

CHEM20212

Computational Chemistry II:
Fundamentals of electronic structure theory

2 Electronic structure of molecules

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Course Overview

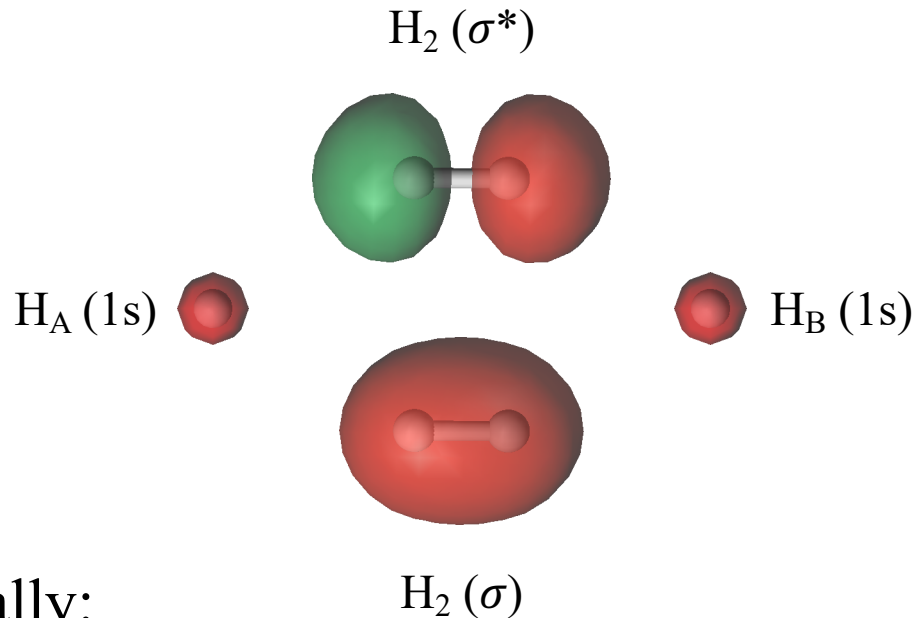
1 Electronic structure of atoms <ul style="list-style-type: none">• Introduction• Hydrogenic atoms• Multi-electron atoms• Ground vs. excited states	4 Hückel theory <ul style="list-style-type: none">• Constructing a Hückel matrix• Molecular orbitals• Benzene anion• Electrophilic and nucleophilic attack
2 Electronic structure of molecules <ul style="list-style-type: none">• Molecular orbitals• Molecular electronic structure• Energy hierarchy	5 Spin Hamiltonians <ul style="list-style-type: none">• A “how-to” guide• Matrix elements• Example: $S = 1/2$• Example: $S = 1$
3 Matrix mechanics <ul style="list-style-type: none">• Vector (Hilbert) spaces• Bra-ket notation• Operators and expectation values• Matrix diagonalisation	6 Workshop

Intended learning objectives

1. Construct approximate wave functions for single and multi-electron atoms
2. Explain the energy hierarchy of multi-electron atoms
3. Differentiate the concepts of ground and excited electronic states, including spin and orbital states
4. Mathematically expand and visualise the spatial wave functions of atoms and simple molecules as a linear combination of MOs and basis functions
5. Mathematically describe the connection between matrix diagonalisation and solution to the Schrödinger equation
6. Construct a Hückel Hamiltonian matrix
7. Employ Bra-Ket notation to evaluate the matrix elements of a simple spin Hamiltonian

Molecular orbitals

- What about molecular wavefunctions? [Ignore spin for now]
 - We construct spatial molecular orbitals (MOs) from a linear combination of spatial atomic orbitals (LCAO)



- Mathematically:

$$\psi_{1s,\sigma}[\vec{r}] = \frac{1}{\sqrt{2}} (\psi_{1s_A}[\vec{r} - \vec{R}_A] + \psi_{1s_B}[\vec{r} - \vec{R}_B])$$
$$\psi_{1s,\sigma^*}[\vec{r}] = \frac{1}{\sqrt{2}} (\psi_{1s_A}[\vec{r} - \vec{R}_A] - \psi_{1s_B}[\vec{r} - \vec{R}_B])$$

Molecular orbitals

- In general, **MOs** are sums over all **AOs** (the set of **AOs** is called the *basis set*):

$$\psi_a[\vec{r}] = \sum_b C_{a,b} \psi_b(\vec{r} - \vec{R}_b)$$

- Note: same number of **MOs** as **AOs**!
- For the H₂ example:

$$\psi_{1s,\sigma}[\vec{r}] = \frac{1}{\sqrt{2}} (\psi_{1s_A}[\vec{r} - \vec{R}_A] + \psi_{1s_B}[\vec{r} - \vec{R}_B])$$
$$\psi_{1s,\sigma^*}[\vec{r}] = \frac{1}{\sqrt{2}} (\psi_{1s_A}[\vec{r} - \vec{R}_A] - \psi_{1s_B}[\vec{r} - \vec{R}_B])$$

$$C_{\sigma,1s(A)} = +\frac{1}{\sqrt{2}} \quad C_{\sigma,1s(B)} = +\frac{1}{\sqrt{2}}$$
$$C_{\sigma^*,1s(A)} = +\frac{1}{\sqrt{2}} \quad C_{\sigma^*,1s(B)} = -\frac{1}{\sqrt{2}}$$

Molecular orbitals

- How about O₂:

$$\psi_{2p,-1}[r, \theta, \phi] = R_{2p}[r]Y_{1,-1}[\theta, \phi]$$

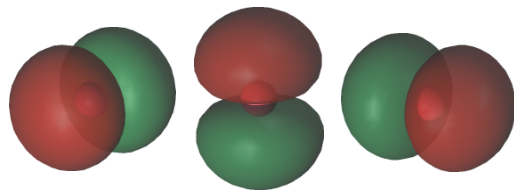
$$\psi_{2p,0}[r, \theta, \phi] = R_{2p}[r]Y_{1,0}[\theta, \phi]$$

$$\psi_{2p,+1}[r, \theta, \phi] = R_{2p}[r]Y_{1,+1}[\theta, \phi]$$

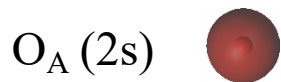
$$\psi_{2p_x}[r, \theta, \phi] = R_{2p}[r]x = R_{2p}[r]r \sin \theta \cos \phi$$

$$\psi_{2p_y}[r, \theta, \phi] = R_{2p}[r]y = R_{2p}[r]r \sin \theta \sin \phi$$

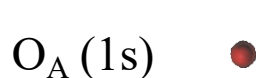
$$\psi_{2p_z}[r, \theta, \phi] = R_{2p}[r]z = R_{2p}[r]r \cos \theta$$



O_A (2p)



O_A (2s)



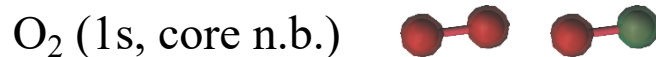
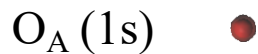
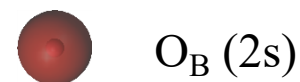
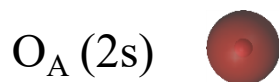
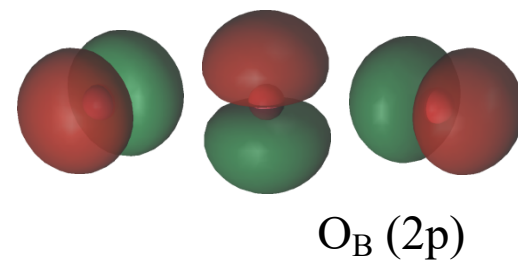
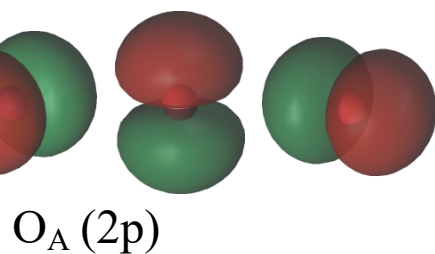
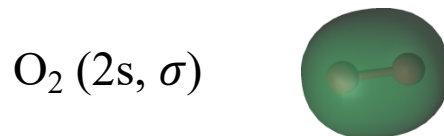
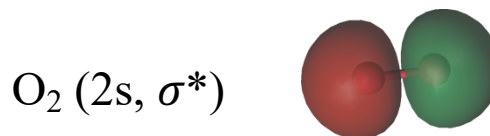
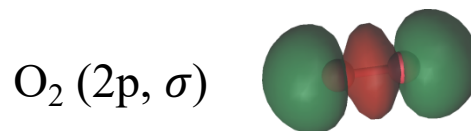
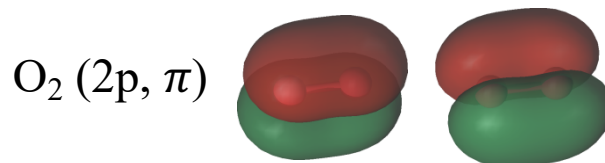
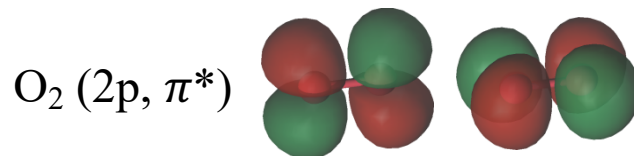
O_A (1s)

$$\psi_{2s}[r, \theta, \phi] = R_{2s}[r]$$

$$\psi_{1s}[r, \theta, \phi] = R_{1s}[r]$$

Molecular orbitals

- How about O_2 :



Molecular orbitals

- Let's sketch one of the 2p π^* MOs:
 - Atoms O_A and O_B lie on the x-axis
 - MO is:

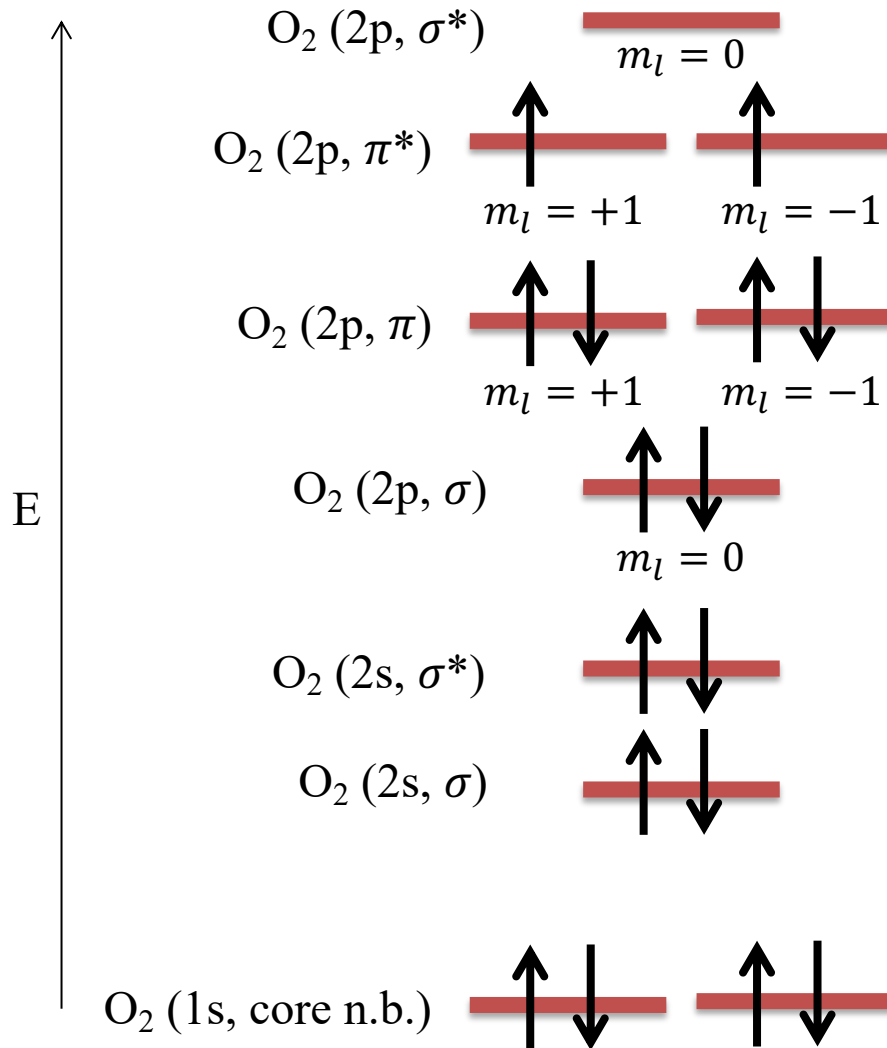
$$\psi_{2p,\pi^*}[\vec{r}] = \frac{1}{\sqrt{2}} \left(\psi_{2p_{z_A}}[\vec{r} - \vec{R}_A] - \psi_{2p_{z_B}}[\vec{r} - \vec{R}_B] \right)$$

- AOs:

$$\psi_{2p_{z_A}}[\vec{r} - \vec{R}_A] = R_{2p}[r - R_A](z - z_A)$$

Molecular electronic structure

- What about electronic states?



- Ground term?

$$- S = \frac{1}{2} + \frac{1}{2} = 1$$

$$- L = 1 - 1 = 0 \equiv \Sigma(S)$$

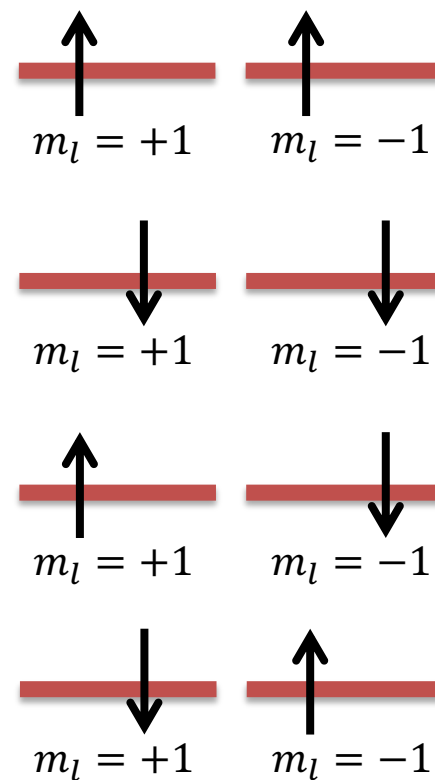
$$- {}^3\Sigma$$

Molecular electronic structure

- A Slater determinant represents a given set of quantum numbers (χ_{m_l, m_s} notation): need multiple determinants to describe O_2 !
- Ground state of O_2 (π^* electrons only):

$$\Psi_{^3\Sigma}[\vec{x}_1, \vec{x}_2] = B_1 \begin{vmatrix} \chi_{+,+}[\vec{x}_1] & \chi_{-,+}[\vec{x}_1] \\ \chi_{+,+}[\vec{x}_2] & \chi_{-,+}[\vec{x}_2] \end{vmatrix} + B_2 \begin{vmatrix} \chi_{+,-}[\vec{x}_1] & \chi_{-,-}[\vec{x}_1] \\ \chi_{+,-}[\vec{x}_2] & \chi_{-,-}[\vec{x}_2] \end{vmatrix} + B_3 \begin{vmatrix} \chi_{+,+}[\vec{x}_1] & \chi_{-,-}[\vec{x}_1] \\ \chi_{+,+}[\vec{x}_2] & \chi_{-,-}[\vec{x}_2] \end{vmatrix} + B_4 \begin{vmatrix} \chi_{+,-}[\vec{x}_1] & \chi_{-,+}[\vec{x}_1] \\ \chi_{+,-}[\vec{x}_2] & \chi_{-,+}[\vec{x}_2] \end{vmatrix}$$

These coefficients tell us how much each determinant contributes to the ground $^3\Sigma$ state

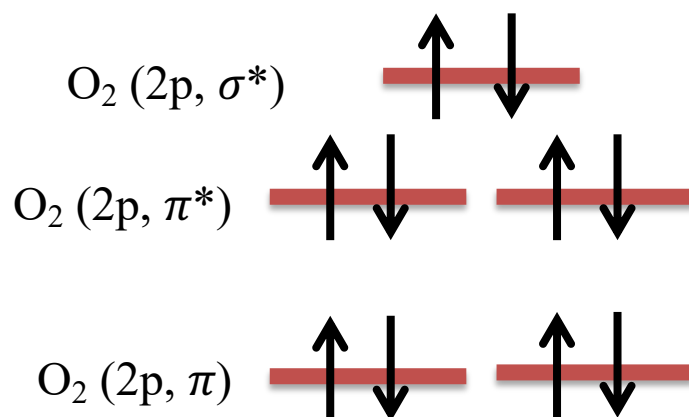


Wavefunction methods

- Hartree-Fock(-Roothan) method:
 - Mean-field theory
 - Single determinant, *all electrons paired*
 - LCAO method for MOs
 - *Good approximation for closed-shell organic molecules*
- Main problems of Hartree-Fock?
 - We haven't *actually included* the $\frac{1}{|\vec{r}_1 - \vec{r}_2|}$ term, so the electrons don't interact with each other correctly
 - This is called a lack of *dynamic correlation*
 - Can be approximated with perturbation theory (*i.e.* MP2) or through other methods (*i.e.* coupled-cluster or DFT)
 - Can't model open-shell molecules (lack of *static correlation*)

Wavefunction methods

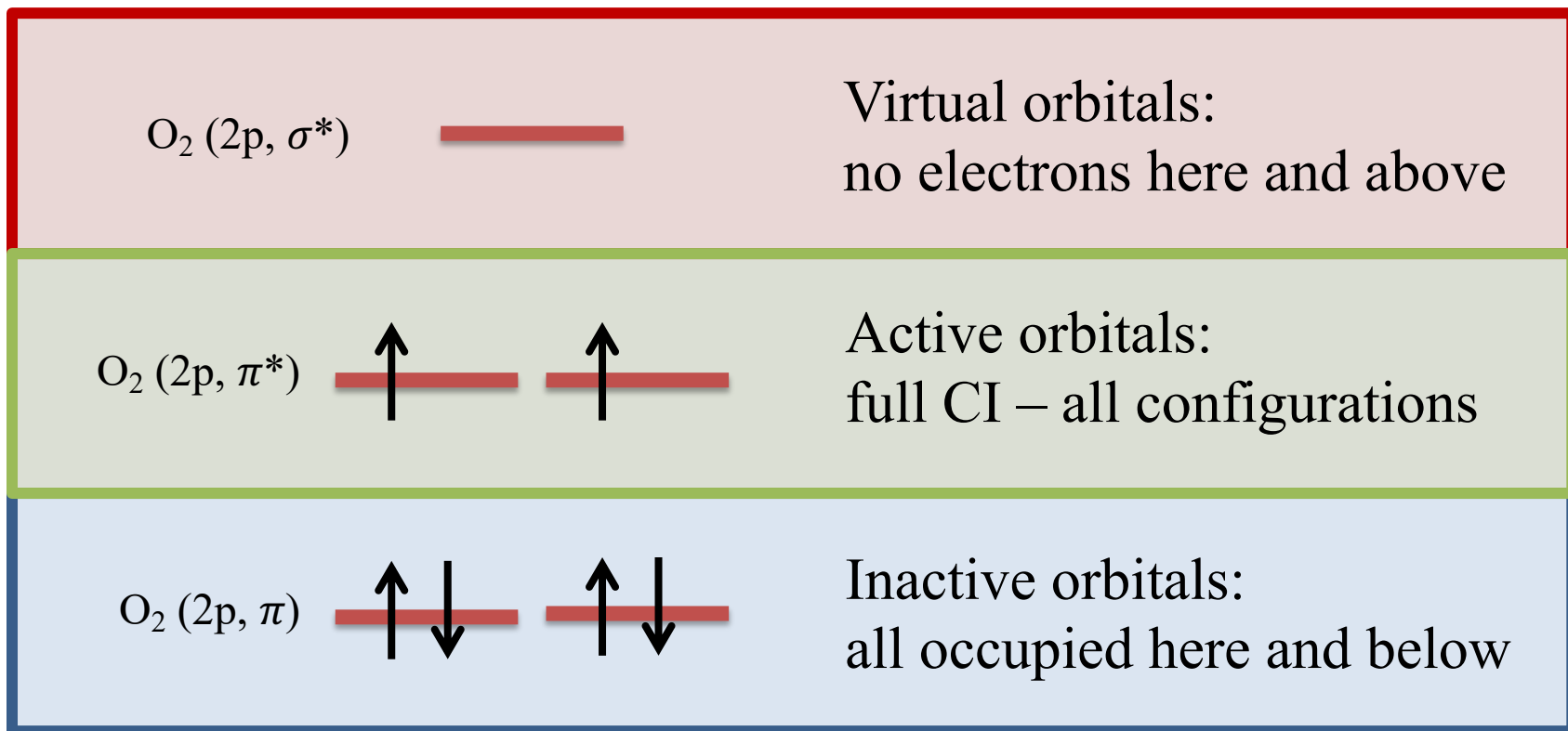
- Open shell molecules require multiple determinants
 - Hartree-Fock method not applicable!
 - Wavefunction is a linear combination of Slater determinants
 - ***Full configuration interaction*** (all electrons can be in all orbitals) approaches the exact non-relativistic solution when combined with an infinite basis set



- Unfortunately, it's very expensive! Usually, the number of configurations is restricted

Wavefunction methods

- The *complete active space* method is a common approach
 - Treats most electrons with Hartree-Fock and only some electrons and orbitals with configuration interaction
 - Allows treatment of excited states



Energy Hierarchy

- Just like atoms, molecules have many electronic states
 - But they also have vibrational and rotational quantum states!
 - For O_2 :

