

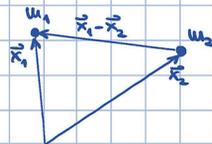
## Chapter 7: The Hydrogen Atom

- One of the "breakthrough applications" that established quantum theory as the mathematical and conceptual foundation of all physical processes.
- For the hydrogen atom the relevant issues discussed in this chapter are:
  - \* The 2-body-problem ( $e^-p^+$ ) can be separated into the motion of the center-of-mass and the relative motion in the center-of-mass system (CMS).
  - \* The proton ( $p^+$ ) and electron ( $e^-$ ) interact via a Coulomb-potential due to the electric attraction.
  - \* The negative energy eigenvalues of the CMS-Hamilton operator are the binding energies of the H-atom.
  - \* Angular momentum is conserved and causes a centrifugal repulsive force that, together with the attractive Coulomb force, leads to an effective potential with a minimum in which the stable H-atom states can form.
  - \* The generalized uncertainty relation can be used to estimate the binding energy of the bound state with the smallest energy ("ground state").
  - \* Due to the spin of the electron there is a doubling (2-fold degeneracy) of the energy levels of the H-atom.

### 7.1. Two-Body Problems

- Assume two particles with masses  $m_1$  and  $m_2$  which interact with each other via a force related to a potential  $V(\vec{x})$  where  $\vec{x} = \vec{r}_1 - \vec{r}_2$  is the distance vector between the particles.

H-atom: Electron with el. charge  $Q_e = -e$  and proton with el. charge  $Q_p = +e$  which interact via the electric field related the Coulomb potential  $V_c(\vec{x}) = -\frac{e^2}{|\vec{x}|}$



Hamilton operator:  $H = \frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} + V(\vec{r}_1 - \vec{r}_2)$

Commutation relations:  $[(X_a)_k, (P_b)_c] = i\hbar \delta_{ab} \delta_{ck}$   $a, b = 1, 2$ ,  $k = 1, 2, 3$

$[(X_a)_k, (X_b)_l] = 0$ ,  $[(P_a)_k, (P_b)_l] = 0$

- Change of variables to **centre-of-mass** and **relative coordinates**:

$M = m_1 + m_2$  total mass  $\vec{V}_i = \frac{\vec{P}_i}{m_i}$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$  reduced mass

$\vec{X}_{cm} = \frac{1}{m_1 + m_2} (m_1 \vec{X}_1 + m_2 \vec{X}_2)$ ;  $\vec{P}_{cm} = M \vec{V}_{cm} = m_1 \vec{V}_1 + m_2 \vec{V}_2 = \vec{P}_1 + \vec{P}_2$

$\vec{X} = \vec{X}_1 - \vec{X}_2$ ;  $\vec{P} = \mu (\vec{V}_1 - \vec{V}_2) = \frac{1}{m_1 + m_2} (m_2 \vec{P}_1 - m_1 \vec{P}_2)$

$$\hookrightarrow \vec{P}_{\text{cm}}^2 = \vec{p}_1^2 + \vec{p}_2^2 + 2\vec{p}_1 \cdot \vec{p}_2, \quad \vec{P}^2 = \frac{1}{(m_1+m_2)^2} (m_2^2 \vec{p}_1^2 + m_1^2 \vec{p}_2^2 + 2m_1 m_2 \vec{p}_1 \cdot \vec{p}_2)$$

$$\begin{aligned} \frac{1}{2M} \vec{P}_{\text{cm}}^2 + \frac{1}{2\mu} \vec{p}^2 &= \frac{1}{2(m_1+m_2)} (\vec{p}_1^2 + \vec{p}_2^2 + 2\vec{p}_1 \cdot \vec{p}_2) + \frac{1}{2(m_1+m_2)} \left( \frac{m_2}{m_1} \vec{p}_1^2 + \frac{m_1}{m_2} \vec{p}_2^2 - 2\vec{p}_1 \cdot \vec{p}_2 \right) \\ &= \frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} \end{aligned}$$

$$\text{Hamilton operator: } H = \frac{\vec{P}_{\text{cm}}^2}{2M} + \frac{\vec{p}^2}{2\mu} + V(\vec{x}) = H_{\text{cm}} + H_{\text{rel}} \quad \text{with}$$

$$H_{\text{cm}} = \frac{\vec{P}_{\text{cm}}^2}{M}$$

kinetic energy of the centre-of-mass: free particle with mass  $M$

$$H_{\text{rel}} = \frac{\vec{p}^2}{2\mu} + V(\vec{x})$$

Energy in the centre-of-mass coordinate system for a particle with mass  $\mu$  in central potential

$$\text{Commutation relations: } [X_{\text{cm},k}, P_{\text{cm},k}] = \frac{m_1}{M} [X_1, P_1] + \frac{m_2}{M} [X_2, P_2] = i\hbar \delta_{kk}$$

$$[X_{e,k}, P_{e,k}] = \frac{m_2}{M} [X_2, P_2] + \frac{m_1}{M} [X_1, P_1] = i\hbar \delta_{kk}$$

$$[X_{\text{cm},k}, P_{e,k}] = \frac{m_1 m_2}{M^2} [X_1, P_1] - \frac{m_1 m_2}{M^2} [X_2, P_2] = 0$$

$$[X_{e,k}, P_{\text{cm},k}] = [X_1, P_1] - [X_2, P_2] = 0$$

$\hookrightarrow$  The location and momentum operators in centre-of-mass and relative coordinates satisfy the canonical commutation relations.

$$\hookrightarrow \text{We also have: } [\vec{P}_{\text{cm}}, \vec{p}] = 0, \quad [\vec{P}_{\text{cm}}, f(\vec{x})] = 0 \Rightarrow [H_{\text{cm}}, H_{\text{rel}}] = 0$$

So it is possible to find simultaneous eigenstates of  $H_{\text{cm}}$  and  $H_{\text{rel}}$  and we can make a (direct) product ansatz for these eigenfunctions:

$$\Psi_{E_{\text{tot}}, E}(\vec{x}_1, \vec{x}_2) = \Psi_{E_{\text{cm}}, E}(\vec{X}_{\text{cm}}, \vec{x}) = \phi_{E_{\text{cm}}}(\vec{X}_{\text{cm}}) \psi_E(\vec{x})$$

$$H \Psi_{E_{\text{tot}}, E}(\vec{x}_1, \vec{x}_2) = [H_{\text{cm}} \phi_{E_{\text{cm}}}(\vec{X}_{\text{cm}})] \psi_E(\vec{x}) + \phi_{E_{\text{cm}}}(\vec{X}_{\text{cm}}) [H_{\text{rel}} \psi_E(\vec{x})] = E_{\text{tot}} \Psi_{E_{\text{tot}}, E}(\vec{x}_1, \vec{x}_2)$$

$$H_{\text{cm}} \phi_{E_{\text{cm}}}(\vec{X}_{\text{cm}}) = \frac{\vec{P}_{\text{cm}}^2}{2M} \phi_{E_{\text{cm}}}(\vec{X}_{\text{cm}}) \Rightarrow \phi_{E_{\text{cm}}}(\vec{X}_{\text{cm}}) = e^{i\vec{P}_{\text{cm}} \cdot \vec{X}_{\text{cm}}}$$

$$H_{\text{rel}} \psi_E(\vec{x}) = \left( \frac{\vec{p}^2}{2\mu} + V(\vec{x}) \right) \psi_E(\vec{x}) = E \psi_E(\vec{x})$$

$$\left. \begin{array}{l} \phi_{E_{\text{cm}}}(\vec{X}_{\text{cm}}) = e^{i\vec{P}_{\text{cm}} \cdot \vec{X}_{\text{cm}}} \\ \psi_E(\vec{x}) \end{array} \right\} E_{\text{tot}} = \frac{\vec{P}_{\text{cm}}^2}{2M} + E$$

The centre-of-mass motion described by  $\phi_{E_{\text{cm}}}(\vec{X}_{\text{cm}})$  corresponds to the free motion of a particle with mass  $M$ . This motion can be separated from the more complicated dynamics within the centre-of-mass frame which corresponds to a particle with mass  $\mu$  moving in the central potential  $V(\vec{x})$ .

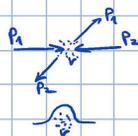
We have to address the latter problem for the hydrogen atom.

## 7.2. Particle in a Central Potential

→ We consider a spinless (spin-0) particle with mass  $m$  in a radial symmetric central potential  $V(r)$ .

Hamilton operator:  $H = \frac{\vec{p}^2}{2m} + V(r)$ ,  $V(r) = -\frac{e^2}{r}$  (H-atom:  $m = \mu = m_e^-$ )

Solutions of  $H\psi = E\psi$  with  $E > 0$ : scattering states



with  $E < 0$ : bound states

↳  $H$  is a scalar operator that is invariant under rotations  $\Rightarrow [H, \vec{L}^2] = 0$ ,  $[H, L_z] = 0$   
Thus there is a COMS of simultaneous eigenstates of the operators  $H$ ,  $\vec{L}^2$  and  $L_z$

→ We already know the simultaneous eigenfunctions of  $\vec{L}^2$  and  $L_z$ , the spherical harmonics, which can describe the complete  $(\theta, \phi)$ -dependence of the eigenfunctions. (→ completeness of spherical harmonic fns.)  
We therefore switch to spherical coordinates to separate out the  $r$ -dependence.

We have:  $\vec{L}^2 = L_i L_i = \epsilon_{ijk} x_j p_k \epsilon_{irs} x_r p_s$

$$\begin{aligned} &= x_j p_k x_i p_s - x_i p_k x_j p_s \\ &= x_j x_i p_k p_s - i\hbar x_j p_i p_s - x_j x_k p_k p_i + 3i\hbar x_j p_i \\ &= \vec{x}^2 \vec{p}^2 - x_i p_i x_k p_k - i\hbar x_j p_i p_s - i\hbar x_j p_i p_s + 3i\hbar x_j p_i \\ &= \vec{x}^2 \vec{p}^2 - (\vec{x}\vec{p})^2 + i\hbar \vec{x}\vec{p} \end{aligned}$$

$$\epsilon_{ijk} \epsilon_{irs} = \delta_{ir} \delta_{ks} - \delta_{is} \delta_{kr}$$

$$p_k x_i = x_j p_k - i\hbar \delta_{ij} \delta_{kl}$$

$$p_k x_k = x_k p_k - 3i\hbar$$

$$\vec{x}\vec{p} = \frac{\hbar}{i} \vec{x} \vec{\nabla} = \frac{\hbar}{i} r \frac{\partial}{\partial r}$$

$$\vec{\nabla} = \vec{e}_r \frac{\partial}{\partial r} + \vec{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \vec{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$$

$$(\vec{x}\vec{p})^2 = -\hbar^2 \left( r \frac{\partial}{\partial r} \right)^2 = -\hbar^2 r \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) = -\hbar^2 r \left( \frac{\partial}{\partial r} + r \frac{\partial^2}{\partial r^2} \right)$$

$$\Rightarrow \vec{p}^2 = \frac{1}{r^2} \vec{L}^2 + \frac{1}{r^2} (\vec{x}\vec{p})^2 - \frac{1\hbar}{r^2} (\vec{x}\vec{p}) = \frac{1}{r^2} \vec{L}^2 - \hbar^2 \left( \frac{\partial}{\partial r} + \frac{2}{r} \frac{\partial}{\partial r} \right)$$

The energy eigenvalue equation can therefore be written as:

$$\left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\vec{L}^2}{2mr^2} + V(r) \right] \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

We look for simultaneous eigenfunctions of  $H$ ,  $\vec{L}^2$  and  $L_z$ , so we can make the

ansatz:  $u(r) Y_{\ell m}(\theta, \phi)$

$$\hookrightarrow \left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2}{2mr^2} \ell(\ell+1) + V(r) \right] u(r) = E u(r)$$

$$\int d\Omega |Y_{\ell m}(\theta, \phi)| = 1$$

For bound state solutions ( $E < 0$ ) the function must be normalized:  $\int d\tau r^2 |u(r)|^2 = 1$  (\*)

→ We rewrite  $u(r) = \frac{f(r)}{r}$  ←  $\vec{L}^2$  only contains derivatives of  $\theta, \phi$

$$\text{and use that } \vec{\nabla}^2 u(r) = \frac{\partial^2}{\partial r^2} u(r) + \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) u(r) = \vec{\nabla}^2 \frac{f(r)}{r}$$

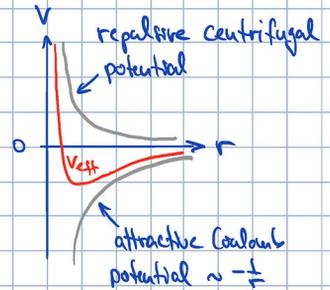
$$= \vec{\nabla}^2 \frac{f(r)-f(0)}{r} + f(0) \vec{\nabla}^2 \frac{1}{r} \quad \vec{\nabla}^2 \frac{1}{r} = -4\pi \delta^3(\vec{x})$$

$$\begin{aligned}
 &= \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \frac{f(r) - f(0)}{r} - 4\pi f(0) \delta^{(3)}(\vec{x}) \\
 &= \frac{f''(r)}{r} - 4\pi f(0) \delta^{(3)}(\vec{x})
 \end{aligned}$$

So since there is no other  $\delta^{(3)}(\vec{x})$ -function in the eigenvalue equation for  $u(r)$  we must have

$$f(0) = 0$$

$$\hookrightarrow \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \underbrace{\frac{\hbar^2 \ell(\ell+1)}{2m r^2} + V(r)}_{V_{\text{eff}}(r)} \right] f(r) = E f(r) \quad (*)$$



This looks like a 1-dimensional Schrödinger equation for a particle in the effective potential  $V_{\text{eff}}(r)$ . The attractive Coulomb potential and the repulsive centrifugal potential make  $V_{\text{eff}}(r)$  have a hollow in which bound states can form.

For bound state solutions the norm condition  $\int_0^\infty dr r^2 |u(r)|^2$  leads to the condition

$$\int_0^\infty dr |f(r)|^2 = 1$$

which gives the condition:  $|f(r)|$  must fall faster than  $\frac{1}{r^{1/2}}$  for large  $r$

$$\left( \lim_{r \rightarrow \infty} |f(r)| = \frac{a}{r^{1/2+\epsilon}} \text{ for } a \in \mathbb{R}, \epsilon > 0 \right)$$

### 7.3. Bound State Energies of Hydrogen

→ We determine the binding energies ( $E < 0$ ) by analyzing the eigenvalue equation concerning the structure of the possible eigenfunctions. This we do by first switching to dimensionless quantities.

→ We define the Bohr radius  $a = \frac{\hbar^2}{me^2}$

$$\frac{\hbar^2}{2\mu r^2} = \frac{me^4}{2\hbar^2 s^2}, \quad -\frac{e^2}{r} = -\frac{me^4}{\hbar^2 s}$$

and rewrite Eq. (\*) in terms of  $\varepsilon$  and  $g(s)$  ← dimensionless

defined by  $E = \frac{me^4}{2\hbar^2} \varepsilon$  and  $g(s) = \sqrt{a} f(as)$ ,  $r = as$  ← dimensionless

$$\hookrightarrow \left[ -\frac{me^4}{2\hbar^2} \frac{d^2}{ds^2} + \frac{me^4}{2\hbar^2} \frac{l(l+1)}{s^2} - \frac{me^4}{\hbar^2} \frac{1}{s} \right] f(as) = \frac{me^4}{2\hbar^2} \varepsilon f(as)$$

$$\Rightarrow \left[ -\frac{d^2}{ds^2} + \frac{l(l+1)}{s^2} - \frac{2}{s} \right] g(s) = \varepsilon g(s), \quad g(0) = 0, \quad \int_0^\infty ds |g(s)|^2 = 1$$

→ Behavior for  $r \rightarrow 0$ : (dominant behavior)

We already know  $g(s) \sim s^2$  with  $s > 0$  for  $s \rightarrow 0$ .  $\Rightarrow -\frac{d^2}{ds^2} g(s) \sim -s(s-1) s^{s-2}$

Thus for the dominant behavior we obtain: (only take smallest exponents)

$$-s(s-1) s^{s-2} + l(l+1) s^{s-2} = 0 \quad \Rightarrow \quad s(s-1) = l(l+1)$$

↳ solutions:  $s = l+1$  or  $s = -l$ . Only the solution  $s = l+1 > 0$  is allowed.

→ Behavior for  $r \rightarrow \infty$ :

$$\text{Dominant terms give: } -\frac{d^2}{ds^2} g(s) = \varepsilon g(s) \quad (D)$$

This can only work together with the norm condition  $\int_0^\infty ds |g|^2 = 1$  if  $\varepsilon = -\tilde{\varepsilon} < 0$  ( $\tilde{\varepsilon} > 0$ ):

$$\Rightarrow g(s) \sim s^k e^{-\sqrt{\tilde{\varepsilon}} s} = s^k e^{-\kappa s} \quad \kappa = \sqrt{\tilde{\varepsilon}} = \sqrt{-\varepsilon}$$

The  $s^k$  term always leads to a subdominant contribution that drops out of Eq. (D) that only contains the dominant terms.

→ Ansatz for the full function  $g(s)$ :

We combine all information on  $g(s)$  into a single ansatz:

$$g(s) = s^{l+1} e^{-\kappa s} \sum_{\nu=0}^{\infty} c_\nu s^\nu = e^{-\kappa s} \sum_{\nu=0}^{\infty} s^{l+1+\nu} c_\nu$$

$$\hookrightarrow -\frac{d^2}{ds^2} g(s) = e^{-\kappa s} \sum_{\nu=0}^{\infty} \left( -\kappa^2 s^{l+1+\nu} + 2\kappa(l+1+\nu) s^{l+\nu} - (l+1+\nu)(l+\nu) s^{l+\nu-1} \right) c_\nu$$

$$\frac{l(l+1)}{s^2} g(s) = e^{-\kappa s} \sum_{\nu=0}^{\infty} l(l+1) s^{l+\nu-1} c_\nu$$

$$-\frac{2}{s} g(s) = e^{-ks} \sum_{v=0}^{\infty} (-2s^{l+v}) c_v$$

We compare coefficients and obtain:

$$e^{-ks} \sum_{v=0}^{\infty} \left[ (k^2 - l^2) s^{l+v} + (2k(l+v) - 2) s^{l+v} + (l(l+1) - (l+1+v)(l+v)) s^{l+v-1} \right] c_v = 0$$

$$\Rightarrow \frac{c_{v+1}}{c_v} = \frac{2[k(l+v) - 1]}{(l+2v)(l+v) - l(l+1)}, \quad v \geq 0$$

Behavior for large  $v$ :  $\frac{c_{v+1}}{c_v} \sim \frac{2k}{v} \Rightarrow c_v \sim \frac{(2k)^v}{v!}$

Thus if the  $c_v$  were  $\neq 0$  for  $v \rightarrow \infty$  we have  $\sum_v c_v s^v \sim e^{2ks}$  and we had

$$g(s) \sim s^{l+1} e^{+ks} \quad \text{which would make } g(s) \text{ not normalizable.}$$

Thus the  $c_v$  must be  $= 0$  for  $v > n_0$ :  $c_{n_0} \neq 0$  with  $c_{n_0+1} = 0$

$$\Rightarrow \text{Thus we must have: } k(l+n_0+1) = 1 \quad \text{for } n_0 \in \mathbb{N}_0$$

$\rightarrow$  We finally find that for given values of  $l, n_0 = 0, 1, 2, \dots$  we can find a normalizable solution  $g(s)$  if

$$2 = -k^2 = -\frac{1}{(l+n_0+1)^2}$$

The integer number  $n_0$  is called radial quantum number and gives the number of zeros  $g(s)$  has for  $0 \leq s < \infty$ .

The integer  $n = l+n_0+1 = 1, 2, 3, \dots$  is called the main quantum number and governs the possible energy eigenvalues:

$$E_n = -\frac{1}{n^2}, \quad n = 1, 2, 3, \dots$$

Thus we find for the bound states the following energy eigenvalues:

$$E_n = \frac{\mu e^4}{2\hbar^2} \quad E_n = -\frac{\mu e^4}{2\hbar^2} \frac{1}{n^2}, \quad n = 1, 2, 3, \dots$$

Degeneracy of the energy eigenvalues:

For each value of  $n$  the values  $l = 0, 1, \dots, n-1$  are allowed.

For each value of  $l$  the values  $m = -l, -l+1, \dots, l-1, l$  are allowed

$\Rightarrow$  Each energy  $E_n$  has  $\sum_{l=0}^{n-1} (2l+1) = n^2$  eigenstates (for a particle without spin)

→ Fine structure Constant:  $\alpha = \frac{e^2}{\hbar c} = (137.035999139(31))^{-1} \approx \frac{1}{137}$

The fine structure constant is a measure to quantify the strength of the electromagnetic interaction (= the strength of the interaction between photons and particles with electric charge).

Numerical values for hydrogen  $G = 10^9$

$$\left. \begin{array}{l} \text{proton mass: } m_p = 0.9383 \text{ GeV}/c^2 \\ \text{electron mass: } m_e = 0.0005 \text{ GeV}/c^2 \end{array} \right\} \begin{array}{l} \text{reduced mass: } m = \mu = \frac{m_e m_p}{m_e + m_p} \approx m_e - \frac{m_e^2}{m_p} + \dots \\ \hookrightarrow m \approx m_e \end{array}$$

$$\text{H ground state binding energy: } E_1 = -\frac{m_e e^4}{2\hbar^2} = -\frac{1}{2} m_e c^2 \alpha^2 \approx -13.6 \text{ eV}$$

→ The H-atom is usually in its ground state unless it is excited to higher- $n$  states by other processes (heat, pressure, exposure to photons that cause transitions, ...). An excited hydrogen state will fall back to the stable ground state with some probability, so the excited states have a finite lifetime.

$E_1$  is the **ionization energy** of hydrogen = energy needed to free the proton and electron from the hydrogen in its ground state.

$E_1 = -13.6 \text{ eV}$  is also called **Rydberg energy**.

**Tabelle 6.1.** Quantenzahlen und Energieeigenwerte

$n = 1$	$l = 0$ (s-Orbital)	$m = 0$	$E_1$ (1-fach)
$n = 2$	$l = 0$ (s)	$m = 0$	} $E_2$ (4-fach)
	$l = 1$ (p)	$m = -1, 0, 1$	
$n = 3$	$l = 0$ (s)	$m = 0$	} $E_3$ (9-fach)
	$l = 1$ (p)	$m = -1, 0, 1$	
	$l = 2$ (d)	$m = -2, -1, 0, 1, 2$	
$n = 4$	$l = 0$ (s)	$m = 0$	} $E_4$ (16-fach)
	$l = 1$ (p)	$m = -1, 0, 1$	
	$l = 2$ (d)	$m = -2, -1, 0, 1, 2$	
	$l = 3$ (f)	$m = -3, -2, -1, 0, 1, 2, 3$	

## 7.4. Groundstate Energy from an Uncertainty Relation

→ We first show that  $[P_k, f(R)] = -i\hbar \frac{X_k}{R} f'(R)$ , where  $f$  is a real-valued function and  $R = |\vec{X}|$ :

↳ Take configuration space representation: acts on everything that might come on the RHS, even on what is not shown!

$$[P_k, f(R)] = -i\hbar \left( \frac{\partial}{\partial X_k} f(|\vec{X}|) - f(|\vec{X}|) \frac{\partial}{\partial X_k} \right) = -i\hbar \frac{\partial R}{\partial X_k} \frac{d}{dR} f(R) = -i\hbar \frac{X_k}{R} f'(R) \quad R = \sqrt{\vec{X}^2}$$

→ We define the (non-Hermitian) linear operators  $A_k = P_k - i\lambda X_k f(R)$ ,  $k=1,2,3$ ,  $\lambda \in \mathbb{R}$  and with  $|\psi\rangle$  an arbitrary normalized state. proper dimension

$$\rightarrow 0 \leq \langle A_k \psi | A_k \psi \rangle = \langle \psi | A_k^\dagger A_k | \psi \rangle = \langle \psi | \vec{P}^2 - i\lambda [P_k, X_k f(R)] + \lambda^2 \vec{X}^2 f^2(R) | \psi \rangle$$

$$[P_k, X_k] f(R) + X_k [P_k, f(R)] = -3i\hbar f(R) - i\hbar R f'(R)$$

$$= \langle \vec{P}^2 \rangle + \lambda^2 \langle \vec{X}^2 f^2(R) \rangle - 3\lambda\hbar \langle f(R) \rangle - \lambda\hbar \langle R f'(R) \rangle \quad \text{for } \lambda \in \mathbb{R}$$

$$\text{Take } f(R) = \frac{1}{R}, \lambda = \hbar \langle \frac{1}{R} \rangle$$

$$x \sim \frac{\hbar}{p} \quad p \sim \frac{\hbar}{x}$$

$$\rightarrow 0 \leq \langle \vec{P}^2 \rangle + \lambda^2 - 2\lambda\hbar \langle \frac{1}{R} \rangle = \langle \vec{P}^2 \rangle - \hbar^2 \langle \frac{1}{R} \rangle^2 \Rightarrow \langle \vec{P}^2 \rangle \geq \hbar^2 \langle \frac{1}{R} \rangle^2$$

→ For an arbitrary normalized state  $|\psi\rangle$  we now have:

$$\langle H \rangle = \frac{1}{2m} \langle \vec{P}^2 \rangle - e^2 \langle \frac{1}{R} \rangle \geq \frac{1}{2m} \langle \vec{P}^2 \rangle - \frac{e^2}{\hbar} \frac{\langle \langle \vec{P}^2 \rangle \rangle^{1/2}}{\hbar} = \frac{p^2}{2m} - \frac{e^2}{\hbar} p =: E(p)$$

We can now search for the minimum of  $E(p) = \frac{p^2}{2m} - \frac{e^2 p}{\hbar}$ ,  $p \geq 0$

$$E'(p) = \frac{p}{m} - \frac{e^2}{\hbar} = 0 \Rightarrow p_{\min} = \frac{m e^2}{\hbar} \Rightarrow E_{\min} = -\frac{m e^4}{2\hbar^2} = -\frac{m c^2 \alpha^2}{2}$$

This is indeed the ground state binding energy  $E_{\min} = E_1$ .

→ For hydrogen ground state the previous estimate as well as the actual calculations give:

$$p_{\text{ground}} := \sqrt{\langle \vec{P}^2 \rangle_0} = \frac{m e^2}{\hbar} = m c \alpha \Rightarrow v_{\text{ground}} := \frac{p_{\text{ground}}}{m_e} = \alpha c = \frac{c}{137} = 2190 \text{ km/s}$$

$$r_{\text{Bohr}} := \langle \frac{1}{|\vec{X}|} \rangle_0^{-1} = \frac{\hbar}{p_{\text{ground}}} = \frac{\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c \alpha} \approx 0.53 \cdot 10^{-8} \text{ cm} = 0.53 \text{ \AA}$$

The quantity  $v_{\text{ground}} = \alpha c$  is a measure for the typical velocity of the electron in the H-atom ground state. Its small size (compared to  $c$ ) is related to the "weakness" of the electromagnetic interaction and indicates that the hydrogen atom is a non-relativistic system. This justifies (a posteriori) the application of non-relativistic quantum mechanics.

The quantity  $r_{\text{Bohr}} = \hbar / (m_e c \alpha)$  is called Bohr radius and is a measure of the size of the H-atom (in its ground state).

## 7.5. Bound State Wave Functions

→ We recall the task for solving the Schrödinger equation for the hydrogen atom we have discussed before:

Schrödinger equation: 
$$\left[ \frac{\nabla^2}{2m} + V(r) \right] \Psi(\vec{x}) = E \Psi(\vec{x}), \quad m = m_e, \quad V(r) = -\frac{e^2}{r}, \quad E = -\frac{m_e c^4}{2\hbar^2} \frac{1}{n^2}$$

$$\Leftrightarrow \left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2}{2m r^2} l(l+1) + V(r) \right] \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

$$n = 1, 2, 3, \dots$$

Ansatz:  $\Psi_{\text{new}}(\vec{x}) = \Psi_{\text{new}}(r, \theta, \phi) = u(r) Y_{lm}(\theta, \phi), \quad \int d^3x |\Psi_{\text{new}}(\vec{x})|^2 = 1$

↳  $\left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2}{2m r^2} l(l+1) + V(r) \right] u(r) = E u(r), \quad \text{with } \int_0^\infty dr r^2 |u(r)|^2 = 1$

We rewrite  $u(r) =: \frac{f(r)}{r}$  with the necessary condition  $f(0) = 0$

↳  $\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2m r^2} + V(r) \right] f(r) = E f(r) \quad \text{with} \quad \int_0^\infty dr |f(r)|^2 = 1$

We rewrite in units of the Bohr radius  $a = \frac{\hbar^2}{m_e e^2}$ :  $E = \frac{\hbar^2}{2m_e a^2} \varepsilon, \quad \varepsilon = -\frac{1}{n^2} (n = 1, 2, \dots), \quad r = a s, \quad g(s) = \frac{1}{a} f(as)$

↳  $\left[ -\frac{d^2}{ds^2} + \frac{l(l+1)}{s^2} - \frac{2}{s} \right] g(s) = \varepsilon g(s), \quad g(0) = 0, \quad \int_0^\infty ds |g(s)|^2 = 1$

We have learned that the following ansatz is possible:

$$g(s) = s^{l+1} e^{-ks} \sum_{\nu=0}^{n_0} c_\nu s^\nu = e^{-ks} \sum_{\nu=0}^{n_0} s^{l+1+\nu} c_\nu \quad \text{with } k = \frac{1}{a} = \frac{1}{a + n_0 a}, \quad n_0 = n - l - 1$$

→ We now rescale further:  $\xi = 2ks = \frac{2r}{a} = \frac{2r}{na} \Rightarrow f(r) = \frac{g(s)}{a^{l+1}} = \frac{g(\frac{r}{na})}{a^{l+1}} = \frac{h(\xi)}{a^{l+1}}$

↳  $\left[ -4 \frac{d^2}{d\xi^2} + 4 \frac{l(l+1)}{\xi^2} - \frac{4n}{\xi} + 1 \right] h(\xi) = 0 \quad \Leftrightarrow \int d\xi |h(\xi)|^2 = \frac{2}{n}$

Ansatz (motivated from results of Chap. 7.3):  $h(\xi) = \xi^{l+1} e^{-\xi/2} \omega(\xi)$

$$\frac{d^2}{d\xi^2} h = e^{-\xi/2} \left[ \xi^{l+1} \frac{d^2}{d\xi^2} \omega + 2 \left( (l+1) \xi - \frac{1}{2} \xi^{2l+1} \right) \frac{d}{d\xi} \omega + \left( (l+1) l \xi^{2l-1} - (l+1) \xi^l + \frac{1}{4} \right) \omega \right]$$

↳  $\xi \omega''(\xi) + \left( (2l+1) + 1 - \xi \right) \omega'(\xi) + \left( (l+1) - (2l+1) \right) \omega(\xi) = 0$

Does not agree with definition in Mathematics!

This is the defining equation of the **Associated Laguerre Polynomials**  $L_r^s(x)$ :

$$x L_r^s(x) + (s+1-x) L_r^{s+1}(x) + (r-s) L_r^s(x) = 0 \quad \Rightarrow h(\xi) = N L_{n-l-1}^{2l+1}(\xi)$$

→ Properties of the associated Laguerre polynomials:

$$L_r^s(x) = \frac{d^s}{dx^s} e^x \frac{d^r}{dx^r} e^{-x} x^r = \sum_{k=0}^{r-1} (-1)^{k+s} \frac{(r!)^2}{k! (k+s)! (r-k-s)!} x^k$$

↳  $L_1^1(x) = -1, \quad L_2^1(x) = -4 + 2x, \quad L_3^1(x) = -6, \quad L_3^0(x) = -18 + 18x - 3x^2$

$L_4^3(x) = -96 + 24x, \quad L_5^3(x) = -120$

$$\int_0^{\infty} dx x^{s+1} e^{-x} [L_r^s(x)]^2 = \frac{(2r-s+1)(r!)^2}{(r-s)!}$$

$$\hookrightarrow \int_0^{\infty} d\xi |\psi(\xi)|^2 = N^2 \int_0^{\infty} d\xi \xi^{2\ell+2} e^{-\xi} [L_{n-\ell}^{2\ell+1}(\xi)]^2 = N^2 \frac{2n [(n+\ell)!]^2}{(n-\ell)!} = \frac{2}{n} \Rightarrow N = \left[ \frac{(n-\ell)! \frac{2}{a^3}}{2n [(n+\ell)!]^2} \right]^{1/2}$$

We have:  $u(r) \stackrel{\text{convention}}{=} -\frac{\psi(r)}{r} = -\frac{\psi(\frac{2r}{ua})}{r a^{1/2}} = \frac{-1}{r a^{1/2}} \left[ \frac{(n-\ell)! \frac{2}{a^3}}{2n [(n+\ell)!]^2} \right]^{1/2} \left( \frac{2r}{ua} \right)^{\ell+1} e^{-\frac{r}{ua}} L_{n-\ell}^{2\ell+1} \left( \frac{2r}{ua} \right)$

→ Full form of the bound state wave functions:

$$\hookrightarrow \Psi_{n\ell m}(r, \theta, \phi, t) = e^{-itE_n/\hbar} \Psi_{n\ell m}(r, \theta, \phi), \quad E_n = -\frac{\mu e^2 a^2}{2\hbar^2}, \quad n=1, 2, 3, \dots$$

$$\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi)$$

$$\begin{aligned} \ell &= 0, 1, \dots, n-1; \\ m &= -\ell, -\ell+1, \dots, \ell-1, \ell \end{aligned}$$

$$R_{n\ell}(r) = - \left[ \frac{(n-\ell)! (2/a)^3}{2n [(n+\ell)!]^2} \right]^{1/2} \left( \frac{2r}{ua} \right)^{\ell} e^{-\frac{r}{ua}} L_{n-\ell}^{2\ell+1} \left( \frac{2r}{ua} \right), \quad a = \frac{\hbar^2}{\mu e^2}$$

Examples:

$$n=1, \ell=0 \text{ ('K-shell, s-orbital')}: R_{10}(r) = \frac{2}{a^{3/2}} e^{-r/a}$$

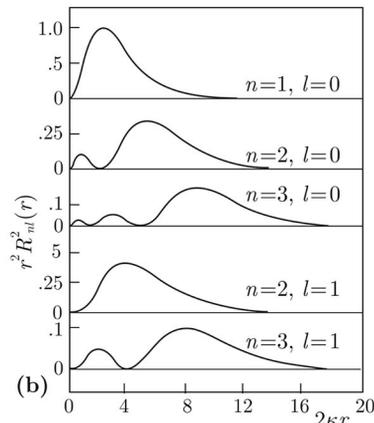
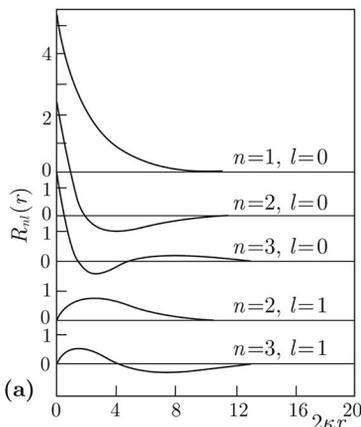
$$n=2, \ell=0 \text{ ('L-shell, s-orbital')}: R_{20}(r) = \frac{2}{(2a)^{3/2}} \left(1 - \frac{r}{2a}\right) e^{-r/2a}$$

$$n=2, \ell=1 \text{ ('L-shell, p-orbital')}: R_{21}(r) = \frac{1}{\sqrt{3}} \frac{1}{(2a)^{3/2}} \left(\frac{r}{a}\right) e^{-r/2a}$$

$$n=3, \ell=0 \text{ ('M-shell, s-orbital')}: R_{30}(r) = \frac{2}{(3a)^{3/2}} \left(1 - \frac{2r}{3a} + \frac{2r^2}{27a^2}\right) e^{-r/3a}$$

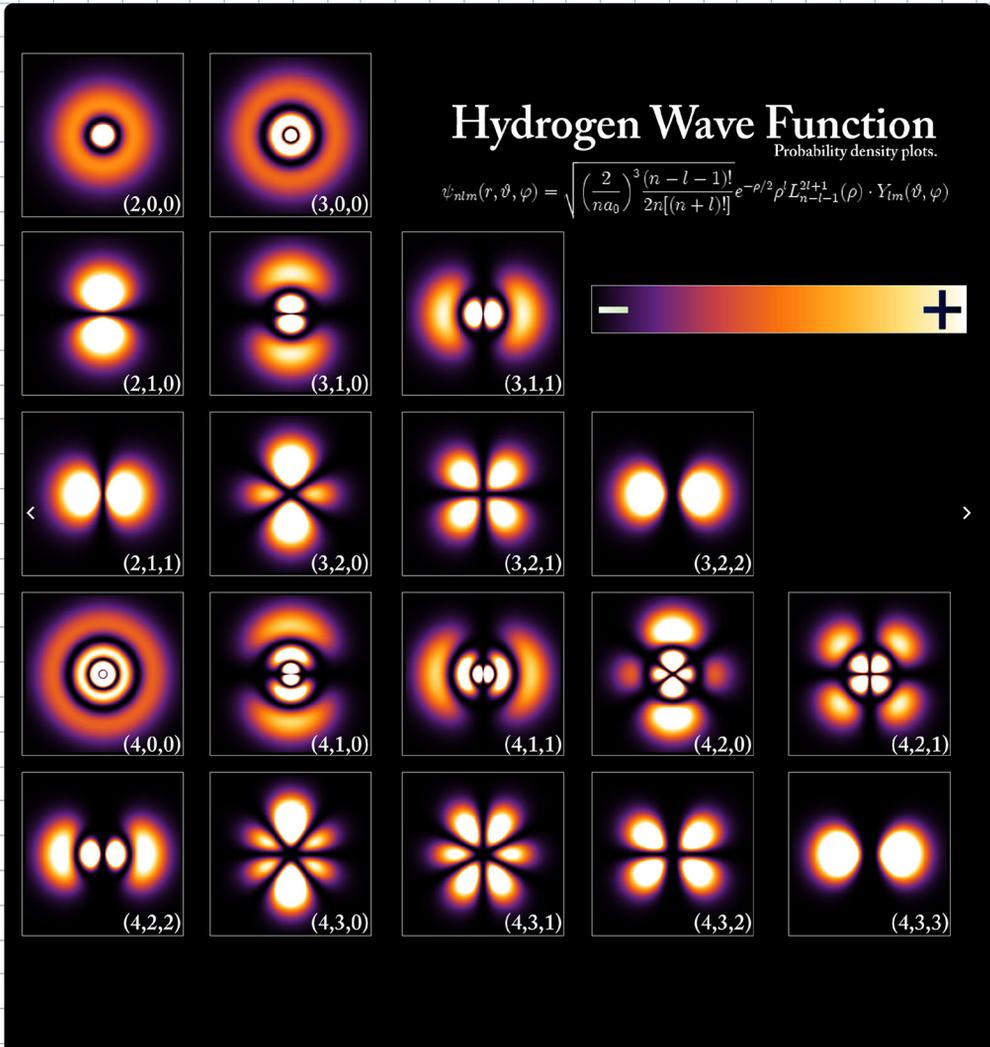
$$n=3, \ell=1 \text{ ('M-shell, p-orbital')}: R_{31}(r) = \frac{4\sqrt{2}}{9} \frac{1}{(3a)^{3/2}} \frac{r}{a} \left(1 - \frac{r}{6a}\right) e^{-r/3a}$$

$$n=3, \ell=2 \text{ ('M-shell, d-orbital')}: R_{32}(r) = \frac{2\sqrt{10}}{27\sqrt{5}} \frac{1}{(3a)^{3/2}} \left(\frac{r}{a}\right)^2 e^{-r/3a}$$



Schwab p. 132

Abb. 6.3. Radiale Wellenfunktion  $R_{nl}(r)$  für das anziehende Coulomb-Potential ( $Z=1$ ). (a) Radiale Wellenfunktion  $R_{nl}$ . (b) Radiale Wahrscheinlichkeitsdichten  $r^2 R_{nl}^2$



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## 7.6. Electron Spin

→ So for the spin of the electron has been neglected. In the non-relativistic approximation that can be applied for the hydrogen the spin does indeed not occur in the Hamiltonian operator, so the calculations of the energy levels are still valid.

The independence of the Hamiltonian operator on the spin operator means that the energy level of a state with spin-up,  $|l, m, \uparrow\rangle$ , and the corresponding state with spin-down  $|l, m, \downarrow\rangle$  (with respect to a given spin axis) are equal.

This results in a degeneracy of  $2k^2$  of each energy level  $E_n$ .

→ In addition to the commuting operators  $H$ ,  $\vec{L}^2$  and  $L_z$  we have to consider  $S_z$  to arrive at a complete set of commuting operators to fully characterize the bound states of the hydrogen atom. (We don't need the operator  $\vec{S}^2$  because since it always gives  $\frac{3}{4}\hbar^2$  for any spin state.)

We can characterize the bound states by their eigenvalues with respect to  $H, \vec{L}^2, L_z, S_z$ :

→ bound states:  $|l, m, \sigma\rangle =: |l, m\rangle \otimes |\sigma\rangle$ ,  $\sigma = \pm \frac{1}{2}$

$$H|l, m, \sigma\rangle = E_n |l, m, \sigma\rangle, \quad \vec{L}^2 |l, m, \sigma\rangle = \hbar^2 l(l+1) |l, m, \sigma\rangle$$

$$L_z |l, m, \sigma\rangle = \hbar m |l, m, \sigma\rangle, \quad S_z |l, m, \sigma\rangle = \hbar \sigma |l, m, \sigma\rangle$$

→ As for the motion of a particle with spin in a magnetic field (Chap. 5.3) we can formulate the spatial bound state wave functions by projections of the bound states location-spin eigenstates that are the direct product of location eigenstates  $|\vec{x}\rangle$  and spin eigenstates  $|\sigma\rangle$ :

$$|\vec{x}, \sigma\rangle =: |\vec{x}\rangle \otimes |\sigma\rangle$$

We can then write each bound state as a 2-component wave function:

$$|l, m, \sigma\rangle \rightarrow \begin{pmatrix} \psi_{l, m, \sigma}^+(\vec{x}) \\ \psi_{l, m, \sigma}^-(\vec{x}) \end{pmatrix} = \begin{pmatrix} \langle \vec{x}, +\frac{1}{2} | l, m, \sigma \rangle \\ \langle \vec{x}, -\frac{1}{2} | l, m, \sigma \rangle \end{pmatrix} = \psi_{l, m}(\vec{r}, \theta, \phi) \begin{pmatrix} \langle \vec{x}, +\frac{1}{2} | \sigma \rangle \\ \langle \vec{x}, -\frac{1}{2} | \sigma \rangle \end{pmatrix}$$

with the normalization  $\langle \psi_{l, m, \sigma} | \psi_{l, m, \sigma} \rangle = \int d^3\vec{x} |\psi_{l, m, \sigma}(\vec{x})|^2 (|\langle +\frac{1}{2} | \sigma \rangle|^2 + |\langle -\frac{1}{2} | \sigma \rangle|^2) = 1$

→ Total angular momentum operator and rotation

The total angular momentum consists of the sum of the orbital angular momentum and the spin:

$$\vec{J} = \vec{L} + \vec{S}$$

Because we have  $[\vec{L}, \vec{S}] = 0$  we have  $\exp(-i\vec{J}\alpha/\hbar) = \exp(-i\vec{L}\alpha/\hbar) \otimes \exp(-i\vec{S}\alpha/\hbar)$  and the rotation acts independently with  $\exp(-i\vec{L}\alpha/\hbar)$  on the orbital and with  $\exp(-i\vec{S}\alpha/\hbar)$  on the spin part of the state.

$$\hookrightarrow e^{-i\vec{J}\alpha/\hbar} |\vec{x}, \sigma\rangle =: e^{-i\vec{L}\alpha/\hbar} |\vec{x}\rangle \otimes e^{-i\vec{S}\alpha/\hbar} |\sigma\rangle$$