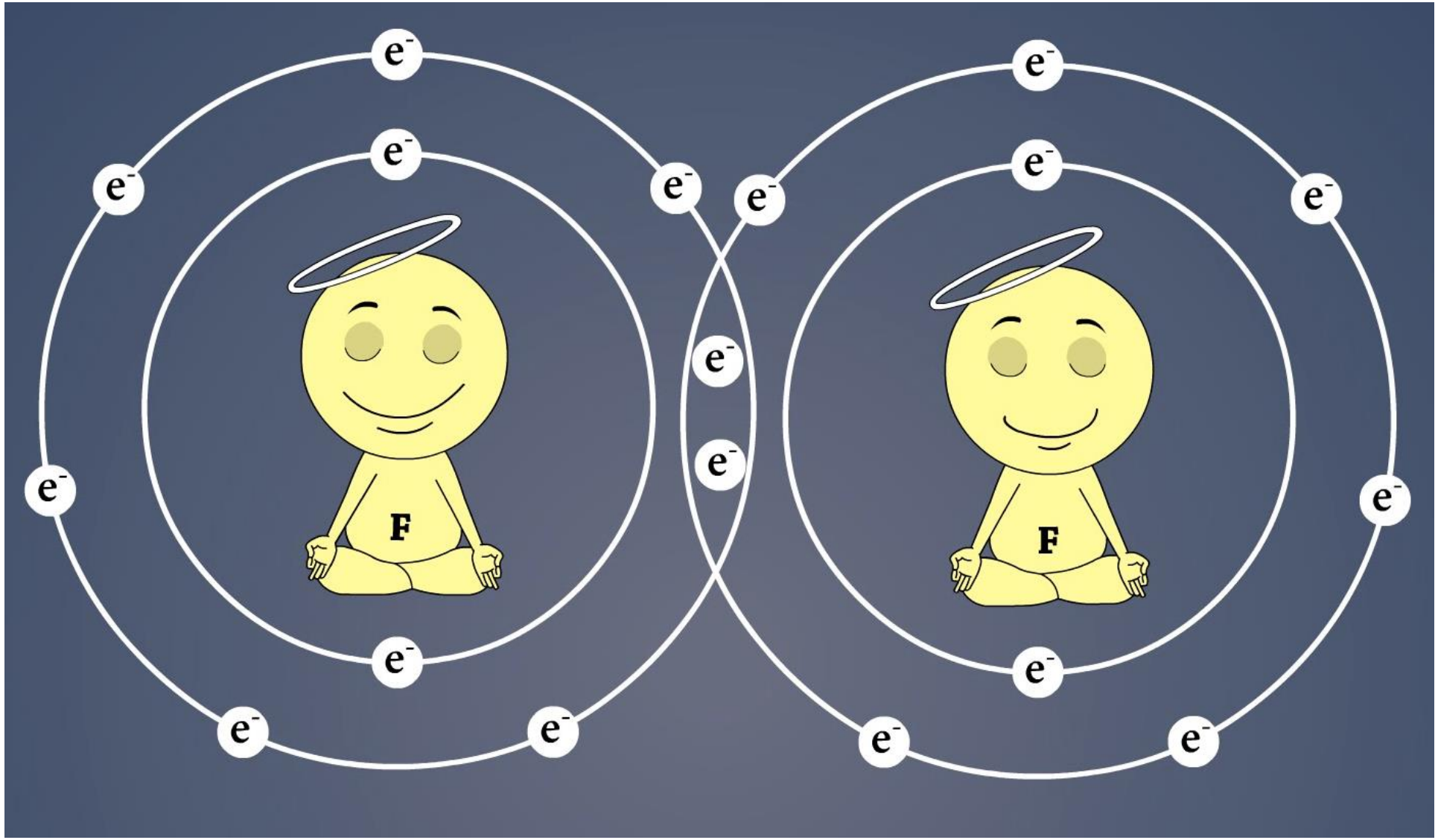
Valence bond theory



Valence Bond and Molecular Orbital Approaches

Valence Bond Theory

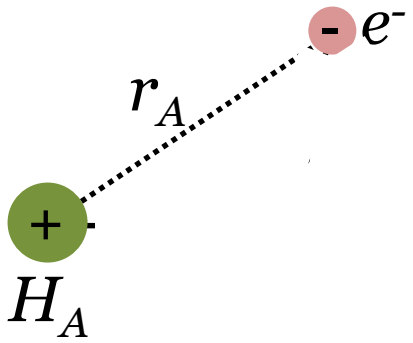
- Extension of Lewis electron dot model
- Overlap of atomic orbitals and sharing of electron pairs
- Works fine for many systems
- Limited to two center two electron bonds

  Delocalization: Resonance
- Cannot describe excited states

Molecular Orbital Theory

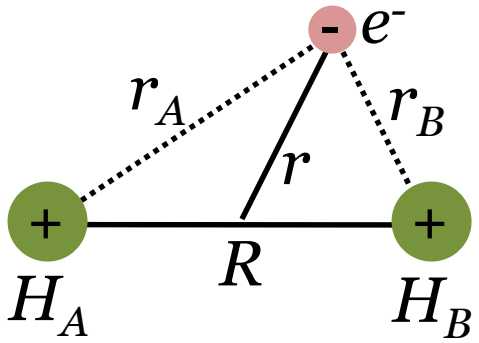
- Electron(s) moving in the joint field of nuclei
- Set up the Hamiltonian: Exactly solvable for H_2^+ but not for more complex molecules
- Molecular orbitals: Linear combination of Atomic Orbitals ***(LCAO***)
- Can handle delocalization, excited states. ***A general theory***
- A bit too general at times (***ionic structure for H_2, for example***)

Hamiltonian: H atom, H_2^+ ion and H_2 molecule

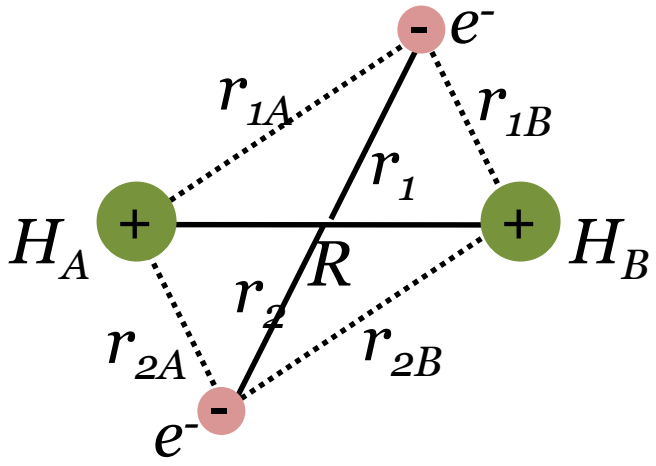


$$\widehat{H}\left(H_{\text{atom}}\right) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - Q\frac{e^2}{r_A}$$

Hamiltonian: H atom, H_2^+ ion and H_2 molecule



$$\widehat{H}\left(H_2^+\right) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{\hbar^2}{2m_e}\nabla_e^2$$
$$-Q\frac{e^2}{r_A} - Q\frac{e^2}{r_B} + Q\frac{e^2}{R}$$



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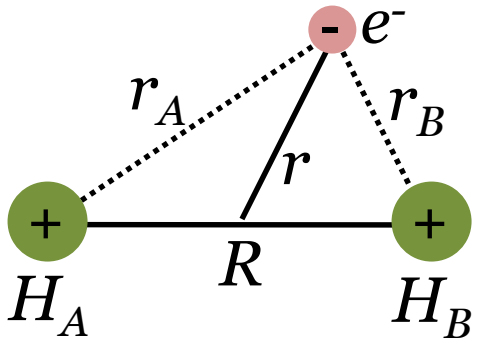
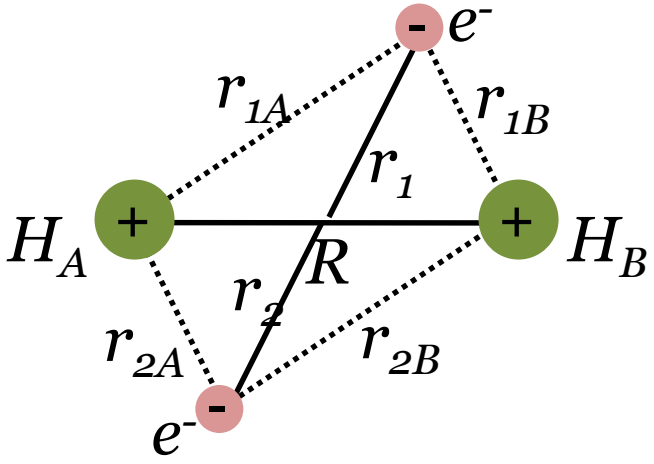


$$\hat{H}\left(H_2^+\right) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - Q\frac{e^2}{r_A} - Q\frac{e^2}{r_B} + Q\frac{e^2}{R}$$

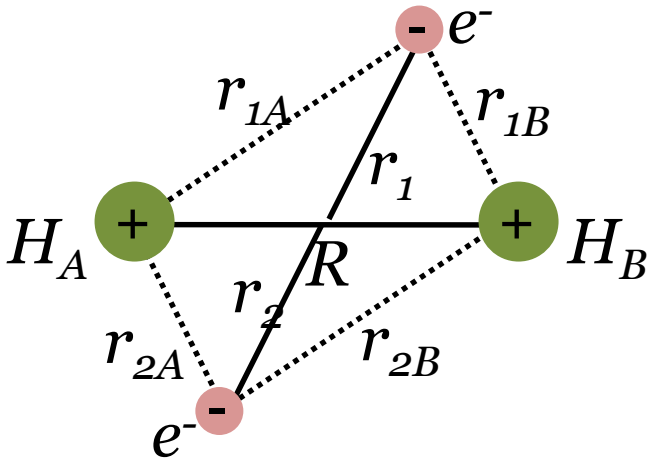


$$\hat{H}\left(H_2\right) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e2}^2 - Q\frac{e^2}{r_{1A}} - Q\frac{e^2}{r_{1B}} - Q\frac{e^2}{r_{2A}} - Q\frac{e^2}{r_{2B}} + Q\frac{e^2}{r_{12}} + Q\frac{e^2}{R}$$

Born Oppenheimer approximation

Nuclei are STATIONARY with respect to electrons

We need methods to find approximate solutions

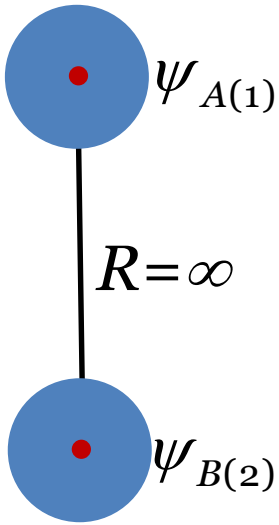


$$\widehat{H}(H_2) = \text{ignore}\left(-\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2\right) - \frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e2}^2 - Q\frac{e^2}{r_{1A}} - Q\frac{e^2}{r_{1B}} - Q\frac{e^2}{r_{2A}} - Q\frac{e^2}{r_{2B}} + Q\frac{e^2}{r_{12}} + Q\frac{e^2}{R}$$

NOT a constant

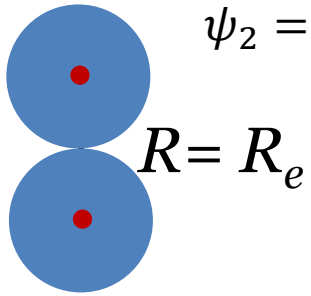
Constant for given R

VBT wavefunctions of H_2



$\Psi = \psi_{A(1)} \cdot \psi_{B(2)}$

ψ_A, ψ_B: **1*s* orbitals**



$\psi_1 = \psi_{A(1)} \cdot \psi_{B(2)}$

$\psi_2 = \psi_{A(2)} \cdot \psi_{B(1)}$

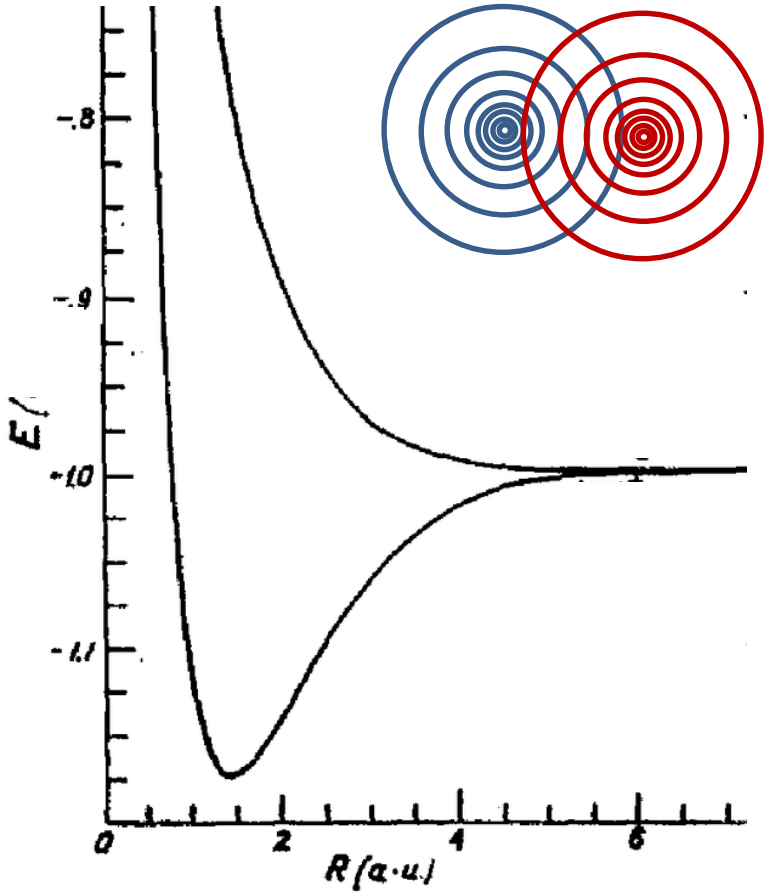
$\hat{H}\Psi = E\Psi$

Heitler and London

$\Psi = c_1\psi_1 + c_2\psi_2$

How do find the energies and coefficients in the expression for the wavefunctions?

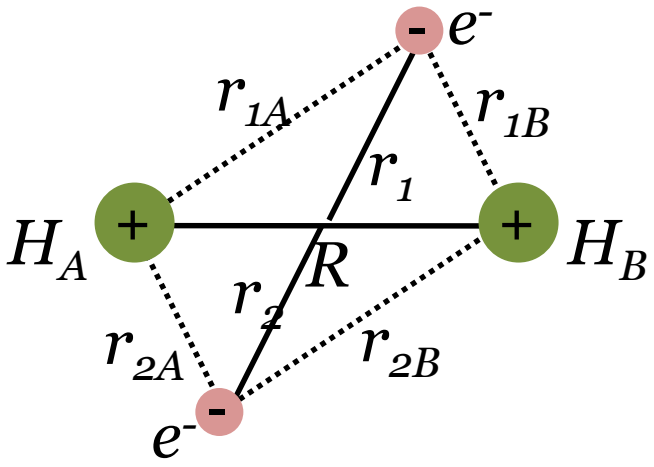
Valence bond theory for H_2: Wavefunction and energy



Hamiltonian operator

Nuclei are STATIONARY with respect to electrons

We need methods to find approximate solutions



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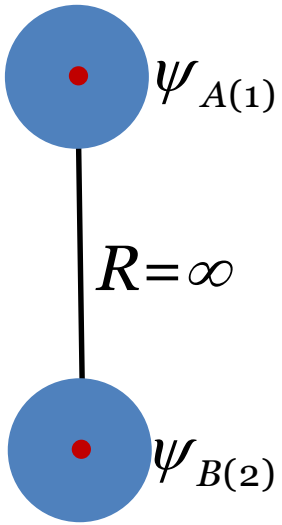
NOT a constant

Constant for given R

VBT wavefunctions of H_2



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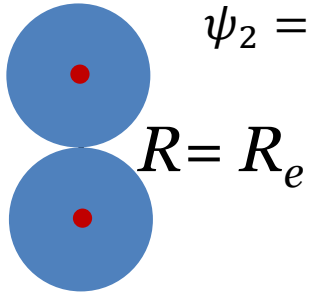
ψ_A, ψ_B: **1*s* orbitals**



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$\psi_2 = \psi_{A(2)} \cdot \psi_{B(1)}$

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

$$\hat{H}(c_1\psi_1 + c_2\psi_2) = E(c_1\psi_1 + c_2\psi_2)$$

$$c_1\langle\psi_1|\hat{H}\psi_1\rangle + c_2\langle\psi_1|\hat{H}\psi_2\rangle = E(c_1\langle\psi_1|\psi_1\rangle + c_2\langle\psi_1|\psi_2\rangle)$$

$\langle\psi_{A(1)}\psi_{B(2)}|\psi_{A(1)}\psi_{B(2)}\rangle$

$= \langle\psi_{A(1)}|\psi_{A(1)}\rangle\langle\psi_{B(2)}|\psi_{B(2)}\rangle$

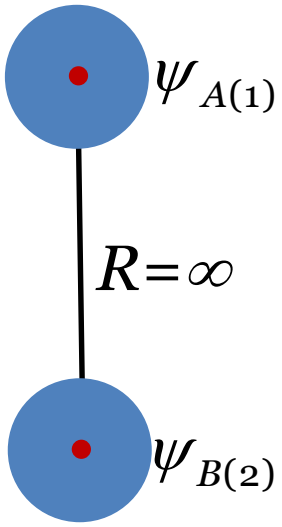
$= 1$

Heitler and London

$\Psi = c_1\psi_1 + c_2\psi_2$

Left multiply by ψ_1 and integrate

VBT wavefunctions of H_2



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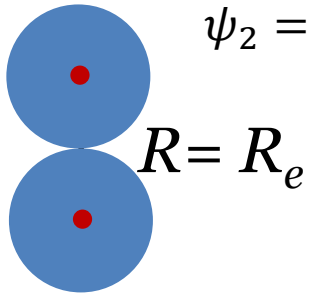

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Heitler and London

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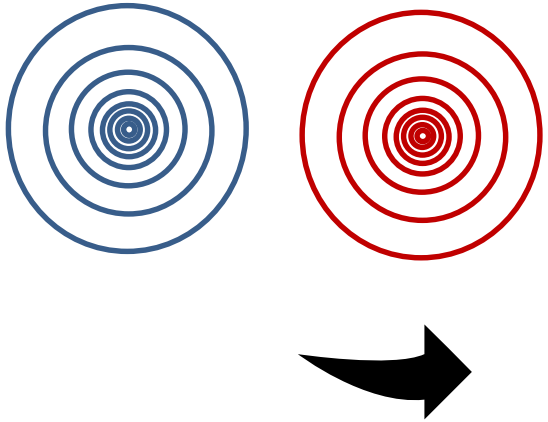

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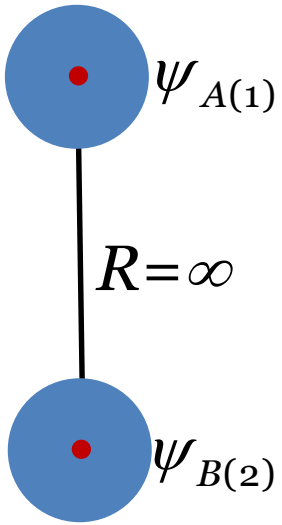
$$c_1\langle\psi_1|\hat{H}\psi_1\rangle + c_2\langle\psi_1|\hat{H}\psi_2\rangle = E(c_1 + c_2\langle\psi_1|\psi_2\rangle)$$

$\langle\psi_{A(1)}\psi_{B(2)}|\psi_{A(2)}\psi_{B(1)}\rangle$

$= \langle\psi_{A(1)}|\psi_{B(1)}\rangle\langle\psi_{B(2)}|\psi_{A(2)}\rangle$

$= S^2$ — **Overlap integral**

VBT wavefunctions of H_2



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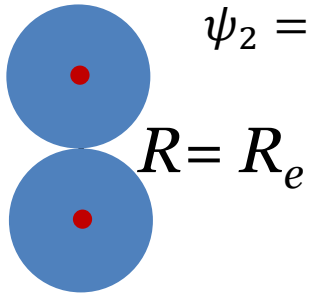

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$$\langle\psi_{A(1)}\psi_{B(2)}|\psi_{A(2)}\psi_{B(1)}\rangle$$

$$= \langle\psi_{A(1)}|\psi_{B(1)}\rangle\langle\psi_{B(2)}|\psi_{A(2)}\rangle$$

$$= S^2$$

Overlap integral

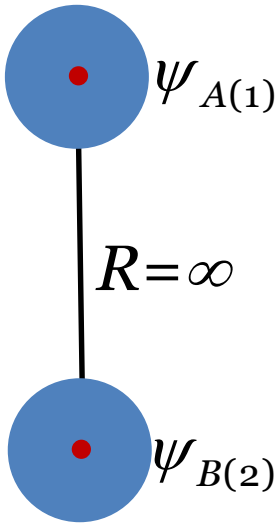
Heitler and London

$\Psi = c_1\psi_1 + c_2\psi_2$

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

Using elliptical coordinates

VBT wavefunctions of H_2



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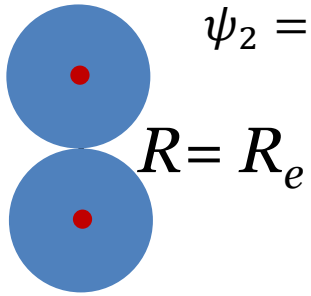
ψ_A, ψ_B: **1s orbitals**



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$\psi_2 = \psi_{A(2)} \cdot \psi_{B(1)}$

Heitler and London

$\Psi = c_1\psi_1 + c_2\psi_2$

S = **Overlap Integral**

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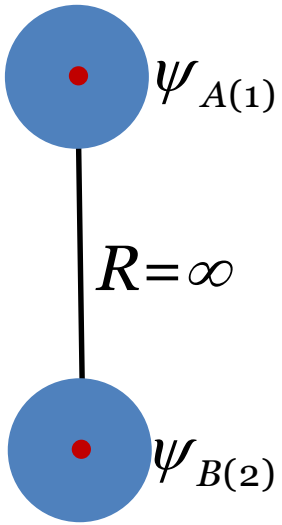
$$\hat{H}(c_1\psi_1 + c_2\psi_2) = E(c_1\psi_1 + c_2\psi_2)$$

$$c_1\langle\psi_1|\hat{H}\psi_1\rangle + c_2\langle\psi_1|\hat{H}\psi_2\rangle = E(c_1 + c_2S^2)$$

H_{11} H_{12}

VBT wavefunctions of H_2



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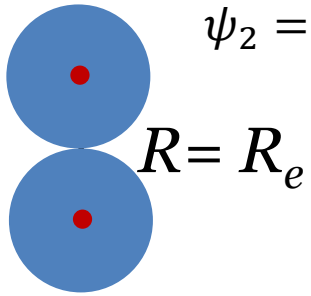

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Heitler and London

$\Psi = c_1\psi_1 + c_2\psi_2$

S = **Overlap Integral**

$\langle \psi_i | \hat{H} \psi_i \rangle = H_{ii}, \langle \psi_i | \hat{H} \psi_j \rangle = H_{ij}$

Secular equation:

$$\begin{vmatrix} H_{11} - E & H_{12} - ES^2 \\ H_{12} - ES^2 & H_{22} - E \end{vmatrix} = 0$$

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

$$\hat{H}(c_1\psi_1 + c_2\psi_2) = E(c_1\psi_1 + c_2\psi_2)$$

$$c_1\langle \psi_1 | \hat{H} \psi_1 \rangle + c_2\langle \psi_1 | \hat{H} \psi_2 \rangle = E(c_1 + c_2 S^2)$$

$$c_1(H_{11} - E) + c_2(H_{12} - ES^2) = 0$$

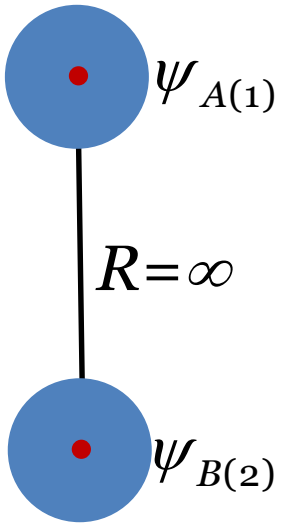
$$c_1(H_{12} - ES^2) + c_2(H_{22} - E) = 0$$

$$\begin{pmatrix} H_{11} - E & H_{12} - ES^2 \\ H_{12} - ES^2 & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$A^{-1}A$

$c = A^{-1}0$

VBT wavefunctions of H_2



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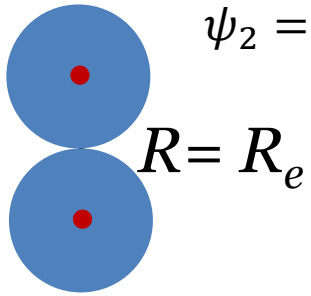
ψ_A, ψ_B: **1s orbitals**



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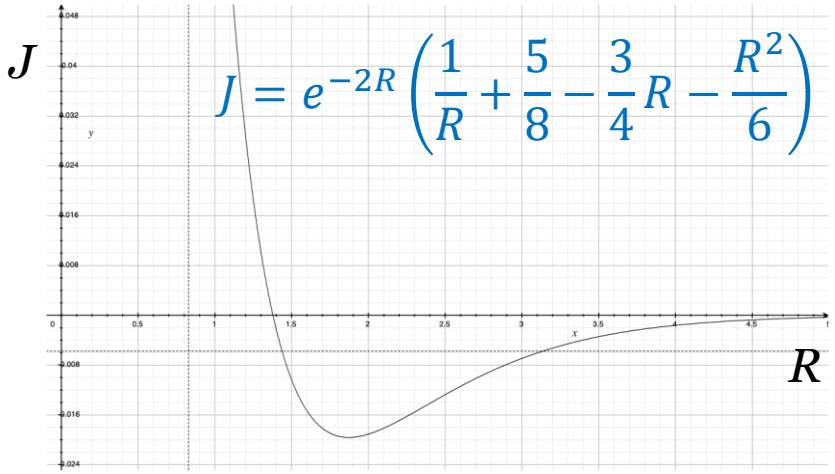

Heitler and London

$\Psi = c_1\psi_1 + c_2\psi_2$

S = **Overlap Integral**

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$H_{11} = -1 + J = H_{22}$

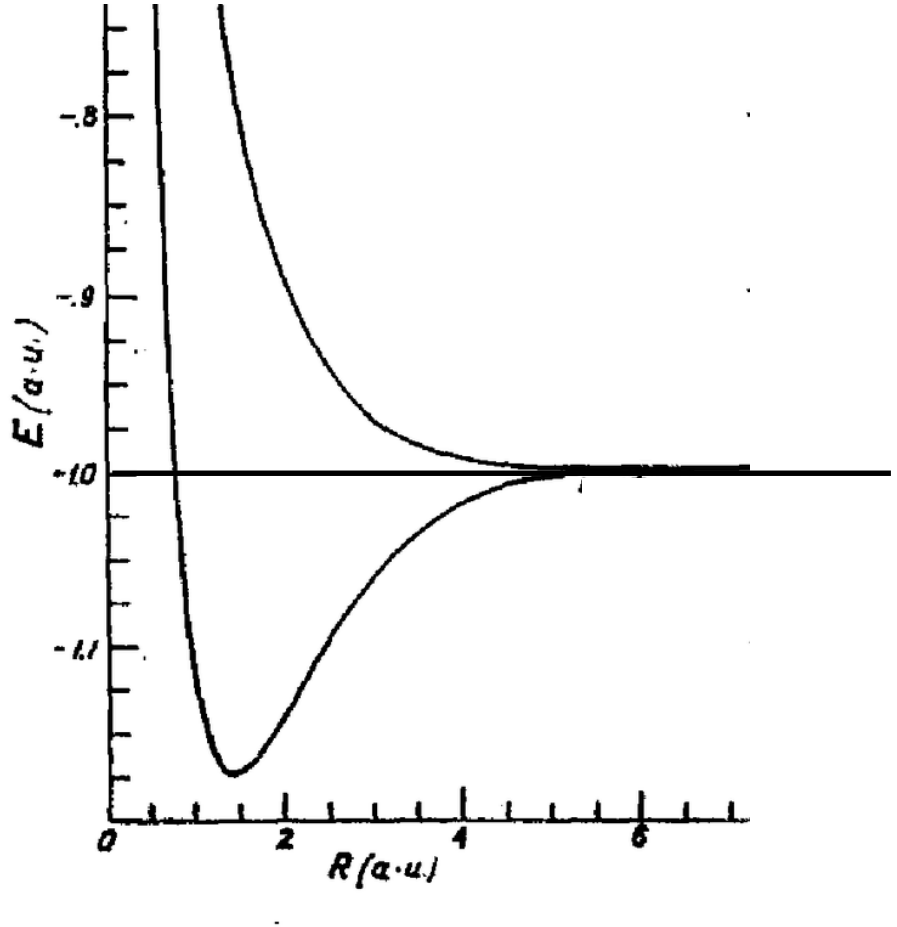
J= **Coulomb Integral**

$H_{12} = -S^2 + K$

K=**Exchange integral**

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

Electronic energies of H_2



Earley, Joseph. (2010). Three Concepts of Chemical Closure and their Epistemological Significance.

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The coefficients

$|c_1| = |c_2| = c$

$\Psi = c(\psi_{A(1)}\psi_{B(2)} \pm \psi_{A(2)}\psi_{B(1)})$

$\langle\Psi|\Psi\rangle = 1$

$\psi_1 = \psi_{A(1)}.\psi_{B(2)}$

$\psi_2 = \psi_{A(2)}.\psi_{B(1)}$

$$c^2\langle(\psi_{A(1)}\psi_{B(2)} \pm \psi_{A(2)}\psi_{B(1)})|(\psi_{A(1)}\psi_{B(2)} \pm \psi_{A(2)}\psi_{B(1)})\rangle = 1$$

$$c^2[\langle\psi_{A(1)}\psi_{B(2)}|\psi_{A(1)}\psi_{B(2)}\rangle \pm \langle\psi_{A(1)}\psi_{B(2)}|\psi_{A(2)}\psi_{B(1)}\rangle \pm \langle\psi_{A(2)}\psi_{B(1)}|\psi_{A(1)}\psi_{B(2)}\rangle + \langle\psi_{A(2)}\psi_{B(1)}|\psi_{A(2)}\psi_{B(1)}\rangle] = 1$$

$$c = \frac{1}{\sqrt{2 \pm 2S^2}}$$

Heitler and London

$$\Psi = c_1\psi_1 + c_2\psi_2$$

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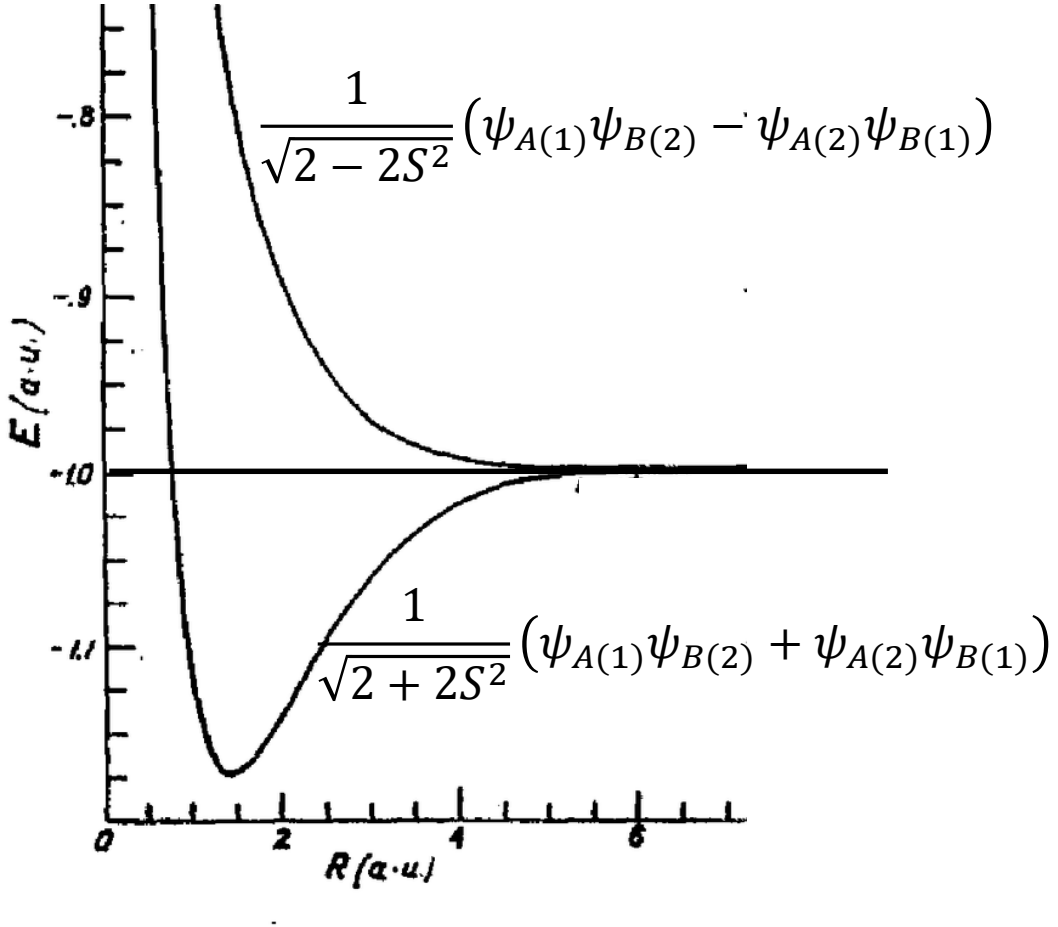
Electronic states of H_2



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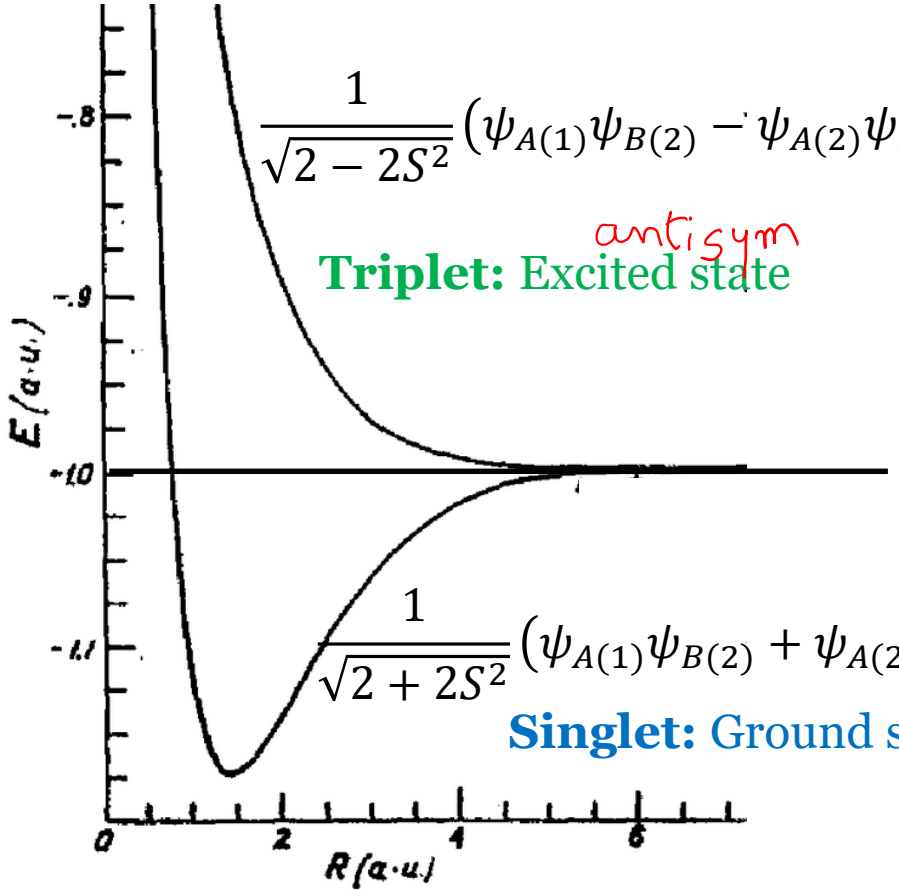
$$E_{\pm} = \frac{J \pm K}{1 \pm S^2}$$

Electronic states of H_2



$$\frac{1}{\sqrt{2-2S^2}}\left(\psi_{A(1)}\psi_{B(2)} - \psi_{A(2)}\psi_{B(1)}\right)\alpha(1)\alpha(2)$$

sym

Triplet: Excited state

antisym

$$\beta(1)\,\beta(2)$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\frac{1}{\sqrt{2+2S^2}}\left(\psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}\right)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Singlet: Ground state

antisym

Electron: Fermion
(spin = ½)

Pauli principle:
Total Wavefunction must be antisymmetric with respect to exchange

$\alpha(1)\alpha(2)$ } sym

$\beta(1)\,\beta(2)$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)]$$

sym

anti

1 and 2: Indistinguishable

Earley, Joseph. (2010). Three Concepts of Chemical Closure and their Epistemological Significance.

Improvement of ground state energy with inclusion of contributions

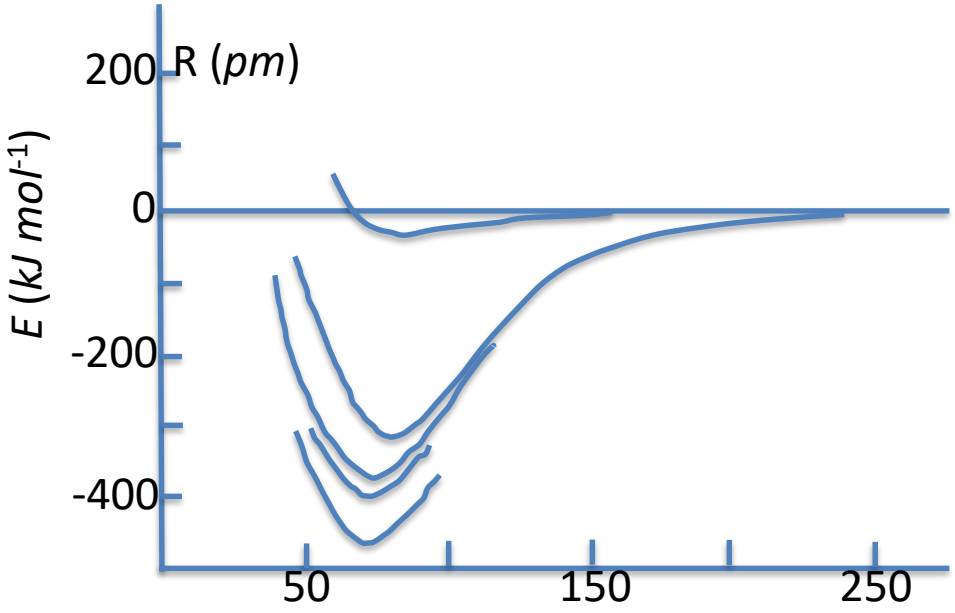
Type of wavefunction	E ($kJ\ mol^{-1}$)	R (pm)
Experimental values	458	74.1

$$(\psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}) + \lambda(\psi_{A(1)}\psi_{A(2)} + \psi_{B(2)}\psi_{B(1)})$$

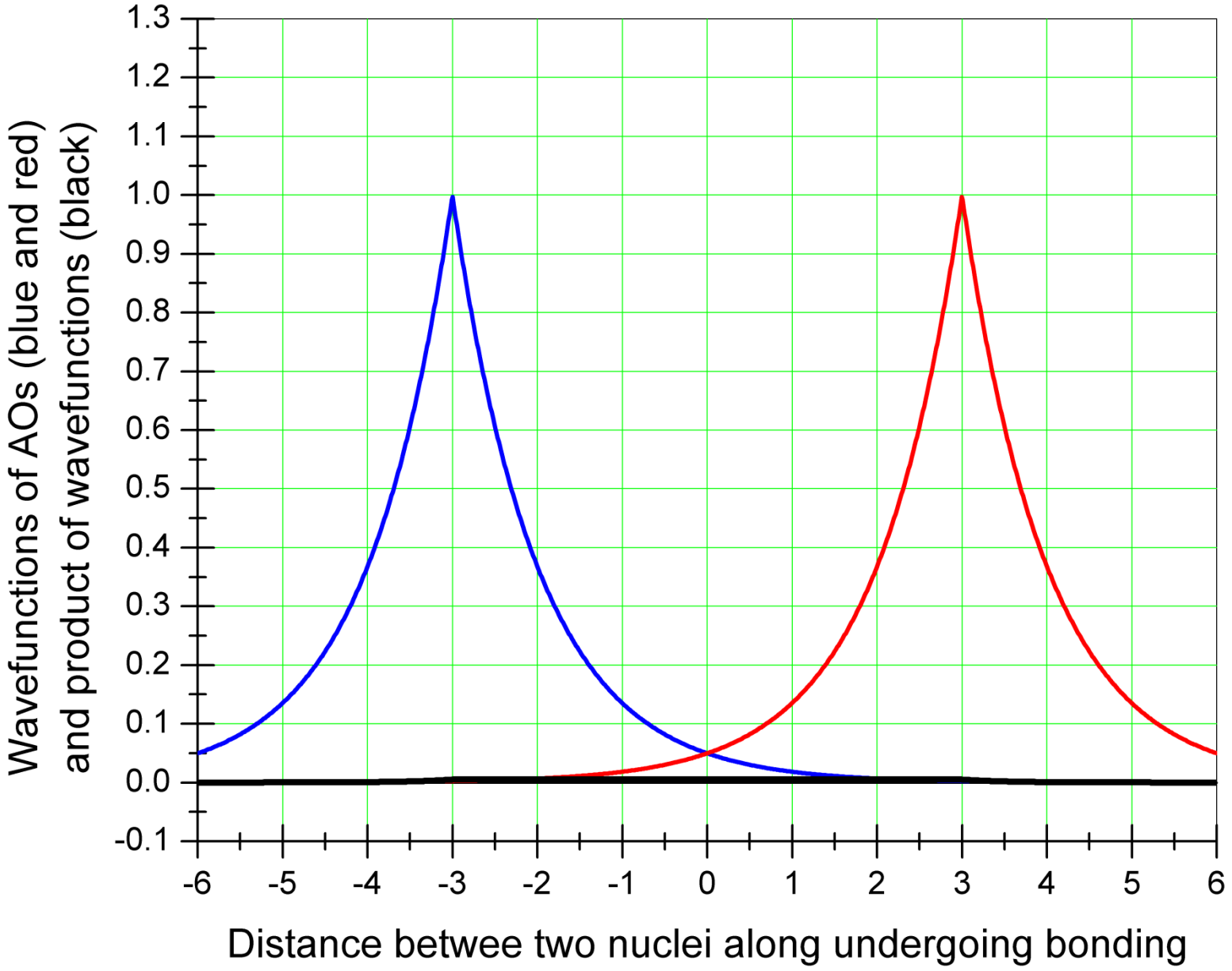
Resonance

H—H ⟷ H^+—H^- ⟷ H^-—H^+

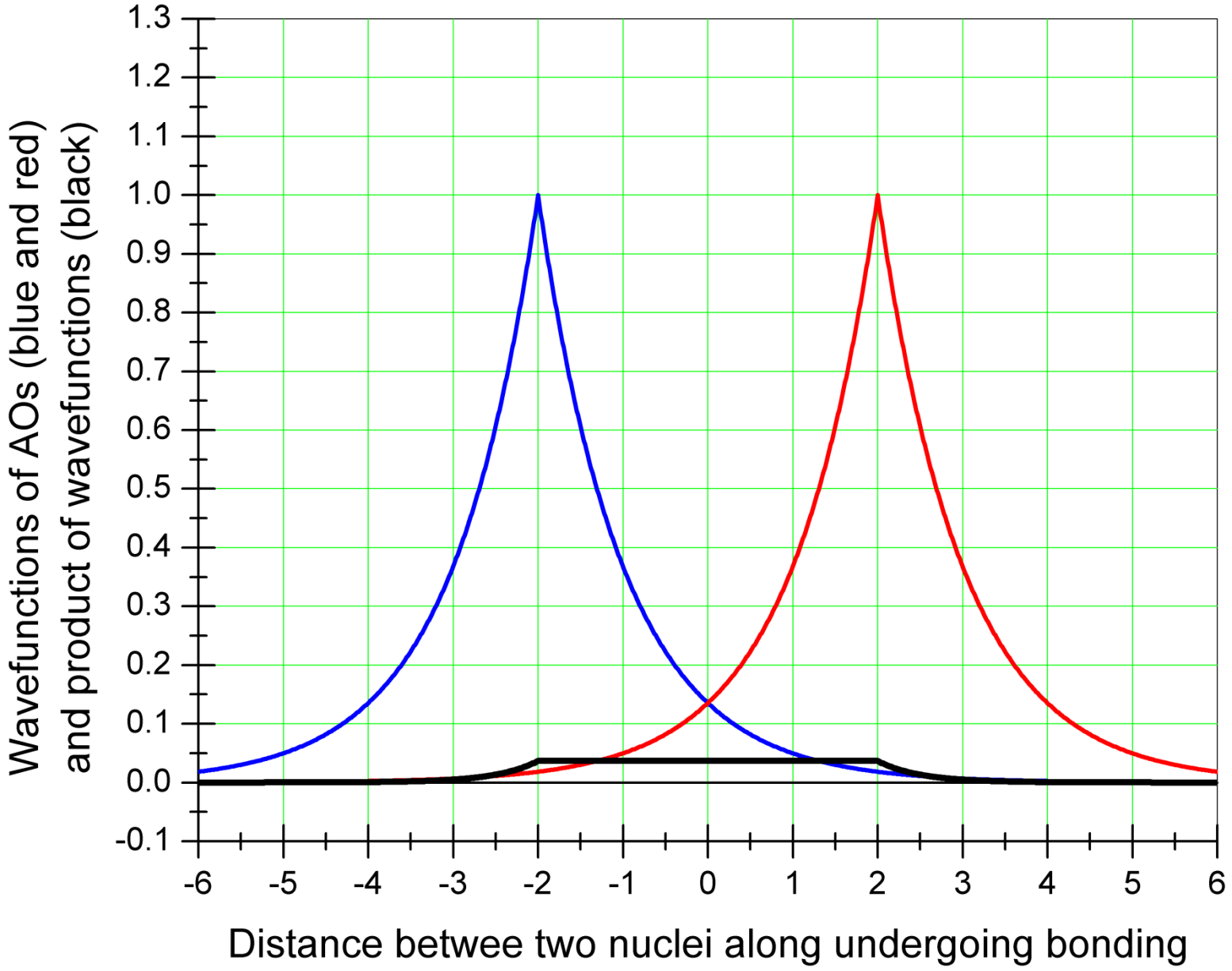
Inclusion of Ionic terms



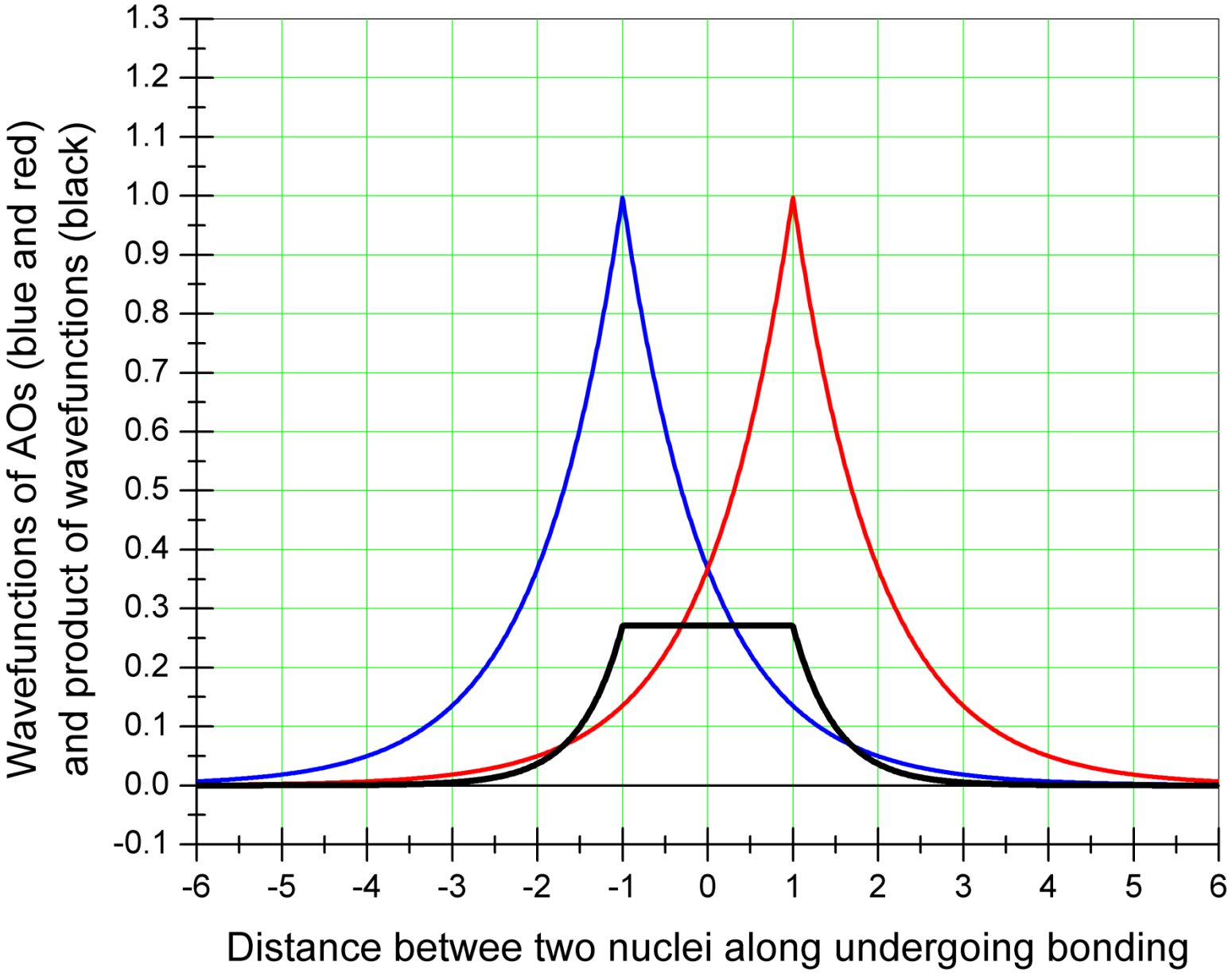
$$\textit{Overlap Integral } S_{AB}(R_1) = \langle 1s_A | 1s_B \rangle = \int 1s_A 1s_B \, d\tau$$



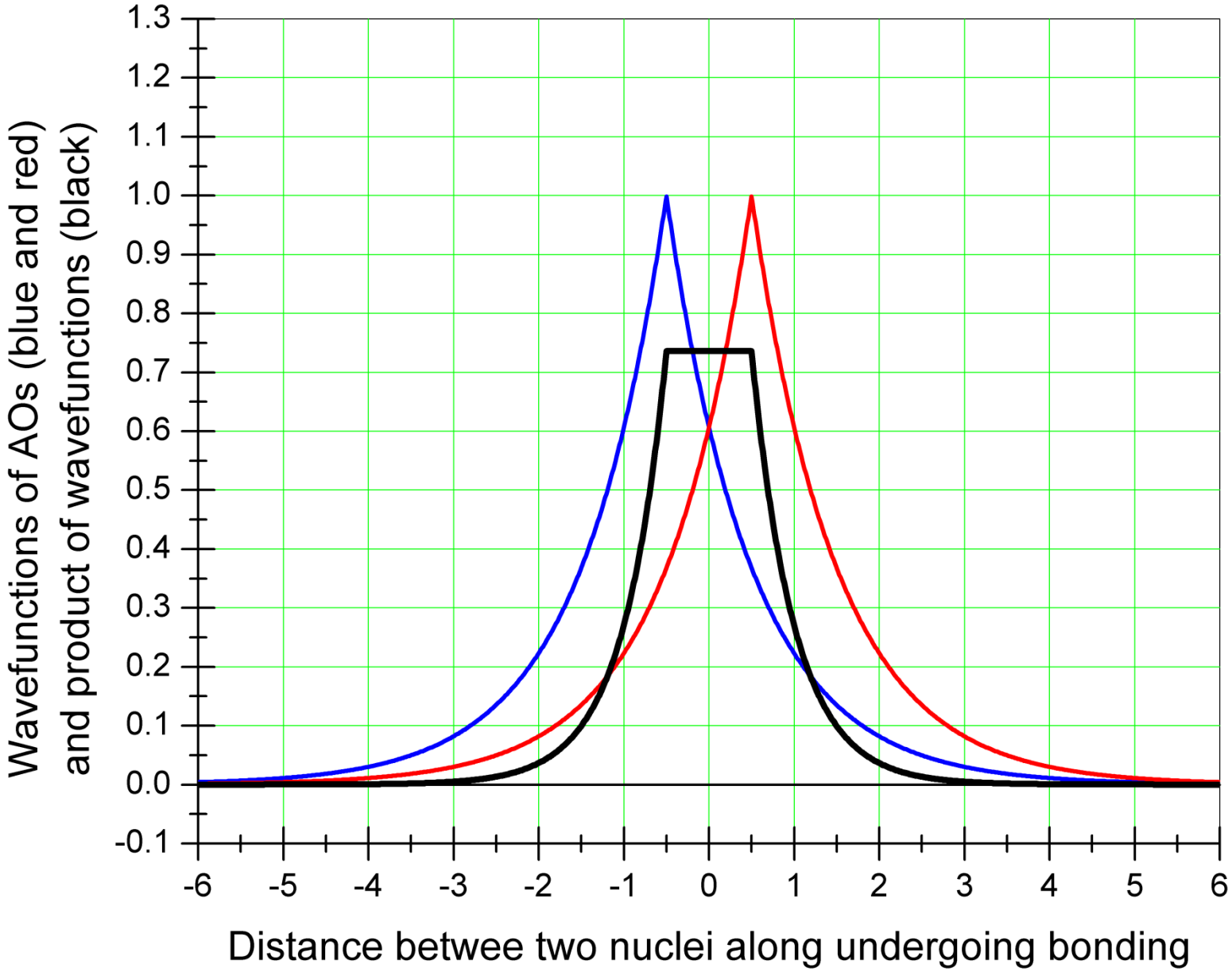
$$\textit{Overlap Integral } S_{AB}(R_2) = \langle 1s_A | 1s_B \rangle = \int 1s_A 1s_B \, d\tau$$



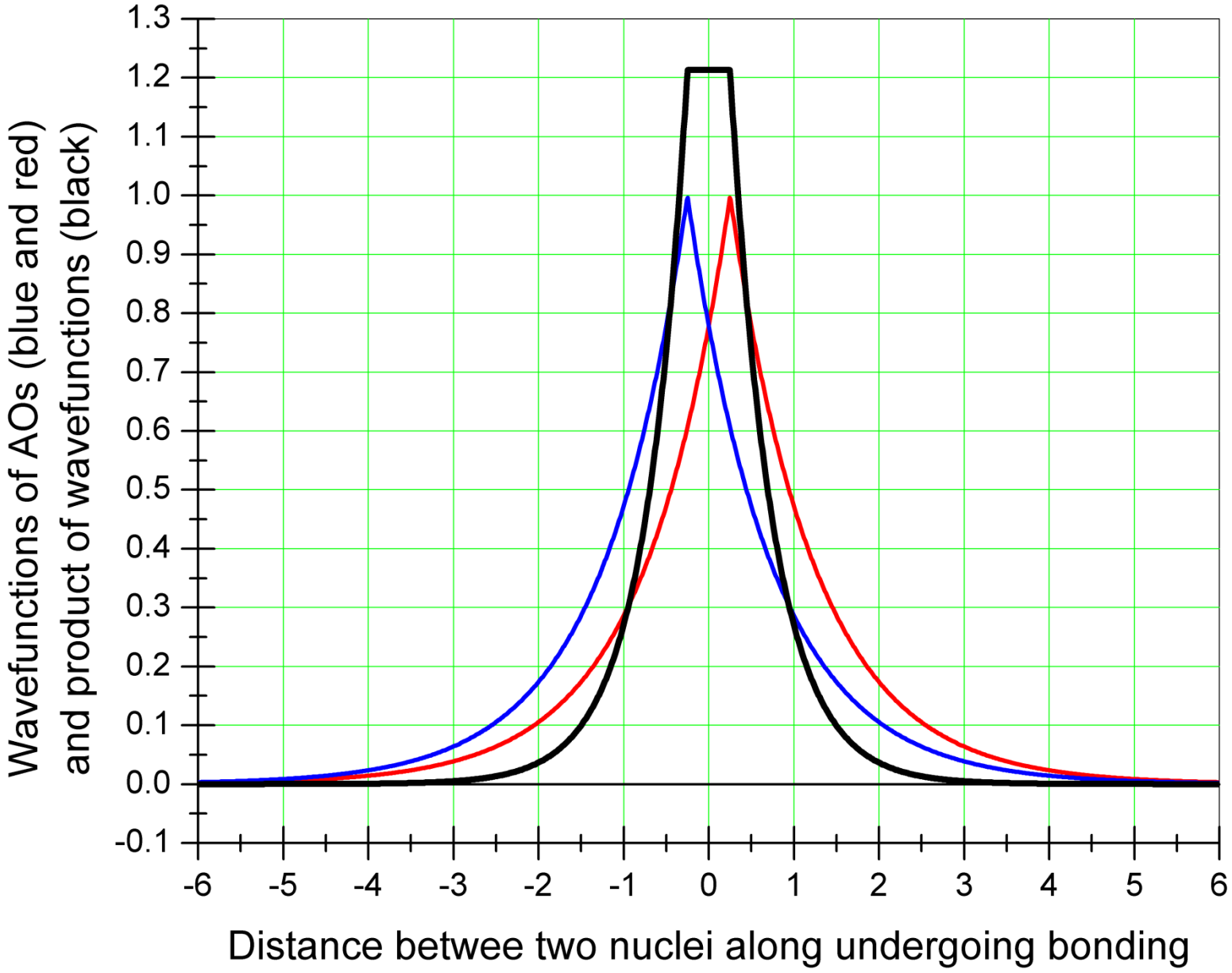
$$\textit{Overlap Integral } S_{AB}(R_3) = \langle 1s_A | 1s_B \rangle = \int 1s_A 1s_B \, d\tau$$



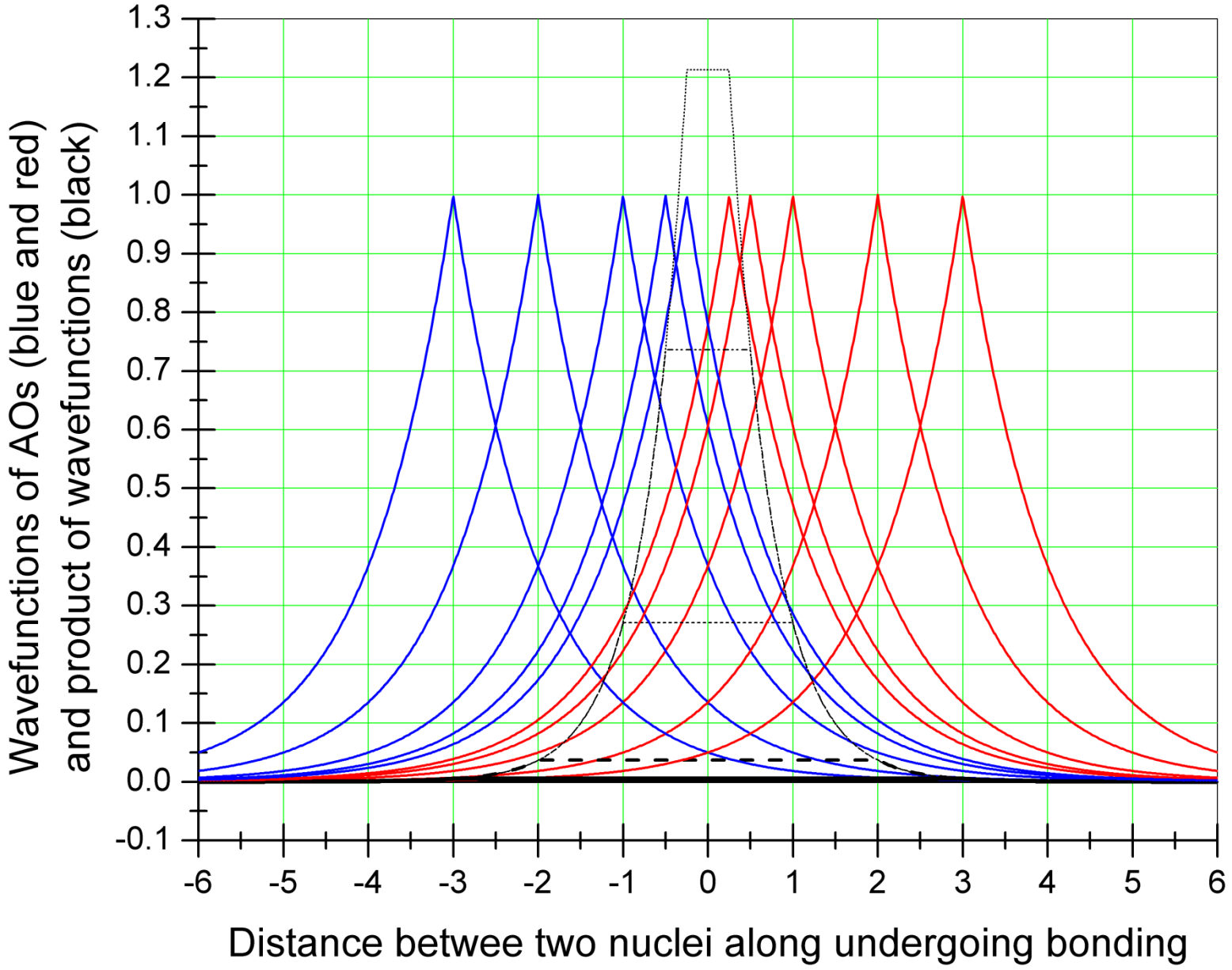
$Overlap\ Integral\ S_{AB}(R_4) = \langle 1s_A | 1s_B \rangle = \int 1s_A 1s_B d\tau$



Overlap Integral $S_{AB}(R_5) = \langle 1s_A | 1s_B \rangle = \int 1s_A 1s_B d\tau$



$$\textit{Overlap Integral } S_{AB}(R) = \langle 1s_A | 1s_B \rangle = \int 1s_A 1s_B \, d\tau$$



$$S_{AB}(R) = \langle \psi_1 | \psi_2 \rangle = \int \psi_1 \psi_2 d\tau$$

Can be negative (area!)