Lecture 8
Molecular Orbitals

Molecular orbital; H_2^+ ion; neutral H_2 molecule

Prof. David A. Kofke
CE 500 – Modeling Potential-Energy Surfaces
Department of Chemical & Biological Engineering
University at Buffalo

University at Buffalo
The State University of New York

A *molecular orbital* (MO) is a 1-electron spatial wavefunction for a molecule
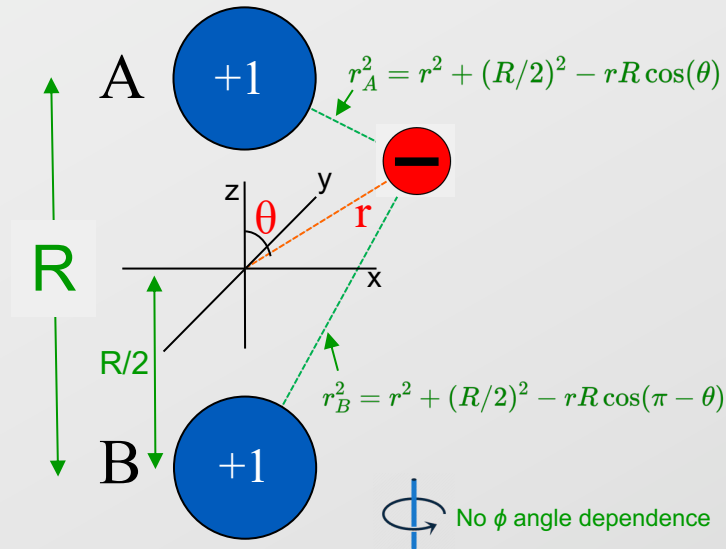
- MOs play a role similar to that of AOs for single atoms
  - Pauli principle limits occupation of a MO to at most 2 electrons
  - Slater determinants formed from MOs are used to approximate molecular multi-electron wavefunctions

- Molecular orbitals are often constructed as a linear combination of atomic orbitals (LCAO)

- MOs form a foundation for understanding of bonding

- Remember that in either case, orbitals are helpful but artificial constructs used to grapple with the many-electron wavefunction

The H_2^+ ion is the simplest multiatomic system, and a useful starting point to study molecules

- 1-electron system
  - no self-consistent field iterations needed
  - ERIs not needed, $\hat{F} = \hat{h}$
  - no Slater determinant

- Complicated analytic solution exists

- Let's construct a MO using a minimal basis set formed from one atomic orbital on each atom:

$$\chi_\alpha(\mathbf{r}), \chi_\beta(\mathbf{r}) \qquad \phi_i(\mathbf{r}) = C_{\alpha,i}\chi_\alpha(\mathbf{r}) + C_{\beta,i}\chi_\beta(\mathbf{r})$$

A +1

$$r_A^2 = r^2 + (R/2)^2 - rR\cos(\theta)$$

θ r

$$r_B^2 = r^2 + (R/2)^2 - rR\cos(\pi - \theta)$$

B +1

No ϕ angle dependence

R

R/2

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Here, α, β are just basis-function indexes, not spin state

- Roothaan-Hall equation for 2 basis functions

$$\begin{bmatrix} F_{\alpha,\alpha} & F_{\alpha,\beta} \\ F_{\beta,\alpha} & F_{\beta,\beta} \end{bmatrix} \begin{bmatrix} C_{\alpha,1} & C_{\alpha,2} \\ C_{\beta,1} & C_{\beta,2} \end{bmatrix} = \begin{bmatrix} 1 & S_{\alpha,\beta} \\ S_{\beta,\alpha} & 1 \end{bmatrix} \begin{bmatrix} C_{\alpha,1} & C_{\alpha,2} \\ C_{\beta,1} & C_{\beta,2} \end{bmatrix} \begin{bmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{bmatrix}$$

- 1-electron system: $\hat{F}^\sigma = \hat{h} + \cancel{\hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\sigma}$

- 2 basis functions: $S_{\alpha,\beta} = S_{\beta,\alpha} \equiv S$

- Secular equation

$$\begin{bmatrix} h_{\alpha,\alpha} - \varepsilon_i & h_{\alpha,\beta} - S\varepsilon_i \\ h_{\beta,\alpha} - S\varepsilon_i & h_{\beta,\beta} - \varepsilon_i \end{bmatrix} \begin{bmatrix} C_{\alpha,i} \\ C_{\beta,i} \end{bmatrix} = 0$$

Use Mathematica to solve for ε that makes determinant zero and evaluate orbitals

- Set up secular matrix
$$\begin{bmatrix} h_{\alpha,\alpha} - \varepsilon_i & h_{\alpha,\beta} - S\varepsilon_i \\ h_{\beta,\alpha} - S\varepsilon_i & h_{\beta,\beta} - \varepsilon_i \end{bmatrix} \begin{bmatrix} C_{\alpha,i} \\ C_{\beta,i} \end{bmatrix} = 0$$

- Use `Det` to get determinant

- Use `Solve` to find ε that make determinant zero

- For each ε, evaluate the basis coefficients $C_{\nu,i}$ for normalized molecular orbital in terms of $h_{\mu,\nu}$ and S

$$\phi_i(\mathbf{r}) = C_{\alpha,i}\chi_\alpha(\mathbf{r}) + C_{\beta,i}\chi_\beta(\mathbf{r})$$

```
hMat = {{h_{α,α}, h_{α,β}}, {h_{β,α}, h_{β,β}}} /. {h_{β,α} → h_{α,β}, h_{β,β} → h_{α,α}};
hMat // MatrixForm
SMat = {{1, S}, {S, 1}};
SMat // MatrixForm

solns = Solve[Det[hMat - e SMat] == 0, e]
{e1, e2} = e /. solns
```

$$\varepsilon_1 = \frac{h_{\alpha,\alpha} - h_{\alpha,\beta}}{1 - S}$$

$$\varepsilon_2 = \frac{h_{\alpha,\alpha} + h_{\alpha,\beta}}{1 + S}$$

First row of matrix

```
Solve[(hMat - e1 SMat)[[1]].{1, C2} == 0, C2]
Solve[(hMat - e2 SMat)[[1]].{1, C2} == 0, C2]
```

Setting determinant to zero makes equations linearly dependent, so satisfying one satisfies both

For each e, we get a different C1, C2

$$\phi 1[\{r\_, \theta\_, \phi\_\}, R\_, \xi\_, s\_] := \frac{\chi\alpha[r, \theta, R, \xi] - \chi\beta[r, \theta, R, \xi]}{(2 - 2 s)^{1/2}}$$

$$\phi 2[\{r\_, \theta\_, \phi\_\}, R\_, \xi\_, s\_] := \frac{\chi\alpha[r, \theta, R, \xi] + \chi\beta[r, \theta, R, \xi]}{(2 + 2 s)^{1/2}}$$

Normalization

$$\langle C_1\chi_\alpha + C_2\chi_\beta | C_1\chi_\alpha + C_2\chi_\beta \rangle$$
$$= C_1^2\langle\chi_\alpha|\chi_\alpha\rangle + 2C_1C_2\langle\chi_\alpha|\chi_\beta\rangle + C_2^2\langle\chi_\beta|\chi_\beta\rangle$$
$$= 1 + 2C_1C_2 s + 1$$
$$= 2 \pm 2s$$

- This defines two states for a single electron interacting with two nuclei

- We can now choose the basis functions as two simple H-atom atomic orbitals, centered on the respective atoms

Homonuclear, so $\zeta_A = \zeta_B \equiv \zeta$

$$\chi_\alpha(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r_A} \qquad \chi_\beta(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r_B}$$

- We now need the integrals for $h_{\mu,\nu}$ and S

$$h_{\mu,\nu} = T_{\mu,\nu} + V_{\mu,\nu} = \left\langle \chi_\mu \Big| -\frac{1}{2}\nabla^2 \Big| \chi_\nu \right\rangle - \left\langle \chi_\mu \Big| \frac{1}{r_A} + \frac{1}{r_B} \Big| \chi_\nu \right\rangle \qquad S = \langle \chi_\alpha | \chi_\beta \rangle$$

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Spatial integrals for a pair of 1s basis functions on two sites separated by a distance R

$$\chi_\mu(r) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta\, r}$$

r is the distance to the atom site
  where the basis function is centered.

Formulas are from J. Autschbach,
Quantum Theory for Chemical Applications,
Oxford University Press, 2021.

Overlap integral: $\langle \chi_\alpha | \chi_\beta \rangle$

```
s[R_, ζ_] := With[{w = R ζ}, (1 + w + w²/3) E^-w]
```

$\alpha\alpha$ Coulomb integral : $\langle \chi_\alpha | \frac{1}{r} | \chi_\alpha \rangle$

```
coulombαα[R_, ζ_] :=
  With[{w = ζ R}, 1/R (1 - Exp[-2 w] (1 + w))]
```

$\alpha\beta$ Coulomb integral : $\langle \chi_\alpha | \frac{1}{r} | \chi_\beta \rangle$

```
coulombαβ[R_, ζ_] :=
  With[{w = ζ R}, 1/R (w + w²) Exp[-w]]
```

$\alpha\alpha$ potential –
energy integral : $-\langle \chi_\alpha | \frac{1}{r_A} + \frac{1}{r_B} | \chi_\alpha \rangle$

```
Vαα[R_, ζ_] := -ζ - coulombαα[R, ζ]
```

$\alpha\beta$ potential –
energy integral : $-\langle \chi_\alpha | \frac{1}{r_A} + \frac{1}{r_B} | \chi_\beta \rangle$

```
Vαβ[R_, ζ_] := -2 coulombαβ[R, ζ]
```

File STO_integrals.nb

$\alpha\alpha$ kinetic –
energy integral : $\langle \chi_\alpha | -\frac{1}{2} \nabla^2 | \chi_\alpha \rangle$

```
Tαα[R_, ζ_] := ζ²/2
```

$\alpha\beta$ kinetic –
energy integral : $\langle \chi_\alpha | -\frac{1}{2} \nabla^2 | \chi_\beta \rangle$

```
Tαβ[R_, ζ_] := ζ coulombαβ[R, ζ] - ζ²/2 s[ζ R]
```

Full 1-electron integrals

```
hαα[R_, ζ_] := Tαα[R, ζ] + Vαα[R, ζ]
hαβ[R_, ζ_] := Tαβ[R, ζ] + Vαβ[R, ζ]
```

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The molecular orbitals describe bonding and antibonding states

$\zeta = 1$

Antibonding

H-atom energy at R→∞

Bonding

Energy, (hartree)

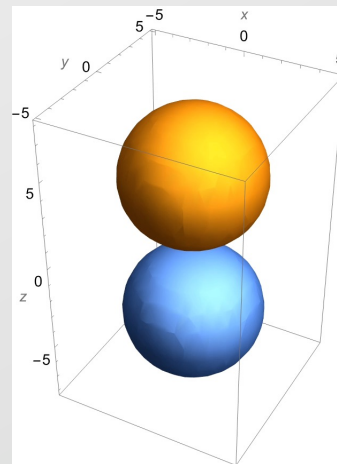Atom separation, R (bohr)
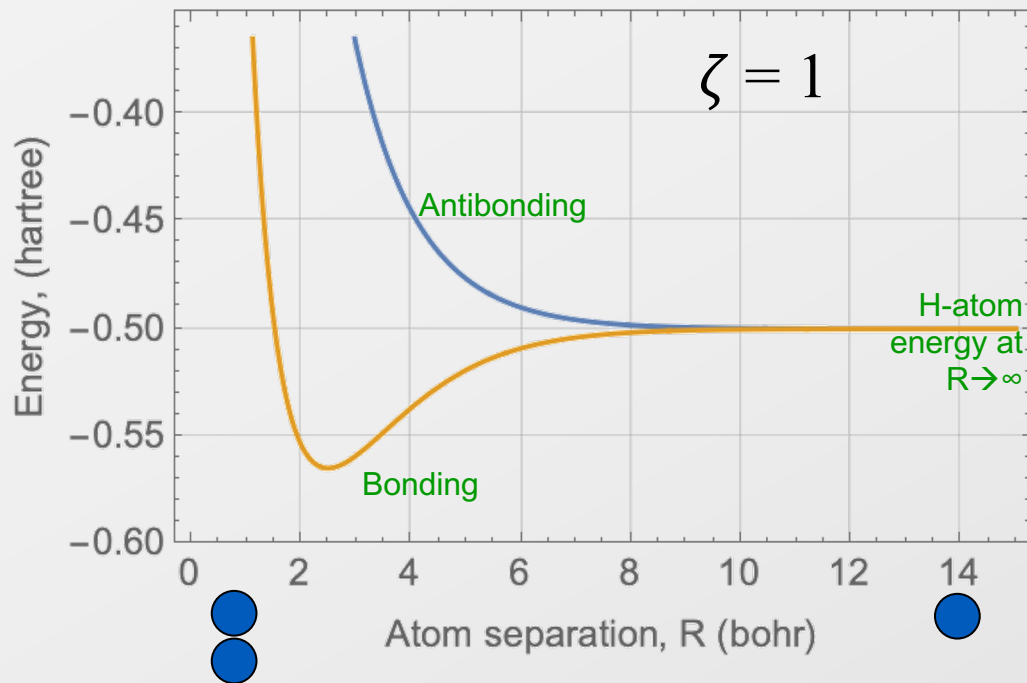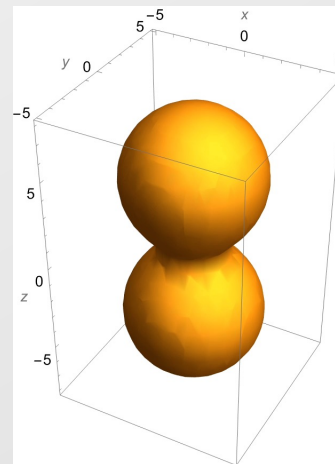
Bonding

gerade (*g*)
symmetry

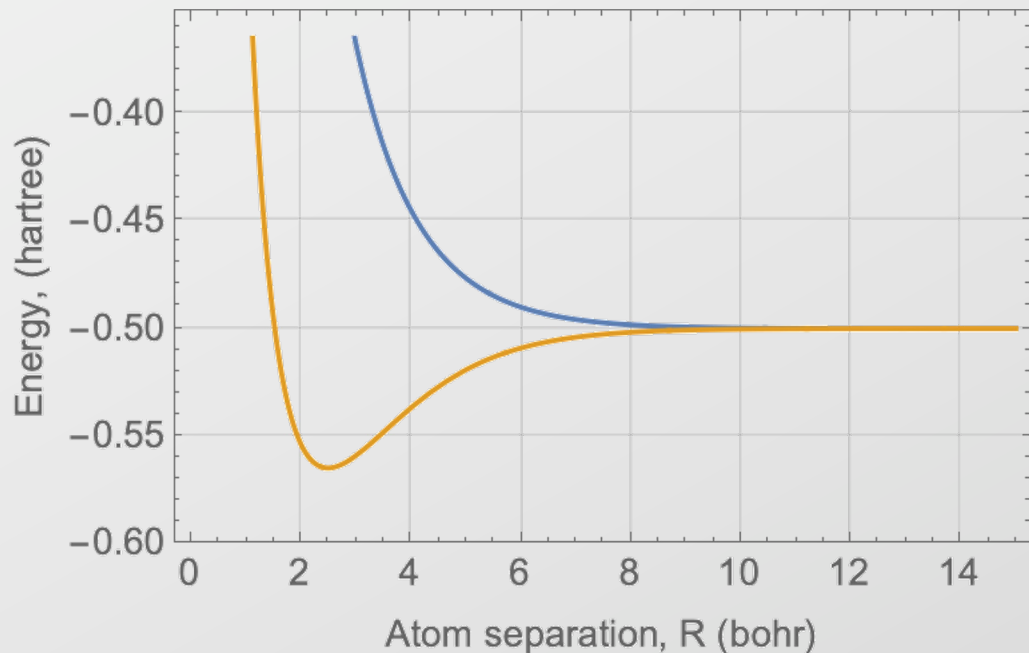"even" point symmetry

Antibonding

ungerade (*u*)
symmetry

"odd"

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Remember that this solution is approximate, and uses only a minimal basis set

- Calculated energy minimum
  - R_e = 2.493 au
  - E = -0.5648 au
  - Bonding energy: 0.0648

- Compare to exact values
  - R_e = 1.997 au
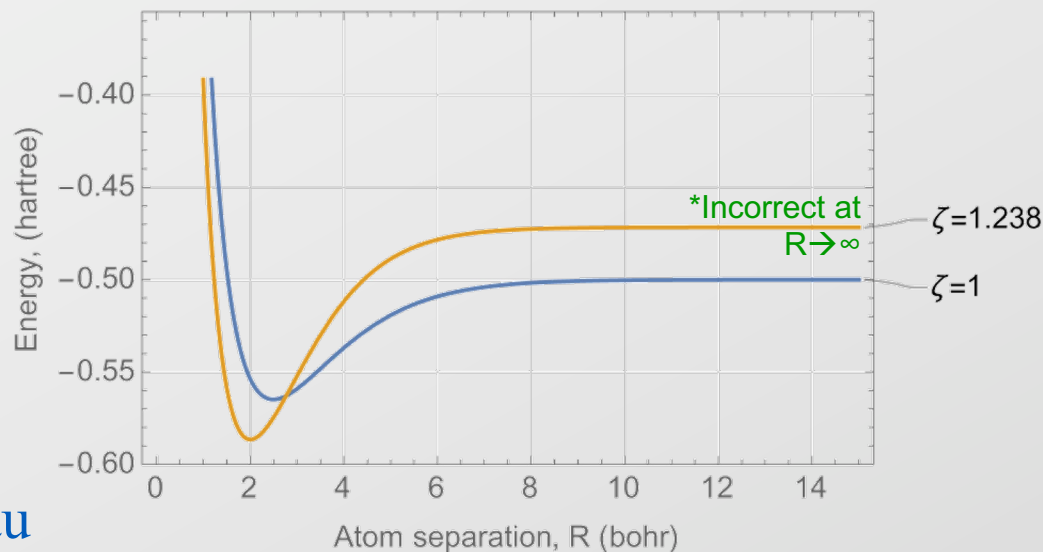 - E = -0.6026 au
  - Bonding energy: 0.1026 au

The approximation can be improved by treating ζ as a variational parameter

- Improved model ($\zeta = 1.238$) (more compact)
  - $R_e = 2.003$ au
  - $E = -0.5865$ au
  - Bonding energy: 0.1048*

- Compare to exact values
  - $R_e = 1.997$ au
  - $E = -0.6026$ au
  - Bonding energy: 0.1026 au

- Improvements possible with multi-ζ basis, or R-dependent ζ

*Incorrect at $R \rightarrow \infty$

$\zeta = 1.238$

$\zeta = 1$

Energy, (hartree)

Atom separation, R (bohr)

Here's a recap of the picture so far

- A MO is a 1-electron wavefunction for a molecule
  - Building block for the full n-electron wavefunction ψ
  - Spatial part can be occupied by up to two electrons, in opposite spin states
  - Shape of MO will be affected by other electron, and electrons in other MOs
- We can form MOs as a LCAO (number of basis functions: N)
  - Coefficients given by minimizing $\langle E \rangle$ according to the variational principle
  - All MOs are computed at once from the same basis set
- The HF/Roothaan-Hall equation performs this minimization while keeping the MOs orthogonal
  - For a 1-electron system, $F_{\mu,\nu} = h_{\mu,\nu}$ and no self-consistent solution needed
- The resulting secular determinant, $|h_{\mu,\nu} - S_{\mu,\nu}E|$, yields N energies
  - Each energy yields a set of coefficients, and thereby a MO
  - N must be at least half the number of electrons, and usually much more

The (neutral) hydrogen molecule has similar features to H_2^+, and a couple of differences

- 2 electrons

- One bonding molecular orbital, occupied by two electrons in different spin states

- If using minimal basis set, molecular orbitals are unchanged

$$\phi1[\{r\_, \theta\_, \phi\_\}, R\_, \zeta\_, s\_] := \frac{\chi\alpha[r, \theta, R, \zeta] - \chi\beta[r, \theta, R, \zeta]}{(2 - 2\,s)^{1/2}}$$

$$\phi2[\{r\_, \theta\_, \phi\_\}, R\_, \zeta\_, s\_] := \frac{\chi\alpha[r, \theta, R, \zeta] + \chi\beta[r, \theta, R, \zeta]}{(2 + 2\,s)^{1/2}}$$

- ERI contribution to Fock matrix will make energies different

$$\varepsilon_1 = h_{1,1} + J_{1,1} = \frac{h_{\alpha,\alpha} + h_{\alpha,\beta}}{1 + S} + [\phi_1\phi_1|\phi_1\phi_1]$$

H$_2$ wavefunction can be formed with both electrons occupying H$_2^+$ molecular orbital

$$\Psi(\tau_1, \tau_2) = \frac{1}{\sqrt{2}} |\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\alpha(s_1)\beta(s_2)|$$

$$= \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)]$$

- Hamiltonian doesn't depend on spin state, so we can drop that part for the rest of the calculation

- We have a filled-shell system, so same spatial orbital is used for both spin states: Restricted Hartree-Fock

- If we employ a more versatile basis set, differences between H$_2^+$ and H$_2$ wavefunctions will emerge

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Expressions for the matrix elements in the Restricted-HF Roothaan equations are here

- Density matrix in terms of basis-set coefficients: $P = 2CC^{\dagger}$

- Energy: $E = \sum_{\mu,\nu} h_{\mu,\nu} P_{\nu,\mu} + \frac{1}{2} \sum_{\mu,\nu} \sum_{\kappa,\lambda} \left([\mu\nu|\kappa\lambda] - \frac{1}{2}[\nu\lambda|\kappa\nu] \right) P_{\nu,\mu} P_{\lambda\kappa}$

- Fock operator: $F_{\mu,\nu} = h_{\mu,\nu} + \sum_{\kappa,\lambda} \left([\mu\nu|\kappa\lambda] - \frac{1}{2}[\mu\lambda|\kappa\nu] \right) P_{\lambda,\kappa}$

- Roothaan-Hall: $FC = SC\varepsilon$

- Iteration is needed to solve for self-consistent C, but h and ERIs do not change with each iteration

- These formulas apply for arbitrary number of basis functions

Suggested Reading/Viewing

- Autschbach Sec. 9.6

- Cramer: https://www.youtube.com/watch?v=BGUtZsnPIGo