

Helium atom

Quantum Chemistry

Lesson 7

Helium atom or ...

- a lesson combining many things we have learnt up to now:
 - the solution of the Schrödinger equation for hydrogen atom
 - variational method
 - perturbation method
- and showing that things need not be easy even for this very simple (two-electron) system
- for the first time, we are going to meet the quantum chemistry in its “full” complexity
- a (limited) *main goal*: **the ground-state energy of the He atom**
(with just a brief remark on excited states)

Contents

1. Time-independent Schrödinger equation
2. Crude approximation: non-interacting electrons
3. Refinement I: perturbation method
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Time-independent Schrödinger equation

Classical Hamilton function

(two electrons moving in the electrostatic field of an infinitely heavy nucleus carrying a charge of $+Ze$)

$$H(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{1}{2m_e} \vec{p}_1^2 + \frac{1}{2m_e} \vec{p}_2^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_1\|} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_2\|} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_2 - \vec{r}_1\|}$$

Hamilton operator (X-representation)

$$\hat{H} = -\frac{\hbar^2}{2m_e} \Delta_1 - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_1} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_2 - \vec{r}_1\|}$$

Schrödinger equation (X-representation)

$$\left[-\frac{\hbar^2}{2m_e} \Delta_1 - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_1} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_2 - \vec{r}_1\|} \right] \Phi = E\Phi$$

Time-independent Schrödinger equation

Classical Hamilton function

(two electrons moving in the electrostatic field of an infinitely heavy nucleus carrying a charge of $+Ze$)

$$H(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{1}{2m_e} \vec{p}_1^2 + \frac{1}{2m_e} \vec{p}_2^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_1\|} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_2\|} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_2 - \vec{r}_1\|}$$

He: $Z = 2$
(general treatment)

$\frac{e^2}{4\pi\epsilon_0} \rightarrow \tilde{e}^2$

Hamilton operator (X-representation)

$$\hat{H} = -\frac{\hbar^2}{2m_e} \Delta_1 - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_1} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_2 - \vec{r}_1\|}$$

Schrödinger equation (X-representation)

$$\left[-\frac{\hbar^2}{2m_e} \Delta_1 - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_1} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_2 - \vec{r}_1\|} \right] \Phi = E\Phi$$

Time-independent Schrödinger equation

Wave function (X-representation)

- $\Phi = \Phi(\vec{r}_1, \xi_1; \vec{r}_2, \xi_2) = \Phi(x_1, y_1, z_1, \xi_1; x_2, y_2, z_2, \xi_2) \rightarrow \Phi(1,2)$

Remarks

- approximations
 - an infinitely heavy nucleus
 - electrostatic approximation
 - spin-less Hamiltonian (commutes with all the spin operators)
 - common eigenvectors of \hat{H} , \hat{S}^2 (total spin), \hat{S}_z (total spin projection): $\Phi(1,2) = \varphi(\vec{r}_1, \vec{r}_2)\Sigma(\xi_1, \xi_2)$
- two identical fermions – antisymmetric (total) wave function: $\Phi(1,2) = -\Phi(2,1)$

Non-interacting electrons

Hamilton operator

$$\hat{H} = -\frac{\hbar^2}{2m_e}\Delta_1 - \frac{\hbar^2}{2m_e}\Delta_2 - \frac{Z\tilde{e}^2}{r_1} - \frac{Z\tilde{e}^2}{r_2} + \frac{\tilde{e}^2}{\|\vec{r}_2 - \vec{r}_1\|} \rightarrow \hat{H}_0 = -\frac{\hbar^2}{2m_e}\Delta_1 - \frac{\hbar^2}{2m_e}\Delta_2 - \frac{Z\tilde{e}^2}{r_1} - \frac{Z\tilde{e}^2}{r_2}$$

Schrödinger equation (orbital part of the wave function only, the spin part cancels out)

$$\left(-\frac{\hbar^2}{2m_e}\Delta_1 - \frac{\hbar^2}{2m_e}\Delta_2 - \frac{Z\tilde{e}^2}{r_1} - \frac{Z\tilde{e}^2}{r_2}\right)\varphi(\vec{r}_1, \vec{r}_2) = E\varphi(\vec{r}_1, \vec{r}_2)$$

Solution (separation of particles)

- $\varphi(\vec{r}_1, \vec{r}_2) = \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)$
- $\left(-\frac{\hbar^2}{2m_e}\Delta_I - \frac{Z\tilde{e}^2}{r_I}\right)\varphi_I(\vec{r}_I) = E_I\varphi_I(\vec{r}_I) \quad [I = 1, 2]$
- $\varphi_I = \Psi_{n_I l_I m_I}, E_{n_1 n_2} = E_{n_1} + E_{n_2}$ (see lesson 3, page 14, hydrogen-like ions)

The ground state

- $\varphi_{GS}(\vec{r}_1, \vec{r}_2) = \Psi_{100}(\vec{r}_1)\Psi_{100}(\vec{r}_2), E_{GS} = 2E_1 \underset{\text{He}}{\approx} -108,8 \text{ eV}$ (experiment: $E_{GS} \approx -79,0 \text{ eV}$, deviation $\approx -38\%$)

Non-interacting electrons

Spin

- *notation:*
 - $|\uparrow\rangle = |\alpha\rangle \rightarrow \alpha(\uparrow) \equiv \alpha(1/2) = 1, \alpha(\downarrow) \equiv \alpha(-1/2) = 0$
 - $|\downarrow\rangle = |\beta\rangle \rightarrow \beta(\uparrow) \equiv \beta(1/2) = 0, \beta(\downarrow) \equiv \beta(-1/2) = 1$
- (normalized) ground-state wave function
 - $\psi_{\text{GS}}(1,2) \sim \hat{A}[\Psi_{100}(1)\Psi_{100}(2)\alpha(1)\beta(2)] = \Psi_{100}(1)\Psi_{100}(2) \times \frac{1}{2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
 - $\psi_{\text{GS}}(1,2) = \Psi_{100}(1)\Psi_{100}(2) \times \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
- remarks
 - antisymmetric spin part of the overall wave function, $S = S_z = 0$ (a singlet state)
 - symmetric orbital part
 - the overall wave function is antisymmetric (as it should be!)

Refinement I: perturbation method

Task to solve

- perturbed problem $P(\varepsilon)$: $\hat{H} = \hat{H}_0 + \hat{H}_P$, $\hat{H}_P = \frac{\tilde{e}^2}{\|\vec{r}_2 - \vec{r}_1\|}$ (perturbation Hamiltonian)
- unperturbed problem P_0 : $\hat{H}_0 = -\frac{\hbar^2}{2m_e} \Delta_1 - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{Z\tilde{e}^2}{r_1} - \frac{Z\tilde{e}^2}{r_2}$ (non-interacting electrons)

Known solution of P_0 (the ground state)

- $\psi_{GS}(1,2) = \Psi_{100}(1)\Psi_{100}(2)\Sigma_A(1,2)$
 - $\Sigma_A(1,2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
 - $\Psi_{100}(\vec{r}) = \frac{1}{\pi^{1/2}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Z}{a_0}r}$, where $a_0 \approx 0,53 \times 10^{-10}$ m (the Bohr radius of the hydrogen atom)

Refinement I: perturbation method

Energy perturbation (1st order)

- $\Delta E_1 = \langle \psi_{GS} | \hat{H}_P | \psi_{GS} \rangle = \langle \Sigma_A | \langle \Psi_{100} | \langle \Psi_{100} | \hat{H}_P | \Psi_{100} \rangle | \Psi_{100} \rangle | \Sigma_A \rangle =$
 $= \langle \Psi_{100} | \langle \Psi_{100} | \hat{H}_P | \Psi_{100} \rangle | \Psi_{100} \rangle \langle \Sigma_A | \Sigma_A \rangle = \langle \Psi_{100} | \langle \Psi_{100} | \hat{H}_P | \Psi_{100} \rangle | \Psi_{100} \rangle$
- $\Delta E_1 = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \Psi_{100}(\vec{r}_1) \Psi_{100}(\vec{r}_2) \frac{\tilde{e}^2}{\|\vec{r}_2 - \vec{r}_1\|} \Psi_{100}(\vec{r}_1) \Psi_{100}(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 =$
 $= \left(\frac{\tilde{e}}{\pi}\right)^2 \left(\frac{Z}{a_0}\right)^6 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} e^{-\frac{2Z}{a_0}(r_1+r_2)} \frac{1}{\|\vec{r}_2 - \vec{r}_1\|} d\vec{r}_1 d\vec{r}_2 = \dots$
- complex calculations ...
 $\Delta E_1 = \frac{5Z\tilde{e}^2}{8a_0} \approx \frac{5}{8}Z \cdot 27,2 \text{ eV} \approx 34,0 \text{ eV}$
 He
- $E_{GS} \approx -108,8 + 34,0 = -74,8 \text{ eV}$ (experiment: $E_{GS} \approx -79,0 \text{ eV}$, deviation $\approx +5 \%$)
 He

Refinement II: variational method

Test wave functions

- non-interacting electrons

$$\psi_{ZS}(1,2) = \Psi_{100}(1)\Psi_{100}(2)\Sigma_A(1,2) = \frac{1}{\pi} \left(\frac{Z}{a_0}\right)^3 e^{-\frac{Z}{a_0}(r_1+r_2)} \Sigma_A(1,2)$$

- proposed form of (normalized) test functions

$$\psi(1,2; \eta) = \frac{1}{\pi} \eta^3 e^{-\eta(r_1+r_2)} \Sigma_A(1,2)$$

Energy functional

$$\begin{aligned} \bullet \quad \mathcal{E}(\eta) &= \langle \psi(\eta) | \hat{H} | \psi(\eta) \rangle = \dots = \pi^{-2} \eta^6 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} e^{-\eta(r_1+r_2)} \hat{H} e^{-\eta(r_1+r_2)} d\vec{r}_1 d\vec{r}_2 = \dots = \\ &= \pi^{-2} \eta^6 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} e^{-\eta(r_1+r_2)} \left[-\frac{\hbar^2}{2m_e} \Delta_1 - \frac{\hbar^2}{2m_e} \Delta_2 - \frac{Z\tilde{e}^2}{r_1} - \frac{Z\tilde{e}^2}{r_2} + \frac{\tilde{e}^2}{\|\vec{r}_2 - \vec{r}_1\|} \right] e^{-\eta(r_1+r_2)} d\vec{r}_1 d\vec{r}_2 = \end{aligned}$$

Refinement II: variational method

Energy functional (continuation)

- ... complex calculations

$$\mathcal{E}(\eta) = \tilde{e}^2 \left[a_0 \eta^2 + \left(-2Z + \frac{5}{8} \right) \eta \right]$$

Functional energy minimum

- $\frac{d\mathcal{E}(\eta)}{d\eta} = 0$

- $\eta_{\min} = \frac{Z - \frac{5}{16}}{a_0} = \frac{Z'}{a_0}$, for He: $Z' = 1,6875$ (interpretation!)

- $\mathcal{E}_{\min} = \tilde{e}^2 \left[a_0 \left(\frac{Z - \frac{5}{16}}{a_0} \right)^2 + \left(-2Z + \frac{5}{8} \right) \frac{Z - \frac{5}{16}}{a_0} \right] = \dots = -\frac{\tilde{e}^2}{a_0} \left(Z - \frac{5}{16} \right)^2 \underset{\text{He}}{\approx} -77,5 \text{ eV}$

(experiment: $E_{\text{GS}} \approx -79,0 \text{ eV}$, deviation $\approx +1.8 \%$)

Excited states

- hydrogen-like orbitals: $\Psi_{100} = 1s$, $\Psi_{200} = 2s$, $\Psi_{21\{-1,0,1\}} = 2p$, ...
- ground state** (singlet, $S = 0, S_z = 0$)
 $\psi(1,2) = \Psi_{100}(1)\Psi_{100}(2) \times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \rightarrow 1s[\uparrow\downarrow]$
- excited singlet states** ($S = 0, S_z = 0$)
 $\psi(1,2) = \frac{1}{\sqrt{2}} [\Psi_{100}(1)\Psi_{200}(2) + \Psi_{100}(2)\Psi_{200}(1)] \times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \rightarrow 1s[\uparrow] 2s[\downarrow]$
 $\psi(1,2) = \Psi_{200}(1)\Psi_{200}(2) \times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \rightarrow 1s[\] 2s[\uparrow\downarrow]$
 ...
- excited triplet states** ($S = 1, S_z = -1, 0, +1$)
 $\psi(1,2) = \frac{1}{\sqrt{2}} [\Psi_{100}(1)\Psi_{200}(2) - \Psi_{100}(2)\Psi_{200}(1)] \times \alpha(1)\alpha(2) \rightarrow 1s[\uparrow] 2s[\uparrow] \quad (S_z = +1)$
 $\psi(1,2) = \frac{1}{\sqrt{2}} [\Psi_{100}(1)\Psi_{200}(2) - \Psi_{100}(2)\Psi_{200}(1)] \times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \rightarrow 1s[\uparrow] 2s[\downarrow] \quad (S_z = 0)$
 $\psi(1,2) = \frac{1}{\sqrt{2}} [\Psi_{100}(1)\Psi_{200}(2) - \Psi_{100}(2)\Psi_{200}(1)] \times \beta(1)\beta(2) \rightarrow 1s[\downarrow] 2s[\downarrow] \quad (S_z = -1)$
 ...
- the perturbation method can be used straightforwardly (degeneracy of triplet states!)
- as well as the variational approach (minimum energy for a given symmetry)

Other uses

- helium-like ions (Li^+ , Be^{2+} , etc.)
 - the formulas given in this presentation with the proton number (Z) value appropriately set ($Z = 3$ for Li^+ , $Z = 4$ for Be^{2+} , etc.)

The end of lesson 7.