The atom



- Stationary states for central potentials
- Solutions for the hydrogen atom
- Magnetic dipole moment of hydrogen
- The independent electron model
- Ground state of atoms
- ✓ The Zeeman effect
- Spin-orbit coupling
- ✓ (X-rays and Auger electrons)
- (Fluorescence)

Spherically symmetric potentials

We will look for stationary states describing the 3d motion of an object in a central potential V(r)

➤ We will not consider the time dependence of the wavefunctions (measurements)

Our stationary states will be used to describe the electron states of the hydrogen atom. They are also eigenstates of L^2 and L_z .

The Schrödinger equation

Stationary states: $\psi(r, \phi, \theta)$

$$-\frac{1}{2m}\left(\frac{h}{2\pi}\right)^{2}\left[\frac{\partial^{2}}{\partial r^{2}} + \frac{2}{r}\frac{\partial}{\partial r}\right]\psi + \frac{1}{2m}\frac{1}{r^{2}}L^{2}\psi + V(r)\psi = E\psi$$

but we already have the spherical harmonics so we can write $\psi(r, \phi, \theta) = R(r)Y_{lm}(\theta, \phi)$ and solve the radial equation:

$$\left[-\frac{1}{2m}\left(\frac{h}{2\pi}\right)^2 \left[\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) - \frac{1}{r^2}l(l+1)\right] + V(r)\right]R(r) = ER(r)$$



$$m \to \mu = \frac{m_p m_e}{m_p + m_e}$$



Hydrogen atom: the results

1. <u>The energy levels</u>:

$$E_n = -\frac{1}{n^2} E_R, \ E_R = 13.6 \ eV$$

where n = 1, 2, ... is the principal quantum number

2. <u>The radial wavefunction</u>: $R_{nl}(r)$ depends on n, lprobability density for electron $P(r) = r^2 |R_{nl}(r)|^2$ average position varies roughly as n^2 (application: *shells*)

Hydrogen atom : the results (cont'd)

- **3**. The spatial dependence of the wavefunction: $\psi_{nlm}(r, \phi, \theta) = R_{nl}(r)Y_{lm}(\theta, \phi) \operatorname{but} |\psi_{nl}(r, \theta)|^2$
- **4**. The <u>parity</u> of hydrogen: $P\psi_{nlm} = (-1)^l \psi_{nlm}$
- 5. 'Orbitals' instead of 'orbits'
- 6. <u>Spin</u>: the complete wavefunction is $\Psi_{nlm_lm_s}$
- 7. <u>Degeneracy</u> of energy levels: $2n^2$

Magnetic dipole moment of hydrogen

In general, μ is due to angular momentum

The hydrogen atom has: (a) orbital angular momentum, *l* (b) spin orbital momentum, *s*

We thus have 'two' magnetic dipole moments:

$$\mu_{L,z} = -\frac{eh}{4\pi m_e}m_l = -m_l\mu_B \text{ and } \mu_{S,z} = -\frac{eh}{2\pi m_e}m_s = -2m_s\mu_B$$

The independent electron model

We describe many-electron atoms by using an 'effective potential' in the Schrödinger equation

- wavefunction: $\Psi_{nlm_lm_s}$ as in hydrogen atom *but*

energy levels: depend on n, l
l = 0, 1, 2, 3, ...
name of the level: s, p, d, f, ...
notation for electronic energy levels: nl, e.g. 1s
energy ordering: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, ...





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19 K	20 Ca	21 Sc	22 Ti	23 ¥	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 ND	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	⁵⁰ Sn	51 Sb	52 Te	53 	54 Xe
55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 ₩	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 TI	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	¹⁰⁶ 106	¹⁰⁷ 107	¹⁰⁸ 108	109 109	110 110	111 111	112 112						
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Series	Če	Pr	Nd	Pm	Sm	Eu	Gd	ть	Dy	Но	Ēr	Tm	Ύb	Ľ
+ Actinide	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Series	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Li

The Pauli principle

'For each set of values for the quantum numbers n, l, m_l, m_s , we can have only one electron'



Applications of the model (i.e.m)

electronic structure of atoms
determine the chemical and electromagnetic properties of the atom
calculate angular momentum of atom (L-S coupling)
explain optical transitions
ground state for light atoms

★ cannot be used for the study of X-rays (heavy atoms)



The ground state of atoms

Hund's rules

1. add spins of valence electrons so that the total spin is maximized

2. add the orbital angular momenta of valence electrons so that $L_z = \sum m_l \left(\frac{h}{2\pi}\right) = \left(\frac{h}{2\pi}\right) m_L$ is max.

3. S and J are added to calculate J

The Zeeman effect

Assume 'spinless' valence electron with n=2, l=1 in a magnetic field (along z-axis) Interaction energy between the magnetic moment and the magnetic field: $U = -\mu_{L, z}B = m_{l}\mu_{B}B$



Spin-orbit coupling

The nucleus produces a magnetic field that interacts with the spin magnetic dipole moment of the electron

$$U = -\mu_{S, z}B = 2m_{s}\mu_{B}B = \pm \mu_{B}B$$

Electron states: eigenstates of $J^{2}, L^{2}, S^{2}, J_{z}$ (i.e.m.)
notation: ${}^{2s+1}A_{j}$