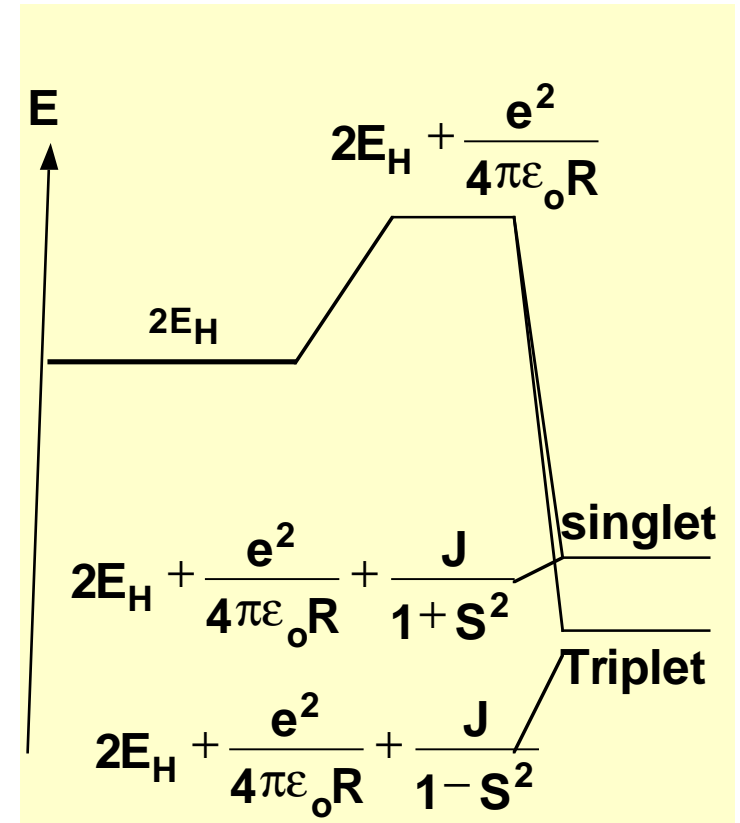
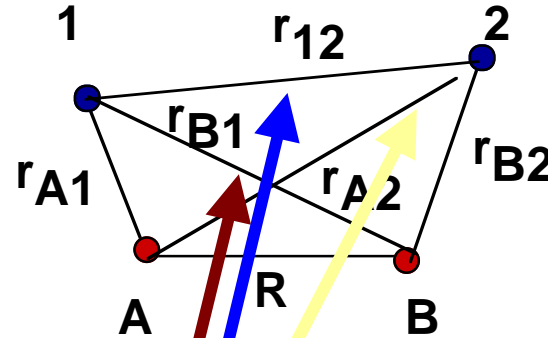
$$-\frac{e^2}{4\pi\epsilon_0} \int B(2)B(2) \frac{1}{r_{2A}} dv_2$$

Int. el.2 with Nuc. A

$$\frac{e^2}{4\pi\epsilon_0} \int B(2)B(2) \frac{1}{r_{12}} A(1)A(1) dv_2 dv_1$$

el 1 with el 2

Basic Theory



Valence Bond Theory

Singlet :

$$E = 2E_H + \frac{J+K}{1+S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$

Triplet :

$$E = 2E_H + \frac{J-K}{1-S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$

$$K = -\frac{e^2}{4\pi\epsilon_0} \int A(1)B(1) \frac{1}{r_{1B}} dv_1$$

Int. overlap dens. with Nuc. B

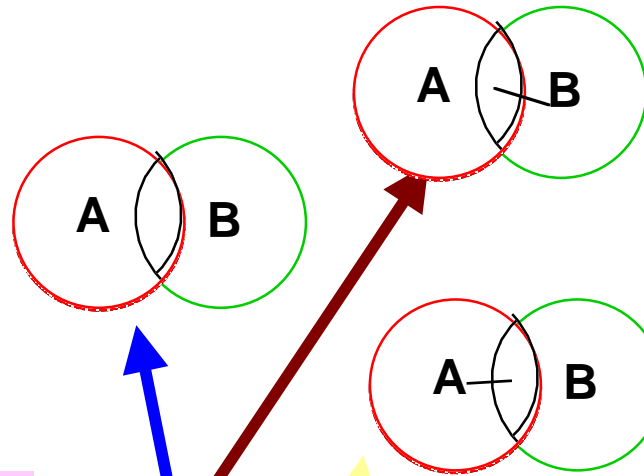
$$-\frac{e^2}{4\pi\epsilon_0} \int A(2)B(2) \frac{1}{r_{2A}} dv_2$$

Int. overlap dens with Nuc. A

$$+\frac{e^2}{4\pi\epsilon_0} \int A(2)B(2) \frac{1}{r_{12}} A(1)B(1) dv_2 dv_1$$

int. overlap dens with itself

Basic Theory



K is negative for singlet since overlap density positive

K enters with opposite sign for triplet since overlap density negative

Valence Bond Theory

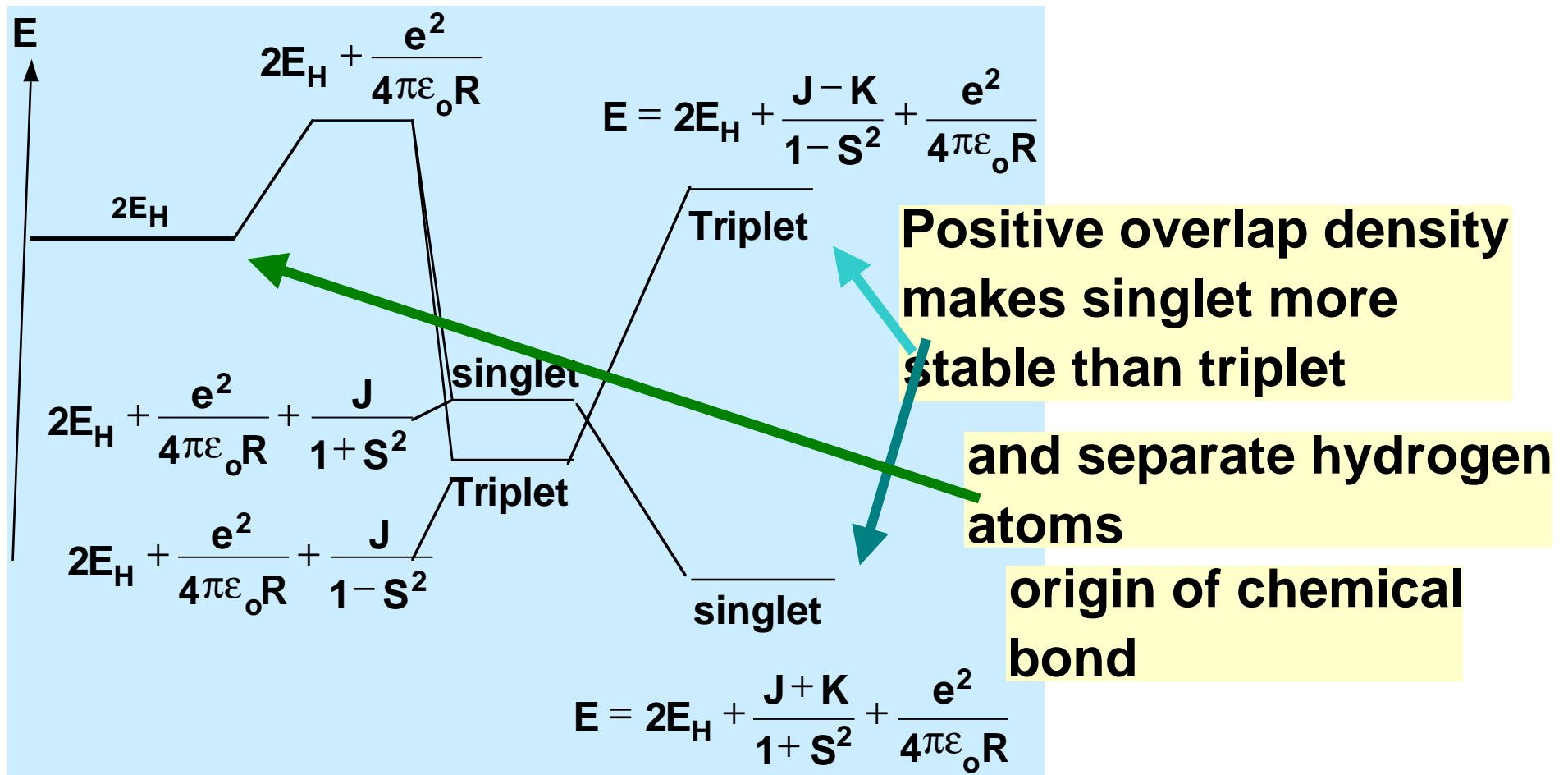
Singlet :

$$E = 2E_H + \frac{J+K}{1+S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$

Basic Theory

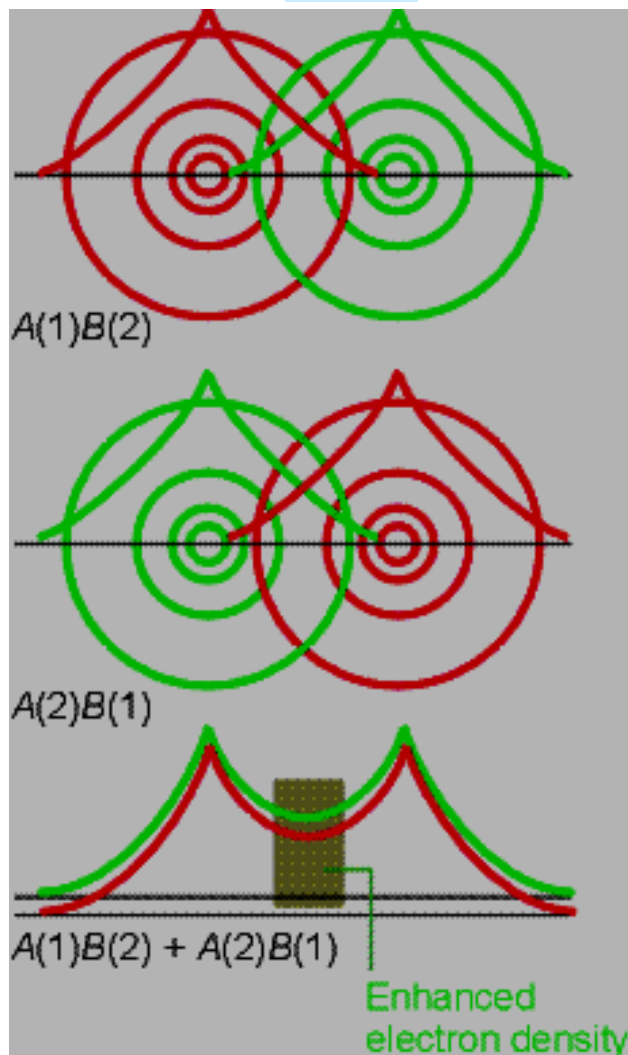
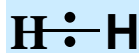
Triplet :

$$E = 2E_H + \frac{J-K}{1-S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$



Valence Bond Theory

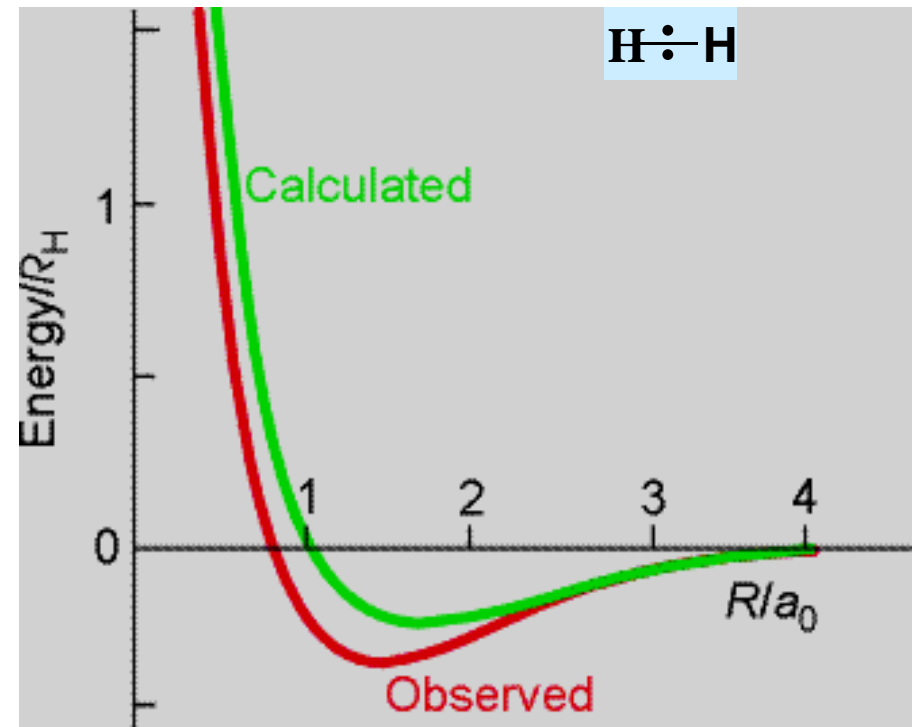
Basic Theory



It is very difficult to represent valence-bond wavefunctions because they refer to two electrons simultaneously. However, this illustration is an attempt. The atomic orbital for electron 1 is represented by the black contours, and that of electron 2 is represented by the green contours. The top illustration represents $A(1)B(2)$, and the middle illustration represents the contribution $A(2)B(1)$. When the two contributions are superimposed, there is interference between the black contributions and between the green contributions, resulting in an enhanced (two-electron) density in the internuclear region.

Valence Bond Theory

Basic Theory



The molecular potential energy curve for the hydrogen molecule showing the variation of the energy of the molecule as the bond length is changed. The calculated curve refers to the valence-bond model.

What you should learn from this lecture

You should know that :

In valence bond theory we start by writing down the Lewis structure of our molecule. Subsequently we write $\psi(r_e, R_N)$ as the product of electron pair functions $\omega_i(r_{2i-1}, r_{2i})$ as $\psi(r_e, R_N) = \omega_1(r_1, r_2) \times \omega_2(r_3, r_4) \times \dots \times \omega_j(r_{2j-1}, r_{2j}) \dots \times \omega_n(r_{2n-1}, r_{2n})$

You should know that the singlet function $\xi_1 = C_1[A(1)B(2) + A(1)B(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ is more stable than the triplet (e.i. $\xi_2 = C_2[A(1)B(2) - A(1)B(2)] \times [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$)

You are not asked to derive the expression for the density of the singlet .

$$\rho_{\text{sing}}(1) = \frac{\rho_{\text{HA}}(1)}{1+S^2} + \frac{\rho_{\text{HB}}(1)}{1+S^2} + \frac{2A(1)B(1)}{1+S^2}$$

However, you should know that density is increased in the bonding region and that contribute to the stability of the singlet

What you should learn from this lecture

You are not asked to derive the expression for the density of the triplet .

$$\rho_{\text{trip}}(1) = \frac{\rho_{\text{HA}}(1)}{1-S^2} + \frac{\rho_{\text{HB}}(1)}{1-S^2} - \frac{2A(1)B(1)}{1-S^2}$$

However, you should know that density is decreased in the bonding region and that contribute to the higher energy of the triplet

You will not be required to derive the energy expression for the singlet

$$E_{\text{sing}} = 2E_{\text{H}} + \frac{J+K}{1+S^2} + \frac{e^2}{4\pi\epsilon_0 R} \quad \text{and the triplet}$$

$$E_{\text{triplet}} = 2E_{\text{H}} + \frac{J-K}{1-S^2} + \frac{e^2}{4\pi\epsilon_0 R}$$

However you should know that the (negative) exchange integral K is responsible for the lower energy of the singlet. It is related to the buildup of charge in the bonding region.