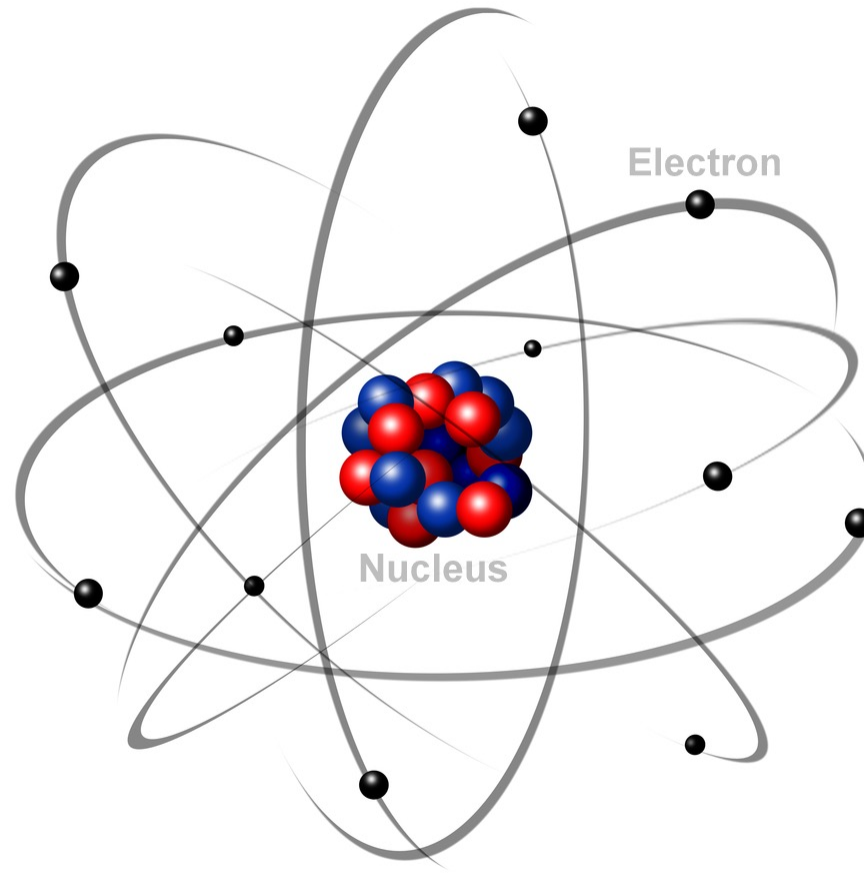# Multi-electron systems with DFT – optimizing, choosing basis sets, XC functional

June 13, 2022

Goals for this session

Review H_2^+ optimization to go over general structure of a computational quantum mechanics calculation

Be able to recognize the steps a molecule optimization code takes

Be able to describe the general types of basis sets, and be able to make general choices and check dependence of results on basis set
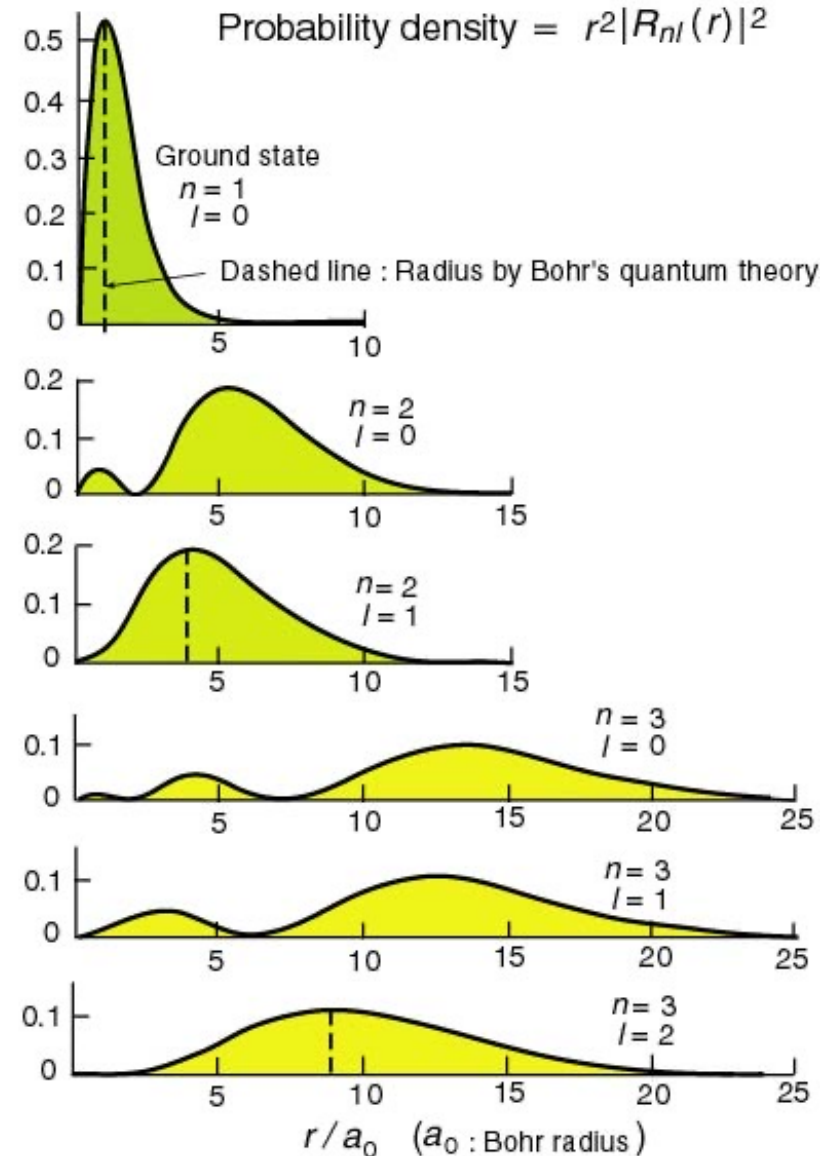
Be able to describe the types of exchange-correlation functionals and their rough hierarchical accuracy

The Hydrogen Atom – Radial Distribution Functions

Probability of finding the electron a given distance from the nuclei

$$prob(0, r') = \int_0^{r'} |R_{nl}(r)|^2 r^2 \, dr \; * $$

$$\iint |Y_l^m(\phi, \theta)|^2 sin\theta \, d\theta d\phi$$

Fig. (C)

Probability density $= r^2 |R_{nl}(r)|^2$

Ground state
$n = 1$
$l = 0$

Dashed line : Radius by Bohr's quantum theory

$n = 2$
$l = 0$

$n = 2$
$l = 1$

$n = 3$
$l = 0$

$n = 3$
$l = 1$

$n = 3$
$l = 2$

r / a_0 (a_0 : Bohr radius)

The Hydrogen Atom – Total Wavefunctions

Table 1: Wave functions and their components

| n	ℓ	m	$R_{n\ell}$	$Y_{\ell m}$	$\psi_{n\ell m} = R_{n\ell} Y_{\ell m}$
1	0	0	$2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$
2	0	0	$\left(\frac{1}{2a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0} e^{-r/2a_0}\cos\theta$
2	1	± 1	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0} e^{-r/2a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$	$\frac{1}{8}\sqrt{\frac{1}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0} e^{-r/2a_0}\sin\theta e^{\pm i\phi}$
3	0	0	$2\left(\frac{1}{3a_0}\right)^{3/2}\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}(r/a_0)^2\right) e^{-r/3a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(27 - 18\frac{r}{a_0} + 2(r/a_0)^2\right) e^{-r/3a_0}$
3	1	0	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\left(1 - \frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}\cos\theta$
3	1	± 1	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\left(1 - \frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$	$\frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$ ${1\over 81}\sqrt{2\over \pi}$ ... ${r\over a_0}\right)$
3	2	0	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$	$\frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2} e^{-r/3a_0}(3\cos^2\theta - 1)$
3	2	± 1	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$	$\pm\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{\pm i\phi}$	$\frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}\sin\theta\cos\theta e^{\pm i\phi}$
3	2	± 2	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2i\phi}$	$\frac{1}{162\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}\sin^2\theta e^{\pm 2i\phi}$

The Hydrogen Atom – Total Wavefunctions

s (n=1, 2, ..; l=0, m=0)
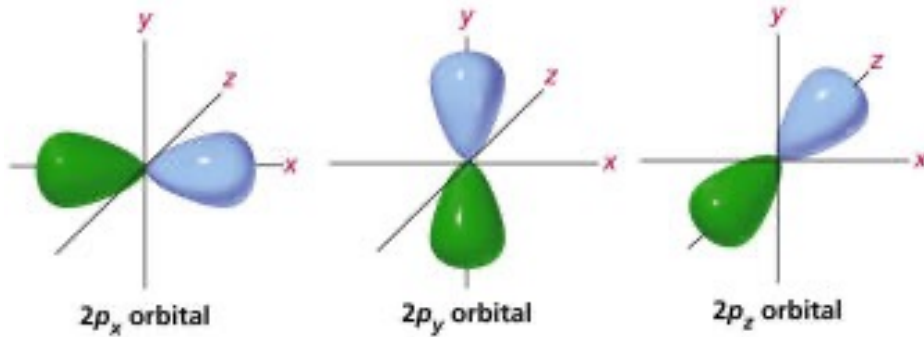
p (n=2, 3, …; l=1, m=-1,0,1)

d (n=3,4,…;l=2, m=-2, -1, 0, 1, 2)

2p_x orbital

2p_y orbital

2p_z orbital
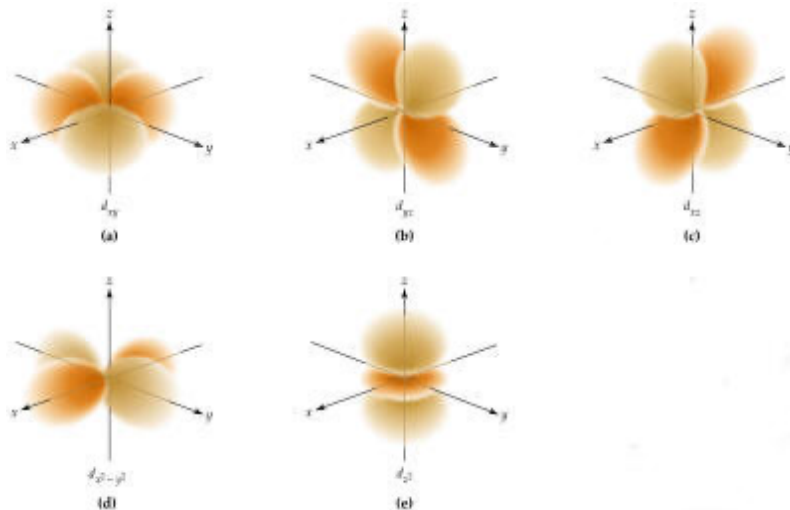
More than 1 electron: He atom Schrodinger Equation

$$H\psi(\vec{r}_1, \vec{r}_2) = \left[\sum_{i=1,2} \left(-\frac{\hbar^2}{2\mu}\nabla^2_{r_i} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) - \frac{\hbar^2}{M}\nabla_{r1} \cdot \nabla_{r2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right]\psi(\vec{r}_1, \vec{r}_2)$$

KE electron   e – nucleus   KE nucleus   electron-electron

$$\mu = \frac{mM}{m + M} \qquad \vec{r}_1 \quad \vec{r}_2 \text{ Distance vectors between electron and nucleus)}$$

$$r_{12} = \left| \vec{r}_1 - \vec{r}_2 \right|$$

Heavy atoms: Born-Oppenheimer approximation, removes KE nucleus term. In atomic units (ie, non-dimensionalized by constants):
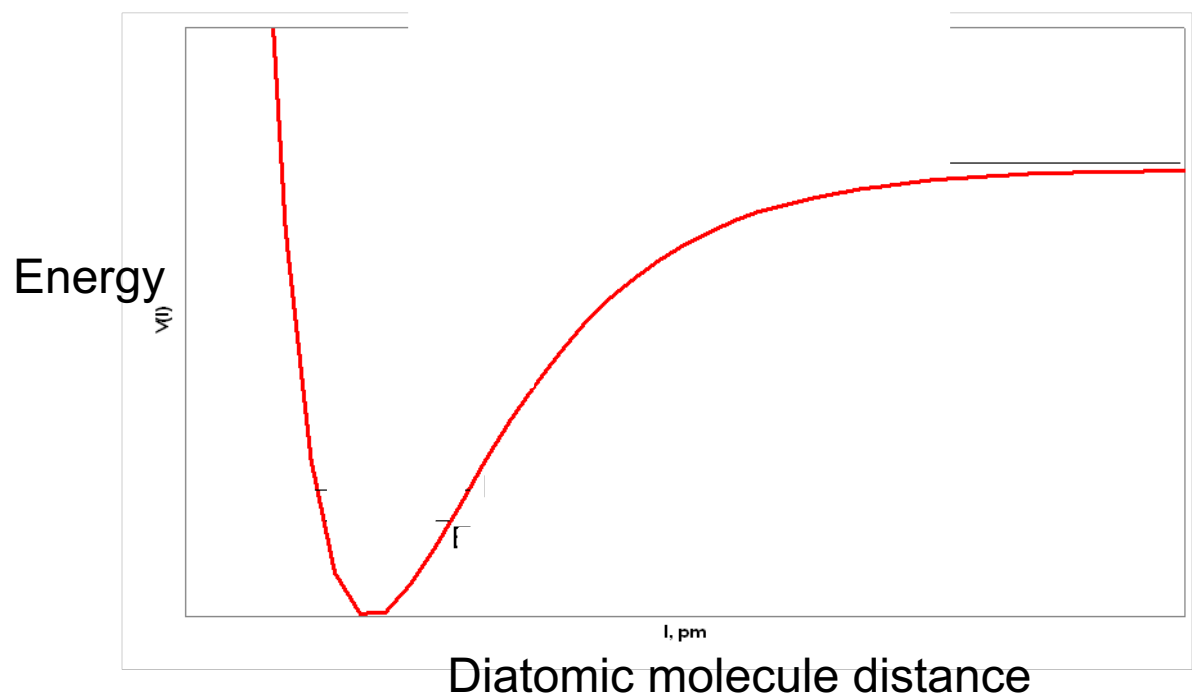
$$H\psi(\vec{r}_1, \vec{r}_2) = \left[-\frac{1}{2}\nabla^2_{r1} - \frac{1}{2}\nabla^2_{r2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right]\psi(\vec{r}_1, \vec{r}_2).$$

Wavefunction now a function of x_1, y_1, z_1, x_2, y_2, z_2 (or r_1, θ_1, ϕ_1, r_2, θ_2, ϕ_2).
Because of electron-electron term, this is not separable in any coordinate system.
Must be solved by approximate methods.

General first step: *ab initio* geometry optimization
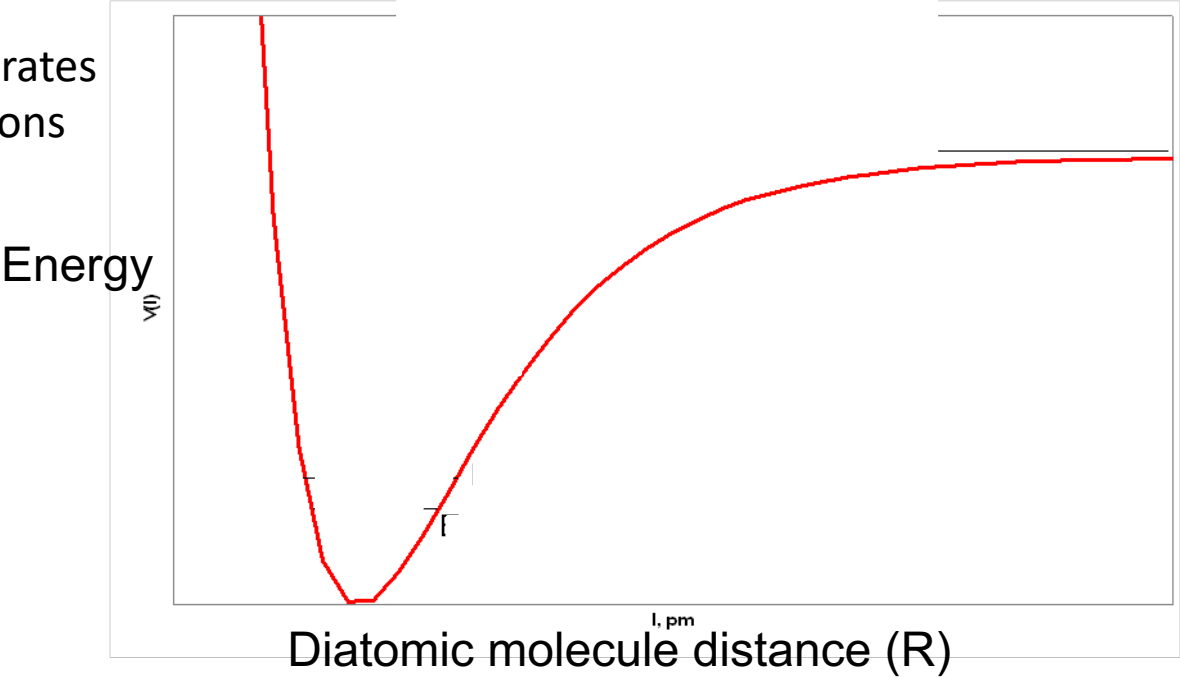

Energy

Diatomic molecule distance

General scheme of an *ab initio* geometry optimization calculation

Born Oppenheimer approximation – nuclei heavier and slower than electrons, so we can think of nuclei as static "atom position", electrons adjust, and potential energy surface is the energy of the system as a function of nuclei positions, with electrons in "optimal" configuration at each set of nuclei position

Build structure – guess of nuclei positions (ie, where are the nuclei)
Do a QM calculation to get the energy
Calculate the forces on atoms (dE / d (atom positions)
Check forces – close enough to 0? Yes – done
No –
Optimizer algorithm generates
  next step for atom positions

Energy

V(l)

l, pm

Diatomic molecule distance (R)

Variational Theorem gives us an approach to get "best" wavefunctions

For any system described by the Hamiltonian H and any satisfactory trial wavefunction Ψ,

$$E = \frac{\int \Psi \hat{H} \Psi d\tau}{\int \Psi \Psi d\tau} \geq E_0$$

where E_0 is the true ground state energy of the system. (This comes from the fact that the solutions of H form a complete Hilbert space.)

See https://adambaskerville.github.io/posts/Variational-Method-Hydrogen/

We get the best wave function given a presumed form of the solution.......

We can guess that the wavefunction will have some form:

For H_2^+ - let's use that the molecular wavefunction is a sum of 1s orbitals on each atom
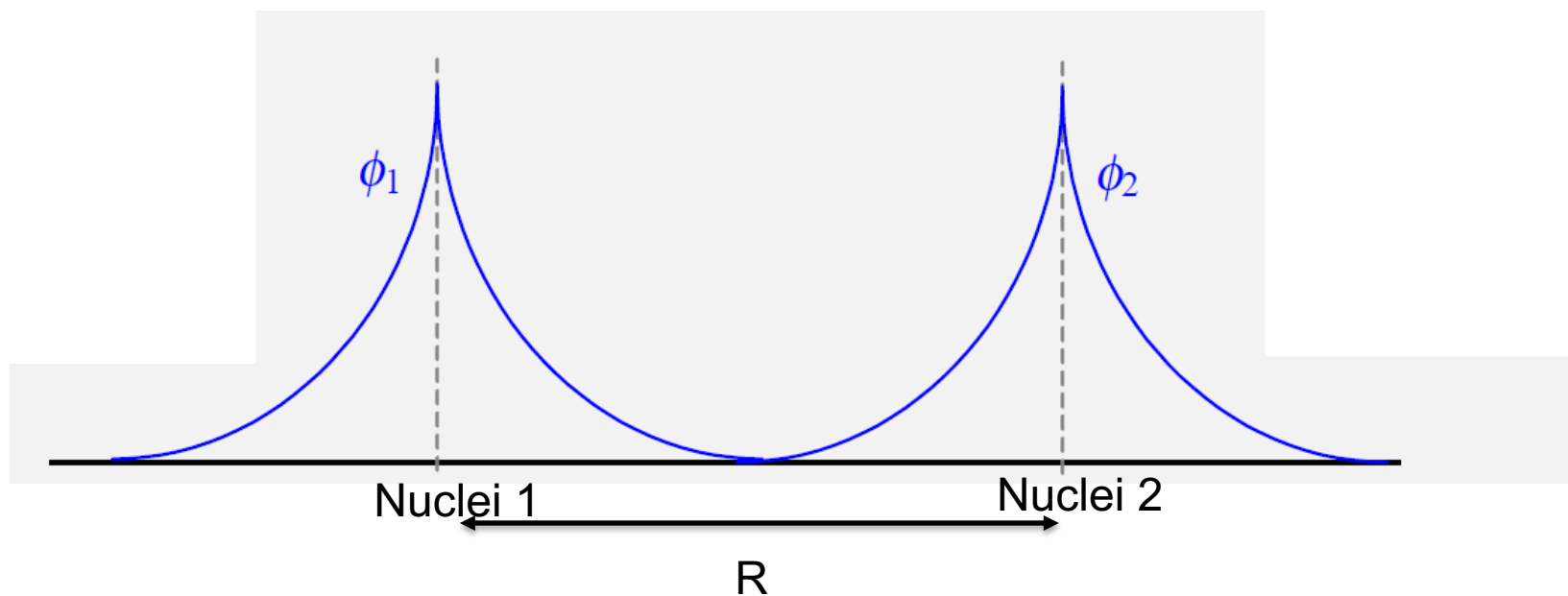
$$\psi = c_1 \phi_1 + c_2 \phi_2$$

If we have Hamiltonian and we have this functional form, problem is minimizing E with respect to c_i's

Solve $\dfrac{\partial E}{\partial c_1} = 0$ and $\dfrac{\partial E}{\partial c_2} = 0$

H$_2$+ Molecule Example – we need to find "best" c's given our assumed ψ function

$$\psi = c_1\phi_1 + c_2\phi_2 \qquad \xrightarrow{\text{H 1s}} \qquad \phi_1 = 2a_0^{-3/2}e^{-r/a_0}$$

$$E = \frac{\int \psi \hat{H} \psi.d\tau}{\int \psi^2.d\tau} = \frac{\int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2).d\tau}{\int (c_1\phi_1 + c_2\phi_2)^2.d\tau}$$

ϕ_1

ϕ_2

Nuclei 1

Nuclei 2

R

$$f(r) = c_1 g(r;1) + c_2 g(r;0.5)$$

Construct $E = \dfrac{\langle f(r)|\hat{H}|f(r)\rangle}{\langle f(r)|f(r)\rangle}$

Solve $\dfrac{\partial E}{\partial c_1} = 0$ and $\dfrac{\partial E}{\partial c_2} = 0$

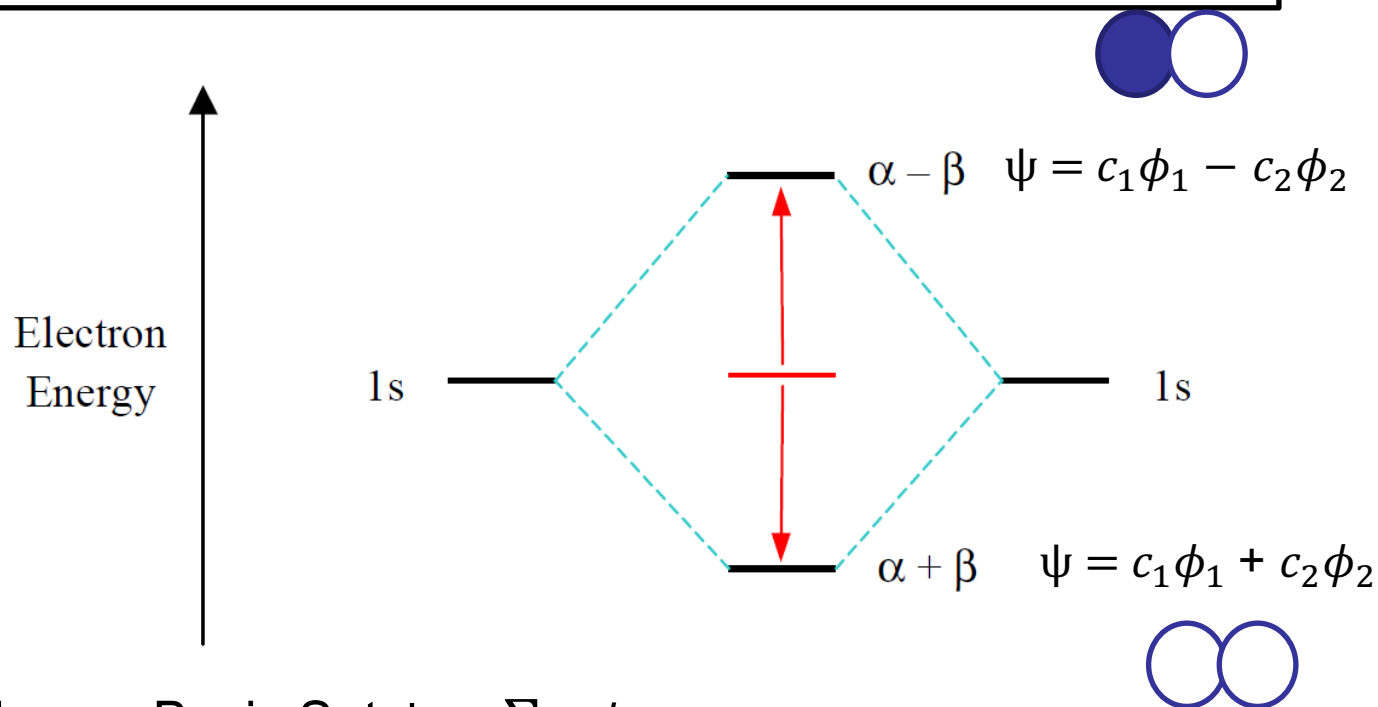The H_2^+ system will be analytically solvable in a single "step" due to no e⁻-e⁻ interaction

$$\begin{pmatrix} \langle g(r;1)|\hat{H}|g(r;1)\rangle - E & \langle g(r;1)|\hat{H}|g(r;0.5)\rangle - \langle g(r;1)|g(r;0.5)\rangle E \\ \langle g(r;1)|\hat{H}|g(r;0.5)\rangle - \langle g(r;1)|g(r;0.5)\rangle E & \langle g(r;0.5)|\hat{H}|g(r;0.5)\rangle - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

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

$$\begin{vmatrix} H_{11} - E & H_{12} - SE \\ H_{12} - SE & H_{22} - E \end{vmatrix} = 0 \implies$$

- Yields Quadratic Function of E
- Both E's are solutions → 1s and 2s orbital energies
- Solve for $c_i(E1)$ and $c_i(E2)$ →

For E1 → $c_1 = c_2$

For E2 → $c_1 = -c_2$

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We can make an orbital energy level diagram

Electron Energy

$\alpha - \beta$ $\quad \psi = c_1\phi_1 - c_2\phi_2$

1s $\qquad\qquad$ 1s

$\alpha + \beta$ $\quad \psi = c_1\phi_1 + c_2\phi_2$

1) Choose Basis Set $\psi = \sum c_i\phi_i$
2) Evaluate H_{ij}, S_{ij} Integrals: $H_{ij} = \int \phi_i \widehat{H} \phi_j \, dv$, $S_{ij} = \int \phi_i \phi_j \, dv$
3) Construct Secular Matrix "A"
4) Solve det |A| = 0 to obtain E (one solution per basis function)
5) Substitute E in Secular Equations to find set of $\{c_i\}$
$\qquad$ → H_{ij} more complicated for multi-electron (add in e-e repulsion), but the methodology is the same!

H$_2$+ molecule example – we have the solutions – what do they look like?

$$\psi = c_1\phi_1 - c_1\phi_2$$
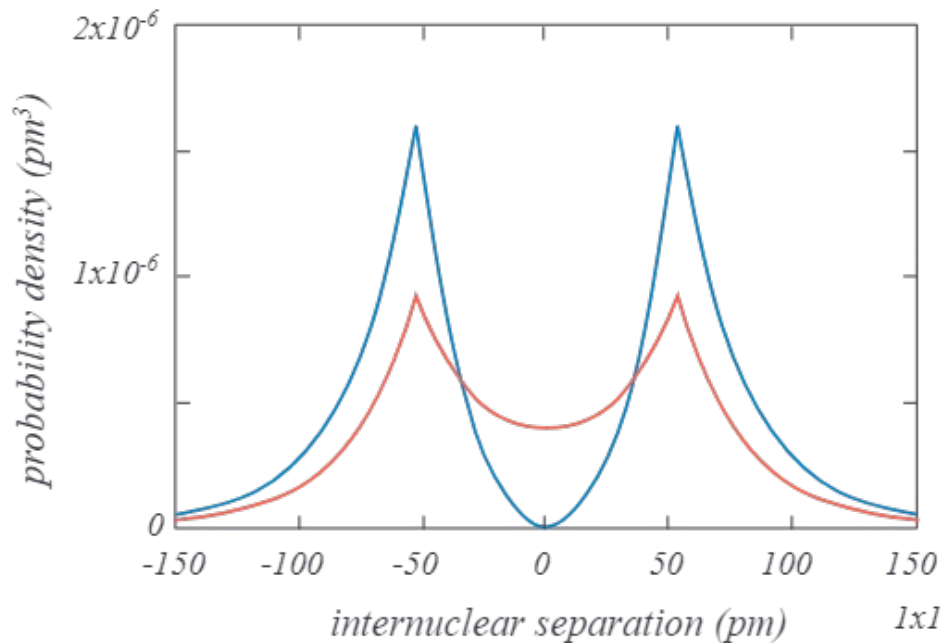
$$\psi = c_1\phi_1 + c_1\phi_2$$
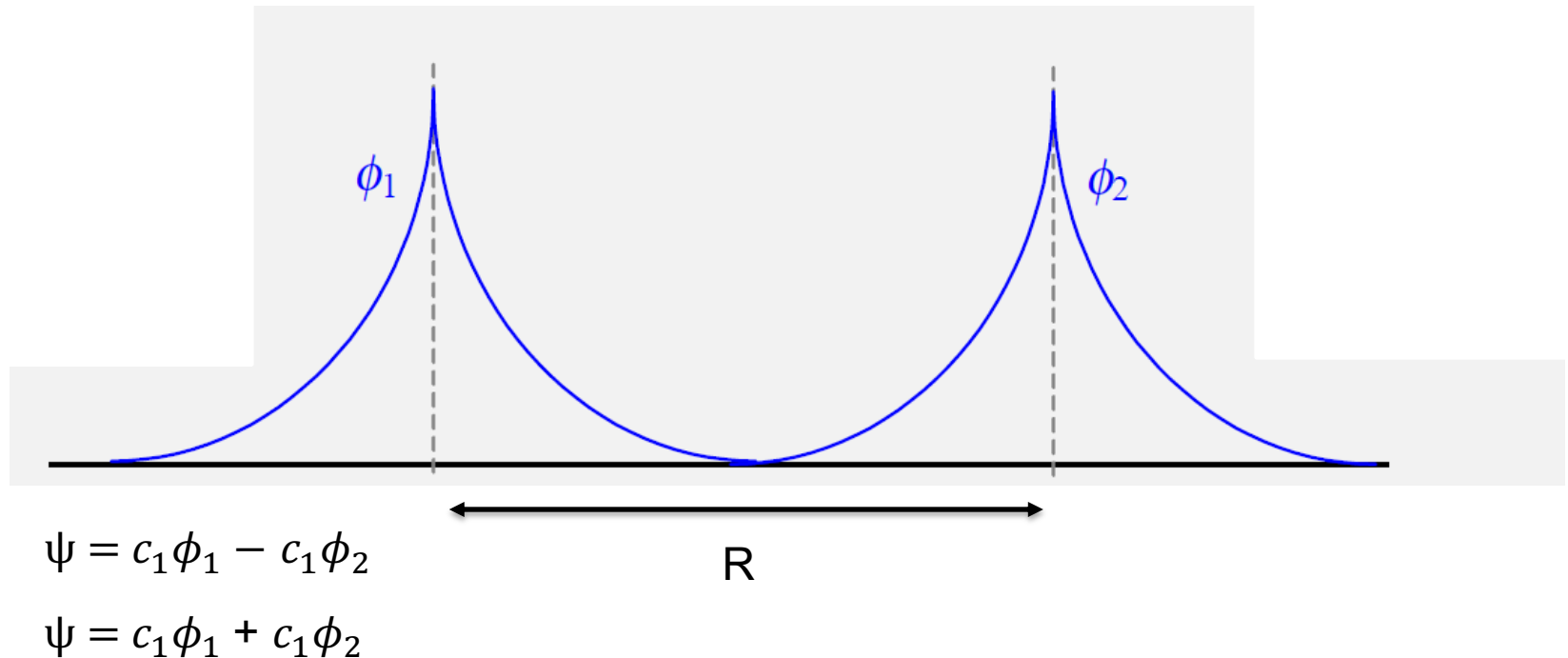
What does the electron density versus distance apart look like?
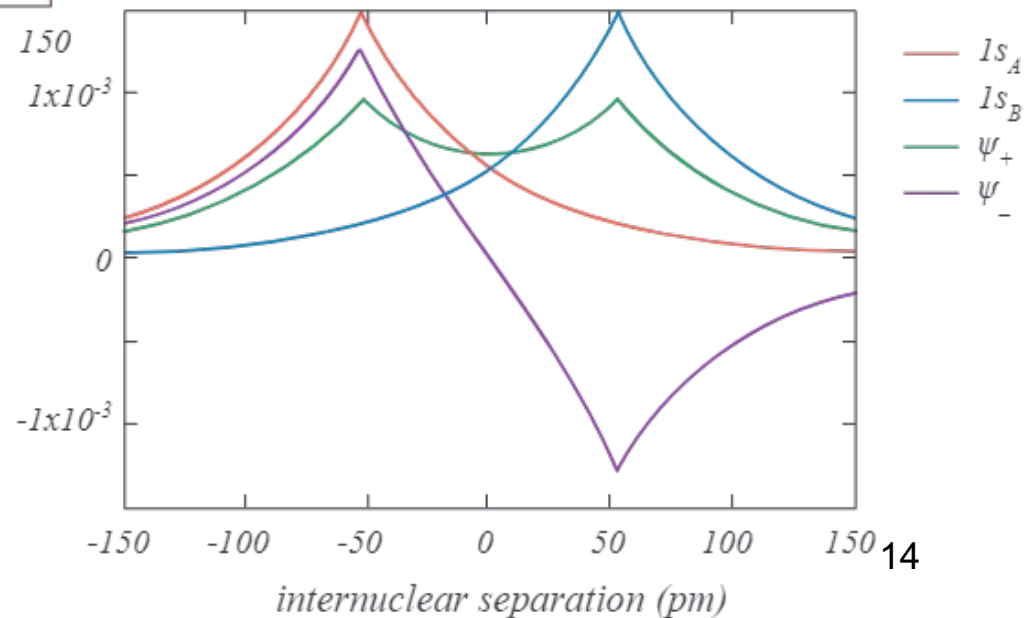What does the anti-bonding wavefunction look like, and what would it's density look like?
How will this change as R is varied?

Bonding orbital has constructive overlap between nuclei, antibonding has a node

$$\psi = c_1\phi_1 + c_2\phi_2$$

$$\psi = c_1\phi_1 - c_2\phi_2$$

Review the steps we took:

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

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

1) Choose Basis Set $\psi = \sum c_i \phi_i$
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4) Solve det |A| = 0 to obtain E (one solution per basis function)
5) Substitute E in Secular Equations to find set of $\{c_i\}$
   → H_{ij} more complicated for multi-electron (add in e-e repulsion), but the methodology is the same!

General scheme of an *ab initio* geometry optimization calculation

Born Oppenheimer approximation – nuclei heavier and slower than electrons, so we can think of nuclei as static "atom position", electrons adjust, and potential energy surface is the energy of the system as a function of nuclei positions, with electrons in "optimal" configuration at each set of nuclei position

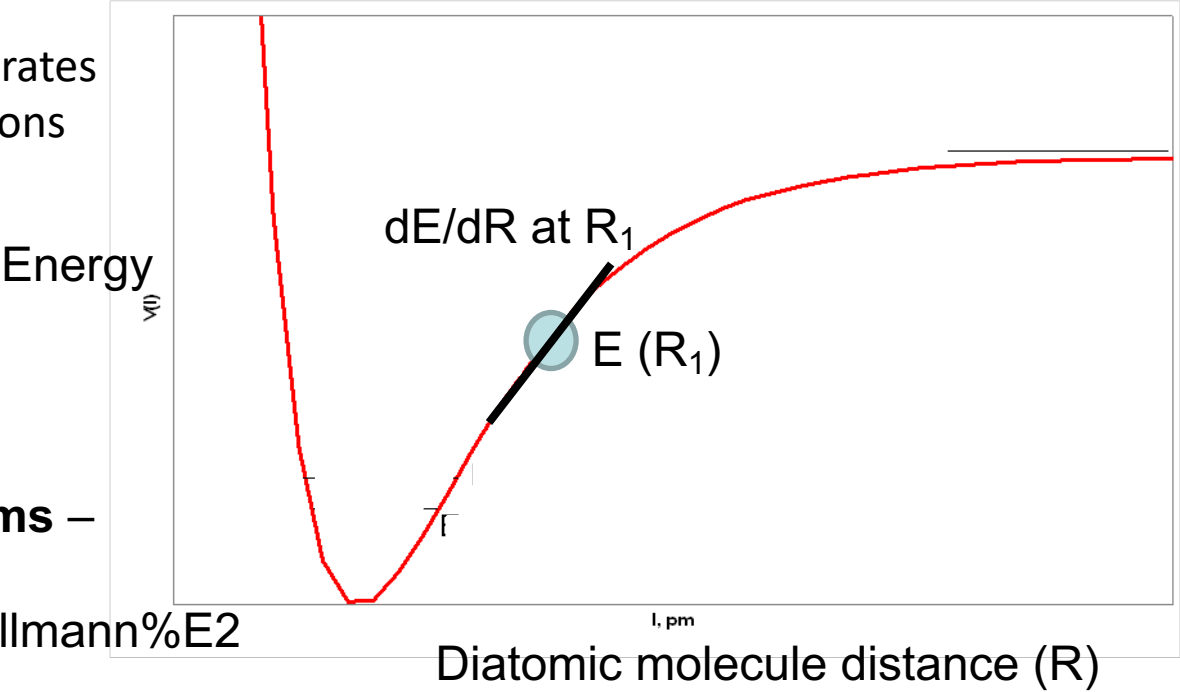Build structure – guess of nuclei positions (ie, where are the nuclei)

Do a QM calculation to get the energy

Calculate the forces on atoms (dE / d (atom positions)

Check forces – close enough to 0? Yes – done

No –

Optimizer algorithm generates
 next step for atom positions

Energy

$V(l)$

dE/dR at R_1

$E (R_1)$

How to get the forces on atoms –
Hellmann-Feynman
https://en.wikipedia.org/wiki/Hellmann%E2%80%93Feynman_theorem

l, pm

Diatomic molecule distance (R)

General scheme of an *ab initio* geometry optimization calculation

Born Oppenheimer approximation – nuclei heavier and slower than electrons, so we can think of nuclei as static "atom position", electrons adjust, and potential energy surface is the energy of the system as a function of nuclei positions, with electrons in "optimal" configuration at each set of nuclei position

Build structure – guess of nuclei positions (ie, where are the nuclei)

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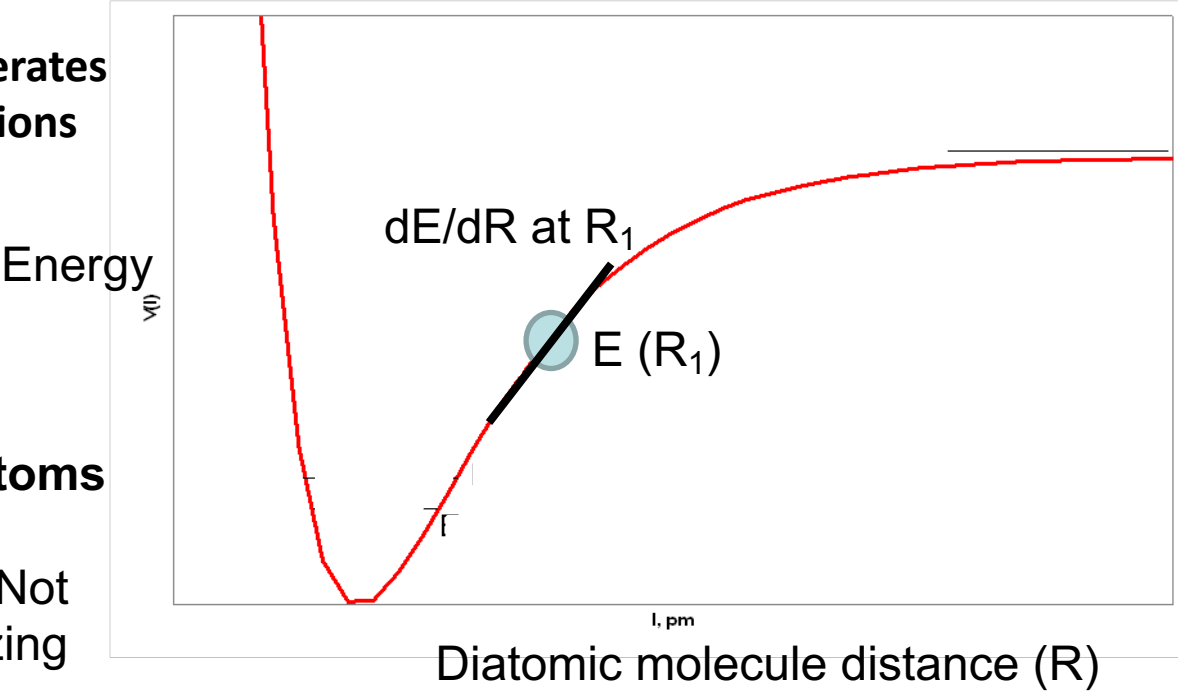*Calculate the forces on atoms (dE / d (atom positions)*
Check forces – close enough to 0? Yes – done
No –
Optimizer algorithm generates
next step for atom positions

How to decide where to put atoms next?

-choice of optimizer algorithm. Not inherently different than minimizing any function.

Energy

dE/dR at R_1

$E (R_1)$

Diatomic molecule distance (R)

Did we use the "right" functional form for the H_2^+ wavefunction?

$\psi = c_1\phi_1 + c_2\phi_2$

H 1s

$\phi_1 = 2a_0^{-3/2}e^{-r/a_0}$

$$E = \frac{\int \Psi\hat{H}\Psi d\tau}{\int \Psi\Psi d\tau} \geq E_0$$

$$E = \frac{\int \psi\hat{H}\psi.d\tau}{\int \psi^2.d\tau} = \frac{\int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2).d\tau}{\int (c_1\phi_1 + c_2\phi_2)^2.d\tau}$$

Legend: ψ_{+^2} (red), ψ_{-^2} (blue)

y-axis: probability density (pm^3)

x-axis: internuclear separation (pm)

Did we use the "right" functional form for the H_2^+ wavefunction?
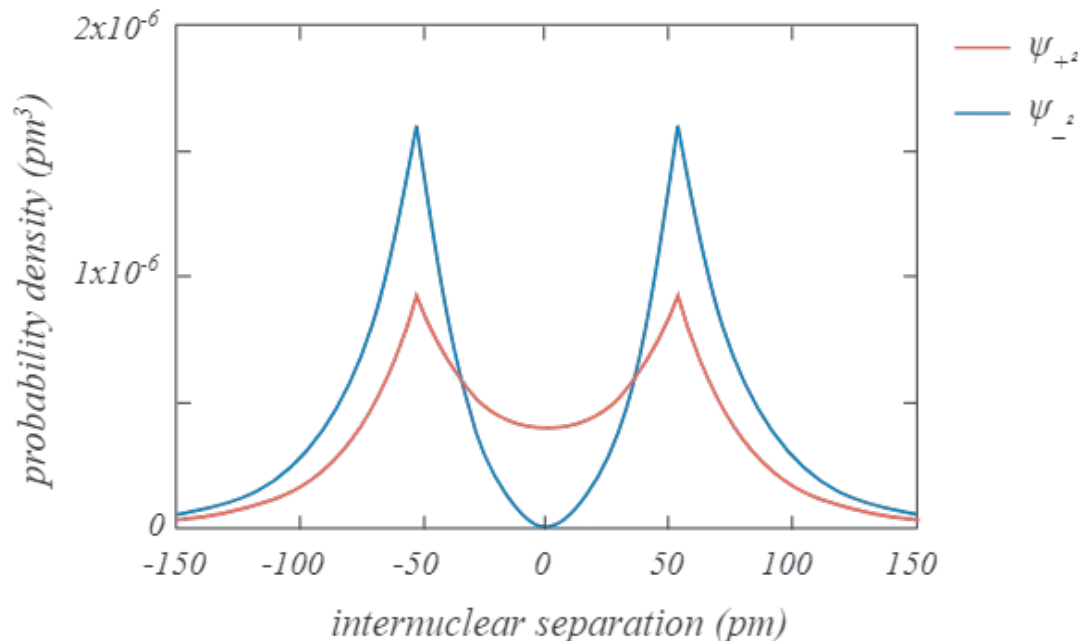
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H 1s

$\phi_1 = 2a_0^{-3/2}e^{-r/a_0}$

$E = \dfrac{\int \Psi\hat{H}\Psi d\tau}{\int \Psi\Psi d\tau} \geq E_0$

$E = \dfrac{\int \psi\hat{H}\psi.d\tau}{\int \psi^2.d\tau} = \dfrac{\int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2).d\tau}{\int (c_1\phi_1 + c_2\phi_2)^2.d\tau}$

There was no "scientific" requirement we made the H_2^+ molecular orbital from H 1s functions.   If we could use any guess function for ψ, what would tell us we made the "best choice"?

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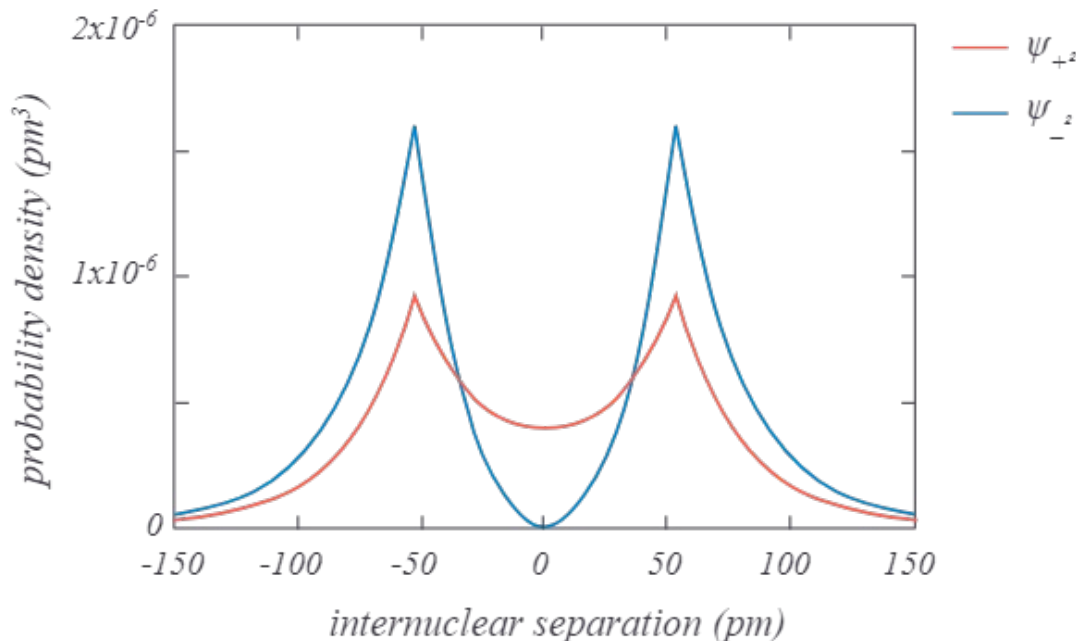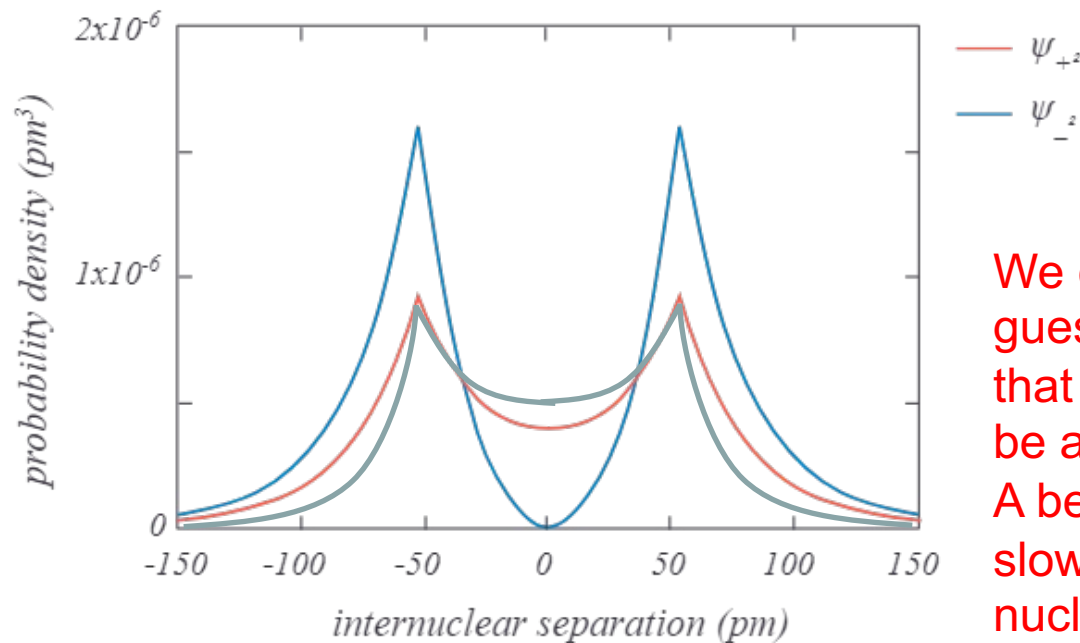# Did we use the "right" functional form for the H_2^+ wavefunction?

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H 1s

$$\phi_1 = 2a_0^{-3/2}e^{-r/a_0}$$

$$E = \frac{\int \Psi\hat{H}\Psi d\tau}{\int \Psi\Psi d\tau} \geq E_0$$

$$E = \frac{\int \psi\hat{H}\psi.d\tau}{\int \psi^2.d\tau} = \frac{\int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2).d\tau}{\int (c_1\phi_1 + c_2\phi_2)^2.d\tau}$$

There was no "scientific" requirement we made the H_2^+ molecular orbital from H 1s functions. If we could use any guess function for ψ, what would tell us we made the "best choice"?


We could keep changing the guess function, and anything that gave us a lower E would be a better function.
A better function would decay slower between the two nuclei and faster outside then a sum of 1s orbitals……

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We chose a "basis set" of 1s orbitals on each atom. We can make (many) other choices…….

Linear combination of functions
If "functions" are atom centered orbitals (typically H like s, p, d, f)
"Linear combination of atomic orbitals" - LCAO
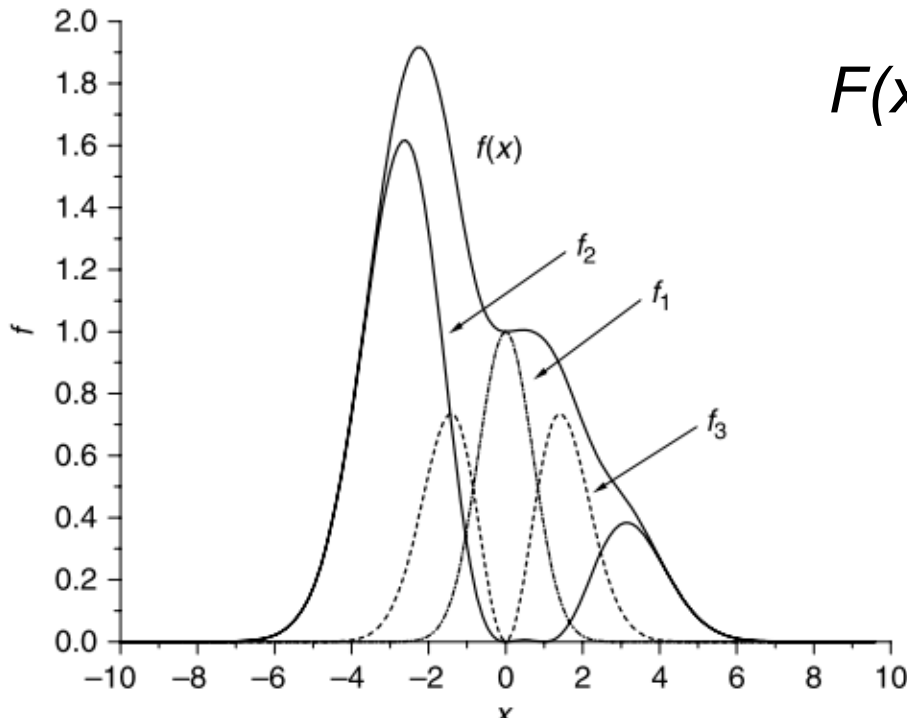
$$F(x) = c_1 f_1(x) + c_2 f_2(x) + c_3 f_3(x)$$
$$= \sum_i c_i f_i$$

$$f_1(x) = \exp(-x^2),$$
$$f_2(x) = x^2 \exp(-x^2/2),$$
$$f_3(x) = \tfrac{1}{10} x^2 (1 - x)^2 \exp(-x^2/4).$$

Hydrogen atomic orbitals are computationally inefficient – "hydrogen-like Gaussians" are common choice

$$E_n = -\frac{1}{n^2}\left(\frac{e^2}{2a_0}\right) = -13.6 \text{ eV} \cdot \frac{1}{n^2} = -13.6 \text{ eV} \quad n = 1,$$

$$R_{10}(r) = 2a_0^{-3/2}e^{-r/a_0}$$

Gaussian Trial Function: $\quad g(r;\zeta) = e^{-\zeta r^2}$

Normalize: $\quad N^2 \int_0^\infty \left(e^{-\zeta r^2}\right)^2 r^2 \, dr = 1 \Rightarrow N = \left(\frac{8\zeta^3}{\pi}\right)^{1/4} \quad \Rightarrow \quad g(r;\zeta) = 2\left(\frac{8\zeta^3}{\pi}\right)^{1/4} e^{-\zeta r^2}$

Evaluate Energy: $\quad E(\zeta = 1) = \left\langle g(r;1) \left| \hat{H} \right| g(r;1) \right\rangle =$ -2.61 eV

Two Gaussians, Equal Weight Trial Function: $\quad b(r) = N\left(g(r;1) + g(r;0.5)\right) \qquad$ E[b(r)] = -8.33 eV

Two Gaussians, Unequal Weight Trial Function: $\quad c(r) = N'\left(g(r;1) + 1.5g(r;0.5)\right) \quad$ E[c(r)] = -9.061 eV

Comparison of 1s and Gaussian functions

Legend:
- Coulomb
- 1s
- Gaussian($\zeta=1$)
- Gaussian($\zeta=1$)+($\zeta=1/2$)
- Gaussian($\zeta=1$)+1.5($\zeta=1/2$)

$$R_{10}(r) = 2a_0^{-3/2}e^{-r/a_0}$$

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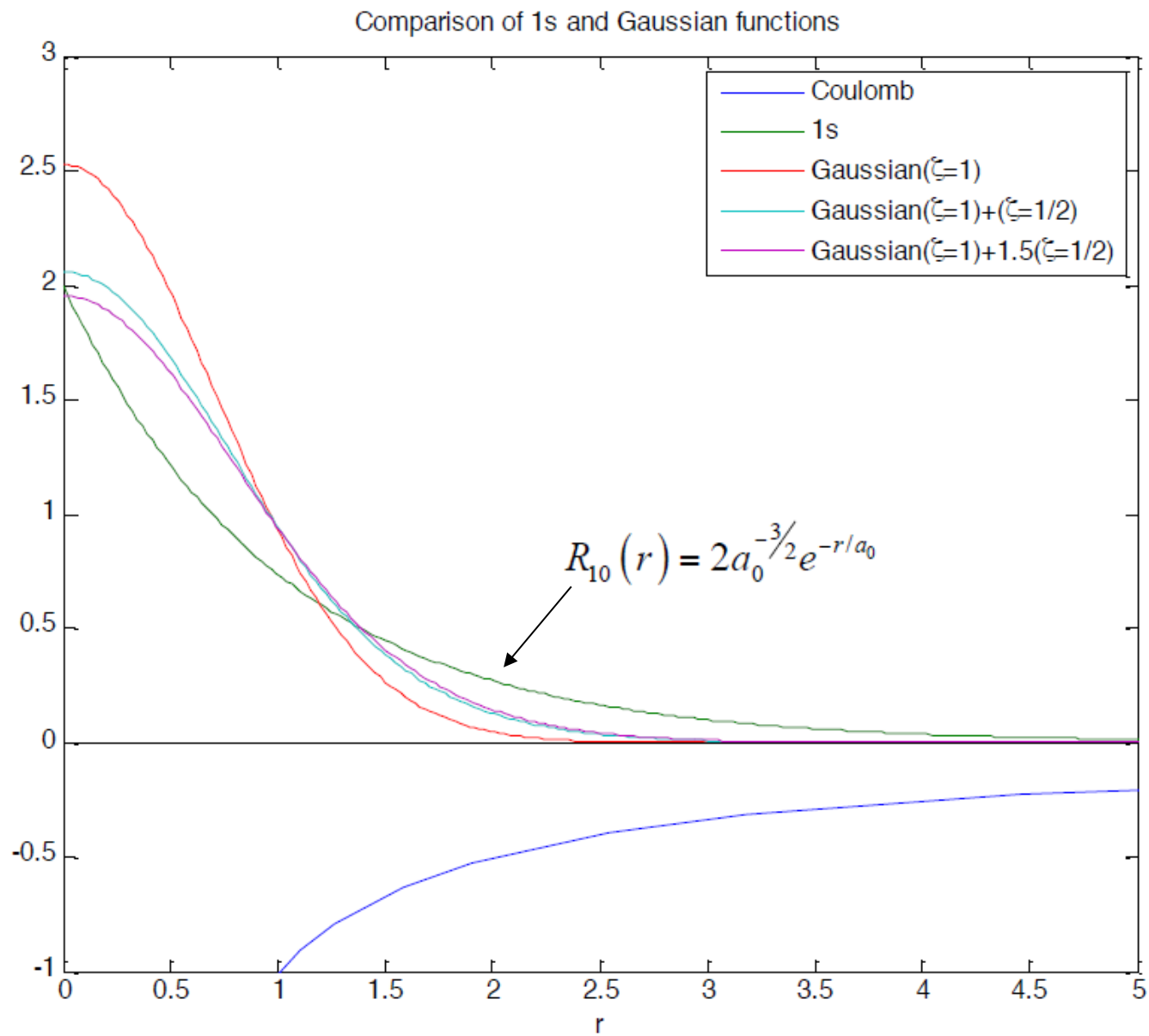
Atomic orbital basis sets common, can be analytical functions, numerical, Slater, Gaussian, etc…

Slater-type orbitals have an exponential term that is more hydrogen like, but are computationally longer to evaluate integrals than Gaussians

- Spherical Harmonic Slaters

$$\phi(\mathbf{r}) = r^L e^{-\zeta r} Y_L^M(\theta, \phi) \tag{4}$$

characterized by 2 integers (L, M; $-L \leq M \leq L$)

- Cartesian Slaters

$$\phi(\mathbf{r}) = x^l y^m z^n e^{-\zeta r} \tag{5}$$

characterized by 3 integers (l, m, n; $L = l + m + n$ is similar to the angular momentum)

- $L = 0, 1, 2, 3, 4, 5, 6$ designated as s, p, d, f, g, h, i
- Very similar to hydrogenic orbitals - useful for calculations on atoms
- Proper analytical structure: exponential decay, s-type Slaters have a nuclear cusp
- Very difficult to compute matrix elements in the case of molecular systems!
- Used by some atomic codes and some molecular codes (e.g., Amsterdam Density Functional (ADF) package)

Gaussians are quicker for a computer to evaluate in integrals, but don't physically look like H-like so need to add more of them together....

Introduced by Boys in 1950.

► Cartesian Gaussians

$$\phi(\mathbf{r}) = x^l y^m z^n e^{-\alpha r^2} \tag{6}$$

characterized by 3 integers (l,m,n; $L = l + m + n$ is referred to as the angular momentum)

► Spherical Harmonic ("pure angular momentum") Gaussians

$$\phi(\mathbf{r}) = r^L e^{-\alpha r^2} Y_L^M(\theta, \phi) \tag{7}$$

characterized by 2 integers (L, M; $-L \le M \le L$)

► Decay at infinity faster than Slaters

► s-type Gaussians do not have a nuclear cusp

► Matrix elements are much easier to compute

Contracted Gaussian-Type Orbitals (CGTO's)

- *Problem:* STO's are more accurate, but it takes longer to compute integrals using them

- *Solution:* Use a linear combination of enough GTO's to mimic an STO

- *Unfortunate:* A combination of n Gaussians to mimic an STO is often called an "STO-nG" basis, even though it is made of CGTO's...

$$\phi_{abc}^{CGTO}(x, y, z) = N \sum_{i=1}^{n} c_i x^a y^b z^c e^{-\zeta_i r^2} \tag{1}$$
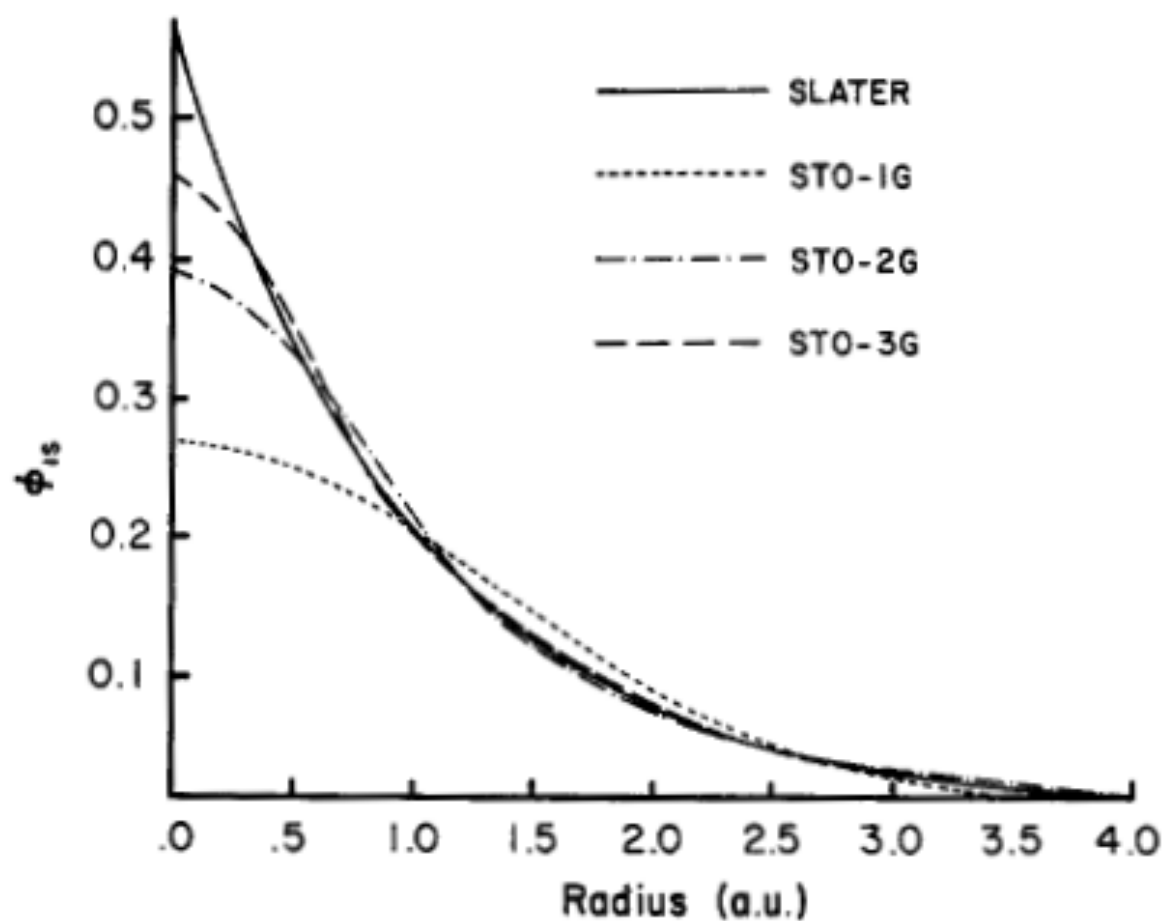
Figure 3.3 Comparison of the quality of the least-squares fit of a 1s Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

Figure from Szabo and Ostlund, Modern Quantum Chemistry.

We can give a C atom one set of 1s, 2s, and 2p orbitals, OR why not give it 2 of them with slightly different decay rates, shapes……

Minimal: One basis function (STO, GTO, or CGTO) for each atomic orbital in the atom

Double-zeta: Two basis functions for each AO

Triple-zeta: Three basis functions for each AO

… and etc. for quadruple-zeta (QZ), 5Z, 6Z, … Having different-sized functions allows the orbital to get bigger or smaller when other atoms approach it

A split-valence basis uses only one basis function for each core AO, and a larger basis for the valence AO's

Examples

H atom, minimal basis: One 1s AO, one (STO, GTO, or CGTO) basis function

C atom, minimal basis: 1s, 2s, $2p_x$, $2p_y$, $2p_z$ AO's (5), so 5 basis functions

C atom, double-zeta basis: Two basis functions per AO, so 10 basis functions

C atom, split-valence double-zeta basis: 9 basis functions (why?)

Polarization functions – why not give H some p-orbitals in basis, C some d's? (p orbital in H-H direction of H_2^+ very helpful in getting more accurate orbital and molecule energy)

- As other atoms approach, an atom's orbitals might want to shift to one side or the other (polarization). An s orbital can polarize in one direction if it's mixed with a p orbital.

- p orbitals can polarize if mixed with d orbitals

- In general, to polarize a basis function with angular momentum l, mix it with basis functions of angular momentum $l + 1$

- This gives "polarized double-zeta", or "double-zeta plus polarization" basis sets, etc

Polarization Functions – Orbital Mixing

– Orbitals are influenced by other nuclei

– Polarization accounts for these influences which distort the **orbital shape**
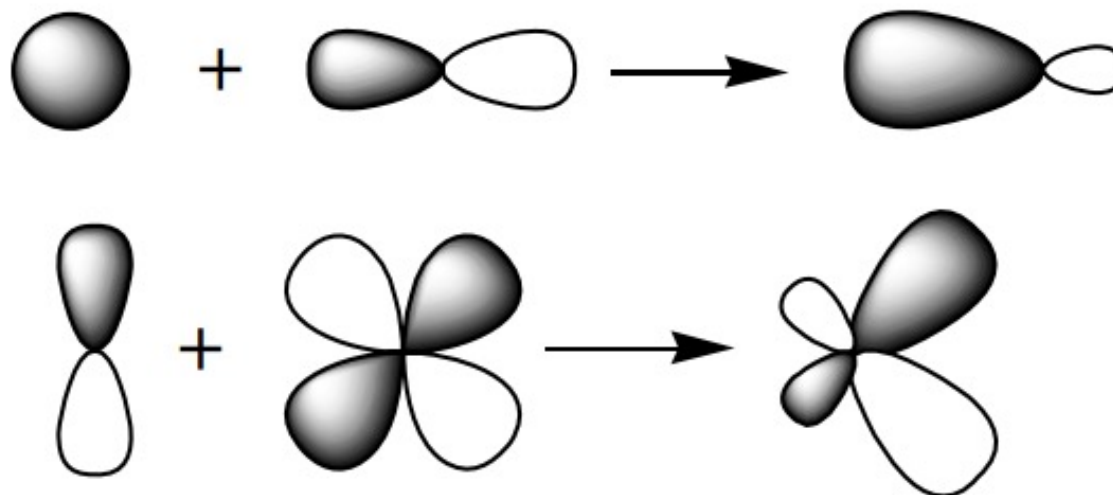
Diffuse functions - Sometimes electrons reside further from nuclei than captured with a typical basis set, especially for ANIONS

- Diffuse functions have small ζ exponents; this means the electron is held far away from the nucleus

- Necessary for anions, Rydberg states, very electronegative atoms (fluorine) with a lot of electron density

- Necessary for accurate polarizabilities or binding energies of van der Waals complexes (bound by dispersion)

- It is very bad to do computations on anions without using diffuse functions; your results could change completely!

Pople Basis Sets

- Developed by the late Nobel Laureate, John Pople, and popularized by the Gaussian set of programs

- STO-3G is a minimal basis set in which each AO is represented by 3 Gaussians (3G), chosen to mimic the behavior of a STO

- Pople's split-valence double-zeta basis set is called 6-31G; the core orbital is a CGTO made of 6 Gaussians, and the valence is described by two orbitals — one CGTO made of 3 Gaussians, and one single Gaussian

The number of gaussian functions summed to describe the inner shell orbital

The number of gaussian functions summed in the second STO

3-21G

The number of gaussian functions that comprise the first STO of the double zeta

More on Pople Basis Sets

- 6-31G* [or 6-31G(d)] is 6-31G with added d polarization functions on non-hydrogen atoms; 6-31G** [or 6-31G(d,p)] is 6-31G* plus p polarization functions for hydrogen

- 6-311G is a split-valence triple-zeta basis; it adds one GTO to 6-31G

- 6-31+G is 6-31G plus diffuse s and p functions for non-hydrogen atoms; 6-31++G has diffuse functions for hydrogen also

Key points from basis sets

Basis set can effect results – is an important choice to make when performing quantum chemistry calculations

Basis set choice is dependent on chemical intuition, computational time constraints, and should consider established norms

For accuracy bigger basis set is better – add polarization, diffuse, more zetas. If they are unnecessary, their coefficients in LCAO will end up being 0….

The notation used is not intuitive – need to look up what it means (6-++31g+*p……)
  6-31 higher numbers mean more basis functions per orbital
  * - polarization function, adds d to sp-block atoms
  ** - polarization, but also adds p to hydrogen
  + adds diffuse functions s and p functions
  ++ includes diffuse functions for hydrogen also

Our H_2^+ example was too easy because we didn't have to worry about e^--e^- interaction. When we have interacting electrons, constructing the terms inside the "secular matrix" becomes more complicated

So we have to go back to more DFT theory to get there…..

Structure of a DFT calculation is still similar, minimize E with respect to n(r) instead of ψ(r)

- **Minimize the energy functional with respect to *n(r)***

$$E_v[n] = T[n] + U[n] + V[n] = T[n] + U[n] + \int d^3r\, n(\mathbf{r})v(\mathbf{r})$$

- **How should we do this?**

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

Kohn-Sham approach – we don't know how to write KE(n), so re-invoke (non-interacting) e's and lump what we get wrong into E_{XC}

- **Write down total kinetic energy functional as sum of non-interacting particle density (n) and the one that represents rest of the kinetic energy functional**

$$T[n] = T_s[n] + T_c[n]$$

where,

$$T_s[n] = -\frac{\hbar^2}{2m} \sum_i^N \int d^3r \, \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$$

We rewrite the exact energy functional as:

$$E[n] = T[n] + U[n] + V[n] = T_s[\{\phi_i[n]\}] + U_H[n] + E_{xc}[n] + V[n]$$

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

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Exchange-correlation functional – hardest part to internalize

- **Exchange correlation functional is decomposed at exchange functional and correlation functional**

$$E_{xc} = E_x + E_c$$

- **There is no "classical physical" way for us to "visualize" or explain what these are – all attempts will feel approximate**

- **Exchange – extra repulsion beyond density-based Coulomb's law associated with the energy penalty of putting two electrons in the same orbital with the same spin**

- **Correlation – electrons will lower their energy by "correlating" their motion to avoid each other.**

- **DFT – we collectively lump these two (and what we got wrong in the KE when we made a non-interacting picture, and what we get wrong letting electrons interact with themselves in Hartree term) into a functional that captures everything we aren't sure how to get right.....**

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Kohn-Sham approach

- **determine orbitals for the Schrodinger equations:**

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r})\right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

where,

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

- **density is determined from these orbitals**

$$n(\mathbf{r}) \equiv n_s(\mathbf{r}) = \sum_i^N f_i \left|\phi_i(\mathbf{r})\right|^2$$

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

Approach – variationally solve K-S eqns, with a "SCF" approach

$$E[\{\psi_i\}] = 2 \sum_i \int \psi_i \left[-\frac{\hbar^2}{2m} \right] \nabla^2 \psi_i \, d^3r + \int V_{\text{ion}}(\mathbf{r}) n(\mathbf{r}) d^3r + \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r \, d^3r' + E_{XC}[n(\mathbf{r})] + E_{\text{ion}}(\{\mathbf{R}_I\}) ,$$

nuclei-nuclei Coulombic

electron kinetic energy   *electron nuclei Coulomb*   *electron electron "average" Coulomb*   *electron exchange +correlation*

Kohn-Sham equations (Kohn and Sham, 1965):

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) ,$$

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r'$$

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

V_H, V_{XC} depend on n(r), but n(r) depends on set of ψ_i's – self-consistent field procedure:
Use "old" coefficients in the ψ_i's (old c_i's) to get n_{old}
Construct "Hamiltonian" and solve for new ψ_i's. Calculate new n
Check if $E(n_{\text{new}}) = E(n_{\text{old}})$ and if not, use a convergence procedure (choose alg.) and keep trying

General scheme of an *ab initio* geometry optimization calculation

Born Oppenheimer approximation – nuclei heavier and slower than electrons, so we can think of nuclei as static "atom position", electrons adjust, and potential energy surface is the energy of the system as a function of nuclei positions, with electrons in "optimal" configuration at each set of nuclei position

Build structure – guess of nuclei positions (ie, where are the nuclei)
          "guess" wavefunctions (ie, where are the electrons)
          iterate on wavefunctions until wavefunction$_{new}$=wavefunction$_{old}$
                  (converged, "self consistent field")
          determine forces on atoms
          check if forces, energy change
            meets convergence criteria
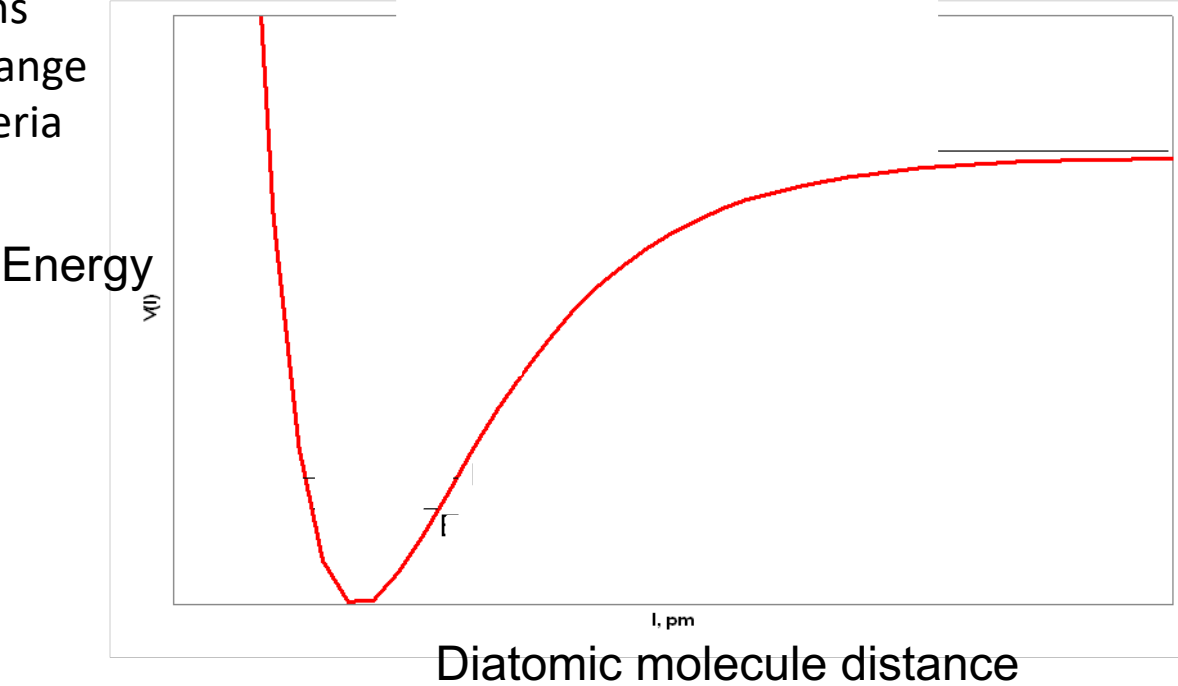
Energy

$V(l)$

l, pm

Diatomic molecule distance

Why quantum mechanics? What properties can we calculate with quantum mechanics?

Properties we can't get from anything other than QM:

Properties we might get more accurately or quickly with QM compared to FF methods:

Why quantum mechanics? What properties can we calculate with quantum mechanics?

Properties we can't get from anything other than QM:
        Electron excitation energies
        NMR shifts
        Work function of a solid/surface
        Electrostatic potential distribution about a molecule/surface
        Electron conductivity (rates of electron motion)

Properties we might get more accurately or quickly with QM compared to FF methods:
        Structures, especially of small systems (molecules, crystals)
        Reaction energies (cohesive energies, thermodynamics)
        Activation barriers (rates of chemical transformation)
        Vibrational frequencies