Atoms with two electrons

The Schrödinger equation for a 3-body system

- The He-atom (or an ion with two electrons)
    - Two electrons + a nucleus with charge +Ze
    - $\Rightarrow$ a 3-body problem

- Exact, analytic solutions are not possible

- We will need approximation methods
    - Perturbation theory

<u>The Schrödinger equation</u>

- In centre-of-mass coordinates:

$$\left(-\frac{\hbar^2}{2\mu}\nabla_{r_1}^2 - \frac{\hbar^2}{2\mu}\nabla_{r_2}^2 - \frac{\hbar^2}{M}\nabla_{r_1}\cdot\nabla_{r_2} - \frac{Ze^2}{4\pi\epsilon_0\,r_1} - \frac{Ze^2}{4\pi\epsilon_0\,r_2} + \frac{e^2}{4\pi\epsilon_0\,r_{12}}\right)\psi(\vec{r_1},\vec{r_2})$$
$$= E\psi(\vec{r_1},\vec{r_2})$$

here: $r_{12} = |\vec{r_1} - \vec{r_2}|$
Simplifications: $M = \infty \quad \Rightarrow \quad \mu = m_{\mathrm{e}}$

- We introduce Atomic units

Atomic units

- Atomic units (a.u) are used to simplify calculations
  - Most constants disappear from Hamiltonians and the Schrödinger

- Starting point : the following natural constants are set to one:

$$e = m_\mathrm{e} = \hbar = \frac{1}{4\pi\varepsilon_0} = 1$$

- Be careful with quantitative calculations

Quantity	atomic unit	value in SI units
Charge	e	$1.602\,176\,565 \times 10^{-19}$ C
Mass	m_e	$9.109\,382\,91 \times 10^{-31}$ kg
Angular momentum	$\hbar$	$1.054\,571\,726 \times 10^{-34}$ J s
Length	a_0	$0.529\,177\,210\,92 \times 10^{-10}$ m
Energy	E_h	$4.359\,744\,34 \times 10^{-18}$ J
Time	$\hbar/E_\mathrm{h}$	$2.418\,884\,326\,502 \times 10^{-17}$ s
Force	E_h/a_0	$8.238\,722\,78 \times 10^{-8}$ N
Velocity	$c\,\alpha$	$2.187\,691\,263\,79 \times 10^{6}$ m s^{-1}
Momentum	$\hbar/a_0$	$1.992\,851\,740 \qquad \times 10^{-24}$ kg m s^{-1}
Charge density	e/a_0^3	$1.081\,202\,338 \times 10^{12}$ C m^{-3}
Electric potential	E_h/e	$27.211\,385\,05$ V
Electric field	$E_\mathrm{h}/(e\,a_0)$	$5.142\,206\,52 \times 10^{11}$ V m^{-1}
Electric dipole moment	$e\,a_0$	$8.478\,353\,26 \times 10^{-30}$ C m
Magnetic flux density	$\hbar/(e\,a_0^2)$	$2.350\,517\,464 \times 10^{5}$ T

- The 2-electron system Hamiltonian in atomic units:

$$\left(-\frac{\nabla_{r_1}^2}{2} - \frac{\nabla_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \psi(\vec{r_1}, \vec{r_2}) = E\psi(\vec{r_1}, \vec{r_2})$$

- Consequences of the term : $\propto \dfrac{1}{r_{12}}$
  - $\psi(\vec{r_1}, \vec{r_2})$ cannot be factorised
  - The exact solutions must be entangled states

Symmetry

- With two electrons, symmetry becomes important
  - Spin will matter, due to symmetry

- Total wave function: product of spatial and spin parts

$$\Psi(q_1, q_2) = \psi(\vec{r}_1, \vec{r}_2)\, \chi(\vec{s}_1, \vec{s}_2)$$

- The Hamiltonian does not depend on spin
  - the wave function can be factorised

The Pauli principle

- The total wave function for two identical fermions is antisymmetric with respect to exchange of the particles

- Two identical fermions cannot occupy the same quantum state simultaneously

- For the product function $\Psi(q_1, q_2)$, we have two options:
  - $\psi(\vec{r}_1, \vec{r}_2)$ symmetric and $\chi(\vec{s}_1, \vec{s}_2)$ anti-symmetric
  - $\psi(\vec{r}_1, \vec{r}_2)$ anti-symmetric and $\chi(\vec{s}_1, \vec{s}_2)$ symmetric

Exchange symmetry

- The exchange operator: P_{12}

$$P_{12}\, \Psi(q_1, q_2) = \Psi(q_2, q_1)$$

- A permutation of spatial coordinates:
  - if $P_{12}\,\Psi(q_1, q_2) = \lambda\Psi(q_1, q_2)$
  - $P_{12}^2\,\Psi(q_1, q_2) = \lambda^2\Psi(q_1, q_2) = \Psi(q_1, q_2)$
  - $\Rightarrow\quad \lambda = \pm 1$

Spin wave functions

- For each of the two spin functions, there are only two options
    - Spin-up or Spin-down

- We define kets in the two spin-spaces:

$$\left\{ \begin{array}{l} |+\rangle_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_1 \\[2mm] |-\rangle_1 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_1 \end{array} \right. \qquad \left\{ \begin{array}{l} |+\rangle_2 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_2 \\[2mm] |-\rangle_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_2 \end{array} \right.$$

- Compound spin function ;
    - four possibilities:

$$\chi_1(\vec{s}_1, \vec{s}_2) \; : \; |+\rangle_1 \otimes |+\rangle_2 = |++\rangle$$
$$\chi_2(\vec{s}_1, \vec{s}_2) \; : \; |+\rangle_1 \otimes |-\rangle_2 = |+-\rangle$$
$$\chi_3(\vec{s}_1, \vec{s}_2) \; : \; |-\rangle_1 \otimes |+\rangle_2 = |-+\rangle$$
$$\chi_4(\vec{s}_1, \vec{s}_2) \; : \; |-\rangle_1 \otimes |-\rangle_2 = |--\rangle$$

-   (assume that the spatial functions are different, so the Pauli principle does not forbid χ_1 and χ_4)

- There are 2 problems with this basis:

- Problem 1 :
    - χ_1 and χ_4 are exchange symmetric , BUT
    - χ_2 and χ_3 are neither symmetric, nor anti-symmetric

- We need a description for the "total spin"
  - In absence of spin-spin interaction: $\left[\, \vec{S}_1 \, , \, \vec{S}_2 \,\right] = 0$
  - $\Rightarrow$ Logical choice : $\vec{S} \equiv \vec{S}_1 + \vec{S}_2$
  - $\Rightarrow$ $\begin{cases} S_z = S_{1z} + S_{2z} \\ S^2 = S_1^2 + S_2^2 + 2\,\vec{S}_1 \cdot \vec{S}_2 \end{cases}$
  - $\Rightarrow$ Quantum numbers S and M_S
  - The action of S^2 and S_z on $\chi_1 , \chi_2 , \chi_3 , \chi_4$ can be calculated (using the Pauli spin matrices)

- Problem 2 :
  - $S_z\,|++\rangle = |++\rangle$
    $S^2\,|++\rangle = 2\,|++\rangle$
  - $S_z\,|+-\rangle = 0$
    $S^2\,|+-\rangle = |+-\rangle + |-+\rangle$
  - $S_z\,|-+\rangle = 0$
    $S^2\,|-+\rangle = |+-\rangle + |-+\rangle$
  - $S_z\,|--\rangle = -|--\rangle$
    $S^2\,|--\rangle = 2\,|--\rangle$
  - χ_2 and χ_3 are not eigenfunctions to S^2
  - $\Rightarrow$ To have a diagonal basis, where all basis functions are either symmetric or anti-symmetric at exchange, we need to replace χ_2 and χ_3

- New functions:
  - $|\,S\,\rangle \propto |+-\rangle + |-+\rangle$
    $|\,A\,\rangle \propto |+-\rangle - |-+\rangle$

- $\Rightarrow$ A basis of four functions: $|\,S\,M_S\,\rangle$

- 3 symmetric functions (a triplet) :

  - $$\begin{cases} |\,1,1\,\rangle & = & |\,+\,+\,\rangle \\ |\,1,0\,\rangle & = & |\,\mathrm{S}\,\rangle = \frac{1}{\sqrt{2}}\left(|\,+\,-\,\rangle + |\,-\,+\,\rangle\right) \\ |\,1,-1\,\rangle & = & |\,-\,-\,\rangle \end{cases}$$

- 1 anti-symmetric function (a singlet) :

  - $$|\,0,0\,\rangle = |\,\mathrm{A}\,\rangle = \frac{1}{\sqrt{2}}\left(|\,+\,-\,\rangle - |\,-\,+\,\rangle\right)$$

The ground state of He

Perturbation Theory

- Assume that the interaction term can be treated as a perturbation:

$$H = H_0 + H'$$

$$H_0 = -\frac{\nabla^2_{r_1}}{2} - \frac{\nabla^2_{r_2}}{2} - \frac{Z}{r_1} - \frac{Z}{r_2}$$

$$H' = \frac{1}{r_{12}}$$

- The zero-order solution can be factorized

$$H_0\, \psi^{(0)}(\vec{r_1}, \vec{r_2}) = E_0 \psi^{(0)}(\vec{r_1}, \vec{r_2})$$
$$\psi^{(0)}(\vec{r_1}, \vec{r_2}) = \psi_1^{(0)}(\vec{r_1})\, \psi_2^{(0)}(\vec{r_2})$$
$$E_0 = E_1 + E_2$$

- The zero order ground state will be both electron is hydrogenic 1s-orbitals, with $Z = 2$

$$\psi^{(0)} = \psi_{1s}\, \psi_{1s} = (R_{1s} Y_{00})\, (R_{1s} Y_{00}) = \psi_{1s^2}$$

Identical electrons - the Pauli principle

- We have
  - $n_1 = n_2 = 1$, $l_1 = l_2 = 0$, $m_{l1} = m_{l2} = 0$
  - The compound spatial wave function HAS to be symmetric

- To avoid violation the Pauli principle, the two spins HAVE to be opposite

$$\Rightarrow \Psi^{(0)} = \psi_{1s^2}\, \chi_{0,0}$$
$$|\,(0)\,\rangle = |\,1s^2\,\rangle \otimes |\,0,0\,\rangle = |\,1s^2, 0\,0\,\rangle$$

$$\Rightarrow 1s^2\,{}^1S \Rightarrow 1s^2\,{}^1S$$

The energy of the ground state

- We define this as the ionization energy E_{ion}

- The zero-order energy (without the perturbation) :

- $$E_0 = E_1 + E_2 = 2E_{1s}(Z=2) = 2\left(-Z^2 hcR_\infty\right)$$
$$\approx 2\left(-54.4\text{ eV}\right) \approx -109\text{ eV}$$

- The perturbation :

$$\Delta E = \langle\, \psi_{1s^2} \,|\, H' \,|\, \psi_{1s^2} \,\rangle$$
$$H' = \tfrac{1}{r_{12}}$$
$$\psi_{1s^2} = \left[\left(\tfrac{Z}{a_m u}\right)^{3/2} 2e^{-\rho}\right]^2 \left[\sqrt{\tfrac{1}{4\pi}}\right]^2$$

$$\Rightarrow \Delta E \approx 34\text{ eV}$$
$$\Rightarrow E(1s^2) \approx -109\text{ eV} + 34\text{ eV} = -75\text{ eV}$$

- This means that 75 eV is the energy needed to remove BOTH electrons from the nucleus
  - Suppose one electron has already been removed; how much energy is needed to remove the other one?

  - $\Rightarrow$ the ionization energy of He$^+$

10

- $E_{\text{ion}}(\text{He}^+) = E_{1\text{s}}(Z = 2) \approx -54.4 \text{ eV}$

- The ionization energy of He :
  $$E_{\text{ion}}(\text{He}) = E(1\text{s}^2) - E_{\text{ion}}(\text{He}^+) \approx -21 \text{ eV}$$

- Experimental value of the heliume ionization energy :
  -24.6 eV
    - The order of magnitude is right, but
    - The energy contribution from the electron-electron interaction is too great to be treated as a perturbation

Excited states of He

- One of the electrons is in the 1s-orbital
- The other in an *nl*-orbital ($n \neq 1$)

$$1s nl$$

Exchange degeneracy

- We have two states with the same energy:
$$\psi_{1s}(\vec{r_1})\,\psi_{nl}(\vec{r_2})$$
and
$$\psi_{nl}(\vec{r_1})\,\psi_{1s}(\vec{r_2})$$

- This is the "exchange degeneracy"

Degenerate perturbation theory

- We must use superposition states

- $(H_0 + H')\,\psi = (E_0 + \Delta E)\,\psi$
  - where:
  - $\psi = \alpha\,\psi_{1s}(\vec{r_1})\,\psi_{nl}(\vec{r_2}) + \beta\,\psi_{nl}(\vec{r_1})\,\psi_{1s}(\vec{r_2})$
  - $E_0 = E_{1s} + E_{nl}$

$$H'\,\psi = \Delta E\,\psi$$
$$H'\begin{pmatrix}\alpha\\\beta\end{pmatrix} = \Delta E \begin{pmatrix}\alpha\\\beta\end{pmatrix}$$

$$H' = \begin{pmatrix} J & K \\ K & J \end{pmatrix}$$

$$J = \int |\psi_{1\mathrm{s}}(\vec{r}_1)|^2 \, \frac{1}{r_{12}} \, |\psi_{nl}(\vec{r}_2)|^2 \, \mathrm{d}\vec{r}_1 \, \mathrm{d}\vec{r}_2$$

$$K = \int \psi_{1\mathrm{s}}^*(\vec{r}_1)\psi_{nl}^*(\vec{r}_2)\frac{1}{r_{12}}\psi_{1\mathrm{s}}(\vec{r}_2)\psi_{nl}(\vec{r}_1) \, \mathrm{d}\vec{r}_1 \, \mathrm{d}\vec{r}_2$$

- J : the "direct integral"
    - Coulomb interaction between the two charge clouds
    - Increases energy
- K : the "exchange integral"
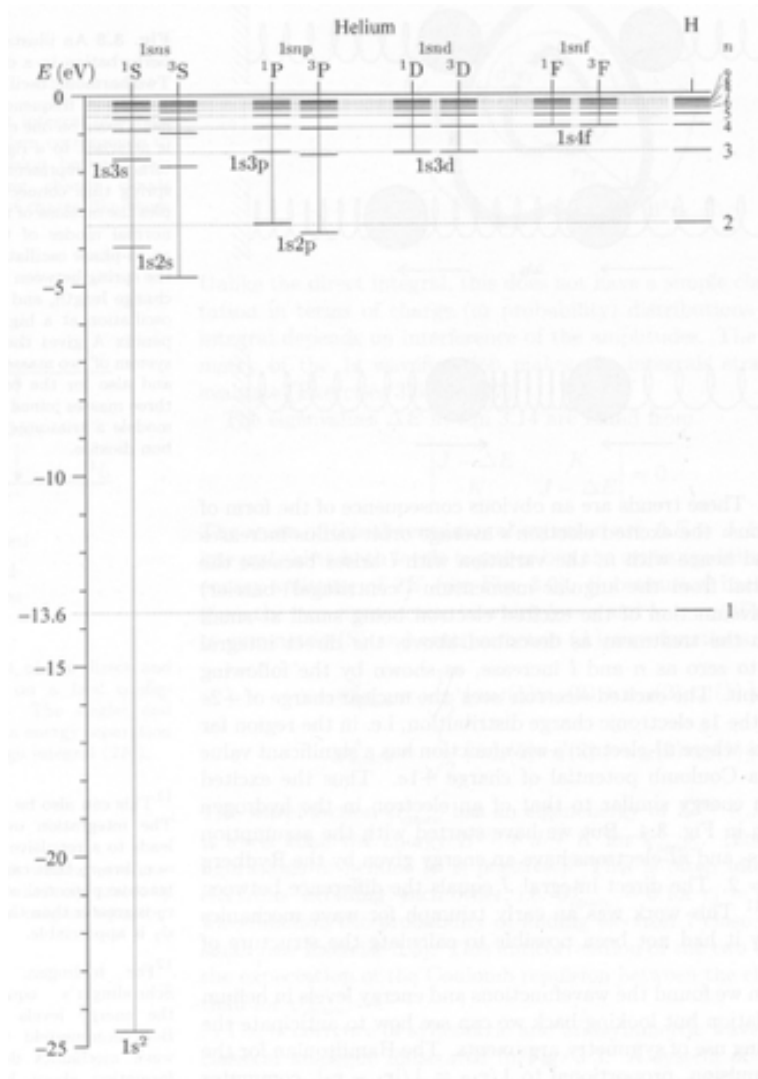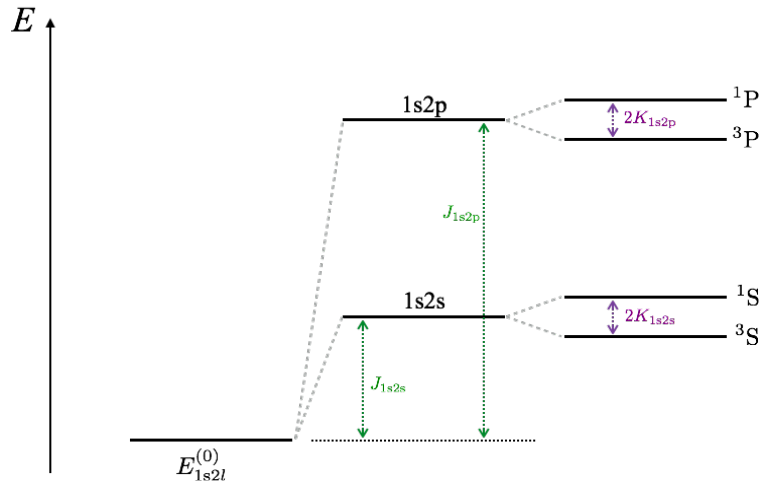   - a quantum interference effect

$$\Delta E = J \pm K$$
$$E_{1\mathrm{s}nl}^{\pm} = E_{1\mathrm{s}nl}^0 + J \pm K$$

- The wave functions are symmetric or anti-symmetric :

$$\begin{cases} \psi_+^{(0)}(\vec{r}_1, \vec{r}_2) \equiv \frac{1}{\sqrt{2}} \left[\psi_{1\mathrm{s}}(\vec{r}_1) \, \psi_{nl}(\vec{r}_2) + \psi_{nl}(\vec{r}_1) \, \psi_{1\mathrm{s}}(\vec{r}_2) \right] \\ \psi_-^{(0)}(\vec{r}_1, \vec{r}_2) \equiv \frac{1}{\sqrt{2}} \left[\psi_{1\mathrm{s}}(\vec{r}_1) \, \psi_{nl}(\vec{r}_2) - \psi_{nl}(\vec{r}_1) \, \psi_{1\mathrm{s}}(\vec{r}_2) \right] \end{cases}$$
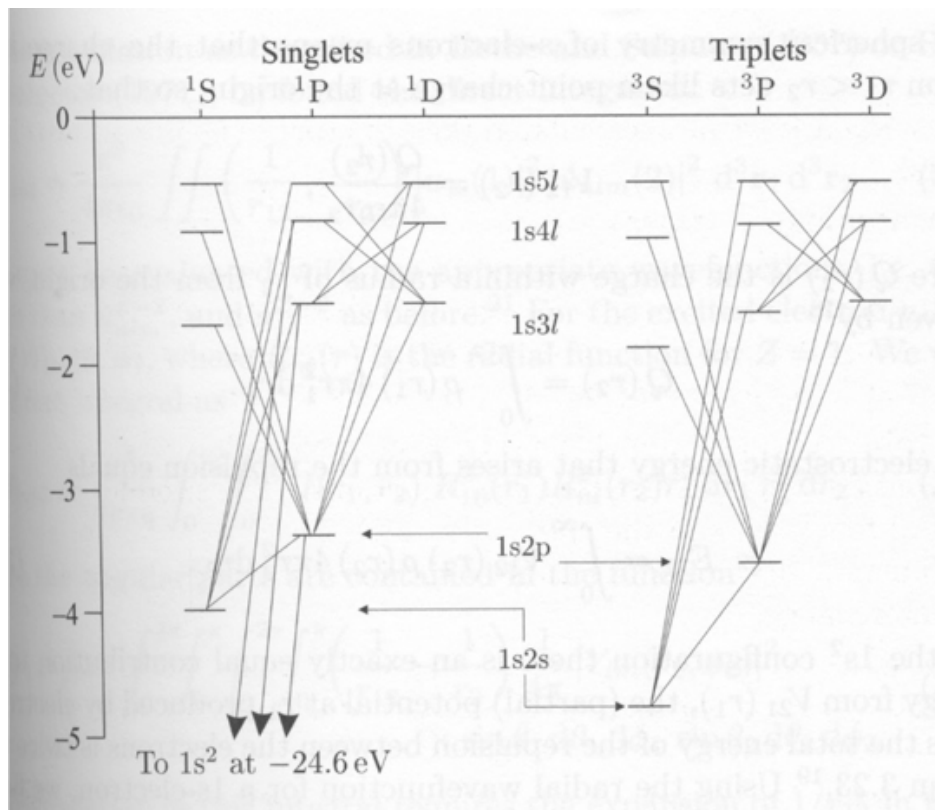
    - entangled states

Transitions in He

- Selection rule for the total spin :
$$\Delta S = 0$$

- A two-electron atom will only have singlets ($S = 0$) and triplets ($S = 1$)

- There will never be transitions between a singlet and triplet

- He gives an appearance of having two separate spectra