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
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.

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

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

• 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\textsubscript{2} or HeH\textsuperscript{+}):

\[
\Psi(\mathbf{x}_1, \mathbf{x}_2) \sim \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2)
\]

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

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

\[ \Psi(x_1, x_2) = \chi_1(x_1)\chi_2(x_2) - \chi_2(x_1)\chi_1(x_2) \]

It can also be written as a determinant:

\[ \Psi(x_1, x_2) = \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) \\ \chi_1(x_2) & \chi_2(x_2) \end{vmatrix} \]

• 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:

\[ \Psi_{SD}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix} \]

Normalisation constant

Shorthand representation, as a ket:

\[ \Psi_{SD}(x_1, x_2, \ldots, x_N) = |\chi_1(x_1) \chi_2(x_2) \cdots \chi_N(x_N)\rangle \]

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

- 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

\[ \psi_2(\mathbf{r}) \]

\[ \psi_1(\mathbf{r}) \]

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

$$\hat{O}(r_1) = -\frac{1}{2} \nabla^2_{r_1} \quad \text{or} \quad \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|r_1 - R_I|}$$

$$\int \int \chi^*_p(1) \chi^*_q(2) \hat{O}(r_1) \chi_s(1) \chi_t(2) d1d2 = \int \chi^*_p(1) \hat{O}(r_1) \chi_s(1) d1 \int \chi^*_q(2) \chi_t(2) d2$$

$$\int \chi^*_p(1) \hat{O}(r_1) \chi_s(1) d1 = \int \psi^*_p(r_1) \hat{O}(r_1) \psi_s(r_1) d_r_1 \int \sigma^*_p(\omega_1) \sigma_q(\omega_1) d\omega_1$$

$$\int \chi^*_q(1) \chi_t(1) d1 = \int \psi^*_q(r_1) \psi_t(r_1) d_r_1 \int \sigma^*_q(\omega_1) \sigma_t(\omega_1) d\omega_1$$

For what combinations of spin orbitals the above integrals are non-zero?
Matrix elements of two-electron operators

The Hamiltonian contains just one kind of two-electron operator

\[ \hat{O}(r_1, r_2) = \frac{1}{|r_1 - r_2|} \]

\[
\int \int \chi^*_p(1) \chi^*_q(2) \hat{O}(r_1, r_2) \chi_s(1) \chi_t(2) d1d2 = \int \int \psi^*_p(r_1) \psi^*_q(r_2) \hat{O}(r_1, r_2) \psi_s(r_1) \psi_t(r_2) dr_1 dr_2
\]

\[
\int \sigma^*_p(\omega_1) \sigma_s(\omega_1) d\omega_1 \int \sigma^*_q(\omega_2) \sigma_t(\omega_2) d\omega_2
\]

For what combinations of spin orbitals the above integrals are non-zero?
1) Kinetic energy

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

\[ E_{\text{kin}} = \int \ldots \int \Psi_{SD}^*(x_1, \ldots, x_{N_{\text{elec}}}) \left( \sum_{i=1}^{N_{\text{elec}}} -\frac{1}{2} \nabla_i^2 \right) \Psi_{SD}(x_1, \ldots, x_{N_{\text{elec}}}) \, dx_1 \ldots dx_{N_{\text{elec}}} \]

In bra-ket notation:

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

which, using the properties of determinants, simplifies to

\[ = \sum_{i=1}^{N_{\text{elec}}} \int \chi_i^*(x) \left( -\frac{1}{2} \nabla^2 \right) \chi_i(x) \, dx = \sum_{i=1}^{N_{\text{elec}}} \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle \]

a sum of the kinetic energies of the \( N_{\text{elec}} \) spin orbitals.
2) Nuclear attraction energy

Leads to an expression similar to the kinetic energy:

\[ E_{e-n} = \langle \Psi_{SD} | \hat{V}_{e-n} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \sum_{i=1}^{N_{elec}} \left( \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|r_i - R_I|} \right) | \Psi_{SD} \rangle \]

\[ = \sum_{i=1}^{N_{elec}} \int \chi_i^*(x) \left( \sum_{I=1}^{N_{nuc}} -\frac{Z_I}{|r - R_I|} \right) \chi_i(x) \, dx = \sum_{i=1}^{N_{elec}} \langle \chi_i | \sum_{I=1}^{N_{nuc}} -\frac{Z_I}{|r - R_I|} | \chi_i \rangle \]

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:

\[ \hat{v}_{ext}(r) = \sum_{I=1}^{N_{nuc}} -\frac{Z_I}{|r - R_I|} \]
3) Electron-electron repulsion energy

The most complicated contribution to the energy

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

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

\[
= \frac{1}{2} \sum_{i=1}^{N_{\text{elec}}} \sum_{j=1}^{N_{\text{elec}}} \left[ \int \int \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \, d\mathbf{x}_1 \, d\mathbf{x}_2 - \int \int \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) \, d\mathbf{x}_1 \, d\mathbf{x}_2 \right]
\]
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:

$$\int \int |\psi_i(\mathbf{r}_1)|^2 |\psi_j(\mathbf{r}_2)|^2 \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 = J_{ij} > 0$$

$$\int \int \frac{[\psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1)][\psi_j^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2)]^*}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 = K_{ij} > 0$$

Coulomb integral

Exchange integral
Interpretation of the electronic energy of a Slater determinant

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

- An electron in orbital \( \psi_i \) has kinetic and nuclear attraction energy \( h_i \)
- It has a Coulomb (electrostatic) interaction energy \( J_{ij} \) with each electron in orbital \( \psi_j \)
- It also has an exchange interaction energy \( K_{ij} \) only with electrons of the same spin in orbital \( \psi_j \). 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:

\[ \psi_1 \quad \psi_2 \quad \psi_3 \]
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)