

10/09/2024

- Brief review of variation theory and the Rayleigh-Ritz method
- Molecular Orbital Theory
 - for H_2^+
 - energies
 - wavefunctions
 - for H_2
 - spinorbitals
 - energy level diagrams
 - for other molecules
- Huckel Theory
- This lecture is designed to help you achieve the following learning objectives
 - Describe variation theory and the use of basis sets

Review

Variation Theory

- For any test wavefunction Ψ_t , the expectation of the energy is greater than the ground state energy E_o , $E = \frac{\int \Psi_t^* \hat{H} \Psi_t d\tau}{\int \Psi_t^* \Psi_t d\tau} = \frac{\langle \Psi_t | \hat{H} | \Psi_t \rangle}{\langle \Psi_t | \Psi_t \rangle} \geq E_o$
- Approximate wavefunctions can be found by trial and error. They can be tested to see whether they are closer to the true wavefunction.

The Rayleigh-Ritz Method

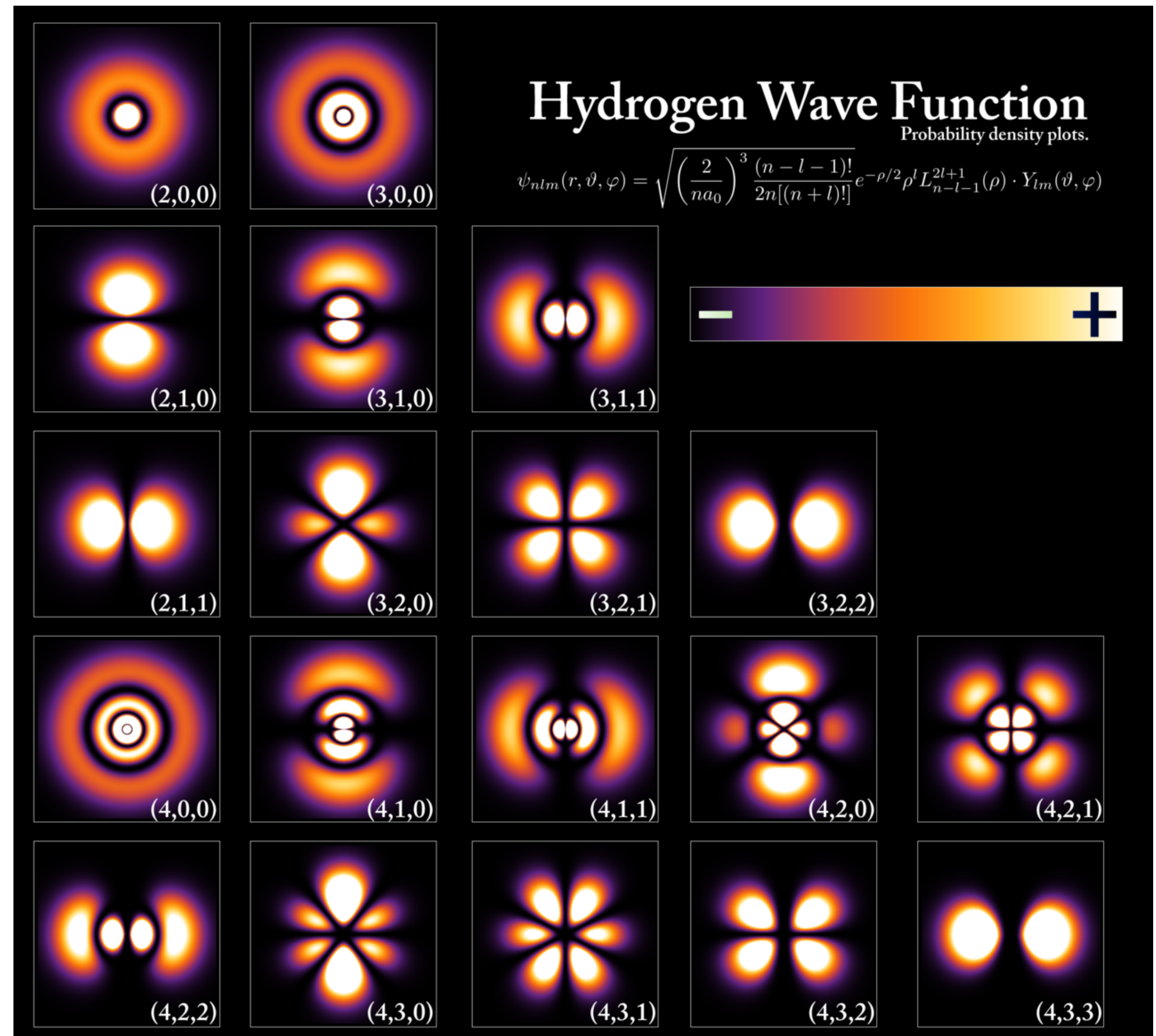
- The method is to find the linear combination of *fixed functions* that is closest to the ground-state wavefunction

- $\Psi_t = \sum_i c_i \Psi_i$

- c_i are coefficients, that are allowed to vary
- Ψ_i are arbitrary functions, not necessarily eigenfunctions of the Hamiltonian operator
- With this form of trial function, linear algebra (instead of multivariate calculus) can be used to optimize Ψ_t

Molecular Orbital Theory

- Based on a linear combination of atomic orbitals (LCAO), $\Psi = \sum_r c_r \chi_r$
- Qualitatively similar to exact solution of H_2^+
- Near an nucleus, \hat{H} is similar to atomic \hat{H}
- Ground-state energy is based on the variation theorem and can be found using the Rayleigh-Ritz method



By PoorLeno (talk) - the English language Wikipedia (log).Original text: I created this work entirely by myself.

MO Theory for H_2^+

H_2^+ energies

- For H_2^+ , the minimum basis set (enclosing both nuclei) is $\Psi = c_A 1s_A + c_B 1s_B$, where $1s_n$ is a $1s$ orbital enclosing nucleus n

- The secular determinant is
$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{vmatrix} = 0$$

- $H_{AA} = \langle 1s_A | \hat{\mathbf{H}} | 1s_A \rangle = \langle 1s_B | \hat{\mathbf{H}} | 1s_B \rangle = H_{BB}$ are *atomic integrals*, centered around one nucleus
- $H_{AB} = \langle 1s_A | \hat{\mathbf{H}} | 1s_B \rangle = H_{BA}$ are *exchange integrals*, dependent on two nuclei
- $S = \langle 1s_A | 1s_B \rangle$ is the overlap integral
 - Near one if the atoms are close
 - Falls to zero as the distance between atoms increases

Matrix elements of Slater-type orbitals

- Instead of the actual hydrogen orbital, we will use Slater-type orbitals, $S_{nlm_l}(r, \theta, \phi) = N_{nl}r^{n-1}e^{-\zeta r}Y_l^{m_l}(\theta, \phi)$
 - These decay exponentially
 - Unlike hydrogenic orbitals, they have no radial nodes
- For these orbitals, the matrix elements are

$$\bullet H_{AA} = \left\langle 1s_A \left| -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right| 1s_A \right\rangle = -\frac{1}{2} + J(R) + \frac{1}{R} \text{ is called the Coulomb integral}$$

$$\bullet H_{AB} = \left\langle 1s_A \left| -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right| 1s_B \right\rangle = -\frac{S(R)}{2} + K(R) + \frac{S(R)}{R} \text{ is called the resonance integral}$$

$$\bullet S(R) = e^{-R} \left(1 + R + \frac{R^2}{3} \right) \text{ is overlap integral}$$

$$\bullet J(R) = \left\langle 1s_A \left| -\frac{1}{r_B} \right| 1s_A \right\rangle = e^{-2R} \left(1 + \frac{1}{R} \right) - \frac{1}{R}; K(R) = -e^{-R}(1 + R)$$

Distance dependence of matrix elements

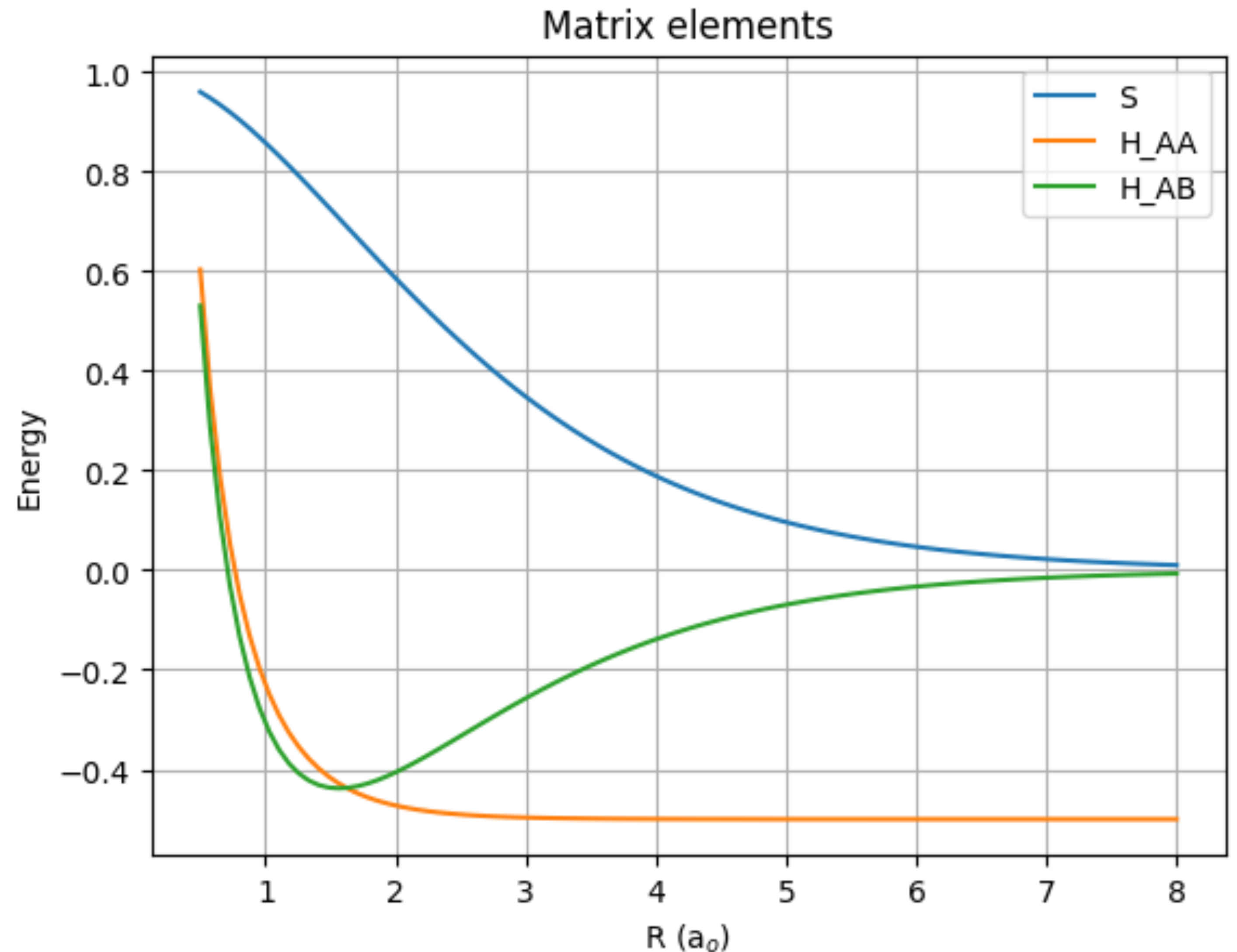
```
[1] import numpy as np

R = np.linspace(0.5, 8., 100)
S = np.exp(-R)*(1+R+R*R/3)
J = np.exp(-2*R)*(1+1/R) - 1/R
K = -np.exp(-R)*(1+R)
```

```
[2] H_AA = -1/2 + J + 1/R
H_AB = -S/2 + K + S/R

import matplotlib.pyplot as plt

plt.plot(R, S, label="S")
plt.plot(R, H_AA, label="H_AA")
plt.plot(R, H_AB, label="H_AB")
plt.legend()
plt.ylabel("Energy")
plt.xlabel("R (a$_o$)")
plt.grid(True);
plt.title('Matrix elements');
```



H_2^+ energies

- Expanding the secular determinant

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{vmatrix} = 0 \text{ leads to}$$

$$(H_{AA} - E)^2 - (H_{AB} - ES)^2 = 0$$

- Based on the quadratic equation,

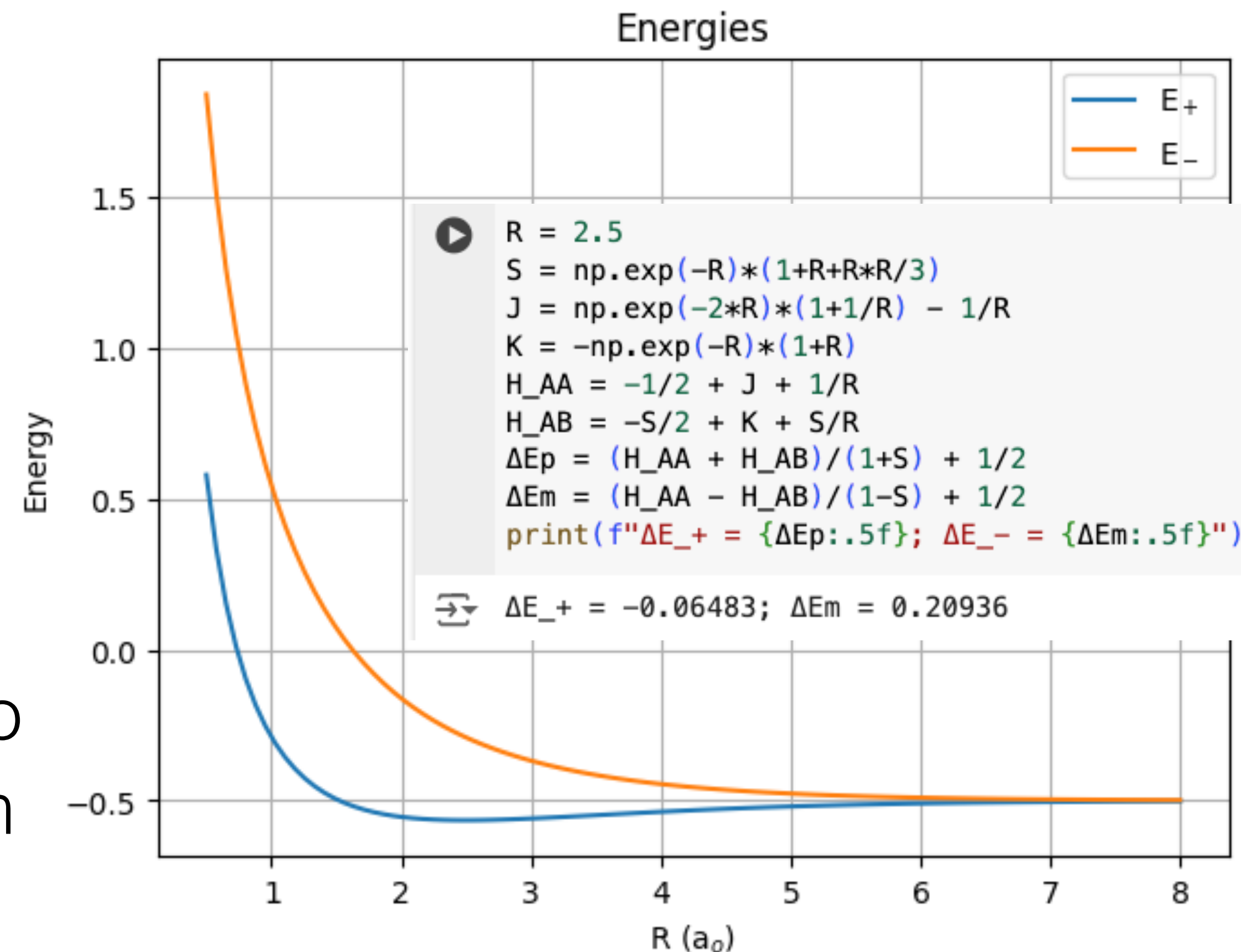
$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S} \text{ are the MO energies}$$

- E_+ is the ground state
- E_- is the first excited state.
- $\Delta E_{\pm} = E_{\pm} - E_{1s}$ is the energy relative to the separated proton and hydrogen atom

$$E_p = (H_{AA} + H_{AB}) / (1 + S)$$

$$E_m = (H_{AA} - H_{AB}) / (1 - S)$$

```
plt.plot(R, Ep, label="E$_+$")
plt.plot(R, Em, label="E$_-$")
plt.legend()
plt.ylabel("Energy")
plt.xlabel("R (a$_0$)")
plt.grid(True)
plt.title('Energies');
```



Assessment of MO energies

MO vs exact energies

	LCAO (minimum basis set)	Exact
Minimum energy	-0.06483 E_h	-0.10264 E_h
Bond length	2.493 a_o = 132 pm	2 a_o = 106 pm

Not that close, but qualitatively similar

H_2^+ wavefunction

- The secular equations are

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

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

- Substituting E_+ into the first equation and using $H_{AA} = H_{BB}$ and $H_{AB} = H_{BA}$, we get,

- $c_A \left(H_{AA} - \frac{H_{AA} + H_{AB}}{1 + S} \right) + c_B \left(H_{AB} - \frac{H_{AA} + H_{AB}}{1 + S} S \right) = 0$

- $c_A \left(\frac{H_{AA}S - H_{AB}}{1 + S} \right) + c_B \left(\frac{H_{AB} - H_{AA}S}{1 + S} \right) = 0$

- Thus $c_A = c_B$.

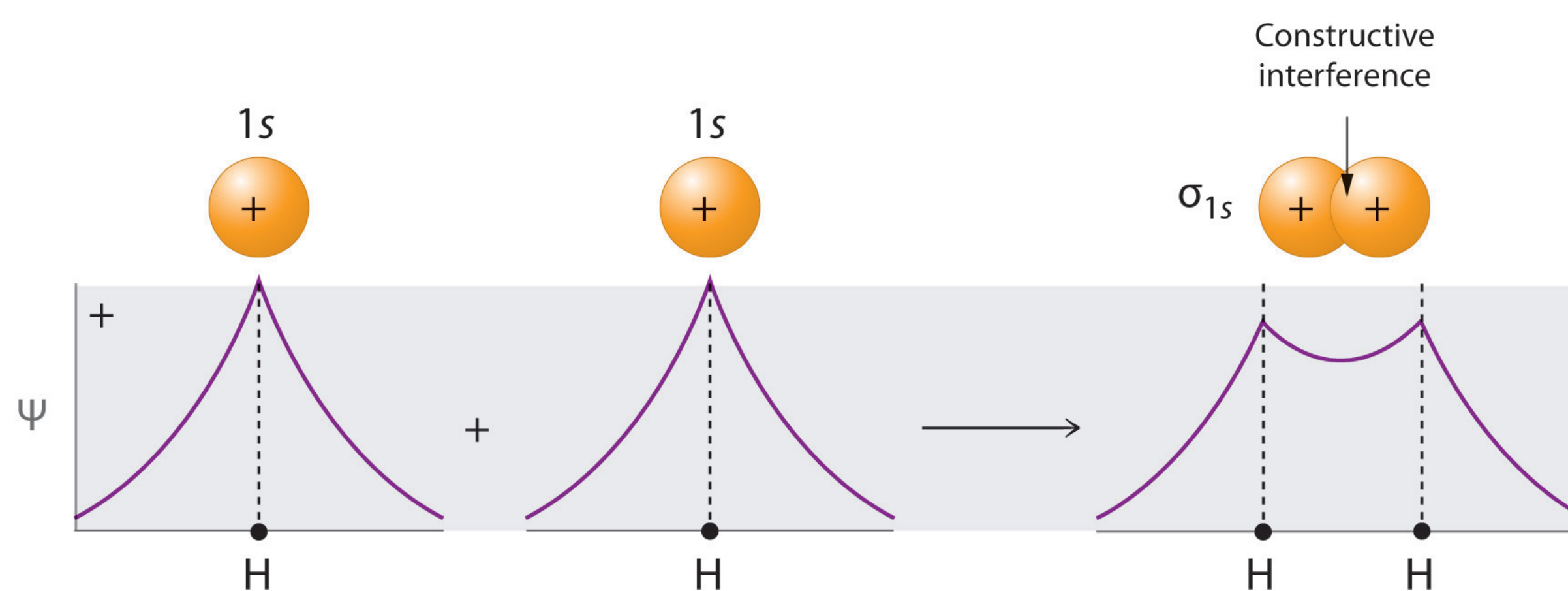
- After normalizing, we find

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

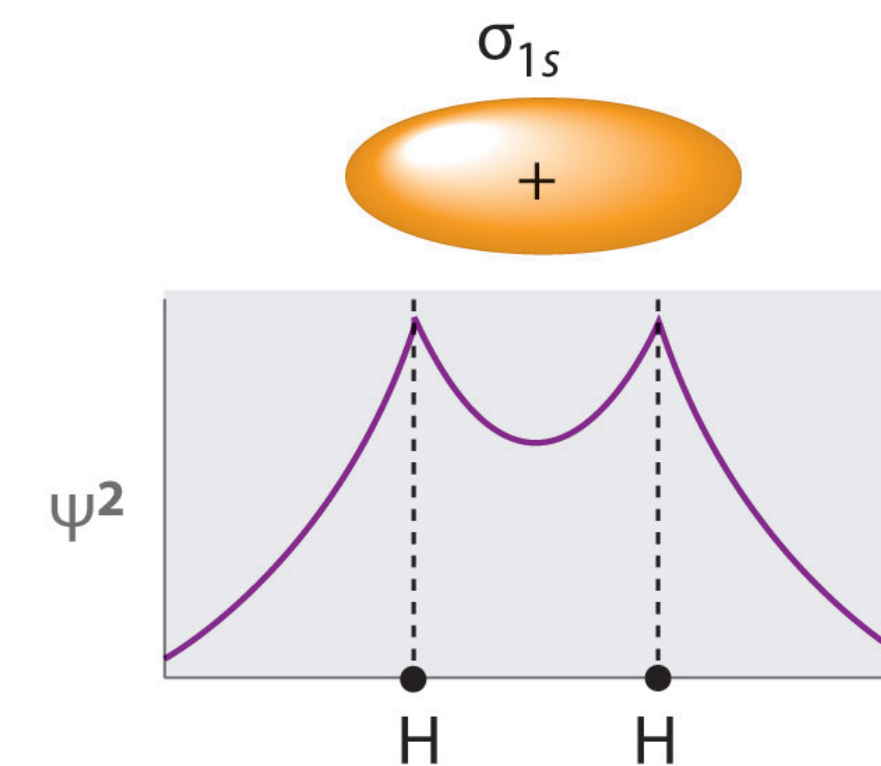
- Likewise,

$$\Psi_- = \frac{1}{\sqrt{2(1 - S)}} (1s_A - 1s_B)$$

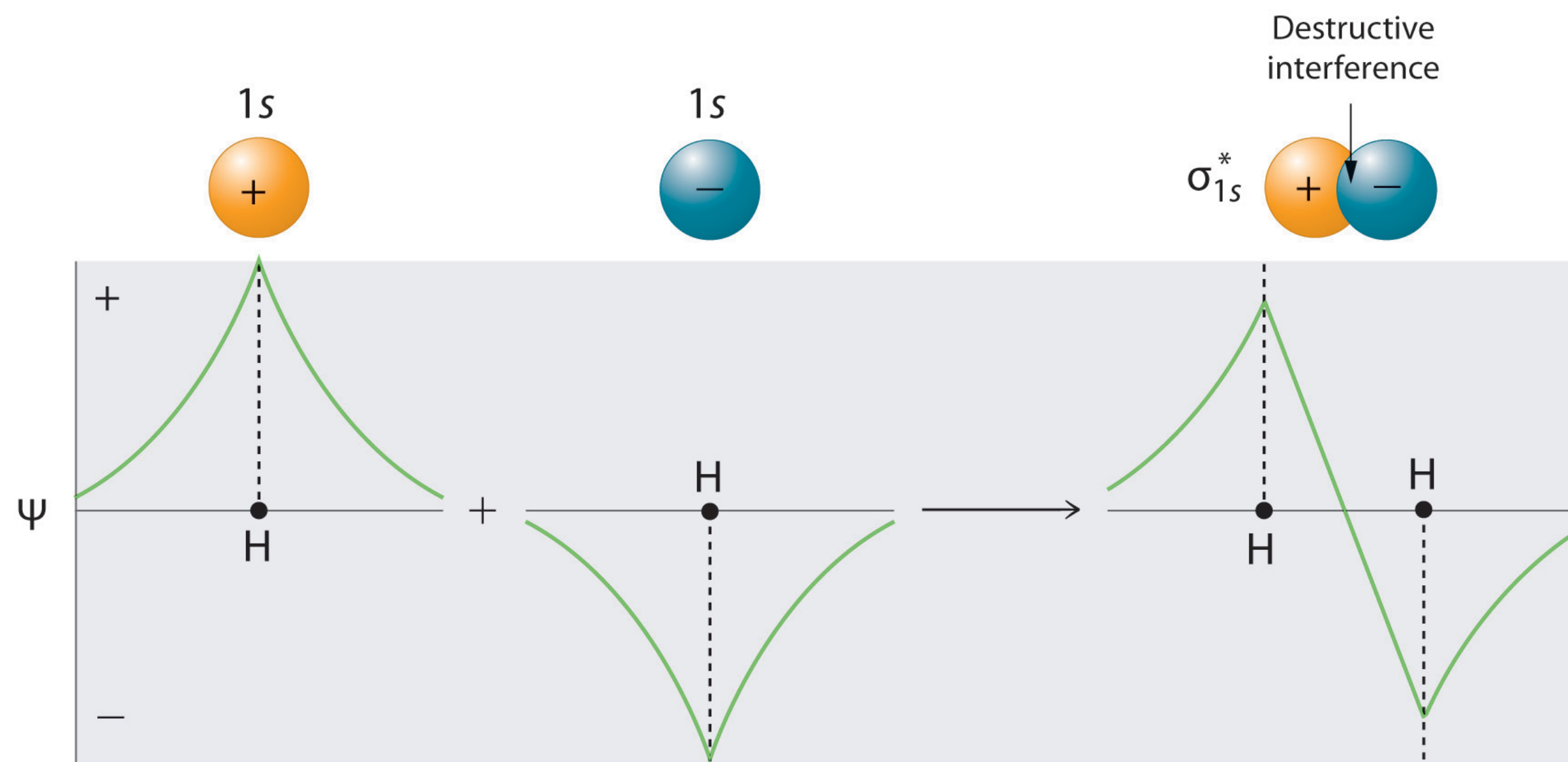
- Ψ_+ is stable and is called the *bonding* orbital
- Ψ_- is unstable and is called the *antibonding* orbital



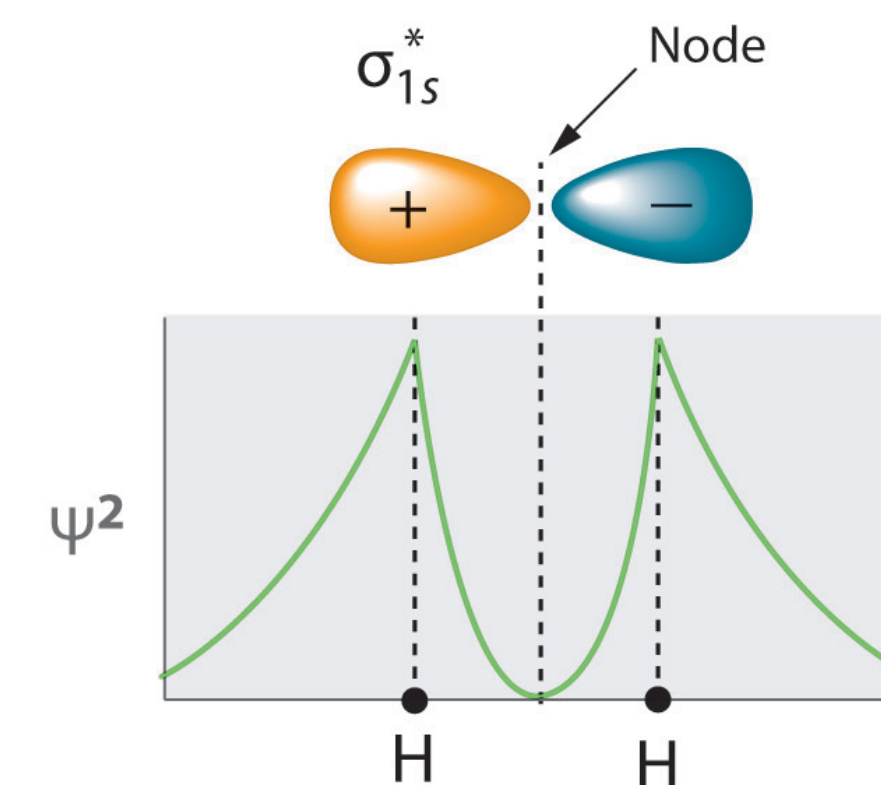
(a) Wave functions combined for σ_{1s}



(b) Bonding probability density



(c) Wave functions combined for σ_{1s}^*



(d) Antibonding probability density

Molecular Orbitals for the H_2 Molecule. (a) The formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H $1s$ atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (c) The formation of an antibonding molecular orbital for H_2 as the difference of the wavefunctions (Ψ) of two H $1s$ atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei. https://chem.libretexts.org/Courses/Knox_College/Chem_321%3A_Physical_Chemistry_I/03%3A_Chemical_Bond/3.04%3A_Molecular_Orbital_Theory

MO theory for H₂

Electronic wavefunctions for H₂

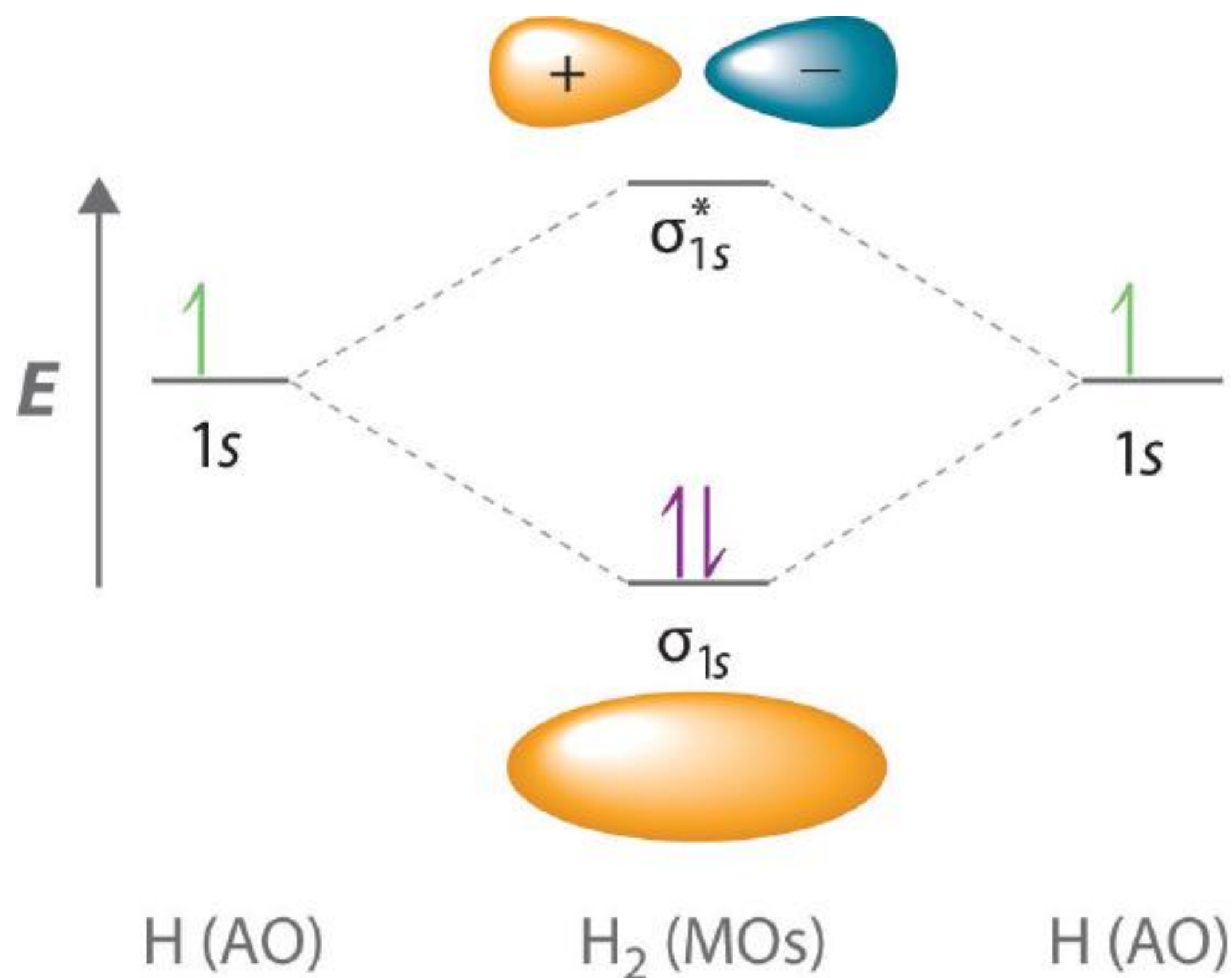
- LCAO leads to one-electron spatial molecular orbitals Ψ_+ and Ψ_-
- Most molecules have more than one electron
- H₂ has two protons and two electrons
- For the *electronic* Schrodinger equation, its Hamiltonian is,
$$\hat{\mathbf{H}} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{R},$$
 only slightly different than for H₂⁺
- What is a two-electron wavefunction using $\Psi_+(n)$ for $n \in \{1,2\}$ that satisfies the Pauli principle?

Assessment of MO energies

MO vs experimental energies

	LCAO (minimum basis set)	Experimental
Minimum energy	-1.0991 E_h	-1.174 E_h
Bond length	1.603 a_o	1.401 a_o

H₂ energy level diagram



- An energy level diagram compares the energies of MOs with the those of the parent atomic orbitals
- σ_{1s} - sum of 1s orbitals
- σ_{1s}^* - difference of 1s orbitals
- Valence electrons are inserted into diagram according to
 - Pauli principle - each orbital can accommodate a maximum of two electrons with opposite spins
 - Hund's rule - orbitals are filled in order of increasing energy

Molecular Orbital Energy-Level Diagram for H₂
https://chem.libretexts.org/Courses/Knox_College/Chem_321%3A_Physical_Chemistry_I/03%3A_Chemical_Bond/3.04%3A_Molecular_Orbital_Theory

Orbital occupancy


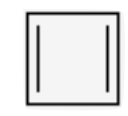
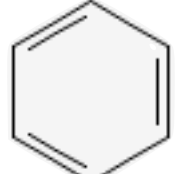

- Bond order is $b = \frac{1}{2} (N_{bonding} - N_{antibonding})$
 - Electrons in antibonding orbitals cancel effect of bonding orbitals
 - Predicts stability of species
- Classifications of MOs
 - HOMO - Highest occupied molecular orbital
 - LUMO - Lowest unoccupied molecular orbital
 - The HOMO and LUMO are frontier orbitals, where most of the reactive and spectroscopic activity occurs
 - Virtual orbitals are not occupied by any electrons

MO theory for other molecules

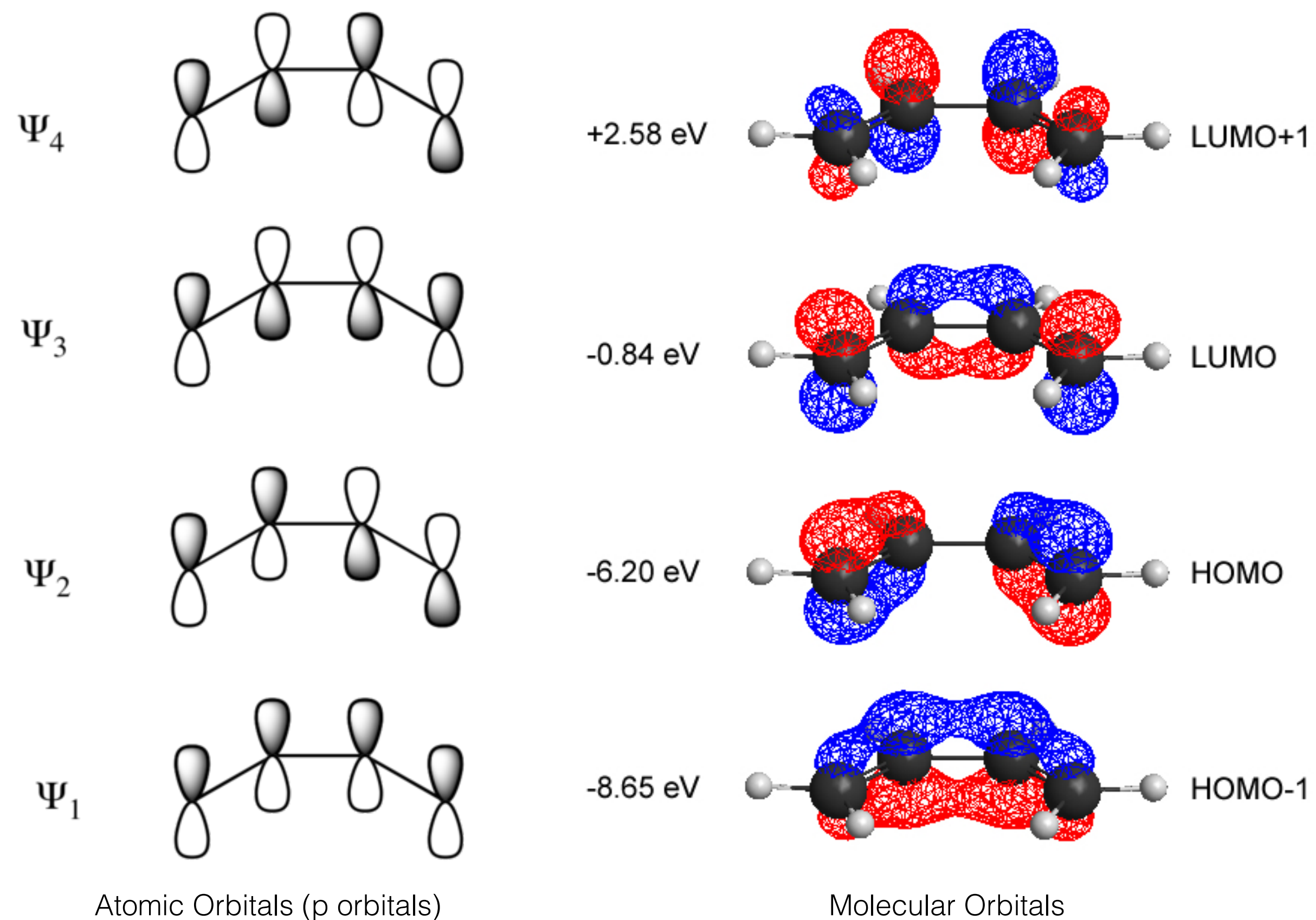
- Can also apply LCAO-MO description
- Criteria for bond formation
 - Non-negligible overlap, which implies valence shell orbitals are involved in bonding
 - Similar energies, as they lead to larger energy changes upon bonding
- For a heteronuclear diatomic molecules, if atom A is more electronegative than atom B, then in the wavefunction $\Psi = c_A\chi_A + c_B\chi_B$
 - $|c_A|^2 > |c_B|^2$ for bonding MOs
 - $|c_A|^2 < |c_B|^2$ for antibonding MOs
- In polyatomic molecules, $\Psi = \sum_o c_o\chi_o$, where χ_o exist for every atom

Huckel Theory

Basics

- Specific type of MO theory with approximations
- For planar conjugated molecules with alternating single and double bonds, e.g.
 - butadiene 
 - cyclobutadiene 
 - benzene 
 - ethylene 
- Based on LCAO, with AOs being p orbitals

1,3-butadiene



Approximations and Examples

- Approximations

- Separate treatment of σ and π orbitals

- Orthonormality, $S_{rs} = \delta_{rs}$

- $$H = \begin{cases} \alpha & \text{for diagonal elements} \\ \beta & \text{for neighboring elements} \\ 0 & \text{otherwise} \end{cases}$$

- Examples

- For butadiene,

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

- For benzene,

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

Benefits

- What does Huckel theory give you?
 - Energy levels, including degeneracy in terms of α and β .
 - Charge density per atom
 - Bond order
 - Dipole moment
- As a caveat, the Huckel method generally gives correct orders for energies, but not necessarily the right absolute values

Review Questions

- How does MO theory relate to variation theory and the Rayleigh-Ritz method?
- How can MO theory be used to predict bond distances and energies?
- What is a bonding and a nonbonding orbital?
- What causes a MO to have a node?
- How are Slater determinants helpful for MOs?
- Explain the purpose of Huckel theory, its approximations, and its relationship with MO theory