

Chapter 22

Diatomic Molecules

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Chem. 4300

The Hydrogen Molecular Ion

Simplest molecule to consider is H_2^+ , with only 1 electron. Hamiltonian is

$$\hat{H}_{\text{H}_2^+} = \underbrace{-\frac{\hbar^2}{2m_p} (\nabla_A^2 + \nabla_B^2)}_{\textcircled{1}} \underbrace{-\frac{\hbar^2}{2m_e} \nabla_e^2}_{\textcircled{2}} \underbrace{-\frac{Z_A q_e^2}{4\pi\epsilon_0 r_A}}_{\textcircled{3}} \underbrace{-\frac{Z_B q_e^2}{4\pi\epsilon_0 r_B}}_{\textcircled{4}} + \underbrace{\frac{Z_A Z_B q_e^2}{4\pi\epsilon_0 R_{AB}}}_{\textcircled{5}}$$

- $\textcircled{1}$ is kinetic energy of nuclei
- $\textcircled{2}$ is kinetic energy of e^-
- $\textcircled{3}$ is Coulomb attraction between e^- and nucleus A
- $\textcircled{4}$ is Coulomb attraction between e^- and nucleus B
- $\textcircled{5}$ is Coulomb repulsion between nuclei A and B

Written in terms of atomic units

$$\hat{H}_{\text{H}_2^+} = -\frac{1}{2} \frac{m_e}{m_p} (\nabla_A^2 + \nabla_B^2) - \frac{1}{2} \nabla_e^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R_{AB}}$$

Born-Oppenheimer (B-O) Approximation

- Since nuclei are much heavier than e^- we separate motion into 2 timescales:
fast time scale of e^- motion and slow time scale of nuclear motion.
- *Born-Oppenheimer approximation* assumes nuclei are fixed in place and solve for e^- wave function in potential of 2 fixed nuclei.
- We then change internuclear spacing and repeat process.
- Not allowing nuclei to move while solving for e^- wave function has 2 effects:
 - ① nuclear kinetic energy terms: ① go away
 - ② nuclear–nuclear repulsion potential energy term ⑤ becomes constant and can be simply added to energy eigenvalue.

With this approximation wave equation for e^- (in atomic units) becomes

$$\underbrace{\left[-\frac{1}{2} \nabla_e^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right]}_{\hat{H}_{el}} \psi_{el}(\vec{r}, R_{AB}) = E(R_{AB}) \psi_{el}(\vec{r}, R_{AB}).$$

Solving this wave equation gives e^- wave function, $\psi_{el}(\vec{r}, R_{AB})$, and its energy for given internuclear distance, R .

Born-Oppenheimer (B-O) Approximation

Next in B-O approximation we take total wave function as

$$\psi(\vec{r}, R_{AB}) \approx \psi_{\text{el}}(\vec{r}, R_{AB})\psi_{\text{nuc}}(R_{AB})$$

Next we assume that $\psi_{\text{el}}(\vec{r}, R_{AB})$ varies so slowly with R_{AB} that

$$-\frac{1}{2} \frac{m_e}{m_p} (\nabla_A^2 + \nabla_B^2) \psi_{\text{el}}(\vec{r}, R_{AB})\psi_{\text{nuc}}(R_{AB}) \approx \psi_{\text{el}}(\vec{r}, R_{AB}) \left[-\frac{1}{2} \frac{m_e}{m_p} (\nabla_A^2 + \nabla_B^2) \psi_{\text{nuc}}(R_{AB}) \right]$$

In other words we assume $(\nabla_A^2 + \nabla_B^2) \psi_{\text{el}}(\vec{r}, R_{AB}) \approx 0$

Putting B-O wave function approximation

$$\hat{H}_{\text{H}_2^+} \psi(\vec{r}, R_{AB}) = E \psi(\vec{r}, R_{AB})$$

into full Schrödinger equation

$$\hat{H}_{\text{H}_2^+} = -\frac{1}{2} \frac{m_e}{m_p} (\nabla_A^2 + \nabla_B^2) - \frac{1}{2} \nabla_e^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R_{AB}}$$

we obtain...

Born-Oppenheimer (B-O) Approximation

$$\psi_{\text{el}}(\vec{r}, R_{AB}) \left[-\frac{1}{2} \frac{m_e}{m_p} (\nabla_A^2 + \nabla_B^2) \right] \psi_{\text{nuc}}(R_{AB}) + \underbrace{\left[-\frac{1}{2} \nabla_e^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right]}_{\hat{H}_{\text{el}}} \psi_{\text{el}}(\vec{r}, R_{AB}) \psi_{\text{nuc}}(R_{AB}) + \frac{Z_A Z_B}{R_{AB}} \psi_{\text{el}}(\vec{r}, R_{AB}) \psi_{\text{nuc}}(R_{AB}) = E \psi_{\text{el}}(\vec{r}, R_{AB}) \psi_{\text{nuc}}(R_{AB})$$

Making the replacement $\hat{H}_{\text{el}} \psi_{\text{el}}(\vec{r}, R_{AB}) = E(R_{AB}) \psi_{\text{el}}(\vec{r}, R_{AB})$ gives

$$\psi_{\text{el}}(\vec{r}, R_{AB}) \left[-\frac{1}{2} \frac{m_e}{m_p} (\nabla_A^2 + \nabla_B^2) + E(R_{AB}) + \frac{Z_A Z_B}{R_{AB}} \right] \psi_{\text{nuc}}(R_{AB}) = \psi_{\text{el}}(\vec{r}, R_{AB}) E \psi_{\text{nuc}}(R_{AB})$$

Dividing both sides by $\psi_{\text{el}}(\vec{r}, R_{AB})$ gives...

Born-Oppenheimer Approximation

Dividing both sides by $\psi_{\text{el}}(\vec{r}, R_{AB})$ and obtain **wave equation for nuclei**:

$$\left[\underbrace{-\frac{1}{2} \frac{m_e}{m_p} (\nabla_A^2 + \nabla_B^2)}_{\text{nuclear kinetic energy}} + \underbrace{E(R_{AB}) + \frac{Z_A Z_B}{R_{AB}}}_{\text{nuclear effective potential}} \right] \psi_{\text{nuc}}(R_{AB}) = E \psi_{\text{nuc}}(R_{AB})$$

General strategy is to

- fix nuclei in position and calculate $\psi_{\text{el}}(\vec{r}, R_{AB})$ and energy, $E(R_{AB})$. Do this for all possible values of R_{AB} , and
- use $E(R_{AB}) + Z_A Z_B / R_{AB}$ as effective nuclear potential energy (Ground state looks like Morse potential) in nuclear wave equation to obtain $\psi_{\text{nuc}}(R_{AB})$ and energies:

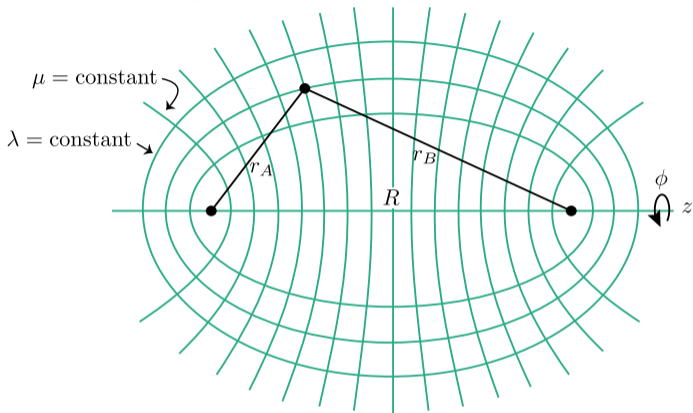
Solving one electron Schrödinger equation for the H_2^+ ion

With B-O approximation out of way let's look at solutions for $\psi_{\text{el}}(\vec{r}, R_{AB})$ of H_2^+ , given the electronic Hamiltonian in atomic units

$$\underbrace{\left[-\frac{1}{2} \nabla_e^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right]}_{\hat{H}_{\text{el}}} \psi_{\text{el}}(\vec{r}, R_{AB}) = E(R_{AB}) \psi_{\text{el}}(\vec{r}, R_{AB}).$$

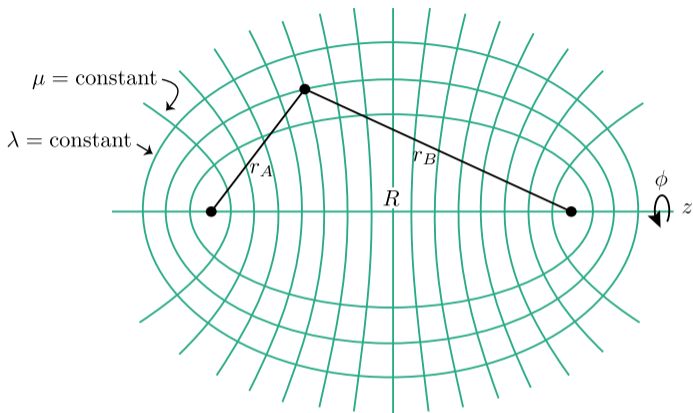
Problem is no longer spherically symmetric. So, what coordinate system should we use?

Spheroidal Coordinates : $\psi_{\text{el}}(\vec{r}, R_{AB})$ to $\psi_{\text{el}}(\lambda, \mu, \phi, R_{AB})$



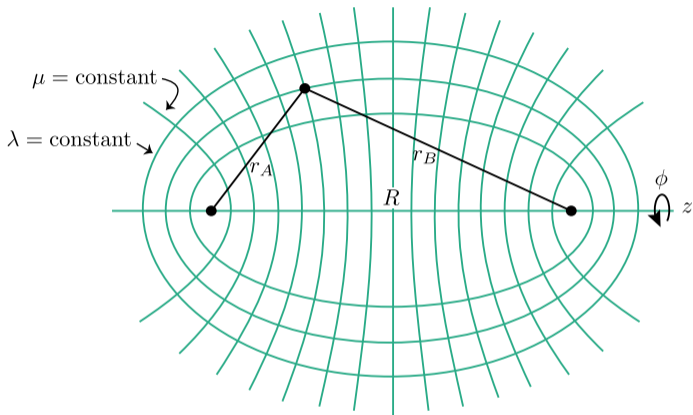
- We can derive exact solution for $\psi_{\text{el}}(\vec{r}, R_{AB})$ using *spheroidal coordinates*, where $\lambda = (r_A + r_B)/R$, $\mu = (r_A - r_B)/R$, and R is internuclear distance.
- Lines of constant λ are ellipses which share foci r_A and r_B .
- Lines of constant μ are hyperbolas with r_A and r_B as foci.
- Ellipses and hyperbolas form orthogonal system of curves.

Spheroidal Coordinates : $\psi_{el}(\vec{r}, R_{AB})$ to $\psi_{el}(\lambda, \mu, \phi, R_{AB})$



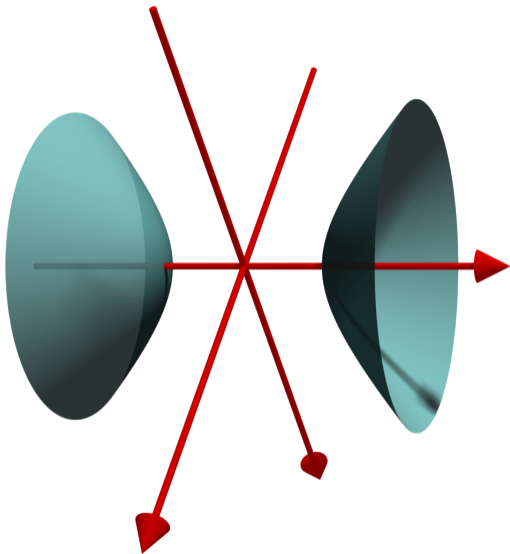
- Variable λ varies over range $1 \leq \lambda \leq \infty$, and plays role analogous to r in usual polar coordinate system.
- Variable μ varies over range $-1 \leq \mu \leq 1$.
- As μ changes point (λ, μ) moves around origin, so μ plays role similar to quantity $\cos \theta$ in polar coordinates.

Spheroidal Coordinates : $\psi_{el}(\vec{r}, R_{AB})$ to $\psi_{el}(\lambda, \mu, \phi, R_{AB})$

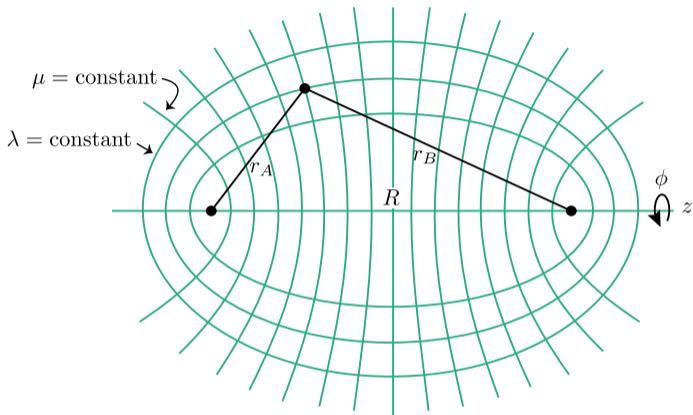


- Three dimensional prolate ellipsoidal coordinates are obtained by rotating figure around z axis.
- Ellipses generate set of confocal ellipsoids
- Hyperbolas generate family of hyperboloids with 2 sheets.
- Surface of constant ϕ are half-planes through x axis.

Two sheet hyperboloid

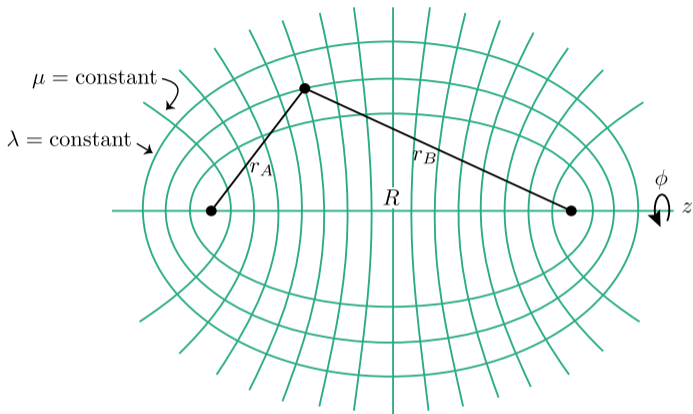


Spheroidal Coordinates : $\psi_{el}(\vec{r}, R_{AB})$ to $\psi_{el}(\lambda, \mu, \phi, R_{AB})$



- Prolate ellipsoidal coordinates in 3D space are obtained by rotating figure around z axis.
- Ellipses generate set of confocal ellipsoids
- Hyperbolas generate family of hyperboloids with 2 sheets.
- Surface of constant ϕ are half-planes through x axis.

Spheroidal Coordinates : $\psi_{el}(\vec{r}, R_{AB})$ to $\psi_{el}(\lambda, \mu, \phi, R_{AB})$



Spheroidal Coordinates allows us to separate wave function into product

$$\psi(\lambda, \mu, \phi) = L(\lambda)M(\mu)\Phi(\phi)$$

Substituting $\psi(\lambda, \mu, \phi)$ into electronic wave equation gives 3 ODEs.

We'll do no derivations, just look at results ...

Solutions to $\Phi(\phi)$

Solutions to $\Phi(\phi)$ which are eigenfunctions of \hat{L}_z ,

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

Each value of $|m|$ leads to different energy. States associated with $\pm m$ are degenerate.

We refer to states by their m value:

$$\left. \begin{array}{ll} m = 0 & \sigma \text{ state,} \\ m = \pm 1 & \pi \text{ state,} \\ m = \pm 2 & \delta \text{ state,} \end{array} \right\} \begin{array}{l} \text{these follow same letter} \\ \text{sequence as } \ell \text{ using} \\ \text{Greek letters instead.} \end{array}$$

States are also labeled by their *inversion symmetry*.

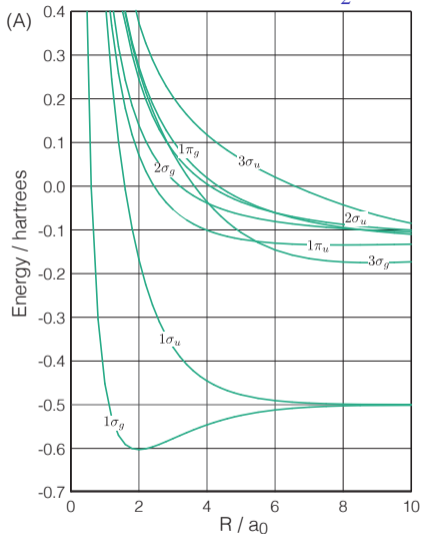
$$\begin{array}{ll} \text{when } \psi_u(\vec{r}) = -\psi_u(-\vec{r}), & \text{odd symmetry,} \\ \text{when } \psi_g(\vec{r}) = \psi_g(-\vec{r}), & \text{even symmetry,} \end{array}$$

Use subscript u for odd wave functions (ungerade)

Use subscript g for even wave functions (gerade).

Wave functions labeled as σ_g , σ_u , π_g , π_u , δ_g , δ_u , and so on.

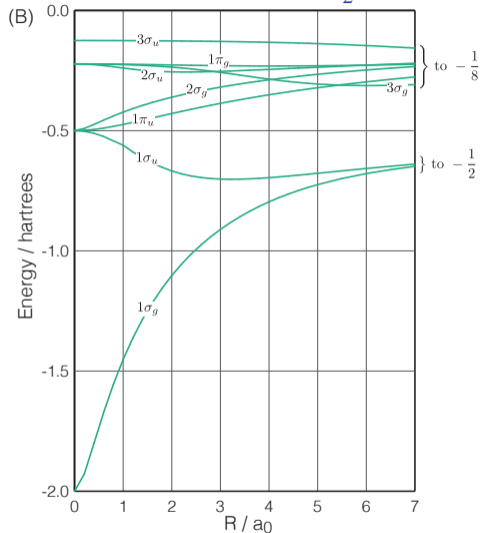
Lowest energy levels of H_2^+ as function of internuclear R



- Minimum in $1\sigma_g$ energy is $R_e \approx 2a_0$, corresponding to equilibrium length of $1\sigma_g$ ground state of H_2^+ .
- As $R \rightarrow \infty$ energy of $1\sigma_g$ state approaches $-0.5E_h$.
As expected, this is energy of electron in $1s$ state of H-atom infinitely separated from isolated proton.
Difference between this energy and energy at equilibrium bond length is binding energy,
 $E_{1\sigma_g}(R_e) - E_{1\sigma_g}(\infty) = 0.1E_h$.
- Both equilibrium distance and binding energy from this exact solution are in excellent agreement with experimentally determined values of $2.00a_0$ and $0.102E_h$, respectively.

with internuclear repulsive energy.

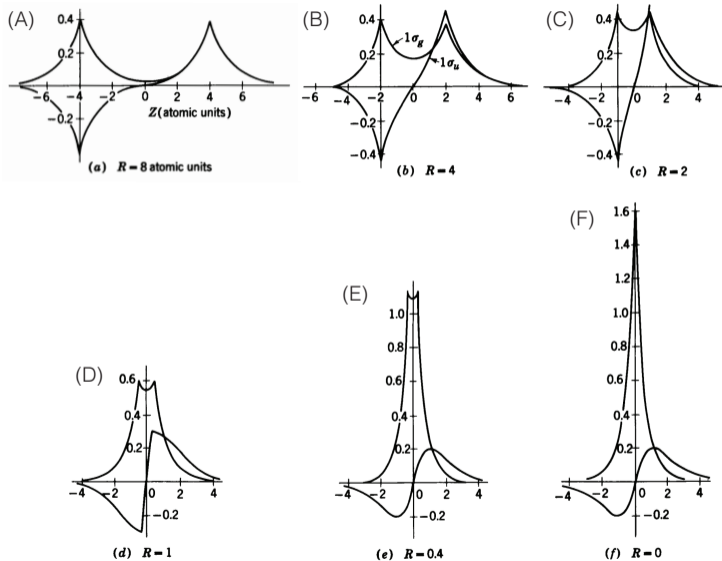
Lowest energy levels of H_2^+ as function of internuclear R



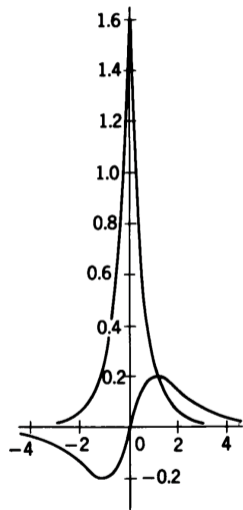
As $R \rightarrow 0$, i.e., both protons at origin form He nucleus, we find energy of $-2E_h$. This is ground state energy of single electron bound to He nucleus.

without internuclear repulsive energy.

Exact solutions for $1\sigma_g$ and $1\sigma_u$ of H_2^+ as a function of R



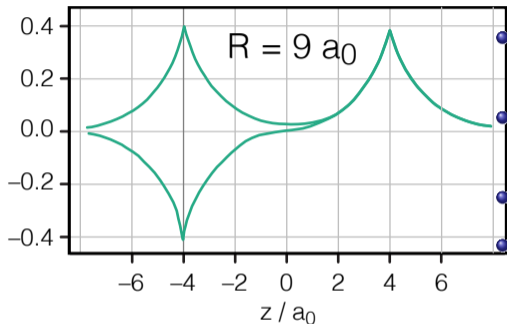
Shape of H_2^+ wave functions



(f) $R = 0$

When $R = 0$ solution becomes identical to He^+ wave function.

Shape of H_2^+ wave functions



- When $R = 8a_0$ observe 2 sharp peaks at $\pm 4a_0$ where nuclei are located.
- When $R \rightarrow \infty$ two peaks correspond to 1s orbital centered on each nucleus.
- In case of H_2^+ only one of these 1s orbitals is occupied.
- Difference between $1\sigma_g$ and $1\sigma_u$ is in how two 1s orbitals are combined.

- Normalization factors aside, in $R \rightarrow \infty$ limit we find (in atomic units)

$$1\sigma_g = e^{-r_A} + e^{-r_B}, \quad \text{and} \quad 1\sigma_u = -e^{-r_A} + e^{-r_B}.$$

- Results suggest approximate approach to describe bonding wave functions as a *linear combination of atomic orbitals* (LCAO) on each nucleus.

- LCAO approach more useful than exact solution—which only works for H^+

Linear Combination of Atomic Orbitals (LCAO)

Linear Combination of Atomic Orbitals (LCAO)

Use variational theorem with LCAO as trial H_2^+ wave function

$$\psi_{\text{guess}}(\vec{r}, R_{AB}) = c_A \phi_{1s_A} + c_B \phi_{1s_B}$$

ϕ_{1s_A} and ϕ_{1s_B} are atomic orbitals associated with e^- in 1s orbital on nuclei A and B, respectively. There are 2 adjustable parameters, c_A and c_B , in ψ_{guess} .

$$\langle \hat{H} \rangle = \int \psi_{\text{guess}}^* \hat{H} \psi_{\text{guess}} d\tau \geq E_0$$

E_0 is true ground state energy. Can't assume trial wave function is normalized so need to minimize energy for

$$E = \frac{\int_V \psi_{\text{guess}}^* \hat{H} \psi_{\text{guess}} d\tau}{\int_V \psi_{\text{guess}}^* \psi_{\text{guess}} d\tau} \geq E_0$$

Even though atomic orbitals are normalized, LCAO wave function is not. Substituting $\psi_{\text{guess}}(\vec{r}, R_{AB})$ we obtain

$$E = \frac{c_A^2 \int_V \phi_{1s_A}^* \hat{H} \phi_{1s_A} d\tau + c_B^2 \int_V \phi_{1s_B}^* \hat{H} \phi_{1s_B} d\tau + 2c_A c_B \int_V \phi_{1s_A}^* \hat{H} \phi_{1s_B} d\tau}{c_A^2 + c_B^2 + 2c_A c_B \int_V \phi_{1s_A}^* \phi_{1s_B} d\tau} \geq E_0$$

Linear Combination of Atomic Orbitals (LCAO)

To simplify equations define

$$H_{AB} \equiv \int_V \phi_{1s_A}^* \hat{H} \phi_{1s_B} d\tau, \quad \text{and} \quad S_{AB} \equiv \int_V \phi_{1s_A}^* \phi_{1s_B} d\tau$$

S_{AB} is called *overlap integral*. These definitions allow us to write

$$E = \frac{c_A^2 H_{AA} + c_B^2 H_{BB} + 2c_A c_B H_{AB}}{c_A^2 + c_B^2 + 2c_A c_B S_{AB}} \geq E_0$$

Next, find values of c_A and c_B where E is at minimum by taking derivative of E wrt c_A and c_B and setting equal to zero,

$$\frac{\partial E}{\partial c_A} = 0, \quad \text{and} \quad \frac{\partial E}{\partial c_B} = 0$$

To make this easier let's move the denominator to the left

$$(c_A^2 + c_B^2 + 2c_A c_B S_{AB}) E = c_A^2 H_{AA} + c_B^2 H_{BB} + 2c_A c_B H_{AB}$$

Linear Combination of Atomic Orbitals (LCAO)

Taking the derivative of both sides

$$\frac{\partial}{\partial c_A} (c_A^2 + c_B^2 + 2c_A c_B S_{AB}) E = \frac{\partial}{\partial c_A} (c_A^2 H_{AA} + c_B^2 H_{BB} + 2c_A c_B H_{AB})$$

gives

$$(2c_A + 2c_B S_{AB})E + (c_A^2 + c_B^2 + 2c_A c_B S_{AB}) \frac{\partial E}{\partial c_A} = 2c_A H_{AA} + 2c_B H_{AB}$$

Doing same with $\partial/\partial c_B$ gives

$$(2c_B + 2c_A S_{AB})E + (c_A^2 + c_B^2 + 2c_A c_B S_{AB}) \frac{\partial E}{\partial c_B} = 2c_B H_{BB} + 2c_A H_{AB}$$

Setting $\partial E/\partial c_A = \partial E/\partial c_B = 0$ leads to two simultaneous equations

$$c_A(H_{AA} - E) + c_B(H_{AB} - ES_{AB}) = 0$$

$$c_A(H_{AB} - ES_{AB}) + c_B(H_{BB} - E) = 0$$

Linear Combination of Atomic Orbitals (LCAO)

Writing these in matrix form gives

$$\begin{pmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

Matrix diagonalization problem can be solved with determinant,

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

In homonuclear example make it little easier since $H_{AA} = H_{BB} = \alpha$.

Also set $H_{AB} = \beta$ and $S = S_{AB}$

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0, \quad \text{which gives} \quad (\alpha - E)^2 - (\beta - ES)^2 = 0$$

Linear Combination of Atomic Orbitals (LCAO)

$$(\alpha - E)^2 - (\beta - ES)^2 = 0$$

which leads to

$$\alpha - E = \pm(\beta - ES) = \pm\beta \mp ES$$

and we find 2 solutions for E :

$$E_+ = \frac{\alpha + \beta}{1 + S} \quad \text{and} \quad E_- = \frac{\alpha - \beta}{1 - S}$$

Putting solution for E_+ back into simultaneous Eqs one can show that $c_A = c_B$.

Put solution for E_- into 2 simultaneous equations and obtain $c_A = -c_B$.

Thus, 2 solutions for wave function are

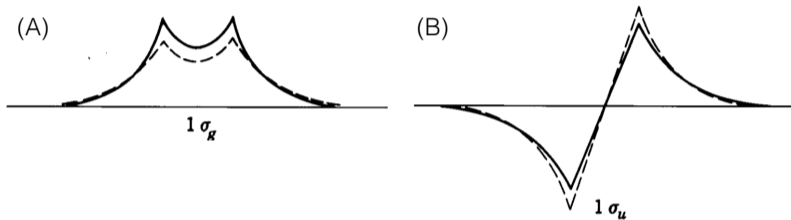
$$\psi_{\sigma_g} = c \left(\phi_{1s_A} + \phi_{1s_B} \right), \quad \text{and} \quad \psi_{\sigma_u} = c \left(\phi_{1s_A} - \phi_{1s_B} \right)$$

Normalizing these two wave functions gives

$$\psi_{\sigma_g} = \frac{1}{\sqrt{2 + 2S}} \left(\phi_{1s_A} + \phi_{1s_B} \right) \quad \text{and} \quad \psi_{\sigma_u} = \frac{1}{\sqrt{2 - 2S}} \left(\phi_{1s_A} - \phi_{1s_B} \right)$$

Linear Combination of Atomic Orbitals (LCAO)

Bring two 1s orbitals together in phase for ψ_{σ_g} and out of phase for ψ_{σ_u}



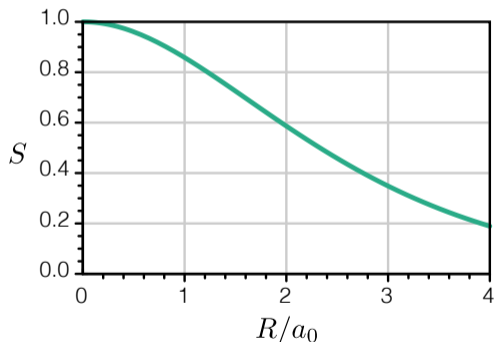
Above is comparison of Exact (solid lines) and LCAO (dashed lines) wave functions ψ_{σ_g} and ψ_{σ_u} for H_2^+ with $R = 2$ for (A) bonding and (B) anti-bonding states.

Simple LCAO approximation is not bad, and is good starting point for refining LCAO method.

LCAO : Overlap Integral S

To finish derivation need to evaluate overlap integral S and energies. Starting with S we find

$$S = \int_V \phi_{1s_A}^* \phi_{1s_B} d\tau = e^{-R_{AB}} \left(1 + R_{AB} + \frac{R_{AB}^2}{3} \right)$$



As expected, overlap integral goes to zero in limit that $R \rightarrow \infty$.

With decreasing R overlap integral increases and reaches value of 1 at $R = 0$.

LCAO : Coulomb Integral

α integral is called Coulomb Integral

$$\alpha = \int_V \phi_{1s_A}^* \hat{H} \phi_{1s_A} d\tau$$

To evaluate α start with electronic Hamiltonian in atomic units

$$\hat{H} = -\frac{1}{2} \nabla_e^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R_{AB}}$$

which can be written
$$\hat{H} = \hat{H}_A - \frac{1}{r_B} + \frac{1}{R_{AB}} \quad \text{or} \quad \hat{H} = \hat{H}_B - \frac{1}{r_A} + \frac{1}{R_{AB}}$$

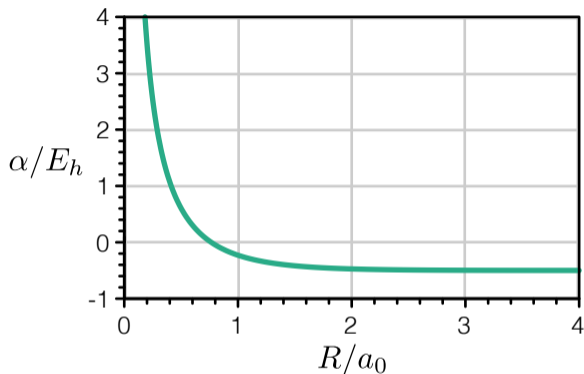
\hat{H}_A or \hat{H}_B are Hamiltonians for e^- in H-atom alone. Thus,

$$\alpha = \int_V \phi_{1s_A}^* \left[\hat{H}_A - \frac{1}{r_B} + \frac{1}{R_{AB}} \right] \phi_{1s_A} d\tau = \int_V \phi_{1s_A}^* \hat{H}_A \phi_{1s_A} d\tau - \int_V \phi_{1s_A}^* \frac{1}{r_B} \phi_{1s_A} d\tau + \frac{1}{R_{AB}}$$

which gives
$$\alpha = E_{1s} + \frac{2E_{1s}}{R_{AB}} \left[1 - e^{-2R_{AB}} (1 + R_{AB}) \right] + \frac{1}{R_{AB}}$$

Coulomb Integral contains energy of e^- in 1s orbital of H-atom, attractive energy of nucleus B for e^- , and repulsive force of nuclei B with A.

LCAO : Coulomb Integral



α decreases monotonically (i.e., no minimum) from ∞ at $R_{AB} = 0$ to $-1/2$ at $R_{AB} = \infty$. In other words, α , which is leading term in

$$E_+ = \frac{\alpha + \beta}{1 + S} \quad \text{and} \quad E_- = \frac{\alpha - \beta}{1 - S}$$

does not give any stability to H_2^+ over 2 infinitely separated nuclei (recall H atom has energy of $-E_h/2$).

LCAO : Exchange Integral

Finally, examine β integral, also called the resonance or Exchange Integral

$$\beta = \int_V \phi_{1s_A}^* \hat{H} \phi_{1s_B} d\tau$$

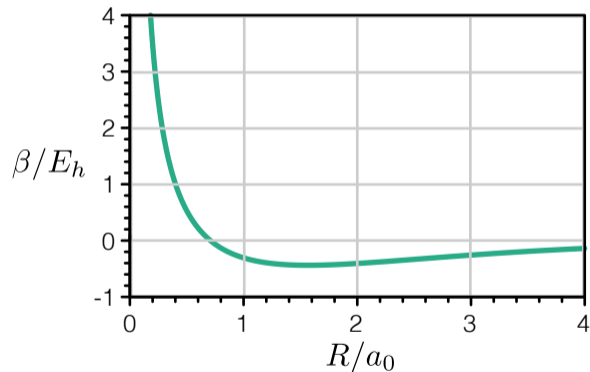
which becomes

$$\beta = \int_V \phi_{1s_A}^* \left[\hat{H}_B - \frac{1}{r_A} + \frac{1}{R_{AB}} \right] \phi_{1s_B} d\tau = \int_V \phi_{1s_A}^* \hat{H}_B \phi_{1s_B} d\tau - \int_V \phi_{1s_A}^* \frac{1}{r_A} \phi_{1s_B} d\tau + \int_V \phi_{1s_A}^* \frac{1}{R_{AB}} \phi_{1s_B} d\tau$$

to obtain

$$\beta = E_{1s} S + 2E_{1s} e^{-R_{AB}} (1 + R_{AB}) + \frac{S}{R_{AB}}$$

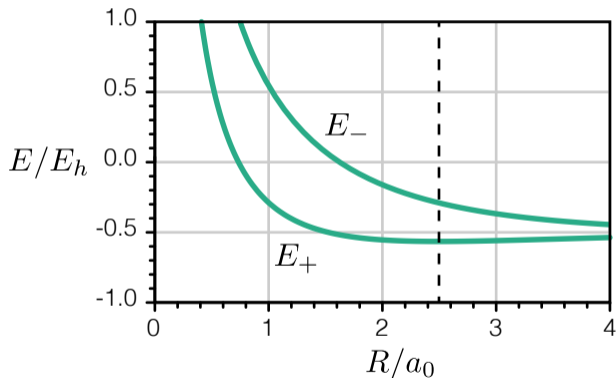
LCAO : Exchange Integral



- β integral goes through a minimum in energy.
- It is stabilization energy from allowing e^- to move (exchange) between 2 nuclei.
- Since both α and β are negative, E_+ will be lowest energy,

$$E_{1\sigma_g} = E_+ = \frac{\alpha + \beta}{1 + S}, \quad (\text{bonding})$$

LCAO : Energy



- LCAO model predicts that energy of ground state has minimum at bond length of $R_e = 2.50a_0$ and has binding energy of $E_+(R_e) - E(\infty) = 0.0648E_h$.
- Predicted bond length is longer than experimentally observed $R_e = 2.00a_0$
- Predicted binding energy is lower than experimentally observed value of $0.102E_h$.

LCAO : Energy

Anti-bonding orbital energy is

$$E_{1\sigma_u} = E_- = \frac{\alpha - \beta}{1 - S}, \quad (\text{anti-bonding})$$

- This orbital gives no stability since β raises total energy in this case.
- Putting lone electron into $\psi_{1\sigma_u}$ would destabilize H_2^+ molecule and cause it to break apart.