CHEM3023: Spins, Atoms and Molecules

Lecture 4

Molecular orbitals

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Learning outcomes

- Be able to manipulate expressions involving spin orbitals and molecular orbitals
- Be able to write down the energies of electronic configurations

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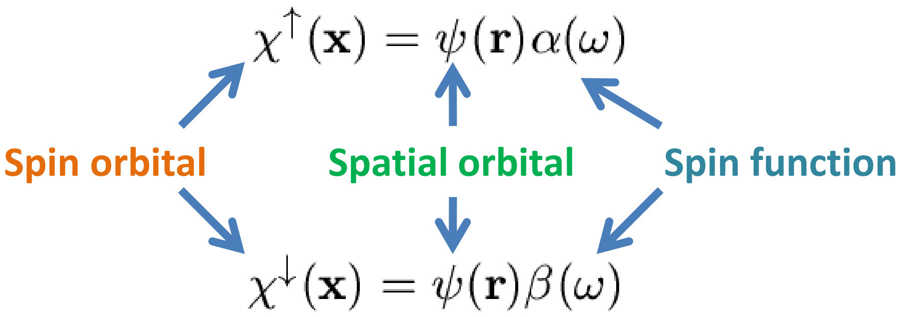
Molecular orbitals

- A wavefunction for a single electron is called a molecular orbital (MO)
- MO with spatial and spin coordinates are called **spin orbitals** and are products of a spatial orbital and a spin function, e.g.



$$\chi^{\uparrow}(\mathbf{x}) = \psi(\mathbf{r})\alpha(\omega)$$

Spin orbital

Spatial orbital

Spin function

$$\chi^{\downarrow}(\mathbf{x}) = \psi(\mathbf{r})\beta(\omega)$$

- Molecules contain many electrons. Can we use MOs to build simple approximate many-electron wavefunctions?
- Let's try using a product of spin orbitals. E.g. for a two-electron molecule (e.g. H_2 or HeH^+):

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) \simeq \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)$$

This wavefunction is not acceptable – it is not antisymmetric (show this!)

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Slater determinants

You can verify that the following wavefunction for two electrons is antisymmetric:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)$$

It can also be written as a determinant:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}$$

- This can be generalised to any number of electrons
- A wavefunction of this form is called a **Slater determinant**
- It obeys antisymmetry by construction (determinants change sign when two rows or columns are interchanged)

Slater determinants

Slater determinant for N electrons:

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \boxed{\frac{1}{\sqrt{N!}}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \ldots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \ldots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \ldots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Normalisation constant

Shorthand representation, as a ket:

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\ldots\chi_N(\mathbf{x}_N)\rangle$$

Spin orbitals in Slater determinants are always orthonormal, i.e.

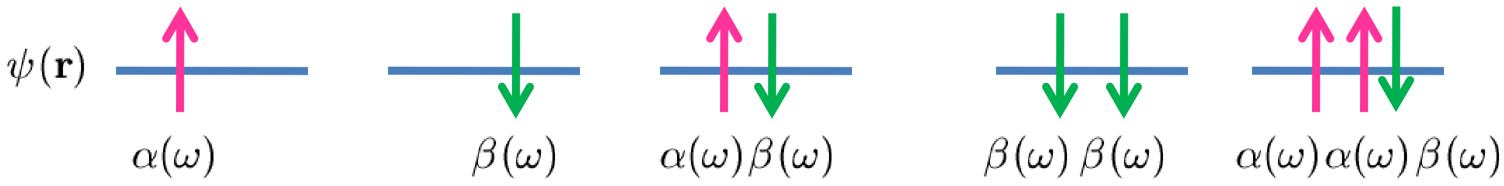
$$\langle\chi_i|\chi_j\rangle = \delta_{ij}$$

The Pauli principle

- A determinant is zero if two or more of its rows or columns are identical
- Therefore a given spin orbital can be included only once in a Slater determinant, as otherwise the determinant would become zero everywhere and such a wavefunction is not acceptable

Allowed

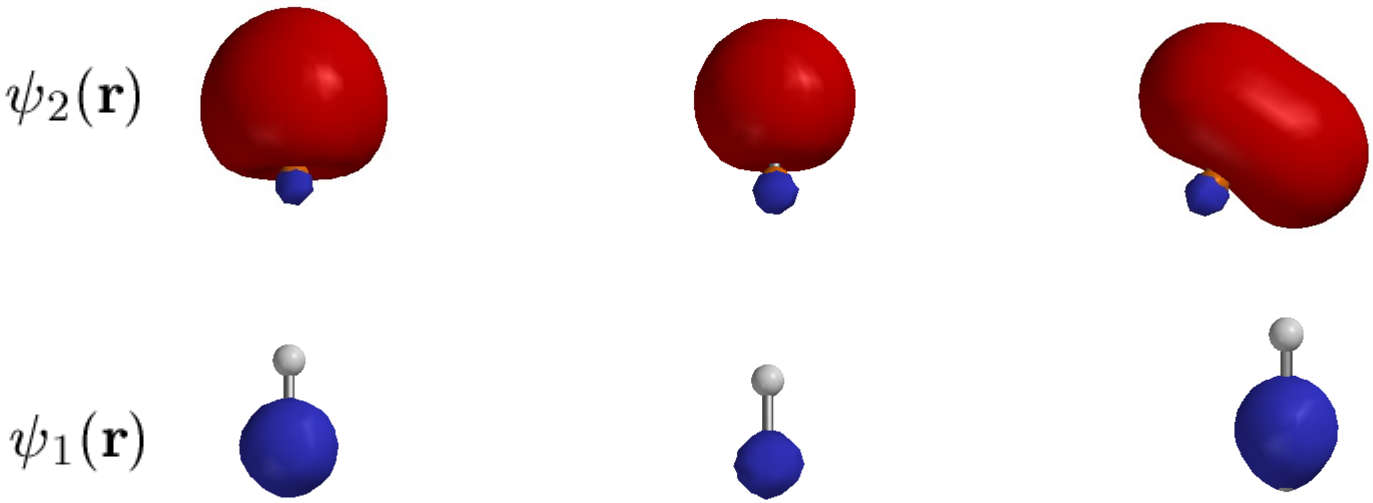
Examples of not allowed cases



- The Pauli principle follows naturally as a spatial orbital can result in at most two spin orbitals (one with up and one with down spin functions)
- In other words, a spatial orbital can be occupied by no more than two electrons of opposite spins

Using Slater determinants

- Even if we decide to use a Slater determinant for our wavefunction, we still need to decide on the form of the molecular orbitals (MOs) as there are infinite choices possible...
- For example, either of the following choices for the two orbitals of the LiH molecule can be used to construct acceptable Slater determinants



Which of the above choices of orbitals produce the “best” Slater determinant?

Electronic energy of a Slater determinant

- We will learn how to perform calculations that **construct the "best" MOs** for a SD of a given molecule
- In order to get to this stage, we first need to derive an expression for the electronic energy of a SD

$$E_{SD} = \frac{\langle \Psi_{SD} | \hat{H}_{elec} | \Psi_{SD} \rangle}{\langle \Psi_{SD} | \Psi_{SD} \rangle} = \langle \Psi_{SD} | \hat{H}_{elec} | \Psi_{SD} \rangle$$

$$\hat{H}_{elec} = -\sum_{i=1}^{N_{elec}} \frac{1}{2}\nabla_i^2 - \sum_{I=1}^{N_{nuc}} \sum_{i=1}^{N_{elec}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i=1}^{N_{elec}} \sum_{j=i+1}^{N_{elec}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Kinetic

Nuclear attraction

Electron-electron repulsion

Matrix elements of one-electron operators

The Hamiltonian contains one-electron operators

$$\hat{O}(\mathbf{r}_1) = -\frac{1}{2}\nabla^2_{\mathbf{r}_1} \quad \text{or} \quad \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|}$$

$$\int\int \chi_p^*(1)\chi_q^*(2)\,\hat{O}(\mathbf{r}_1)\chi_s(1)\chi_t(2)d1d2 = \int \chi_p^*(1)\hat{O}(\mathbf{r}_1)\chi_s(1)d1 \int \chi_q^*(2)\chi_t(2)d2$$

$$\int \chi_p^*(1)\hat{O}(\mathbf{r}_1)\chi_s(1)d1 = \int \psi_p^*(\mathbf{r}_1)\hat{O}(\mathbf{r}_1)\psi_s(\mathbf{r}_1)d\mathbf{r}_1 \int \sigma_p^*(\omega_1)\sigma_q(\omega_1)d\omega_1$$

$$\int \chi_q^*(1)\chi_t(1)d1 = \int \psi_q^*(\mathbf{r}_1)\psi_t(\mathbf{r}_1)d\mathbf{r}_1 \int \sigma_q^*(\omega_1)\sigma_t(\omega_1)d\omega_1$$

For what combinations of spin orbitals the above intergrals are non-zero?

Matrix elements of two-electron operators

The Hamiltonian contains just one kind of two-electron operator

$$\hat{O}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\int\int \chi_p^*(1)\chi_q^*(2)\, \hat{O}(\mathbf{r}_1, \mathbf{r}_2)\, \chi_s(1)\chi_t(2) d1d2 = \int\int \psi_p^*(\mathbf{r}_1)\psi_q^*(\mathbf{r}_2)\hat{O}(\mathbf{r}_1, \mathbf{r}_2)\psi_s(\mathbf{r}_1)\psi_t(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$\int \sigma_p^*(\omega_1)\sigma_s(\omega_1)d\omega_1 \int \sigma_q^*(\omega_2)\sigma_t(\omega_2)d\omega_2$$

For what combinations of spin orbitals the above intergrals are non-zero?

1) Kinetic energy

The expectation value of the kinetic energy is an integral involving the coordinates of all the electrons

$$E_{kin} = \int \ldots \int \Psi^*_{SD}(\mathbf{x}_1, \ldots, \mathbf{x}_{N_{elec}}) \left(\sum_{i=1}^{N_{elec}} -\frac{1}{2}\nabla_i^2 \right) \Psi_{SD}(\mathbf{x}_1, \ldots, \mathbf{x}_{N_{elec}})\, d\mathbf{x}_1 \ldots d\mathbf{x}_{N_{elec}}$$

In bra-ket notation:

$$E_{kin} = \langle \Psi_{SD} | \hat{T}_{elec} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \left(\sum_{i=1}^{N_{elec}} -\frac{1}{2}\nabla_i^2 \right) | \Psi_{SD} \rangle$$

which, using the properties of determinants, simplifies to

$$= \sum_{i=1}^{N_{elec}} \int \chi_i^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2 \right) \chi_i(\mathbf{x})\, d\mathbf{x} = \sum_{i=1}^{N_{elec}} \langle \chi_i | -\frac{1}{2}\nabla^2 | \chi_i \rangle$$

a sum of the kinetic energies of the N_{elec} spin orbitals.

2) Nuclear attraction energy

Leads to an expression similar to the kinetic energy:

$$E_{e-n} = \langle \Psi_{SD} | \hat{V}_{e-n} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \sum_{i=1}^{N_{elec}} \left(\sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) | \Psi_{SD} \rangle$$

$$= \sum_{i=1}^{N_{elec}} \int \chi_i^*(\mathbf{x}) \left(\sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|} \right) \chi_i(\mathbf{x})\, d\mathbf{x} = \sum_{i=1}^{N_{elec}} \langle \chi_i | \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|} | \chi_i \rangle$$

which is equal to the sum of the nuclear attraction energies of N_{elec} spin orbitals. The nuclear attraction potential for each electron (also called "the external potential") is clearly a one-electron operator:

$$\hat{v}_{ext}(\mathbf{r}) = \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

3) Electron-electron repulsion energy

The most complicated contribution to the energy

$$E_{e-e} = \langle \Psi_{SD} | \hat{V}_{e-e} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \left(\sum_{i=1}^{N_{elec}} \sum_{j=i+1}^{N_{elec}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) | \Psi_{SD} \rangle$$

is written as a double sum of "two-electron integrals":

$$= \frac{1}{2} \sum_{i=1}^{N_{elec}} \sum_{j=1}^{N_{elec}} \left[\int\int \chi_i^*(\mathbf{x_1}) \chi_j^*(\mathbf{x_2}) \frac{1}{r_{12}} \chi_i(\mathbf{x_1}) \chi_j(\mathbf{x_2}) \, d\mathbf{x_1} d\mathbf{x_2} - \int\int \chi_i^*(\mathbf{x_1}) \chi_j^*(\mathbf{x_2}) \frac{1}{r_{12}} \chi_j(\mathbf{x_1}) \chi_i(\mathbf{x_2}) \, d\mathbf{x_1} d\mathbf{x_2} \right]$$

Electronic energy of Slater determinant

$$E_{SD} = \sum_{i=1}^{N_{elec}} \int \chi_i^*(\mathbf{x}) \hat{h}\, \chi_i(\mathbf{x}) d\mathbf{x}$$

$$+\frac{1}{2}\sum_{i=1}^{N_{elec}}\sum_{j=1}^{N_{elec}} \left[\int\int \chi_i^*(\mathbf{x_1})\chi_j^*(\mathbf{x_2})\frac{1}{r_{12}}\chi_i(\mathbf{x_1})\chi_j(\mathbf{x_2})\, d\mathbf{x_1} d\mathbf{x_2} - \int\int \chi_i^*(\mathbf{x_1})\chi_j^*(\mathbf{x_2})\frac{1}{r_{12}}\chi_j(\mathbf{x_1})\chi_i(\mathbf{x_2})\, d\mathbf{x_1} d\mathbf{x_2} \right]$$

where $\hat{h} = -\frac{1}{2}\nabla^2 + \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}$

- To understand the meaning of the terms in the above energy expression, we need to re-write it in terms of spatial orbitals

- We will assume that we have an even number of electrons and that each spatial orbital is doubly occupied:

$$|\Psi_{SD}\rangle = |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\, \psi_1(\mathbf{r}_2)\beta(\omega_2)\, \psi_2(\mathbf{r}_3)\alpha(\omega_3)\ \ldots \psi_{N_{elec}/2}(\mathbf{r}_{N_{elec}-1})\alpha(\omega_{N_{elec}-1})\, \psi_{N_{elec}/2}(\mathbf{r}_{N_{elec}})\beta(\omega_{N_{elec}})\rangle$$

Electronic energy in terms of the spatial orbitals

After we integrate out the spin variable, we obtain the following result for the energy of a SD in terms of spatial orbitals:

$$E_{SD} = 2 \sum_{i=1}^{N_{elec}/2} \int \psi_i^*(\mathbf{r}) \hat{h}\, \psi_i(\mathbf{r}) d\mathbf{r}$$

$$+ \sum_{i=1}^{N_{elec}/2} \sum_{j=1}^{N_{elec}/2} \left[2 \int \int \psi_i^*(\mathbf{r_1}) \psi_j^*(\mathbf{r_2}) \frac{1}{r_{12}} \psi_i(\mathbf{r_1}) \psi_j(\mathbf{r_2})\, d\mathbf{r_1} d\mathbf{r_2} - \int \int \psi_i^*(\mathbf{r_1}) \psi_j^*(\mathbf{r_2}) \frac{1}{r_{12}} \psi_j(\mathbf{r_1}) \psi_i(\mathbf{r_2})\, d\mathbf{r_1} d\mathbf{r_2} \right]$$

The electron-electron interactions above contain the following two integrals:

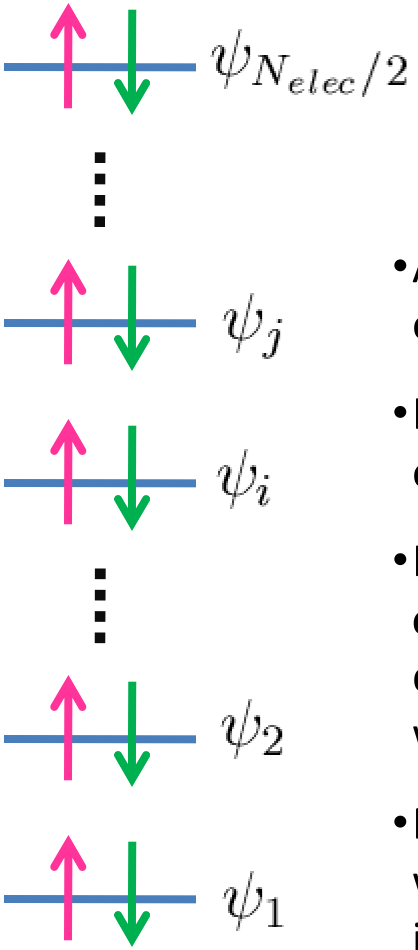
$$\int \int \frac{|\psi_i(\mathbf{r_1})|^2 |\psi_j(\mathbf{r_2})|^2}{r_{12}} d\mathbf{r_1} d\mathbf{r_2} = J_{ij} > 0$$

$$\int \int \frac{[\psi_i^*(\mathbf{r_1}) \psi_j(\mathbf{r_1})][\psi_i^*(\mathbf{r_2}) \psi_j(\mathbf{r_2})]^*}{r_{12}} d\mathbf{r_1} d\mathbf{r_2} = K_{ij} > 0$$

Coulomb integral

Exchange integral

Interpretation of the electronic energy of a Slater determinant

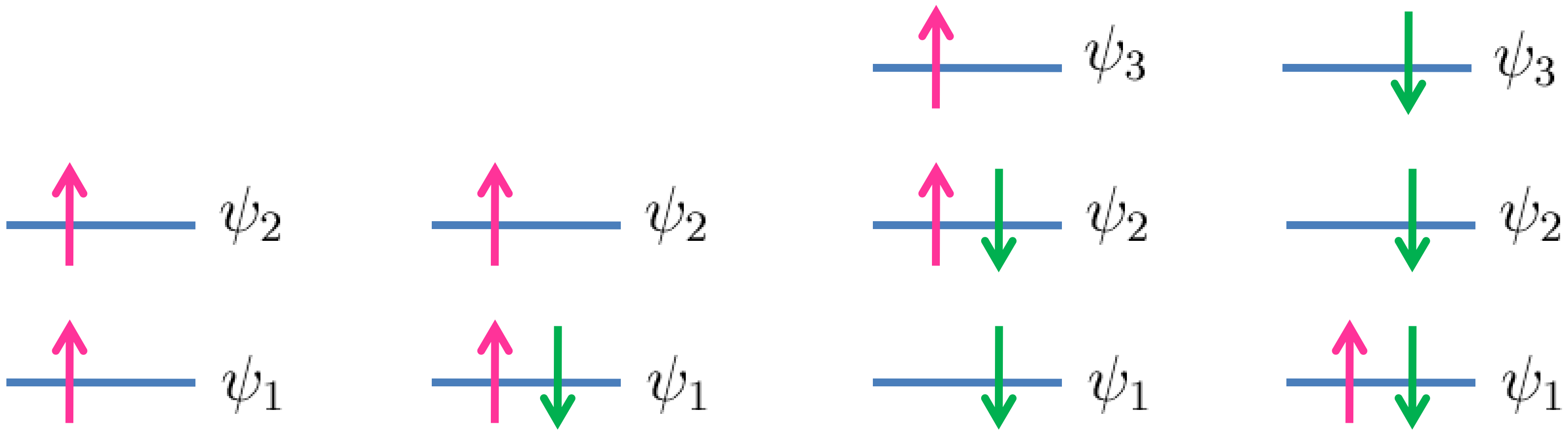


$$E_{SD} = 2\sum_{i=1}^{N_{elec}/2} h_i + \sum_{i=1}^{N_{elec}/2}\sum_{j=1}^{N_{elec}/2}(2J_{ij} - K_{ij})$$

- An electron in orbital ψ_i has kinetic and nuclear attraction energy h_i
- It has a Coulomb (electrostatic) interaction energy J_{ij} with each electron in orbital ψ_j
- It also has an exchange interaction energy K_{ij} **only with electrons of the same spin** in orbital ψ_j. This is a purely quantum effect and is a consequence of the antisymmetry we have introduced in our wavefunctions
- No exchange integrals appear in the energy expression if we represent the wavefunction as a Hartree product instead of a Slater determinant

Electronic configurations

- Now that we know what interactions contribute to the energy of a Slater determinant wavefunction we can write down the energy of any electronic configuration
- Let’s try the following examples:



Summary / Reading assignment

- Many-electron wavefunctions (Cramer, pages 119-122)
- Antisymmetry and Slater determinant wavefunctions (Cramer, pages 122-126)
- Optional: Derivation of energy expression of a Slater determinant (Szabo and Ostlund, pages 67-88)