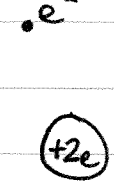
Helium Atom



	Position	mass	charge
nucleus	$\vec{R}$	M (4 amu)	$+2e$
e^-_1	$\vec{r}_1$	m_e	$-e$
e^-_2	$\vec{r}_2$	m_e	$-e$

Full Hamiltonian:

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2\right]\psi(\vec{R},\vec{r}_1,\vec{r}_2)$$

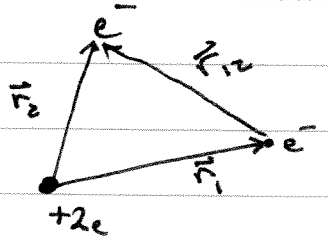
$$+\left[\frac{-2e^2}{4\pi\varepsilon_0|\vec{R}-\vec{r}_1|} - \frac{2e^2}{4\pi\varepsilon_0|\vec{R}-\vec{r}_2|} + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\right]\psi(\vec{R},\vec{r}_1,\vec{r}_2)$$

$$= E\psi(\vec{R},\vec{r}_1,\vec{r}_2)$$

Assume that the nucleus is fixed at the origin (reasonable since $M \gg m_e$)

$$\left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{r_1} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{r_2} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{12}}\right]\psi(\vec{r}_1,\vec{r}_2)$$

$$= E\psi(\vec{r}_1,\vec{r}_2)$$



$r_1 = |\vec{r}_1|$

$r_2 = |\vec{r}_2|$

$r_{12} = |\vec{r}_{12}|$

$$\hat{H}_H(1) = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{r_1}$$

$$\hat{H}_H(2) = -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{r_2}$$

$$\hat{H} = \hat{H}_H(1) + \hat{H}_H(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

To be more general, let's give the nucleus a $+Z$ charge:

$$\hat{H} = \frac{-\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

Atomic units : make writing solutions much easier.

$\hbar = 1$ a.u. of angular momentum

$m_e = 1$ a.u. of mass

$e = 1$ a.u. of charge

$a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2} = 1$ a.u. of length

$4\pi\varepsilon_0 = 1$ a.u. of permittivity

$\frac{m_e e^4}{(4\pi\varepsilon_0)^2\hbar^2} = 1$ a.u. of energy $= 1$ Hartree.

Conversions: $M_p = 1\text{amu} = \frac{1.661\times10^{-27}\text{kg}}{1\text{amu}} \times \frac{1\text{a.u.}}{9.11\times10^{-31}\text{kg}} = 1822.2$ a.u.

$$c = 2.99\times10^8\ \frac{\text{m}}{\text{s}} \times \frac{1\text{a.u}}{0.529177\times10^{-10}\text{m}} \times \frac{2.42\times10^{-17}\text{s}}{\text{a.u.}} = 136.7\ \text{a.u.}$$

$$\hat{H} = \underbrace{-\frac{\nabla_1^2}{2} - \frac{Z}{r_1}}_{\hat{H}_H(1)} + \underbrace{-\frac{\nabla_2^2}{2} - \frac{Z}{r_2}}_{\hat{H}_H(2)} + \underbrace{\frac{1}{r_{12}}}_{\hat{H}'}$$

Trial function:

$$\phi(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = \underbrace{\psi_{n_1 l_1 m_1}(r_1,\theta_1,\phi_1)\psi_{n_2 l_2 m_2}(r_2,\theta_2,\phi_2)}_{\text{product of H-atom wavefunctions}}$$

$$\hat{H}_H(1)\,\psi_{n_1 l_1 m_1} = E_{n_1}\,\psi_{n_1 l_1 m_1}$$

$$\hat{H}_H(2)\,\psi_{n_2 l_2 m_2} = E_{n_2}\,\psi_{n_2 l_2 m_2}$$

$$\left(\hat{H}_H(1)+\hat{H}_H(2)\right)\Phi = \psi_{n_2 l_2 m_2}\,\hat{H}_H(1)\,\psi_{n_1 l_1 m_1} + \psi_{n_1 l_1 m_1}\,\hat{H}_H(2)\,\psi_{n_2 l_2 m_2}$$

$$= (E_{n_1}+E_{n_2})\,\psi_{n_1 l_1 m_1}\,\psi_{n_2 l_2 m_2}$$

$$= \left(\frac{-Z^2 e^2}{n_1^2 8\pi\varepsilon_0 a_0} - \frac{Z e^2}{n_2^2 8\pi\varepsilon_0 a_0}\right)\Phi$$

$$= -\frac{Z^2}{2}\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)\Phi$$

Ground State: $n_1 = n_2 = 1$

$l_1 = l_2 = 0$

$m_1 = m_2 = 0$

E_0 (without H') $= -\frac{Z^2}{2}(1+1) = -Z^2$

if $Z=2$, $E_0 = -4$ a.u. $= -108.8$ eV

$$\psi_{1s^2} = 1s(1)\cdot 1s(2) = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Z r_1}\;\frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Z r_2}$$

Experimentally,

$He \longrightarrow He^+ + e^-$ 24.59 eV (1^{st} IE)

$He^+ \longrightarrow He^{2+} + e^-$ 54.42 eV (2^{nd} IE)

$He \longrightarrow He^{2+} + 2e^-$ 79.01 eV

% error $= \frac{108.8-79.0}{79.0} =$ 37.7% (not good)

Including $e^- - e^-$ repulsion

$$E = \langle 1s(1)\,1s(2) \mid \hat{H} \mid 1s(1)\,1s(2)\rangle$$

$$= \langle 1s(1)\,1s(2) \mid \hat{H}_H(1) + \hat{H}_H(2) + \hat{H}' \mid 1s(1)\,1s(2)\rangle$$

$$= \langle 1s(1)\,1s(2) \mid \hat{H}_H(1) \mid 1s(1)\,1s(2)\rangle + \langle 1s(1)\,1s(2) \mid \hat{H}_H(2) \mid 1s(1)\,1s(2)\rangle + \langle 1s(1)\,1s(2) \mid \hat{H}' \mid 1s(1)\,1s(2)\rangle$$

$$= \langle 1s(1) \mid \hat{H}_H(1) \mid 1s(1)\rangle \underbrace{\langle 1s(2) \mid 1s(2)\rangle}_{\to 1} + \langle 1s(2) \mid \hat{H}_H(2) \mid 1s(2)\rangle \underbrace{\langle 1s(1) \mid 1s(1)\rangle}_{\to 1} + \langle 1s(1)\,1s(2) \mid \hat{H}' \mid 1s(1)\,1s(2)\rangle$$

$$= E_{1s} + E_{1s} + \langle 1s(1)\,1s(2) \mid \hat{H}' \mid 1s(1)\,1s(2)\rangle$$

$$= -Z^2 + \langle 1s(1)\,1s(2) \mid \hat{H}' \mid 1s(1)\,1s(2)\rangle$$

$$\langle H' \rangle = \frac{Z^6}{\pi^2} \int_0^{2\pi} d\phi_1 \int_0^{\pi} \sin\theta_1\, d\theta_1 \int_0^{\infty} dr_1 \int_0^{2\pi} d\phi_2 \int_0^{\pi} \sin\theta_2\, d\theta_2 \int_0^{\infty} dr_2 \; (r_1^2 e^{-2Zr_1}) \frac{1}{r_{12}} (r_2^2 e^{-2Zr_2})$$

r_{12} depends on all of the coordinates! This makes it painful.

Expansion of $\frac{1}{r_{12}}$ (Derivable, but very difficult)

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_l^m(\theta_1, \phi_1)^* Y_l^m(\theta_2, \phi_2)$$

$r_<$ = smaller of r_1 & r_2

$r_>$ = larger of r_1 & r_2

$$\langle H' \rangle = \frac{Z^6}{\pi^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \int_0^\infty dr_1 \int_0^\infty dr_2 \, e^{-2Zr_1} e^{-2Zr_2} \frac{r_<^l}{r_>^{l+1}} r_1^2 r_2^2$$

$$\times \int_0^{2\pi} d\phi_1 \int_0^{\pi} d\theta_1 \; Y_l^m(\theta_1,\phi_1)^* \left(\frac{Y_0^0(\theta_1,\phi_1)}{Y_0^0(\theta_1,\phi_1)} \right) \sin\theta_1$$

$$\times \int_0^{2\pi} d\phi_2 \int_0^{\pi} d\theta_1 \; Y_l^m(\theta_2,\phi_2) \left(\frac{Y_0^0(\theta_2,\phi_2)}{Y_0^0(\theta_2,\phi_2)} \right)^* \sin\theta_2$$

$Y_0^0 = \frac{1}{\sqrt{4\pi}}$, so:

$$\langle H' \rangle = \frac{Z^6 (4\pi)^2}{\pi^2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \int_0^\infty dr_1 \int_0^\infty dr_2 \, e^{-2Zr_1} e^{-2Zr_2} \frac{r_<^l}{r_>^{l+1}} r_1^2 r_2^2$$

$$* \quad \delta_{l,0} \quad \delta_{m,0}$$

$$* \quad \delta_{l,0} \quad \delta_{m,0}$$

$$= 16 Z^6 \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \int_0^\infty \int_0^\infty e^{-2Zr_1} e^{-2Zr_2} \frac{r_<^l}{r_>^{l+1}} r_1^2 r_2^2 \, dr_1 dr_2 \, \delta_{l0} \delta_{m0}$$

$$= 16 Z^6 \int_0^\infty dr_1 \int_0^\infty dr_2 \, e^{-2Zr_1} e^{-2Zr_2} \frac{1}{r_>} r_1^2 r_2^2$$

$$= 16 Z^6 \left[\int_0^\infty dr_2 \, e^{-2Zr_2} r_2^2 \left(\int_0^{r_2} dr_1 \, e^{-2Zr_1} \frac{r_1^2}{r_2} + \int_{r_2}^\infty dr_1 \, e^{-2Zr_1} \frac{r_1^2}{r_1} \right) \right]$$

$$= 16 Z^6 \left[\int_0^\infty dr_2 \, e^{-2Zr_2} r_2 \left(\int_0^{r_2} dr_1 \, e^{-2Zr_1} r_1^2 \right) + \int_0^\infty dr_2 \, e^{-2Zr_2} r_2^2 \left(\int_{r_2}^\infty dr_1 \, e^{-2Zr_1} r_1 \right) \right.$$

$$\int x e^{ax}\,dx = \frac{e^{ax}}{a^2}(ax-1)$$

$$\int x^2 e^{ax}\,dx = e^{ax}\left(\frac{x^2}{a} - \frac{2x}{a^2} - \frac{2}{a^3}\right)$$

$$\int_0^\infty e^{-ax} x^n\,dx = \frac{n!}{a^{n+1}}$$

After evaluating these integrals:

$$\langle H' \rangle = \frac{5Z}{8}$$

for $Z = 2$ $\quad \langle H' \rangle = \frac{5}{4}$

$$E = -4 + \frac{5}{4} = -\frac{11}{4}\text{ a.u.} = -74.82\text{ eV}$$

$$\%\text{ error} = \frac{74.82 - 79.01}{79.01} = 5.3\%$$ much better!

Can we do better? We've now introduced the $e^- - e^-$ repulsion, and gone from 38% error → 5.3%

The wavefunction we are using is:

$$\phi(\vec{r}_1, \vec{r}_2) = \frac{1}{\pi} Z^3 e^{-Zr_1} e^{-Zr_2}$$

We can do a variational treatment just by treating Z as a variational parameter

$$\phi(\vec{r}_1, \vec{r}_2) = \frac{1}{\pi} \alpha^3 e^{-\alpha r_1} e^{-\alpha r_2}$$

(This is like picking an effective nuclear charge)

This is justified because e^1 screens the full nuclear charge for e^2 and vice versa!

We should expect α to fall between

Z (no screening) and $Z-1$ (full screening)

So far, we've had the following

$$\hat{H} = \hat{H}_H(1) + \hat{H}_H(2) + \frac{1}{r_{12}}$$

$$-Z^2 \qquad + \frac{5}{8}Z$$

If We're a bit more careful about Z (in potential) vs. α in wavefunction, this is:

$$E(\alpha) = \left(\alpha^2 - 2Z\alpha + \frac{5}{8}\alpha\right)$$

goes back to $-Z^2 + \frac{5}{8}Z$ when $Z = 2$

α^2: from kinetic energies; $-2Z\alpha$: from e^--nucleus; $\frac{5}{8}\alpha$: from e^--e^- repulsion

$$\frac{\partial E}{\partial \alpha} = 2\alpha - 2Z + \frac{5}{8} = 0$$

$\alpha = Z - \frac{5}{16}$ ← between Z & $Z-1$

$\alpha = \frac{27}{16}$ ← for Helium

$$E = \left(Z - \frac{5}{16}\right)^2 - 2Z\left(Z - 5/16\right) + \frac{5}{8}\left(Z - \frac{5}{16}\right)$$

$$E = -\left(Z - \frac{5}{16}\right)^2$$

for $Z = 2$

$$E = -\left(2 - \frac{5}{16}\right)^2 = -2.85 \text{ a.u.} = -77.48 \text{ eV}$$

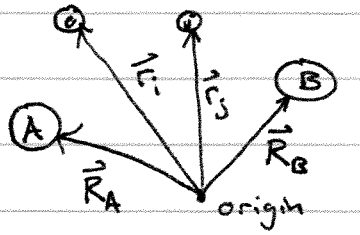
$$\% \text{ error} = \frac{|77.48 - 79.01|}{79.01} \times 100 = 1.9\%$$

Ignore $e^- - e^-$ repulsion $\longrightarrow$ 38% error

Include $e^- - e^-$ repulsion, use 1s (H-atom) $\longrightarrow$ 5.3% error

adjust wavefunction with screening $\longrightarrow$ 1.9% error

Molecules



$\vec{R}_A$ = position of nucleus A

$\vec{r}_i$ = position of electron i

$r_{iA} = |\vec{r}_{iA}| = |\vec{r}_i - \vec{R}_A|$

= distance from electron i to nucleus A

$r_{ij} = |\vec{r}_{ij}| = |\vec{r}_i - \vec{r}_j|$

= distance from electron i to electron j

$R_{AB} = |\vec{R}_{AB}| = |\vec{R}_A - \vec{R}_B|$

= distance from A to B

Full molecular Hamiltonian for N electrons and M nuclei:

$$H = \underbrace{-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2}_{\text{KE of electrons}} \underbrace{-\frac{\hbar^2}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2}_{\text{KE of nuclei}} \underbrace{-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{e^2 Z_A}{4\pi\varepsilon_0 r_{iA}}}_{e^- \text{-nuclear attraction}}$$

$$+ \underbrace{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}}_{e^- \text{-}e^- \text{ repulsion}} + \underbrace{\sum_{A=1}^{M-1}\sum_{B=A+1}^{M}\frac{e^2 Z_A Z_B}{4\pi\varepsilon_0 R_{AB}}}_{\text{nuclear-nuclear repulsion}}$$

Sum over unique pairs

Z_A = charge on nucleus A

In atomic unity

$$\hat{H} = -\sum_{i=1}^{N}\frac{\nabla_i^2}{2} - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{1}{r_{ij}}$$

$$+ \sum_{A=1}^{M-1}\sum_{B=A+1}^{M}\frac{Z_A Z_B}{R_{AB}}$$

The Born-Oppenheimer Approximation

Since $M_A \gg m_e$ (nuclear mass ≫ electron mass)

electrons move much faster than nuclei, and it is reasonable to treat the electrons as if they are moving in a stationary field due to the nuclei!

Consequences: $-\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 \rightarrow 0$ (KE of nuclei is ignored)

$\sum_{A=1}^{M-1} \sum_{B=A+1}^{M} \frac{Z_A Z_B}{R_{AB}}$ is a constant

(adds a constant to energy eigenvalues, but has no effect on electron wavefunctions)

$$\hat{H}_{elect} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{r_{ij}}$$

$$\hat{H}_{elect} \phi_{elect} = E_{elect} \phi_{elect}$$

$\phi_{elect}(\{\vec{r}_i\}; \{\vec{R}_A\})$ depends explicitly on electron coordinates, but only parametrically on nuclear positions.

1) Specify $\{\vec{R}_A\}$ ← molecular geometry
2) solve for ϕ_{elect}, E_{elect}
3) $E_{elect} = E_{elect}(\{\vec{R}_A\})$ ← electronic energy depends on where nuclei were set.
4) $V(\vec{R}) = E_{elect} + \sum_{A=1}^{M-1} \sum_{B=A+1}^{M} \frac{Z_A Z_B}{R_{AB}}$

Assuming Φ_{elect} & E_{elect} have been determined:

$$\hat{H}_{nucl} = -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + \langle \phi_{elec} | \hat{H}_{elect} | \phi_{elect} \rangle + \sum_A \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$

$$= -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + E_{elect}(\{\vec{R}\}) + \sum_A \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$

"Born-Oppenheimer" potential for the nuclei

$$= -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + V(\{\vec{R}\})$$

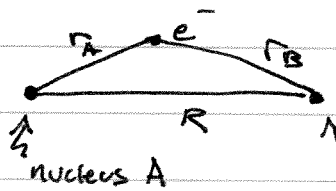
$\hat{H}_{nucl} \phi_{nucl} = E \phi_{nucl}$ describes translation, rotation, and vibration of a molecule

E is the Born-Oppenheimer approximation to the total energy

$$\Phi(\{\vec{r}\}, \{\vec{R}\}) = \phi_{elect}(\{\vec{r}\}; \{\vec{R}\}) \phi_{nucl}(\{\vec{R}\})$$

is the Born-Oppenheimer approximation to the <u>total</u> wavefunction.

<u>Molecular orbitals</u>



We can combine orbitals on each of the 2 atoms into a set of molecular orbitals

$\psi_{bonding} = c(1s_A + 1s_B)$ ← why is this "bonding"

$\psi_{anti\text{-}bonding} = c(1s_A - 1s_B)$

(H_2)

For multi-electron atoms, the simplest MO picture is to put as many electrons as possible into bonding orbitals: (e.g. for 2 electrons:

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{bonding}(1)\,\alpha(1) & \psi_{bonding}(1)\,\beta(1) \\ \psi_{bonding}(2)\,\alpha(2) & \psi_{bonding}(2)\,\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \underbrace{\psi_{bonding}(1)\,\psi_{bonding}(2)}_{\text{both electrons in } \psi_{bonding}} \underbrace{\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)}_{\text{one up \& one down but we don't know which is which.}}$$

$$E_{MO} = \int d\vec{r}_1 \int d\vec{r}_2\, \psi^* \hat{H} \psi \quad \leftarrow \quad \hat{H} = \underline{\text{electronic hamiltonian}}$$

$\Delta E_{binding} = E_{MO} - 2E_{1s} = 260\ \frac{kJ}{mol}$

(Experimentally this is $457\ \frac{kJ}{mol}$)

(what's missing?)

Let's simplify this further: H_2^+

$$\hat{H} = \frac{-\hbar^2}{2m_e}\nabla_e^2 - \frac{Z^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right) + \underbrace{\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{R}}_{\text{constant because } R \text{ is fixed}}$$

$\hat{H}\,\psi_j(\vec{r}_e; R) = E_j\,\psi_j(\vec{r}_e; R)$

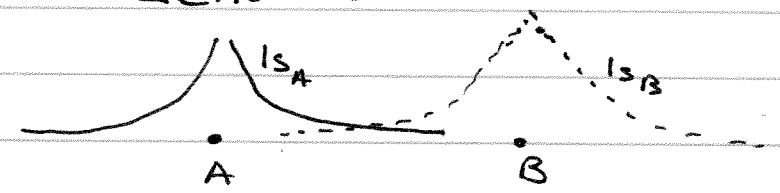
(R: a parameter (nuclear separation); ψ_j: a molecular orbital)

$$\phi_{trial} = c_1\,1s_A + c_2\,1s_B$$

$1s_A$: 1s orbital around nucleus A; $1s_B$: 1s orbital around nucleus B

This is a Linear Combination of Atomic Orbitals

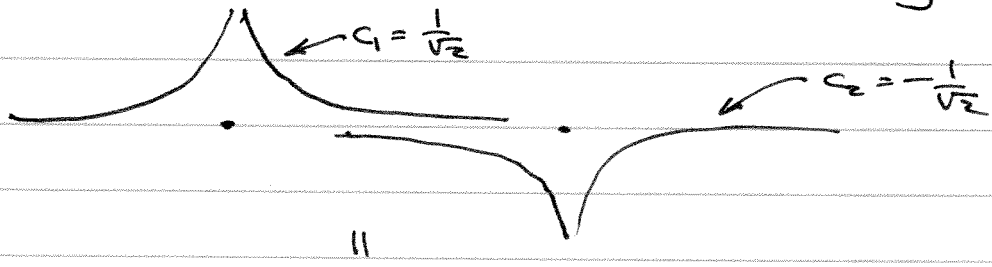
LCAO-MO

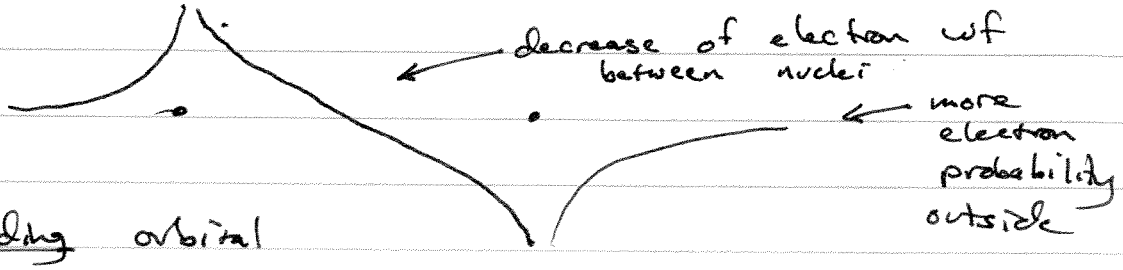


If $c_1 = c_2 = \frac{1}{\sqrt{2}}$

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

Buildup of electron wavefunction between nuclei = bonding





Anti-bonding orbital

Energetics of Molecular Orbitals

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \quad ; \quad |\phi\rangle \; |1s_A\rangle + |1s_B\rangle$$

Denominator first:

$$\langle \phi | \phi \rangle = \left(\langle 1s_A| + \langle 1s_B|\right)\left(|1s_A\rangle + |1s_B\rangle\right)$$

$$= \langle 1s_A | 1s_A\rangle + \langle 1s_A | 1s_B\rangle + \langle 1s_B | 1s_A\rangle + \langle 1s_B | 1s_B\rangle$$

$$= 1 + \int 1s_A^* \, 1s_B \, d\vec{r} + \int 1s_B^* \, 1s_A \, d\vec{r} + 1$$

(integrals: all space)

$$= 1 + S(R) + S(R) + 1$$

(overlap depends on how far nuclei are from each other.)

$$= 2 + 2S(R)$$

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

Numerator:

$$\langle \phi | \hat{H} | \phi \rangle = \cancel{1s_A} \; \left(\langle 1s_A| + \langle 1s_B|\right) \hat{H} \left(|1s_A\rangle + |1s_B\rangle\right)$$

$$\hat{H} = \frac{-\hbar^2}{2m_e}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

$$\left(-\frac{\nabla^2}{2} - \frac{1}{r_A}\right)|1s_A\rangle = E_{1s}\,|1s_A\rangle$$

$$\left(-\frac{\nabla^2}{2} - \frac{1}{r_B}\right)|1s_B\rangle = E_{1s}\,|1s_B\rangle$$

$$\langle \phi | \hat{H} | \phi \rangle = \left(\langle 1s_A| + \langle 1s_B|\right)\left[\left(E_{1s} - \frac{1}{r_B} + \frac{1}{R}\right)|1s_A\rangle + \left(E_{1s} - \frac{1}{r_A} + \frac{1}{R}\right)|1s_B\rangle\right]$$

We have to solve

$$J(R) = \langle 1s_A | \frac{1}{R} - \frac{1}{r_B} | 1s_A \rangle$$

"coulomb integral" (interacting with nucleus B)

↑ electron on atom A

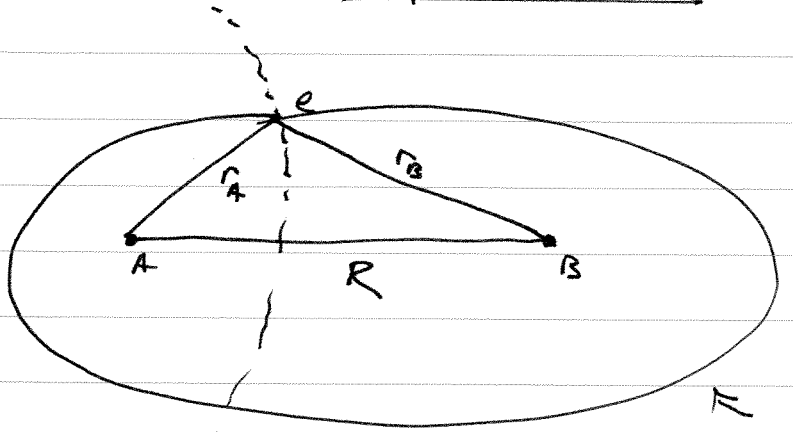
$$K(R) = \langle 1s_A | \frac{1}{R} - \frac{1}{r_B} | 1s_B \rangle$$

"exchange integral"

$$S(R) = \langle 1s_A | 1s_B \rangle$$

"overlap integral"

How to do these: elliptic coordinates



points of constant λ $(r_A + r_B)$

points of constant μ $(r_A - r_B)$

$$\lambda = \frac{r_A + r_B}{R} \qquad \mu = \frac{r_A - r_B}{R} \qquad \phi$$

$$1 \le \lambda \le \infty \qquad -1 \le \mu \le 1 \qquad 0 \le \phi \le 2\pi$$

$$d\vec{r} = dx\,dy\,dz \leftarrow \text{cartesian}$$

$$d\vec{r} = r^2 \sin\theta\, d\theta\, dr\, d\phi \leftarrow \text{spherical}$$

$$d\vec{r} = \frac{R^3}{8}(\lambda^2 - \mu^2)\, d\lambda\, d\mu\, d\phi \leftarrow \text{elliptic}$$

We'll do the <u>overlap</u> integral first:

$$S(R) = \int d\vec{r}\; 1s_A^* \, 1s_B$$

$$= \frac{Z^3}{\pi} \int d\vec{r}\; e^{-Zr_A} e^{-Zr_B}$$

$$= \frac{Z^3 R^3}{8\pi} \int_0^{2\pi} d\phi \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu\; (\lambda^2-\mu^2)\, e^{-Z(r_A+r_B)}$$

$$= \frac{Z^3R^3}{4} \int_1^{\infty} d\lambda \int_{-1}^{1} d\mu\; (\lambda^2-\mu^2)\, e^{-ZR\lambda}$$

$$= \frac{R^3Z^3}{4} \int_1^{\infty} e^{-ZR\lambda} d\lambda \int_{-1}^{1} (\lambda^2-\mu^2)\, d\mu$$

$$= \frac{R^3Z^3}{4} \int_1^{\infty} d\lambda\, e^{-ZR\lambda} \left[\lambda^2\mu - \frac{\mu^3}{3}\right]_{-1}^{1}$$

$$= \frac{R^3Z^3}{4} \int_1^{\infty} \left(2\lambda^2 - \frac{2}{3}\right) e^{-ZR\lambda} d\lambda$$

$$= \frac{R^3Z^3}{2} \left[\left(\frac{1}{ZR} - \frac{2}{Z^2R^2} + \frac{2}{Z^3R^3}\right) e^{-ZR} - \frac{1}{3ZR}\, e^{-ZR} \right]$$

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

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

The others are pretty much the same:

$$J(R) = \left\langle 1s_A \left| \frac{1}{R} - \frac{1}{r_B} \right| 1s_A \right\rangle$$

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

$$K(R) = \langle 1s_A | \frac{1}{R} - \frac{1}{r_A} | 1s_B \rangle$$

$$= \frac{S(R)}{R} - e^{-R}(R+1)$$

Remember:

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

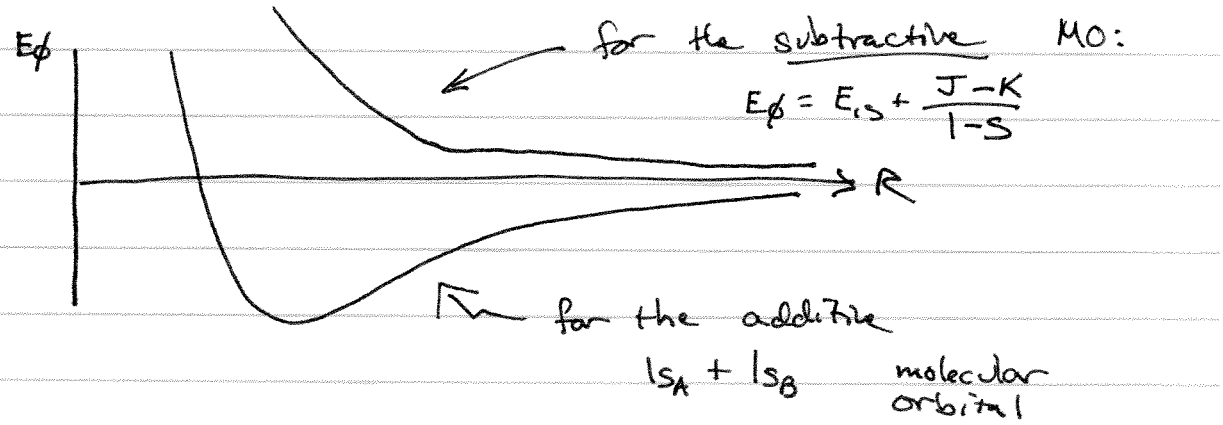
$$|\phi\rangle = |1s_A\rangle + |1s_B\rangle \quad \leftarrow \underline{\text{bonding}} \text{ MO}$$

$$\hat{H} = -\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

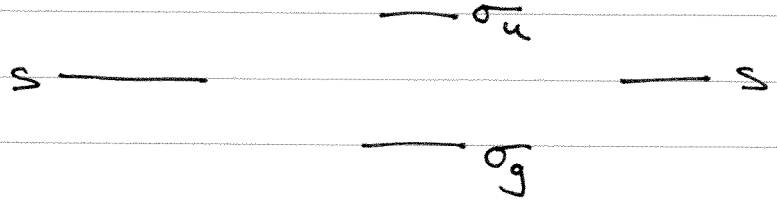
$$E_\phi = \frac{(\langle 1s_A| + \langle 1s_B|)\left(\frac{-\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right)(|1s_A\rangle + |1s_B\rangle)}{(\langle 1s_A| + \langle 1s_B|)\cdot(|1s_A\rangle + |1s_B\rangle)}$$

$$= \frac{2E_{1s}(1 + S(R)) + 2J(R) + 2K(R)}{2 + 2S(R)}$$

$$E_\phi = E_{1s} + \frac{J(R) + K(R)}{1 + S(R)}$$



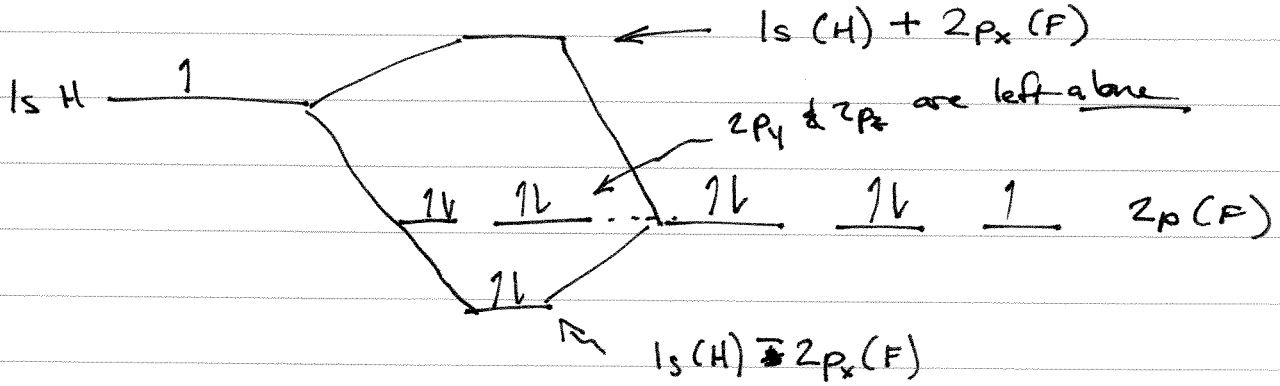
For Homonuclear diatomics:



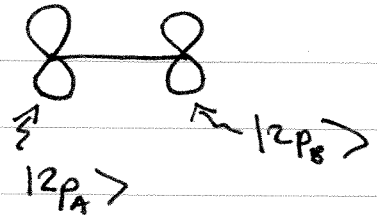
In general, when we take the linear combinations of $2n$ atomic orbitals (n from each atom) we have

$2n$ orbitals
- n lower in energy (g or bonding) than separated
- n higher in energy (u or anti-bonding) than separated

For Heteronuclear diatomics, we'll often leave uncombined some of the atomic orbitals



Hückel Theory: Ethene



Molecular orbitals: $|\psi\rangle = c_A|A\rangle + c_B|B\rangle$

$S = \langle A | B \rangle$

$\alpha_A = \langle A | \hat{H} | A \rangle$
$\alpha_B = \langle B | \hat{H} | B \rangle$ $\Big\} = \alpha$

$\beta = \langle A | \hat{H} | B \rangle = \langle B | \hat{H} | A \rangle$

To do the variational energies

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 = (\alpha - E)^2 - (\beta - ES)^2 = 0$$

Hückel theory has 3 rules:

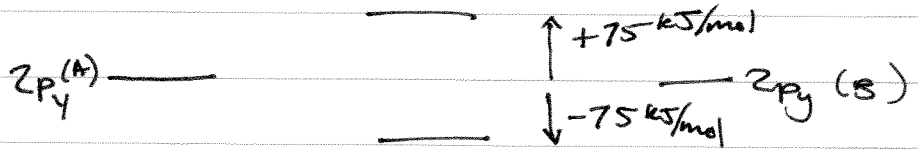
1) Overlap is <u>zero</u> between adjacent p orbitals ($S = 0$)
2) $\langle A | \hat{H} | B \rangle = 0$ <u>unless</u> B is a neighbor of A
3) All $\langle A | \hat{H} | B \rangle$ that remain are <u>identical</u>.

Ethene:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \qquad (\alpha - E)^2 - \beta^2 = 0$$

$$E_I = \alpha \pm \beta$$

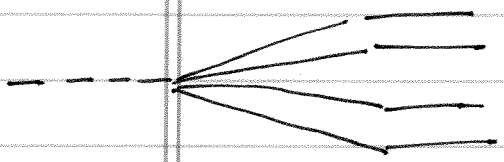
$\beta \sim -75\ kJ/mol$



$$\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix} = 0$$

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

$E = \alpha \pm 1.62\beta,\ \alpha \pm 0.62\beta$



2 pi bonding orbitals

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix}$$

$E = \alpha \pm 2\beta,\ \alpha \pm \beta,\ \alpha \pm \beta$ ← 6 roots!