Atomic Spectra in Astrophysics

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WiSe 2016/2017

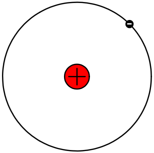
The Hydrogen Atom

Contents

- importance of hydrogen, origin
- the hydrogen spectrum
- (brief) history of atom models
- quantum mechanics and solution of the central-force problem

Hydrogen

- discovered 1766 by Cavendish (metal + acid), and found as constituent of water by de Lavoisir (1787) → hydrogen = generator of water
- simplest atom: proton & electron

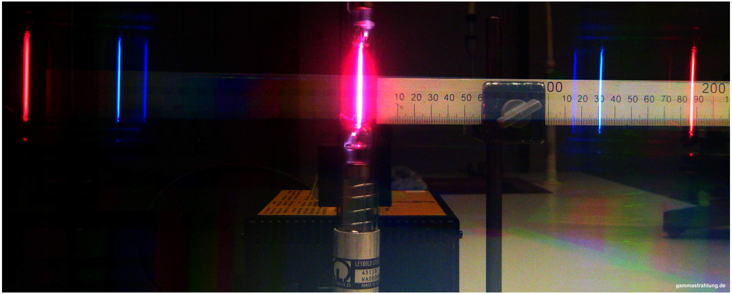


mass	1.6738×10^{-27} kg
E_{ion}	$\approx 13.6\,\text{eV}$

- isotopes: deuterium (1 neutron) and tritium (2 neutrons)
- origin: Big Bang; deuterium from primordial nucleosynthesis (1 min after BB at 60 MK $\hat{=}$ 80 keV);
  recombination at 378 000 yr ($z = 1100$) → transparent universe
- fuel for stars (fusion) via proton-proton chain reaction or CNO cycle

The hydrogen spectrum I

- Spectrum of a Balmer lamp:



  → low pressure gas-discharge tube (H. Geißler 1857) filled with hydrogen

- Ångström (1862): spectral lines of hydrogen in spectrum of sun

The hydrogen spectrum II

- Balmer (1885): spectral lines of hydrogen given by

$$\lambda = \frac{hm^2}{m^2 - n^2} \qquad (n = 2, m = 3, 4, 5, \ldots) \tag{1}$$

  with $h = 3645.6 \times 10^{-10}$ m and 10^{-10} m $= 1$ Å, typical size of an atom
  predicted lines for $m >$ were found in A stars

- Rydberg (1888): generalization to other series

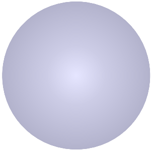
$$\frac{1}{\lambda} = R_\mathrm{H}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad , R_\mathrm{H} = 1.096775854 \times 10^7\,\mathrm{m}^{-1} \tag{2}$$

  generalization to H-like ions (e.g. He II, Li III):

$$\frac{1}{\lambda} = Z^2 R_X \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{3}$$

Atom models I

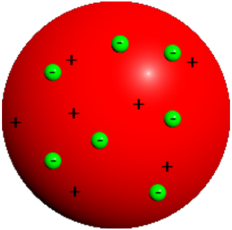
- Parmenides (500 v. Chr.): atoms (*indivisible*) as building blocks of the world



- J. Dalton (1803): chemical elements consist of atoms of different mass

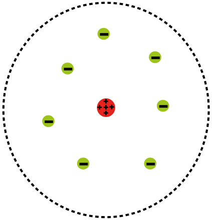
Atom models II

- J.J. Thomson (1900): atoms contain negatively charged electrons in a positively charged continuum (cathode rays experiments)



Atom models III

- Rutherford (1910): positively charged nucleus is smaller (10^{-15} m) than atom (scattering of helium nuclei on gold foil)



Problems of Rutherford model

Why do electrons not fall into nucleus? → circular orbit

Why don't they emit like electric dipole, what about spectral lines?

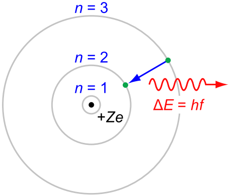
→ Bohr model

Bohr model I

Bohr's postulates (1913) to explain observations:

Motion of electrons in atoms obeys quantum rules

1. Electrons orbit in atoms the nucleus on so-called *stationary orbits* with discrete energies E_n. (The angular momentum is restricted to integer multiples of a fixed unit $L = n\hbar$ $(n = 1, 2, 3, \ldots)$.)
2. Atoms can only gain or lose energy by the transition of an electron from one stationary orbit to another stationary orbit, this energy is discrete and given by $\Delta E = E_n - E_{n+1} = h\nu$ for the involved photon of frequency ν.



Postulate (1) can be also written as phase space integral

$$\frac{1}{2\pi}\oint p\,dq = n\hbar \quad (n = 1, 2, 3, \ldots) \qquad (4)$$

Bohr model II

Application to the hydrogen atom:
Electron orbits in a Coulomb potential (polar coordinates) with

$$F = -\frac{Ze^2}{4\pi\varepsilon_0 r_n^2} \tag{5}$$

with stationary radius r_n, balanced by centrifugal force

$$F_\mathrm{z} = m_\mathrm{r}\frac{v_n^2}{r_n} = m_\mathrm{r} r_n \omega_n^2 \tag{6}$$

with reduced mass m_r so that 0 is in nucleus with mass m_c

$$m_\mathrm{r} = \frac{m_2}{1+\frac{m_2}{m_1}} = \frac{m_e}{1+\frac{m_e}{m_c}} \tag{7}$$

Force balance yields

$$\frac{Ze^2}{4\pi\varepsilon_0 r_n^2} = m_\mathrm{r} r_n \omega_n^2 \tag{8}$$

Bohr model III

As $v_n = r_n \omega_n$ the momentum and position are

$$\begin{aligned} p_n = m_\mathrm{r} v_n &= m_\mathrm{r} r_n \omega_n, \quad q_n = r_n \phi_n && (9) \\ \frac{1}{2\pi} \oint p_n dq_n &= \frac{1}{2\pi} m_\mathrm{r} r_n^2 \omega_n \int_0^{2\pi} d\phi = m_\mathrm{r} r_n^2 \omega_n = n\hbar && (10) \\ \rightarrow \omega_n &= \frac{n\hbar}{m_\mathrm{r} r_n^2} \quad (n = 1, 2, 3, \ldots) && (11) \end{aligned}$$

Inserting force balance to elimnate ω_n:

$$\begin{aligned} r_n &= \frac{4\pi n^2 \hbar^2 \varepsilon_0}{Z m_\mathrm{r} e^2} \quad (n = 1, 2, 3, \ldots) && (12) \\ \omega_n &= \frac{Z^2 m_\mathrm{r} e^4}{16\pi^2 n^3 \hbar^3 \varepsilon_0^2} && (13) \end{aligned}$$

Bohr model IV

This can be used to obtain the *kinetic energy* of the electron

$$E_{\mathrm{kin}} = \frac{m_{\mathrm{r}}}{2} v_n^2 = \frac{m_{\mathrm{r}}}{2} r_n^2 \omega_n^2 = \frac{Z^2 m_{\mathrm{r}} e^4}{32\pi^2 n^2 \hbar^2 \varepsilon_0^2} \tag{14}$$

Its potential energy is given by $qV(r) = -\int F dr$:

$$E_{\mathrm{pot}} = -\frac{Ze^2}{4\pi\varepsilon_0 r_n} = -\frac{Z^2 m_{\mathrm{r}} e^4}{16\pi^2 n^2 \hbar^2 \varepsilon_0^2} \tag{15}$$

Bohr model V

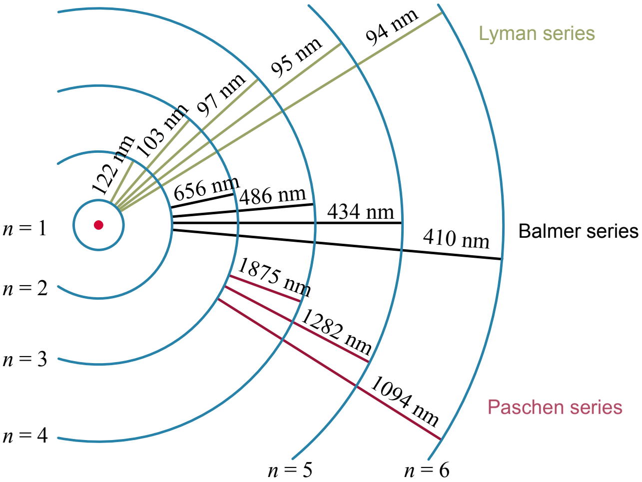
both forces are conservative forces, → conservation of energy and the energy levels are therefore

$$\begin{aligned} E_n &= E_{\text{kin}} + E_{\text{pot}} = -\frac{Z^2 m_{\text{r}} e^4}{32\pi^2 n^2 \hbar^2 \varepsilon_0^2} && (16) \\ &= -\frac{Z^2 m_e e^4}{32\pi^2 n^2 \hbar^2 \varepsilon_0^2 \left(1 + \frac{m_e}{m_c}\right)} \quad (n = 1, 2, 3, \ldots) && (17) \end{aligned}$$

from 2nd Bohr's postulate ($\Delta E = h\nu$) and by $\nu = c/\lambda$:

$$\frac{1}{\lambda} = \frac{Z^2 m_e e^4}{32\pi^2 c \varepsilon_0^2 \left(1 + \frac{m_e}{m_c}\right)} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{18}$$

Bohr model VI



$$\lambda = 911.8\,\text{Å}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)^{-1}$$

Bohr model VII

comparison to Rydberg's formula $1/\lambda = Z^2 R_X \left(1/n_1^2 - 1/n_2^2\right)$ for hydrogen-like atoms suggests:

$$R_X = \frac{R_\infty}{1 + \frac{m_e}{m_c}} \tag{19}$$

$$R_\infty = \frac{m_e e^4}{32\pi^2 c \varepsilon_0^2} = 1.097373177 \times 10^7 \mathrm{m}^{-1} \tag{20}$$

Application: Pickering lines of He II → blackboard
note: R_∞ sometimes used for atomic energies

Bohr model VIII

Problems and limits of Bohr model

Experiments:
H-like spectra of alkali metals need more than one quantum number for discription (e.g. Na D line ≈ 5890 Å transition $3s - 3p$)

no explanation of other spectra

Theory:
Heisenberg's uncertainty principle contradicts electron orbits
→ blackboard

Street light using sodium lamp. Orange light from Na D line

The Schrödinger equation I

wave equation, used for explanation of hydrogen spectrum

Schrödinger (1926)

$$\imath\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \tag{21}$$

$$\text{e.g. } \imath\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left(-\frac{\hbar^2}{2m}\Delta + V(\vec{r},t)\right)\psi(\vec{r},t) \tag{22}$$

- derived from *de Broglie* and dispersion relation:
  $p = \hbar k$ and $E = \hbar\omega$
- describes unperturbed evolution in time of non-relativistic quantum systems, linear PDE of 2nd order with complex solutions ψ
- linearity: superposition principle of solutions
- probability of presence (find particle at position x): $|\psi(\vec{r},t)|^2$

The Schrödinger equation II

Stationary Schrödinger Eq. ($\partial/\partial t = 0$),
separation: $\psi(\vec{r}, t) = \varphi(\vec{r})\, f(t)$ → blackboard

$$\begin{aligned} \hat{H}\varphi(\vec{r}) &= E\varphi(\vec{r}) && (23) \\ \psi(x, t) &= \varphi(x)\, e^{-\imath \frac{E}{\hbar} t} && (24) \end{aligned}$$

with eigenvalues E (energy) of Hamilton operator:

- the probability density $|\psi(x, t)|^2 = |\psi(x)|^2$ (Why?) does not depend on t, same holds for expectation values of dynamic variables
- as $H(x, p) = \frac{p^2}{2m} + V(x)$ is classical Hamiltonian $\equiv$ total energy $\rightarrow \langle H \rangle = E$ (Why?)
- general solution is a *linear* combination of separable solutions:

$$\psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-\imath E_n t/\hbar} \qquad (25)$$

The Central-force problem I

3D: Potential is of form $V(\vec{r}) = V(|\vec{r}|)$
The Laplace operator in 3D for spherical coordinates:

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \qquad (26)$$

Use separation: $\varphi(r,\theta,\phi) = R(r)\cdot Y(\theta,\phi)$, thus

$$-\frac{\hbar^2}{2m}\frac{Y}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}\right) - \frac{\hbar^2}{2m}R\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} - \frac{\hbar^2}{2m}\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + V(r)\,R\,Y = E\,R\,Y \qquad (27)$$

with eigenvalue E

The Angular Equation I

Multiply $\cdot r^2$, and $\frac{1}{RY}$, again: obtain another separation constant

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{1}{R}\left(\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}\right)+r^2V(r)-Er^2 &= \frac{\hbar^2}{2m}\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} \qquad (28)\\
&\quad +\frac{\hbar^2}{2m}\frac{1}{Y\sin^2\theta}\,\frac{\partial^2 Y}{\partial\phi^2}\\
&= \frac{\hbar^2}{2m}[-\ell(\ell+1)] \qquad (29)
\end{aligned}$$

Next separation: $Y(\theta,\phi)=\Theta(\theta)\cdot\Phi(\phi)$

$$\frac{\Phi}{\Theta\Phi\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}+\frac{\Theta}{\Theta\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}=-\ell(\ell+1) \qquad (30)$$

The Angular Equation II

term Φ/Φ and Θ/Θ cancels out, multiply $\sin^2\theta$

$$\frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta}+\ell(\ell+1)\sin^2\theta=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=m^2 \qquad (31)$$

with new separation constant m:

$$\frac{\partial^2\Phi}{\partial\phi^2}+m^2\Phi=0 \quad\Rightarrow\quad \text{solution: } \Phi(\phi)=e^{\pm\imath m\phi} \qquad (32)$$

as rotation around $\phi=2\pi$ in space means same as original state:

$$\Phi(\phi+2\pi)\overset{!}{=}\Phi(\phi) \quad\Rightarrow\quad m=0,\pm1,\pm2,\ldots \qquad (33)$$

The Angular Equation III

The other equation is for Θ

$$\sin\theta \frac{\partial}{\partial\theta} \sin\theta \frac{\partial\Theta}{\partial\theta} + [\ell(\ell+1)\sin^2\theta - m^2]\,\Theta = 0 \tag{34}$$

can be solved by so-called *associated Legendre polynoms*:

$$\begin{aligned}
\Theta(\theta) &= P_\ell^m(\cos\theta) && (35)\\
&= (-1)^m\,(1-\cos^2\theta)^{\frac{|m|}{2}} \frac{d^{|m|}}{d(\cos\theta)^{|m|}} P_\ell(\cos\theta) && (36)\\
P_\ell(\cos\theta) &= \frac{1}{2^\ell \ell!} \frac{d^\ell}{d(\cos\theta)^\ell} (\cos^2\theta - 1)^\ell && (37)
\end{aligned}$$

Eq. (37) implies integer $\ell > 0$. Eq. (36) says $P_\ell^m = 0$ for $|m| > \ell$ and for ℓ are $(2\ell+1)$ values of m.
Other solutions unphysical (e.g. not normalizable) → blackboard

The Angular Equation IV

From normalization condition $\int_0^{2\pi}\int_0^{\pi}|Y|^2\sin\theta d\theta d\phi$ follows *Spherical harmonics*

$$Y_\ell^m(\theta,\phi) \quad = \quad \epsilon\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\, e^{\imath m\phi}\, P_\ell^m(\cos\theta) \tag{38}$$

$$\text{where } \epsilon = \begin{cases} (-1)^m & \text{for } m \geq 0 \\ 1 & \text{for } m \leq 0 \end{cases} \tag{39}$$

E.g.: $P_0 = 1$, $P_0^0 = 1$ and $P_1^0 = \cos\theta$, and therefore
$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$ and $Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$ or $Y_1^{\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm\imath\phi}$

Hydrogen atom - The Radial Equation I

The *radial equation*

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2m_\mathrm{r}r^2}{\hbar^2}[V(r)-E]R=\ell(\ell+1)R \tag{40}$$

Substitution $u(r)\equiv rR(r)\rightarrow R=\frac{u}{r},\ \frac{dR}{dr}=\frac{r\frac{du}{dr}-u}{r^2},\ \frac{d}{dr}r^2\frac{dR}{dr}=r\frac{d^2u}{dr^2}$ and so

$$-\frac{\hbar^2}{2m_\mathrm{r}}\frac{d^2u}{dr^2}+\left[V+\frac{\hbar^2}{2m_\mathrm{r}}\frac{\ell(\ell+1)}{r^2}\right]u=Eu \tag{41}$$

→ like 1D Schrödinger equation but with *effective potential* (with centrifugal term)

$$V_\mathrm{eff}=V+\frac{\hbar^2}{2m_\mathrm{r}}\frac{\ell(\ell+1)}{r^2} \tag{42}$$

Hydrogen atom - The Radial Equation II

Now for specific potential V (Coulomb potential)

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \tag{43}$$

so the radial equation becomes

$$-\frac{\hbar^2}{2m_\mathrm{r}}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m_\mathrm{r}}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \tag{44}$$

Define $\kappa = \frac{\sqrt{-2m_\mathrm{r}E}}{\hbar}$ and consider only bound states, where $E < 0$. Divide Eq. (44) by E

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{m_\mathrm{r}e^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{\kappa r} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right] u \tag{45}$$

Hydrogen atom - The Radial Equation III

Substitute $\rho \equiv \kappa r$ and $\rho_0 \equiv \frac{m_r e^2}{2\pi\epsilon_0 \hbar^2 \kappa}$:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right] u \tag{46}$$

for $\rho \to \infty$ we obtain $\frac{d^2u}{d\rho^2} = u$ and therefore

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \tag{47}$$

For $\rho \to \infty$ we get $e^{\rho} \to \infty$, so we need $B = 0$ and hence $u(\rho) \sim Ae^{-\rho}$
For $\rho \to 0$ (and $\ell \neq 0$):

$$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u \tag{48}$$

Hydrogen atom - The Radial Equation IV

Can be solved with

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell} \tag{49}$$

Again: For $\rho \to 0$ the term $\rho^{-\ell} \to \infty$, thus $D \overset{!}{=} 0$ and $u(\rho) \sim C\rho^{\ell+1}$
Let's introduce $v(\rho)$:

$$u(\rho) = \rho^{\ell+1}\, e^{-\rho}\, v(\rho) \tag{50}$$

Radial equation then reads

$$\rho \frac{d^2 v}{d\rho^2} + 2(\ell + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0 \tag{51}$$

Hydrogen atom - The Radial Equation V

Assuming that $v(\rho)$ can be written as a power series in ρ:

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j \tag{52}$$

$$\rightarrow \frac{dv}{d\rho} = \sum_{j=0}^{\infty} j a_j \rho^{j-1} \overset{j \rightarrow j+1}{=:} \sum_{j=0}^{\infty} (j+1) a_{j+1} \rho^j \tag{53}$$

$$\rightarrow \frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) a_{j+1} \rho^{j-1} \tag{54}$$

Hydrogen atom - The Radial Equation VI

So that radial equation now reads

$$\sum_{j=0}^{\infty} j(j+1)a_{j+1}\rho^j + 2(\ell+1)\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j \tag{55}$$

$$-2\sum_{j=0}^{\infty} ja_j\rho^j + [\rho_0 - 2(\ell+1)]\sum_{j=0}^{\infty} a_j\rho^j = 0 \tag{56}$$

The coefficients for any j must yield

$$j(j+1)a_{j+1} + 2(\ell+1)(j+1)a_{j+1} - 2ja_j + [\rho_0 - 2(\ell+1)]a_j = 0 \tag{57}$$

$$\text{or} \qquad a_{j+1} = \frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}a_j \tag{58}$$

Hydrogen atom - The Radial Equation VII

Starting with $a_0 = A$ (A yet to be fixed) and check for large j:

$$a_{j+1} \simeq \frac{2j}{j(j+1)} a_j = \frac{2}{j+1} a_j \quad \Rightarrow \quad a_j \simeq \frac{2^j}{j!} A \tag{59}$$

But if this were the exact solution:

$$v(\rho) = A \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = A e^{2\rho} \quad \Rightarrow \quad u(\rho) = A \rho^{\ell+1} e^{\rho} \tag{60}$$

where $e^{\rho} \to \infty$ for $\rho \to \infty$. So, series (60) must have maximum $j_{\max}$, such that

$$a_{j_{\max}+1} = 0 \quad \Rightarrow \quad 2(j_{\max} + \ell + 1) - \rho_0 = 0 \quad \text{in Eq. (58)} \tag{61}$$

Hydrogen atom - The Radial Equation VIII

Defining $n \equiv j_{\mathrm{max}} + \ell + 1 \rightarrow \rho_0 = 2n$, recalling that

$$\rho_0 = \frac{m_{\mathrm{r}} e^2}{2\pi\epsilon_0 \hbar^2 \kappa} \quad \text{and} \quad \kappa = \frac{\sqrt{-2m_{\mathrm{r}} E}}{\hbar} \tag{62}$$

$$\rightarrow \; E = -\frac{\hbar^2 \kappa^2}{2m_{\mathrm{r}}} = -\frac{mre^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2} \tag{63}$$

Bohr formula

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)\right]\frac{1}{n^2} = \frac{E_1}{n^2} \quad n = 1, 2, 3, \ldots \tag{64}$$

→ allowed energies of the Hydrogen atom

Hydrogen atom - The Radial Equation IX

Eq. (62) and $\rho = 2n$ also yield *Bohr radius*:

$$\begin{aligned} \kappa &= \left(\frac{m_\mathrm{r} e^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an} && (65)\\ \text{where} \quad a &= \frac{4\pi\epsilon_0\hbar^2}{m_\mathrm{r} e^2} = 0.529\times 10^{-10}\,\mathrm{m} && (66)\\ \text{and} \quad \rho &= \frac{r}{an} && (67) \end{aligned}$$

Now, for normalization we remember that for the *radial equation*

$$\begin{aligned} u(r) &\equiv rR(r) \qquad \text{and our approach:} && (68)\\ u(\rho) &= \rho^{\ell+1}e^{-\rho}v(\rho) && (69)\\ \rightarrow R_{n\ell} &= \frac{1}{r}\rho^{\ell+1}e^{-\rho}v(\rho) && (70) \end{aligned}$$

where $v(\rho) = \sum_{j=0}^{j_\mathrm{max}=n-\ell-1} a_j\rho^j$

Hydrogen atom - The Radial Equation X

Consider *ground state*, i.e. $n = 1$

Binding energy of hydrogen atom

$$E_1 = -\left[\frac{m_\mathrm{r}}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6\,\mathrm{eV} \tag{71}$$

So, $1 = n = j_\mathrm{max} + \ell + 1 \rightarrow \ell \overset{!}{=} 0$ and therefore also $m = 0$ (Why?)

$$\varphi_{100}(r,\theta,\phi) = R_{10}\,Y_0^0(\theta,\phi) \tag{72}$$

Our recursion formula $a_{j+1} = \frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}a_j$ with $j = 0$ yields $a_1 = 0$ (and hence also for $a_2, a_3, \ldots \rightarrow v(\rho) = a_0\rho^0 = \mathrm{const.}$

$$R_{10}(r) = \frac{a_0}{a}e^{-r/a} \tag{73}$$

Hydrogen atom - The Radial Equation XI

Using Normalization condition $\int_0^\infty |R|^2 r^2 dr \overset{!}{=} 1$ to determine a_0:

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|a_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2 dr = |a_0|^2 \frac{a}{4} \overset{!}{=} 1 \tag{74}$$

$$\rightarrow \quad a_0 = \frac{2}{\sqrt{a}} \tag{75}$$

With $Y_0^0 = \frac{1}{\sqrt{4\pi}}$:

$$\varphi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \tag{76}$$

- independent of ϕ and θ → spherical symmetric with $|\varphi|^2 \sim e^{-2r/a}$
- so-called s orbital

Hydrogen atom - The Radial Equation XII

For the first excited state $n = 2 \rightarrow E_2 = E_1/2^2 = -3.4\,\text{eV}$ and

$$j_{\max} = \underbrace{n}_{=2} - \ell - 1 = \begin{cases} \ell = 0 & \Rightarrow \quad j_{\max} = 1 \\ \ell = 1 & \Rightarrow \quad j_{\max} = 0 \end{cases} \tag{77}$$

$\rightarrow m = 0, +1, -1.$
Note: 4 different $\varphi_{n\ell m}$ for one energy (= eigenvalue of $\hat{H}$)
→ *degeneracy*

So for $\ell = 0$ → Recursion formula gives $a_1 = -a_0$ $(j = 0)$
and $a_2 = 0$ $(j = 1)$ → our polynomial $v(\rho) = a_0(1 - \rho)$:

$$\ell = 0 \qquad R_{20}(r) = \frac{a_0}{2a}\left(1 - \frac{r}{2a}\right) e^{-r/2a} \tag{78}$$

$$\ell = 1 \qquad R_{21}(r) = \frac{a_0}{4a^2} r e^{-r/2a} \tag{79}$$

where a_0 needs to be determined from normalization

Hydrogen atom - The Radial Equation XIII

The number of different φ for any n, because of $\ell = 0, 1, \ldots, n-1$ and for each ℓ exist $(2\ell + 1)$ values of m, is:

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = n^2 \qquad \text{(Proof!)} \tag{80}$$

So, our polynomial $v(\rho)$ can be written as

$$\begin{aligned}
v(\rho) &= L^{2\ell+1}_{n-\ell-1}(2\rho) && (81)\\
L^{p}_{q-p}(x) &\equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) && (82)\\
& \quad \text{with the } q\text{th Laguerre polynomial:} && (83)\\
L_q(x) &\equiv e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right) && (84)
\end{aligned}$$

Full solution I

Now, the full solution reads:

$$\varphi_{n\ell m}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^{\ell} L^{2\ell+1}_{n-l-1}\left(\frac{2r}{na}\right) Y^m_\ell(\theta,\phi)$$

$\varphi_{n\ell m}$ e.g. with $n=2$, $\ell=1$, $m=0$:

$$\varphi_{210}(r,\theta,\phi) = \frac{1}{\sqrt{4\pi}}\left(\frac{1}{2a}\right)^{3/2} \frac{r}{a} e^{-r/(2a_0)} \cos\theta \qquad (85)$$

- independent of ϕ → rotationally symmetric w.r.t. the z-axis
- so-called p orbital → illustration of the probability of presence

Full solution II

Summary:

- found stationary solutions for Coulomb potential (eigenfunctions for eigenvalues $E \leftrightarrow \hat{H}$)
- analytic solutions (real) → only certain functions for bound states due to normalization constraints, characterized by *discrete quantum numbers*
- quantum number n → from radial equation → associated Laguerre polynomials
- quantum numbers ℓ, m → possible values depend on n and ℓ → spherical harmonics → associated Legendre polynomials
- eigenvalues E denpend only on n → degeneracy (only for pure Coulomb potential, central force)
- all solutions and quantum numbers verified by experiments
- but: one more quantum number, not deducible from *Schrödinger equation* (i.e. differential equation): *spin* quantum number

Full solution III

quantum number	value / symbol	formula
n	$1, 2, 3, \ldots$ $K, L, M, \ldots$ (shells)	$E_n = -R_\infty / n^2$
ℓ	$0, 1, 2, 3, \ldots, n-1$ $s, p, d, f, \ldots$ (orbitals)	$\lvert\vec{L}\rvert = \sqrt{\ell(\ell+1)}\hbar$
m_ℓ	$0, \pm 1, \pm 2, \ldots, \pm \ell$	$L_z = m_\ell \hbar$
m_s	$\pm \frac{1}{2}$	$S_z = m_s \hbar$

The angular momentum operator I

In classical mechanics angular momentum $\vec{L}$ from cross product:

$$\vec{L} = \vec{r} \times \vec{p} \tag{86}$$

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} yp_z - zp_y \\ zp_x - xp_z \\ xp_y - yp_x \end{pmatrix} \tag{87}$$

In quantum mechanics: $p_x \rightarrow \frac{\hbar}{\imath}\frac{\partial}{\partial x} \equiv \frac{\hbar}{\imath}\partial_x$, so that

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \frac{\hbar}{\imath}\begin{pmatrix} y\partial_z - z\partial_y \\ z\partial_x - x\partial_z \\ x\partial_y - y\partial_x \end{pmatrix} \tag{88}$$

Again, we are interested in the eigenvalues and eigenfunctions.

The angular momentum operator II

Unfortunately:

$$
\begin{aligned}
[L_x, L_y]f &= \left(\frac{\hbar}{\imath}\right)^2 (y\partial_x - x\partial_y)\, f = \imath\hbar L_z f \qquad \text{(Proof!)} && (89)\\
\Rightarrow \qquad [L_x, L_y] &= \imath\hbar L_z && (90)\\
\text{and} & && (91)\\
[L_y, L_z] &= \imath\hbar L_x, \qquad [L_z, L_x] = \imath\hbar L_y && (92)
\end{aligned}
$$

As L_x, L_y, L_z do not commutate, from generalized uncertainty principle:

$$\sigma^2_{L_x}\sigma^2_{L_y} \geq \frac{\hbar}{2}|\langle L_z\rangle| \qquad (93)$$

→ incompatible observables, no common eigenfunctions of L_x and L_z, etc.

The angular momentum operator III

Fortunately:

$$[L^2, L_x] \equiv [L_x^2 + L_y^2 + L_z^2, L_x] = 0 \qquad \text{(Proof!)} \tag{94}$$

→ hopefully: eigenfunction f exists, so that

$$L^2 f = \lambda f \quad \text{and} \quad L_z f = \mu f \tag{95}$$

Let's introduce the *ladder operator*

$$\begin{aligned} L_\pm &\equiv L_x \pm \imath L_y \qquad \text{with:} && (96)\\ [L_z, L_\pm] &= [L_z, L_x] \pm \imath [L_z, L_y] = \imath\hbar L_y \pm \imath(-\imath\hbar L_x) && (97)\\ &= \pm\hbar(L_x \pm \imath L_y) = \pm\hbar L_\pm && (98)\\ \text{and } [L^2, L_\pm] &= 0 && (99) \end{aligned}$$

The angular momentum operator IV

So, with $[L_z, L_\pm] = \pm\hbar L_\pm$:

$$\begin{aligned} L^2(L_\pm f) &= L_\pm(L^2 f) = L_\pm(\lambda f) = \lambda(L_\pm f) \qquad (100) \\ L_z(L_\pm f) &= (L_z L_\pm - L_\pm L_z)f + L_\pm L_z f \qquad (101) \\ &= \pm\hbar L_\pm f + L_\pm(\mu f) = (\mu \pm \hbar)(L_\pm f) \qquad (102) \end{aligned}$$

→ $(L_\pm f)$ is an eigenfunction of L^2 as well as f, with same eigenvalue λ
→ $(L_\pm f)$ is also an eigenfunction of L_z, with *new* eigenvalue $\mu \pm \hbar$

Therefore: L_+ raising operator → increases eigenvalue of L_z
L_- lowering operator → lowers eigenvalue by $\hbar$

→ Consecutive application of L_+ until reaching f_t with $L_z^2 = L^2$, such that $L_+ f_t = 0$ with eigenvalue of f_t, let's call $\hbar\ell$, i.e. $L_z f_t = \hbar\ell f_t$ and $L^2 f_t = \lambda f_t$

The angular momentum operator V

With help of the following relation

$$\begin{aligned} L_{\pm} L_{\mp} &= (L_x \pm \imath L_y)(L_x \mp \imath L_y) = L_x^2 + L_y^2 \mp \imath (L_x L_y - L_y L_x) && (103) \\ &= L^2 - L_z^2 \mp \hbar L_z && (104) \\ \rightarrow L^2 &= L_{\pm} L_{\mp} + L_z^2 \mp \hbar L_z && (105) \end{aligned}$$

we find a relation for the eigenvalue λ of L^2 in terms of the maxium eigenvalue of L_z:

$$\begin{aligned} L^2 f_t &= (L_- L_+ + L_z^2 + \hbar L_z) f_t && (106) \\ &= (0 + \hbar^2 \ell^2 + \hbar \ell) f_t = \hbar^2 \ell(\ell + 1) f_t && (107) \\ \rightarrow \lambda &= \hbar^2 \ell(\ell + 1) && (108) \end{aligned}$$

The angular momentum operator VI

Analogously, there is a minimum eigenvalue of L_z with eigenfunction f_b:

$$\begin{aligned} L_- f_b &= 0 \quad \text{with} \quad L_z f_b = \hbar \ell_b f_b \quad \text{and} \quad L^2 f_b = \lambda f_b & (109)\\ \rightarrow L^2 f_b &= (L_+ L_- + L_z^2 - \hbar L_z) f_b & (110)\\ &= (0 + \hbar^2 \ell_b^2 - \hbar \ell) f_b = \hbar^2 \ell_b (\ell_b - 1) f_b & (111)\\ \rightarrow \lambda &= \hbar^2 \ell_b (\ell_b - 1) & (112) \end{aligned}$$

Hence by combining both results for λ (e.v. of L^2), we get

$$\ell(\ell+1) = \ell_b(\ell_b - 1) \quad \rightarrow \quad \ell_b = -\ell \qquad (113)$$

→ eigenvalues of L_z are $m\hbar$ with $m = -\ell, \ldots, 0, \ldots, \ell$ in N integer steps, i.e. $\ell = -\ell + N \Rightarrow \ell = N/2 \rightarrow \ell$ is integer or *half-integer*

The angular momentum operator VII

Eigenfunctions of L_z, L^2 characterized by ℓ and m:

$$L^2 f_\ell^m = \hbar^2 \ell(\ell+1) f_\ell^m \qquad L_z f_\ell^m = \hbar m f_\ell^m \tag{114}$$

$$\text{where} \quad \ell = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \quad m = -\ell, \ldots, 0, \ldots, \ell \tag{115}$$

Note: by pure algebra we found the eigenvalues of L_z and L^2

ℓ is also called the azimuthal quantum number and m the magnetic quantum number

→ now find eigenfunctions f

The angular momentum operator VIII

Remember that $\vec{L} = \frac{\hbar}{\imath}\vec{r} \times \nabla$ and with the unit vectors $\hat{r}$ etc.

$$\begin{aligned} \nabla &= \hat{r}\partial_r + \hat{\theta}\frac{1}{r}\partial_\theta + \hat{\phi}\frac{1}{r\sin\theta}\partial_\phi & (116) \\ \Rightarrow \vec{L} &= \frac{\hbar}{\imath}\left[r(\hat{r}\times\hat{r})\partial_r + (\hat{r}\times\hat{\theta})\partial_\theta + (\hat{r}\times\hat{\phi})\frac{1}{\sin\theta}\partial_\phi\right] & (117) \end{aligned}$$

As $(\hat{r}\times\hat{r}) = 0$, $(\hat{r}\times\hat{\theta}) = \hat{\phi}$, and $(\hat{r}\times\hat{\phi}) = -\hat{\theta}$

$$\vec{L} = \frac{\hbar}{\imath}\left(\hat{\phi}\partial_\theta - \hat{\theta}\frac{1}{\sin\theta}\partial_\phi\right) \qquad (118)$$

Unit vectors $\hat{\theta}$, $\hat{\phi}$ in Cartesian coordinates:

$$\begin{aligned} \hat{\theta} &= (\cos\theta\cos\phi)\hat{x} + (\cos\theta\sin\phi)\hat{y} + -(\sin\theta)\hat{z} & (119) \\ \hat{\phi} &= -(\sin\phi)\hat{x} + (\cos\phi)\hat{y} & (120) \end{aligned}$$

The angular momentum operator IX

$$\vec{L} = \frac{\hbar}{\imath}\Bigg[(-\sin\phi\hat{x} + \cos\phi\hat{y})\partial_\theta - \tag{121}$$

$$(\cos\theta\cos\phi\hat{x} + \cos\theta\sin\phi\hat{y} - \sin\theta\hat{z})\frac{1}{\sin\theta}\partial_\phi\Bigg] \tag{122}$$

$$\Rightarrow L_x = \frac{\hbar}{\imath}(-\sin\phi\partial_\theta - \cos\phi\cot\theta\partial_\phi) \tag{123}$$

$$L_y = \frac{\hbar}{\imath}(+\cos\phi\partial_\theta - \sin\phi\cot\theta\partial_\phi) \tag{124}$$

$$L_z = \frac{\hbar}{\imath}\partial_\phi \tag{125}$$

$$L_\pm = L_x + \imath L_y = \frac{\hbar}{\imath}[(-\sin\phi \pm \imath\cos\phi)\partial_\theta - \tag{126}$$

$$(\cos\phi \pm \imath\sin\phi)\cot\theta\partial_\phi] \tag{127}$$

$$= \pm\hbar e^{\pm\imath\phi}(\partial_\theta \pm \imath\cot\theta\partial_\phi) \qquad \text{as:}\ \cos\phi \pm \imath\sin\phi = e^{\pm\imath\phi} \tag{128}$$

The angular momentum operator X

Now we can find eigenfunction $f_\ell^m(\theta,\phi)$ of L_z:

$$L_z f_\ell^m(\theta,\phi) = \frac{\hbar}{\imath}\partial_\phi f_\ell^m(\theta,\phi) = \hbar m\, f_\ell^m(\theta,\phi) \quad \Rightarrow \quad f_\ell^m(\theta,\phi) = g(\theta)e^{\imath m\phi} \tag{129}$$

Analogously, $f_\ell^m(\theta,\phi)$ is an eigenfunction of L^2 with e.v. $\hbar\ell(\ell+1)$:

$$L^2 f_\ell^m(\theta,\phi) = (L_+L_- + L_z^2 - \hbar L_z)\, f_\ell^m(\theta,\phi) = \hbar^2\ell(\ell+1)\, f_\ell^m(\theta,\phi) \tag{130}$$

As $\partial_\theta f = e^{\imath m\phi}\frac{dg}{d\theta}$ and $\partial_\phi f = \imath m e^{\imath m\phi} g$ with our expression for $L_\pm$ and L_z we obtain (Proof!)

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dg}{d\theta}\right) + [\ell(\ell+1)\sin^2\theta - m^2]g = 0 \tag{131}$$

→ this is $\Theta(\theta)$ of the spherical harmonics $Y_\ell^m(\theta,\phi)$ and – of course – $f(\phi) = e^{\imath m\phi}$ is $\Phi(\phi)$!

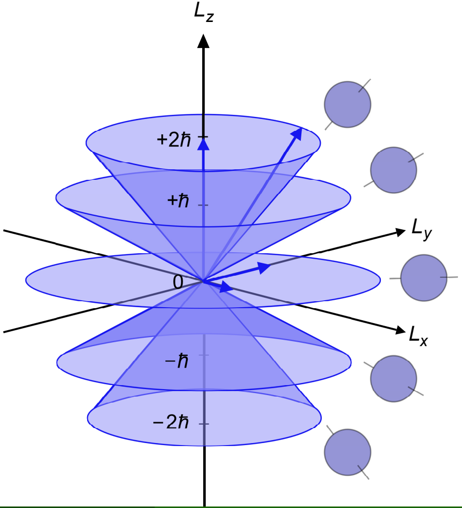
The angular momentum operator XI

⇒ The *spherical harmonics* are the eigenfunctions of L^2 and L_z :

$$H\psi = E\psi \qquad L^2\psi = \hbar^2\ell(\ell+1)\psi \qquad L_z\psi = \hbar m\psi \tag{132}$$

Note 1: Found from analytical solution of the central-force problem that ℓ and m → *integer*
but from algebraic solution for angular momentum operator → ℓ and m also *half-integer*

Note 2: Absolute value of $\vec{L}$ is discrete, but also its *component* L_z → vector cone (see right figure), as J_x, J_y unknown



The spin operator I

Classical mechanics:
$\vec{L} = \vec{r} \times \vec{p}$ (motion of center of mass) and spin $\vec{S} = \mathbf{I}\vec{\omega}$ (motion about center of mass)

Quantum mechanics of hydrogen atom:
$\vec{L}\rightarrow$ orbital angular momentum of electron orbiting nucleus
and $\vec{S}$ spin $\rightarrow$ angular momentum of electron itself $\rightarrow$ not a function of position variables r, θ, ϕ

Spin as *intrinsic* angular momentum cannot be decomposed into orbital angular momenta of constituent parts (e.g. electron is point-like)

The spin operator II

However, analogously to algebraic theory of angular momentum we postulate:

$$[S_x, S_y] = \imath\hbar S_z, \qquad [S_y, S_z] = \imath\hbar S_x, \qquad [S_z, S_x] = \imath\hbar S_y \tag{133}$$

And with *ket* notation (as eigenstates of spin are not functions):

$$S^2 \left|sm\right\rangle = \hbar^2 s(s+1) \left|sm\right\rangle; \qquad S_z \left|sm\right\rangle = \hbar m \left|sm\right\rangle \tag{134}$$

$$S_\pm |sm\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}\, |s(m\pm 1)\rangle \tag{135}$$

These relations do not exclude *half-integer* values of s, m. Interestingly, every elementary particle has specific, fixed value of s, e.g. 1/2 for electrons

The spin operator III

Theory of spin 1/2

simplest nontrival quantum system → only two possible eigenstates:

$|\frac{1}{2}\frac{1}{2}\rangle$ → spin up

$|\frac{1}{2}(-\frac{1}{2})\rangle$ → spin down

Thus, general state can be written as 2-element column matrix (spinor):

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \quad \text{where} \tag{136}$$

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{spin up} \qquad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{spin down} \tag{137}$$

The spin operator IV

The spin operators S_z, S^2, etc. are 2×2 matrices. From their eigenvalues $(s = 1/2)$:

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+; \quad S^2\chi_- = \frac{3}{4}\hbar^2\chi_-; \quad S_z\chi_+ = \frac{1}{2}\hbar^2\chi_+; \quad S_z\chi_- = -\frac{1}{2}\hbar^2\chi_- \tag{138}$$

$$S_+\chi_- = \hbar\chi_+; \quad S_-\chi_+ = \hbar\chi_-; \quad S_+\chi_+ = S_-\chi_- = 0 \tag{139}$$

together with $S_\pm \equiv S_x \pm \imath S_y$, so that

$$S_x = \frac{1}{2}(S_+ + S_-) \quad S_y = \frac{1}{2\imath}(S_+ - S_-) \tag{140}$$

and therefore

$$S_x\chi_+ = \frac{\hbar}{2}\chi_-; \quad S_x\chi_- = \frac{\hbar}{2}\chi_+; \quad S_y\chi_+ = -\frac{\hbar}{2\imath}\chi_-; \quad S_y\chi_- = \frac{\hbar}{2\imath}\chi_+; \tag{141}$$

The spin operator V

we find the algebraic representation of the spin operators

$$S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{142}$$

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix}; \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{143}$$

One defines the *Pauli spin matrices* by $\sigma_x = S_x/\frac{\hbar}{2}$ etc.
Note: S_x, S_y, S_z, S^2 are Hermitian (i.e. self-adjoint:
$S_x = S_x^\dagger = \overline{S_x}^\mathsf{T} = \overline{S_x^\mathsf{T}}$) → observables,
while S_+, S_- are not Hermitian → not observable

We already know the eigenspinors (eigenstates) and eigenvalues of S_z:

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{eigenvalue: } +\frac{\hbar}{2}; \qquad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{eigenvalue: } -\frac{\hbar}{2} \tag{144}$$

The spin operator VI

For a particle in the general state

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_{+} + b\chi_{-} \tag{145}$$

the probability to *get* for S_z the value $+\frac{\hbar}{2}$ is of course $|a|^2$ and to *get* the value $-\frac{\hbar}{2}$ is $|b|^2$, so

$$|a|^2 + |b|^2 = 1 \qquad \text{(i.e. normalized spinor)} \tag{146}$$

Accurate language

The probability $|a|^2$ to *get* $+\hbar/2$ for a measurement of S_z doesn't mean that the particle *is* in the state $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$. In fact, the particle *is* in the state χ.

The parity operator

The action of the parity operator P is just $\vec{r} \rightarrow -\vec{r}$:

$$P\psi(x, y, z) = \psi(-x, -y, -z) \tag{147}$$

Obviously $P^2 = PP = \mathbf{1}$ → only two eigenvalues:

$+1$ → eigenstate of positive parity (even parity): $\psi(\vec{r}) = \psi(-\vec{r})$
-1 → eigenstate of negative parity (odd parity): $\psi(\vec{r}) = -\psi(-\vec{r})$

For a potential $V(x, y, z) = V(-x, -y, -z)$, e.g. Coulomb potential
→ parity is *good quantum number* (i.e. conserved quantity)

Parity of eigenfunctions of hydrogen atom $\psi(r, \theta, \phi) = R(r) P_\ell^m(\cos\theta) e^{\imath m \phi}$

Parity transformation $\theta \rightarrow \pi - \theta$, $\phi \rightarrow \phi + \pi$, $r \rightarrow r$
⇒ parity depends only on transformation of associated Legendre polynoms
even ℓ → even parity and odd ℓ → odd parity (Proof!)

Application: Electron in magnetic field I

spin + charged particle → magnetic dipole:

$$\vec{\mu} = \gamma \vec{S} \qquad \text{where } \gamma := \text{gyromagnetic ratio} \tag{148}$$

Note: in classical electrodynamics: $\gamma = \frac{q}{2m}$
in QM: $\gamma = g_J \frac{q}{2m} = g_S \frac{q}{2m} \approx 2.002 \frac{q}{2m}$
magnetic dipole in magnetic field $\vec{B}$ experiences torque $\vec{M}$:

$$\vec{M} = \vec{\mu} \times \vec{B} \tag{149}$$

→ torque tries to line $\vec{\mu}$ up parallel to field ("compass needle")
Energy (and therefore Hamiltonian):

$$H = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{B} \cdot \vec{S} \tag{150}$$

Application: Electron in magnetic field II

Larmor precession

Spin-$\frac{1}{2}$ particle in a homogeneous magnetic field along z-direction
$\vec{B} = B_0 \vec{e}_z$
Hamiltonian (matrix!):

$$H = -\gamma B_0 S_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{151}$$

Hamiltonian H and Spin operator S_z share same eigenstates:

$$\chi_+, \quad \text{energy } E_+ = -\tfrac{\gamma B_0 \hbar}{2} \tag{152}$$

$$\chi_-, \quad \text{energy } E_- = +\tfrac{\gamma B_0 \hbar}{2} \tag{153}$$

where energy is lowest for dipole moment parallel to magnetic field
(otherwise: → torque tries to align)

Application: Electron in magnetic field III

→ time-dependent solution of $\imath\hbar\partial_t\chi = H\chi$ expressed with stationary states:

$$\chi(t) = a\chi_+ e^{-\imath E_+ t/\hbar} + b\chi_- e^{-\imath E_- t/\hbar} = \begin{pmatrix} ae^{+\imath\gamma B_0 t/\hbar} \\ be^{-\imath\gamma B_0 t/\hbar} \end{pmatrix} \tag{154}$$

fix coefficients by initial conditions, e.g.

$$\chi(t=0) = \begin{pmatrix} a \\ b \end{pmatrix}, \qquad \text{where } |a|^2 + |b|^2 = 1 \tag{155}$$

Then (for real a, b) we can write $a = \cos(\alpha/2)$ and $b = \sin(\alpha/2)$, with constant α, so

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{+\imath\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-\imath\gamma B_0 t/2} \end{pmatrix} \tag{156}$$

Application: Electron in magnetic field IV

therefore the expectation value of the spin as a function of time:

$$\begin{aligned}
\langle S_x\rangle &= \chi(t)^\dagger S_x \chi \\
&= \left(\cos(\alpha/2)e^{-\imath\gamma B_0 t/2} \quad \sin(\alpha/2)e^{+\imath\gamma B_0 t/2}\right)\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \cos(\alpha/2)e^{+\imath\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-\imath\gamma B_0 t/2} \end{pmatrix} \\
&= +\frac{\hbar}{2}\sin\alpha\cos(\gamma B_0 t) \\
\langle S_y\rangle &= -\frac{\hbar}{2}\sin\alpha\sin(\gamma B_0 t) \\
\langle S_z\rangle &= +\frac{\hbar}{2}\cos\alpha
\end{aligned}$$

$\rightarrow \langle\vec{S}\rangle$ tilted at constant angle α to z-axis, precesses about the field at

Larmor frequency of a spinning electron

$$\omega = \gamma B_0 = 1.7606\times 10^{11}\,\mathrm{rad\,s^{-1}\,T^{-1}}\cdot B_0 \;\rightarrow\; f = 28\,\mathrm{GHz\,T^{-1}}\cdot B_0$$

Addition of angular momenta I

Now, two spin-$\frac{1}{2}$ particles (e.g. electron and proton in ground state of hydrogen, so $\ell = 0$), composite system is in a *linear combination* of

$$\uparrow\uparrow,\ \uparrow\downarrow,\ \downarrow\uparrow,\ \downarrow\downarrow \tag{157}$$

What is the *total* angular momentum of the atom?
We define

$$\vec{S} \equiv \vec{S}^{(1)} + \vec{S}^{(2)} \tag{158}$$

The *z*-component: simply adds, each composite state is eigenstate of S_z

$$\begin{aligned} S_z\chi_1\chi_2 &= (S_z^{(1)} + S_z^{(2)})\chi_1\chi_2 = (S_z^{(1)}\chi_1)\chi_2 + \chi_1(S_z^{(2)}\chi_2) && (159)\\ &= (\hbar m_1\chi_1)\chi_2 + \chi_1(\hbar m_2\chi_2) = \hbar(m_1+m_2)\chi_1\chi_2 && (160) \end{aligned}$$

Addition of angular momenta II

Thus, $m = m_1 + m_2$:

$$\begin{aligned}
&\uparrow\uparrow && m = 1 && (161)\\
&\uparrow\downarrow && m = 0 && (162)\\
&\downarrow\uparrow && m = 0 && (163)\\
&\downarrow\downarrow && m = -1 && (164)
\end{aligned}$$

problem: two states with $m = 0 \rightarrow$ apply lowering operator $S_- = S_-^{(1)} + S_-^{(2)}$ to state $\uparrow\uparrow$ to obtain the correct state:

$$\begin{aligned}
S_-(\uparrow\uparrow) &= (S_-^{(1)}\uparrow)\uparrow + \uparrow(S_-^{(2)}\uparrow) && (165)\\
&= (\hbar\downarrow)\uparrow + \uparrow(\hbar\downarrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow) && (166)
\end{aligned}$$

Addition of angular momenta III

Therefore, the states with $s = 1$ in $|s\,m\rangle$ notation

$$\left.\begin{array}{lcl} |1\,1\rangle & = & \uparrow\uparrow \\ |1\,0\rangle & = & \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\,-1\rangle & = & \downarrow\downarrow \end{array}\right\} \rightarrow \text{triplet: } s = 1 \qquad (167)$$

And orthogonal state $|s\,m\rangle = |0\,0\rangle$

$$|0\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)\Big\} \rightarrow \text{singlet: } s = 0 \qquad (168)$$

→ system of two spin-$\frac{1}{2}$ particles has total spin 1 or 0. Let us *proof:* triplet states are eigenvectors of S^2 with eigenvalues $2\hbar^2$ and singlet state is eigenvector with eigenvalue 0:

Addition of angular momenta IV

$$S^2 = (\vec{S}^{(1)} + \vec{S}^{(2)}) \cdot (\vec{S}^{(1)} + \vec{S}^{(2)}) = (S^{(1)})^2 + (S^{(2)})^2 + 2\vec{S}^{(1)} \cdot \vec{S}^{(2)} \quad (169)$$

Remember: $S_x\chi_+ = \frac{\hbar}{2}\chi_-$, $S_y\chi_+ = -\frac{\hbar}{2\imath}\chi_-$, $S_z\chi_+ = \frac{\hbar}{2}\chi_+$, $S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+$ etc.

$$\begin{aligned}
\vec{S}^{(1)} \cdot \vec{S}^{(2)}(\uparrow\downarrow) &= (S_x^{(1)} \uparrow)(S_x^{(2)} \downarrow) + (S_y^{(1)} \uparrow)(S_y^{(2)} \downarrow) + (S_z^{(1)} \uparrow)(S_z^{(2)} \downarrow) \\
&= \left(\frac{\hbar}{2} \downarrow\right)\left(\frac{\hbar}{2} \uparrow\right) + \left(\frac{\imath\hbar}{2} \downarrow\right)\left(-\frac{\imath\hbar}{2} \uparrow\right) + \left(\frac{\hbar}{2} \uparrow\right)\left(-\frac{\hbar}{2} \downarrow\right) \\
&= \frac{\hbar^2}{4}(2 \downarrow\uparrow - \uparrow\downarrow) & (170) \\
&\text{and} & (171) \\
\vec{S}^{(1)} \cdot \vec{S}^{(2)}(\downarrow\uparrow) &= \frac{\hbar^2}{4}(2 \uparrow\downarrow - \downarrow\uparrow) & (172)
\end{aligned}$$

Addition of angular momenta V

So we get

$$\vec{S}^{(1)} \cdot \vec{S}^{(2)}|1\,0\rangle = \frac{\hbar}{4}\frac{1}{\sqrt{2}}(2\downarrow\uparrow - \uparrow\downarrow + 2\uparrow\downarrow - \downarrow\uparrow) = -\frac{\hbar^2}{4}|1\,0\rangle \tag{173}$$

$$\vec{S}^{(1)} \cdot \vec{S}^{(2)}|0\,0\rangle = \frac{\hbar}{4}\frac{1}{\sqrt{2}}(2\downarrow\uparrow - \uparrow\downarrow - 2\uparrow\downarrow + \downarrow\uparrow) = -\frac{3\hbar^2}{4}|0\,0\rangle \tag{174}$$

and therefore

$$S^2|1\,0\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2\frac{\hbar^2}{4}\right)|1\,0\rangle = 2\hbar^2|1\,0\rangle \tag{175}$$

$$S^2|0\,0\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - 2\frac{\hbar^2}{4}\right)|0\,0\rangle = 0 \tag{176}$$

and of course $S^2|1\,-1\rangle = 2\hbar^2|1\,-1\rangle$ and $S^2|1\,1\rangle = 2\hbar^2|1\,1\rangle$

Addition of angular momenta VI

Thus, answer to the general problem of combining *any* s_1, s_2 or *angular momenta*:

$$s = (s_1 + s_2), (s_1 + s_2 - 1), \ldots, |s_1 - s_2| \tag{177}$$

and also, e.g. for hydrogen atom, net angular momentum of electron (spin + orbital) j

$$j = \ell + \frac{1}{2} \qquad \text{or} \qquad j = \ell - \frac{1}{2} \tag{178}$$

and with proton, total angular momentum of hydrogen atom:

$$J = \ell + 1 \qquad \text{or} \qquad J = \ell - 1 \tag{179}$$

Addition of angular momenta VII

Therefore, state $|s\,m\rangle$ with total spin s and z-component m → linear combination of composite states $|s_1\,m_1\rangle\,|s_2\,m_2\rangle$:

$$|s\,m\rangle = \sum_{m_1+m_2=m} C^{s_1\,s_2\,s}_{m_1\,m_2\,m}|s_1\,m_1\rangle\,|s_2\,m_2\rangle \tag{180}$$

with *Clebsch-Gordan coefficients* $C^{s_1\,s_2\,s}_{m_1\,m_2\,m}$. E.g.

$$|2\,1\rangle = \frac{1}{\sqrt{3}}|2\,2\rangle|1\,-1\rangle + \frac{1}{\sqrt{6}}|2\,1\rangle|1\,0\rangle - \frac{1}{\sqrt{2}}|2\,0\rangle|1\,1\rangle \tag{181}$$

Note that the z-components have to add to $m = 1$

→ For two particles of spin 2 and spin 1 with total spin 2 and total z-component 1: measure $S_z^{(1)}$ and get $2\hbar$ (probability $\frac{1}{3}$), $\hbar$ (probability $\frac{1}{6}$), or 0 (probability $\frac{1}{2}$)

The helium atom I

Hamiltonian of helium ($Z = 2$), neglecting spin

$$H = \left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1}\right] + \left[-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2}\right] + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

→ without repulsion term :

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\psi_{n'\ell' m'}(\vec{r}_2) \tag{182}$$

with $a = \frac{a_\mathrm{H}}{2}$ and $E = 4E_\mathrm{H}$,

$$E = 4(E_n + E_{n'}) \quad \rightarrow \quad E_0 = 8 \cdot (-13.6\,\mathrm{eV}) = -109\,\mathrm{eV} \tag{183}$$

(But measured: $-79\,\mathrm{eV} = -24.6\,\mathrm{eV} - 54.4\,\mathrm{eV}$, because we neglected $\mathrm{e}^-\mathrm{e}^-$-interaction)

$$\text{with} \quad \psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} \tag{184}$$

The helium atom II

Electrons are *identical particles*, therefore

$$\psi(\vec{r}_1,\vec{r}_2) \neq \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \quad \text{but} \tag{185}$$

$$\psi_-(\vec{r}_1,\vec{r}_2) = A[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] \quad \text{(fermions)} \tag{186}$$

- two electrons cannot occupy same state → *Pauli exclusion principle* (Proof!)
- ψ for fermions *must be* antisymmetric under exchange:

  $$\psi(\vec{r}_1,\vec{r}_2) = -\psi(\vec{r}_2,\vec{r}_1) \tag{187}$$

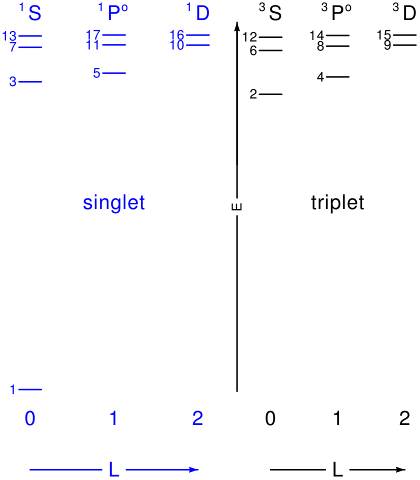
  with $\psi \rightarrow \psi(\vec{r}_1,\vec{r}_2)\chi(\vec{r}_1,\vec{r}_2)$
- as the ground state $\psi_0 \sim e^{r_1+r_2}$ of helium is symmetric → spin state must be antisymmetric → singlet, electrons oppositely aligned

  $$\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \tag{188}$$

The helium atom III

Excited helium atom:

- combination $\psi_{n\ell m}\psi_{100}$ (What about $\psi_{n\ell m}\psi_{n'\ell' m'}$?)
- symmetric $\psi_{n\ell m}\psi_{100}$ → antisymmetric spin configuration (singlet) or antisymmetric $\psi_{n\ell m}\psi_{100}$ → symmetric spin configuration (triplet)
- thus, two different kinds of excited states: singlet and triplet
- singlet states have sligthly higher E than corresponding triplets (because of symmetric ψ → closer e^-e^- → larger E_{repuls})



The helium atom IV

Intercombination

Note that

- total wavefunction must be antisymmetric by

$$\psi(\vec{r}_1, \vec{r}_2) = \begin{cases} \psi_\mathrm{a}(\vec{r}_1, \vec{r}_2)\chi_\mathrm{s}(\vec{r}_1, \vec{r}_2) \\ \psi_\mathrm{s}(\vec{r}_1, \vec{r}_2)\chi_\mathrm{a}(\vec{r}_1, \vec{r}_2) \end{cases} \tag{189}$$

- the interchange operator can be written as $P_{12} = P_{12}^{\psi}\, P_{12}^{\chi}$
- Hamiltonian does not depend on spin $\rightarrow [H, P_{12}^{\psi}] = 0$
- time evolution operator $U(t) = e^{-\frac{\imath}{\hbar}Ht} \rightarrow [U, P_{12}] = 0$
- if for any t_0: $P_{12}|\psi(t_0)\rangle = -|\psi(t_0)$, then for all times:

$$P_{12}|\psi(t)\rangle = P_{12}U(t)|\psi(t_0)\rangle = U(t)P_{12}|\psi(t_0)\rangle \tag{190}$$

$$= -U(t)|\psi(t_0)\rangle = -|\psi(t)\rangle \tag{191}$$

The helium atom V

→ symmetry of $\psi(\vec{r}_1, \vec{r}_2)$ does not change with time → symmetry of $\chi(\vec{r}_1, \vec{r}_2)$ does not change with time

Selection rule for multiplicity

Transitions between different multiplicities are forbidden:

$$\Delta s = 0 \tag{192}$$

(exact Hamiltonian depends on spin → small modification of selection rule)

Parity

ψ composed of $\psi_{n\ell m}\psi_{100} = R_{n\ell}\, Y_\ell^m\, R_{10}\, Y_0^0$
→ parity good quantum number, odd for odd ℓ, even for even ℓ

odd parity indicated by small letter o right from captial letter for net orbital angular momentum → e.g. $^1\mathrm{P}^\mathrm{o}$

Multi-electron atoms I

Analogously, ground-state electron configurations of other atoms described by

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_i} \right] + \sum_{i\neq j} \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r_i} - \vec{r_j}|} \qquad (193)$$

- neglect repulsion term → each electron occupies a one-particle hydrogenic state (n, ℓ, m) → *orbital*
- due to Pauli exclusion principle → only two e^- per orbital:
- n^2 wavefunction for each shell n, e.g. $n = 1$ → two electrons, $n = 2$ → eight electrons, etc.
- Periodic system: horizontal rows ↔ filling out each shell
- How to fill $n = 2$ ($\ell = 0$ or $\ell = 1$) with *single* e^-? → *screening* by inner electrons, favor lowest ℓ, e.g. $E_{n=2}^{\ell=0} < E_{n=2}^{\ell=1}$, $E_{n=4}^{\ell=0} < E_{n=3}^{\ell=2}$ (larger ℓ → larger $\langle r \rangle$ → stronger screening of nucleus → less binding energy)

Multi-electron atoms II

Total angular momentum

- state of electron represented by pair $n\ell$, where ℓ is a letter, e.g. s for $\ell = 0$ – m not listed, but exponent for number of electrons in ℓ, e.g. He $\rightarrow 1s^2$ (i.e. two electrons in $n = 1, \ell = 0$)
- total *orbital* angular momentum indicated by capital L (letter), total spin by captial S (multiplicity, number), and total angular momentum by capital J (number)
- total configuration of atom listed as

$$^{2S+1}L_J \tag{194}$$

- e.g. groundstate of hydrogen $S = 1/2$, $L = S$, $J = 1/2 \rightarrow {}^2S_{1/2}$

LS-coupling of multi-electrons

If spin-orbit interaction negligible: $\vec{L} = \sum \vec{\ell}_i$, $\vec{S} = \sum \vec{s}_i$ and $\vec{J} = \vec{L} + \vec{S}$

Multi-electron atoms III

Spectroscopic nomenclature for atomic states

Table : Angular momenta of electrons

ℓ	0	1	2	3	...
letter	s	p	d	f	...
name	sharp	principal	diffuse	fundamental	?

Ground-state electron configurations of first elements

Z	El.	Configuration	
1	H	$1s$	$^2S_{1/2}$
2	He	$1s^2$	$^1S_0$
3	Li	(He)$2s$	$^2S_{1/2}$
4	Be	(He)$2s^2$	$^1S_0$
5	B	(He)$2s^2\,2p$	$^2P^\circ_{1/2}$
...			
21	Sc	(Ar)$4s^2\,3d$	$^2D_{3/2}$

Multi-electron atoms IV

Note: Screening effect becomes larger for larger $\ell \rightarrow$ overlap of shells

$1s$	$2s$	$3s$	$4s$	$5s$	$6s$	$7s$	$8s$	$9s$	$10s$
	$2p$	$3p$	$4p$	$5p$	$6p$	$7p$	$8p$	$9p$	$10p$
		$3d$	$4d$	$5d$	$6d$	$7d$	$8d$	$9d$	$10d$
			$4f$	$5f$	$6f$	$7f$	$8f$	$9f$	$10f$
				$5g$	$6g$	$7g$	$8g$	$9g$	$10g$
					$6h$	$7h$	$8h$	$9h$	$10h$
						$7i$	$8i$	$9i$	$10i$
							$8k$	$9k$	$10k$
								$9l$	$10l$
									$10m$

→ for determining the energy order of terms of a one-electron system, just go along the diagonals, e.g. 1s 2s 2p 3s 3p 4s 3d 4p 5s.

Multi-electron atoms V

How to distribute electrons to shells?
→ find configuration of minium energy

→ Hund's rules (minimum energy principle)

1. The total angular momentum J of completely filled shells (n) or subshells (ℓ) is 0. E.g. He: $1s^2$, Be: (He)$2s^2$, Ne: (He)$2s^2\,2p^6$
2. Spins of electrons are pereferably parallel, i.e. electron are distributed on subshells with m_ℓ, such that multiplicity $2S+1$ is maximal. E.g. N → (He) $2s^2\,2p^3$: in $2p$ shell: $\uparrow\uparrow\uparrow \rightarrow {}^4S$.
   (sometimes referred to as the 1st rule or S rule)
3. For states of same S, electrons are distributed such that largest angular momentum L is achieved (larger $\ell \rightarrow$ larger $\langle r \rangle \rightarrow$ larger $\Delta x_{\mathrm{e}^-\mathrm{e}^-}$ → less repulsion), e.g. $E({}^1D_2) < E({}^1S_0)$.
   (sometimes referred to as the 2nd rule or L rule)

Multi-electron atoms VI

4. If outermost subshell half-filled or less: configuration with lowest total angular momentum $J = |L - S|$ (i.e. with smallest J) is preferred.
   If outermost subshell more than half-filled: configuration with highest $J = L + S$ is preferred.

→ reason: electron-electron interaction
→ only valid for LS coupling (no spin-orbit interaction → light atoms, $Z < 10$)

Example: groundstate of carbon $1s^2\,2s^2\,2p^2$

two e$^-$ in $2p^2 \rightarrow {}^1S$, ${}^1D$, or ${}^3P$? $\boxed{}\,\boxed{\uparrow\downarrow}\,\boxed{}$, $\boxed{}\,\boxed{}\,\boxed{\uparrow\downarrow}$, $\boxed{}\,\boxed{\uparrow}\,\boxed{\uparrow}$

Using S rule → largest mulitplicity S preferred, i.e. ${}^3P$

$J = L + S \rightarrow L = 1$ and $S = -1, 0, +1 \rightarrow {}^3P_0$, ${}^3P_1$, or ${}^3P_2$

Using J rule → smallest J, i.e. $J = 0$

$\Rightarrow {}^3P_0$

Spin-orbit interaction I

When solved Schrödinger equation for hydrogen, used simple Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \tag{195}$$

But: electron orbiting around nucleus → from electrons point of view: proton orbits electron
→ setting up magnetic field $\vec{B}$, exerting a torque on spining electron to align its magnetic moment $\vec{\mu}_{\mathrm{e}}$ along $\vec{B}$

$$H^{\mathrm{so}} = -\vec{\mu}_{\mathrm{e}} \cdot \vec{B} = -\left(-\frac{e}{m}\vec{S}\right)\vec{B} \tag{196}$$

Spin-orbit interaction II

From Biot-Savart law (→ blackboard):

$$B = \frac{\mu_0 I}{2r} \tag{197}$$

where current $I = e/T$ with $L = rmv = 2\pi m r^2/T$ and $\vec{B}||\vec{L}$, so

$$\vec{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \vec{L} \tag{198}$$

used $c = 1/\sqrt{\epsilon_0 \mu_0}$ to eliminate μ_0. So the *Spin-Orbit Interaction* is described by

$$H^{\mathrm{so}} = \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} \tag{199}$$

where factor $1/2$ is from *Thomas precession*: back transformation into rest frame of proton (electron: not an inertial system, accelerated)

Spin-orbit interaction III

Now: $[H,\vec{L}] \neq 0$ and $[H,\vec{S}] \neq 0 \rightarrow$ not longer separatly conserved quantities, instead:

$$\vec{J} \equiv \vec{L} + \vec{S} \tag{200}$$

commutes with H, as well as L^2, S^2,J_z and

$$J^2 = (\vec{L}+\vec{S})\cdot(\vec{L}+\vec{S}) = L^2 + S^2 + 2\vec{L}\cdot\vec{S} \tag{201}$$

$$\rightarrow\ \vec{L}\cdot\vec{S} = \frac{1}{2}(J^2 - L^2 - S^2) \tag{202}$$

with eigenvalues (where $s = \frac{1}{2}$ in our case):

$$\frac{\hbar^2}{2}[j(j+1) - \ell(\ell+1) - s(s+1)] \tag{203}$$

Spin-orbit interaction IV

For $H^{\rm so}$ we also need $\left\langle \frac{1}{r^3} \right\rangle$:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)n^3a^3} \tag{204}$$

Thus the energy of SO interaction is

$$E^{\rm so} = \langle H^{\rm so}\rangle = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2}\frac{(\hbar^2/2[j(j+1)-\ell(\ell+1)-\frac{3}{4}]}{\ell(\ell+\frac{1}{2})(\ell+1)n^3a^3} \tag{205}$$

$$= \frac{E_n^2}{mc^2}\frac{n[j(j+1)-\ell(\ell+1)-\frac{3}{4}]}{\ell(\ell+\frac{1}{2})(\ell+1)} \sim \frac{E_n^2}{mc^2} \tag{206}$$

Spin-orbit interaction V

However, only half of the truth, need correction for relativistic motion of electron, at least for larger Z, which is

$$E^{\mathrm{r}} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{\ell+\frac{1}{2}} - 3\right] \tag{207}$$

So in total we have $E_n + E^{\mathrm{so}} + E^{\mathrm{r}}$:

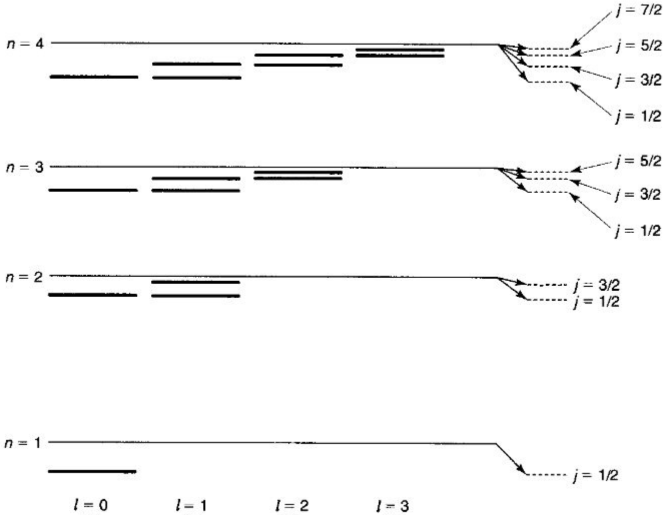
Fine-structure energy levels of hydrogen

$$E_{nj} = -\frac{13.6\,\mathrm{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right] \tag{208}$$

→ breaks degeneracy in ℓ (different eigenvalues of H for same n)
→ m_ℓ and m_s are not longer “good” quantum numbers (stationary states now linear combinations of states with different m_ℓ, m_s)

Spin-orbit interaction VI

→ n, ℓ, s, j, m_j "good" quantum numbers (write $|j\,m_j\rangle$ as linear combination of $|\ell\,m_\ell\rangle|s\,m_s\rangle$ with help of Clebsch-Gordan coefficents)



Fine structure splitting of hydrogen

LS coupling I

For light elements $Z < 10$, total angular momentum $\vec{J} = \vec{L} + \vec{S}$, where $\vec{L} = \sum \vec{\ell}$ and $\vec{S} = \sum \vec{s}$ of single electrons

Example: *LS*-coupling of np^4 electrons

- equivalent p electrons: must differ in either m_ℓ or m_s → for 2p: 3 m_ℓ states $\times$ 2 m_s states $=$ 6 different states, each electron in one of these states (Paul exclusion principle)
- 4 electrons in 6 states: $\begin{pmatrix} 6 \\ 4 \end{pmatrix}$ combinations $= \frac{6!}{(6-4)!4!} = 15$ configurations (see below)
- However: degeneracy, only L and S are "good" quantum numbers
- Spins can couple to either $S = 0$ (e.g. ↑↓,↑,↓) or $S = 1$ (e.g. ↑↓,↑,↑)
- Four electrons with $\ell = 1$ → angular momenta can couple to $L = 0, 1, 2$ (at maximum two electrons in $m_\ell = +1$)

LS coupling II

- therefore:
  $\rightarrow$ possible states ^{2S+1}L:
  $$^1S,\ ^1P,\ ^1D,\ ^3S,\ ^3P,\ ^3D$$
  However, some states forbidden, because of Pauli exclusion principle (complicated to find out, which one),
  so rule for equivalent electrons (same *n and* ℓ):
  $$L + S \text{ must be even}$$
  $\rightarrow$ only ^1S, ^3P, ^1D allowed (see below)

LS coupling III

LS coupling for np^4 electrons

$m_\ell = -1$	$m_\ell = 0$	$m_\ell = +1$	M_L	M_S	Total/Term
↑↓		↑↓	0	0	$^1S_0$
↑↓	↓	↓	-1	-1	$^3P_{0,1,2}$
↑↓	↑	↓	-1	0	
↑↓	↑	↑	-1	1	
↓	↑↓	↓	0	-1	
↑	↑↓	↓	0	0	
↑	↑↓	↑	0	1	
↓	↓	↑↓	1	-1	
↑	↓	↑↓	1	0	
↑	↑	↑↓	1	1	
↑↓	↑↓		-2	0	$^1D_2$
↑↓	↓	↑	-1	0	
↓	↑↓	↑	0	0	
↓	↑	↑↓	1	0	
	↑↓	↑↓	2	0	

jj-coupling I

For heavy atoms ($Z > 10$, e.g. Pb $Z = 82$)
→ spin-orbit interactions ≈ spin-spin interactions
→ for each electron individual combination of $\vec{\ell}$ and $\vec{s}$ to individual $\vec{j}$:

$$\vec{J} = \sum \vec{j} = \sum (\vec{\ell} + \vec{s}) \tag{209}$$

→ resulting angular momentum (S,P,...) of electrons not longer useful

But: pure *jj* coupling only in heaviest atoms

Zeeman effect

Summary: Spin and orbit I

Hydrogen

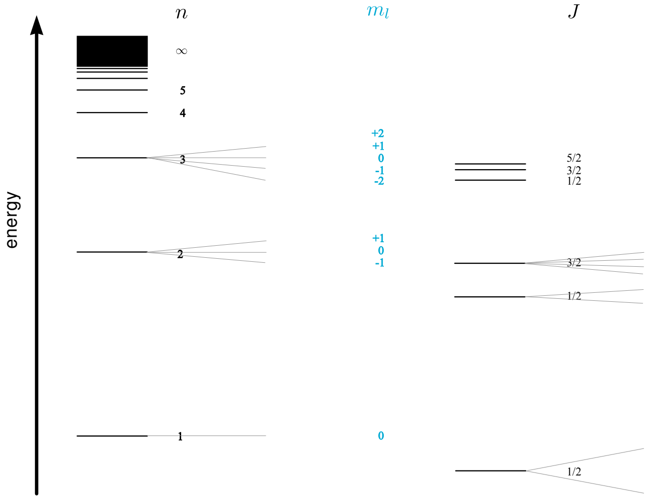
- Bohr formula from Schrödinger Eq. → degeneracy of solutions $\phi_{n\ell m_\ell}$, i.e. same eigenvalue E for different ℓ and m_ℓ

$$E_n = -\frac{13.6\,\mathrm{eV}}{n^2} \tag{210}$$

- take spin-orbit interaction (and relativistic corrections) into account: interaction of internal magnetic field caused by electron orbit with electron spin → fine structure splitting, breaks E degeneracy

$$E_{nj} = -\frac{13.6\,\mathrm{eV}}{n^2}\left[1+\frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)\right] \tag{211}$$

Summary: Spin and orbit II



Bohr: solution of
Schrödinger Eq.
w/o spin

fine structure
spin-orbit interaction
+ relativistic correction

Zeeman effect in QM I

An atom in an external magnetic field $\vec{B}_{\text{ex}}$ adds interaction term to hamiltonian, i.e. energy shift:

$$\begin{aligned} H_{\text{Z}} &= -\left(\vec{\mu}_\ell + \vec{\mu}_s\right) \cdot \vec{B}_{\text{ext}} \qquad (212) \\ &= -\left(-\frac{e}{2m}\vec{L} - \frac{e}{m}\vec{S}\right) \cdot \vec{B}_{\text{ext}} = \frac{e}{2m}(\vec{L} + 2\vec{S}) \cdot \vec{B}_{\text{ext}} \qquad (213) \end{aligned}$$

For $B_{\text{ext}} \ll B_{\text{SO}}$: fine structure dominates → H_{Z} treated as small perturbation

For $B_{\text{ext}} \gg B_{\text{SO}}$: H_{Z} dominates → H_{SO} treated as small perturbation

For $B_{\text{ext}} \approx B_{\text{SO}}$: degenerate perturbation theory

Zeeman effect in QM II

Estimation of internal magnetic field B_{SO}:

$$\vec{B} = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2 r^3}\vec{L} \tag{214}$$

$$\text{e.g. for } L = \hbar,\ r = a \tag{215}$$

$$B = \frac{1.60\times10^{-19}\,\mathrm{C}\cdot1.05\times10^{-34}\,\mathrm{J\,s}}{4\pi\,8.9\times10^{-12}\,\mathrm{C}^2/\mathrm{N\,m}^2\,9.1\times10^{-31}\,\mathrm{kg}\,(3.0\times10^8\,\mathrm{m/s})^2\,(0.53\times10^{-10}\,\mathrm{m})^3} \tag{216}$$

$$= 12.3\,\mathrm{J\,s\,C}^{-1}\,\mathrm{m}^2 = 12.3\,\mathrm{T} \tag{217}$$

→ magnetic field $B_{\mathrm{ext}} \gg 10\,\mathrm{T}$ is "strong" Zeeman field
→ magnetic field $B_{\mathrm{ext}} \ll 10\,\mathrm{T}$ is "weak" Zeeman field

e.g. magnetic field of the Earth $\approx 1\,\mathrm{G} = 10^{-4}\,\mathrm{T}$ is "weak" Zeeman field

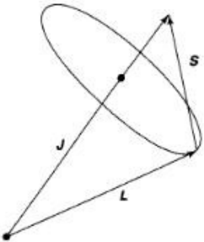
Zeeman effect in QM III

Weak-field Zeeman effect

- for $B_{\text{ext}} \ll B_{\text{int}} \rightarrow$ fine structure dominates
- good quantum numbers: n, ℓ, j, m_j (but not m_ℓ and m_s as $\vec{L}$ and $\vec{S}$ are not separately conserved in spin-orbit coupling)
- from 1st order perturbation theory:

$$E_{\text{Z}} = \langle n\ell j m_j | H_{\text{Z}} | n\ell j m_j \rangle = \frac{e}{2m} \vec{B}_{\text{ext}} \cdot \langle \vec{L} + 2\vec{S} \rangle \tag{218}$$

- as $\vec{J} = \vec{L} + \vec{S} \rightarrow \vec{L} + 2\vec{S} = \vec{J} + \vec{S}$, with constant $\vec{J} = \vec{L} + \vec{S}$



so *time average* of $\vec{S}$ is its projection along $\vec{J}$:

$$\bar{S} = \frac{(\vec{S} \cdot \vec{J})}{J^2} \vec{J} \tag{219}$$

Zeeman effect in QM IV

and $\vec{L} = \vec{J} - \vec{S} \rightarrow L^2 = J^2 + S^2 - 2\vec{J}\cdot\vec{S}$ and therefore

$$\vec{S}\cdot\vec{J} = \frac{1}{2}(J^2 + S^2 - L^2) = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - \ell(\ell+1)] \quad (220)$$

which implies

$$\langle\vec{L} + 2\vec{S}\rangle = \left\langle \left(1 + \frac{\vec{S}\cdot\vec{J}}{J^2}\right)\vec{J}\right\rangle \quad (221)$$

$$= \left[1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)}\right]\langle\vec{J}\rangle = g_J\,\langle\vec{J}\rangle \quad (222)$$

with the *Landé g-factor* g_J. Note: For single-electron system, if only "orbit magnetism" ($S = 0$) $\rightarrow g_J = 1$, if only "spin magnetism" ($\ell = 0$) $\rightarrow g_J \approx 2$

Zeeman effect in QM V

With z-axis aligned with $\vec{B}_{\text{ext}}$:

$$E_\text{Z} = \mu_\text{B} g_J B_\text{ext} m_j \tag{223}$$

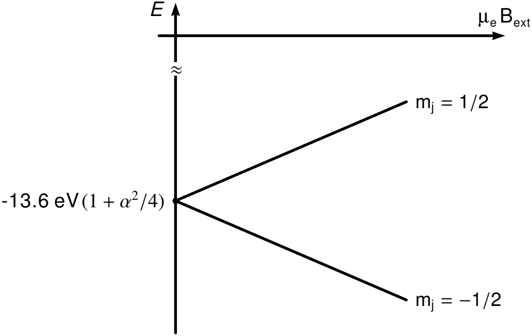
and the *Bohr magneton*

$$\mu_\text{B} = \frac{e\hbar}{2m} = 5.788 \times 10^{-5}\,\text{eV}\,\text{T}^{-1} \tag{224}$$

$\rightarrow$ total energy is $E_{nj} + E_\text{Z}$, e.g. ground state of hydrogen ($n = 1$, $\ell = 0$, $j = \frac{1}{2} \rightarrow g_J = 2$) splits into 2 levels:

$$E = -13.6\,\text{eV}\left(1 + \frac{\alpha^2}{4}\right) \pm \mu_\text{B} B_\text{ext} \tag{225}$$

Zeeman effect in QM VI



Weak-field splitting of the hydrogen ground state, slope $dE/d(\mu_B B_{ext}) = \pm 1$

Zeeman effect in QM VII

Strong-field Zeeman effect (Paschen-Back effect)

- for $B_\text{ext} \gg B_\text{int}$ → Zeeman effect dominates
- let $\vec{B}_\text{ext} = \vec{e}_z B_\text{ext}$
- good quantum numbers: n, ℓ, m_ℓ, m_s – but not j, m_j, as total angular momentum $\vec{J}$ not conserved for external torque (but L_z and S_z are conserved)
- Zeeman Hamiltonian:

$$H_\text{Z} = \frac{e}{2m} B_\text{ext}(L_z + 2S_z) \tag{226}$$

- so "unperturbed" energies:

$$E_{nm_\ell m_s} = -\frac{13.6\,\text{eV}}{n^2} + \mu_B B_\text{ext}(m_\ell + 2m_s) \tag{227}$$

Zeeman effect in QM VIII

- from 1st order perturbation theory: fine-structure correction

$$E_{\mathrm{fs}} = \langle n\ell m_\ell m_s | (H_{\mathrm{rel.}} + H_{\mathrm{SO}}) | n\ell m_\ell m_s \rangle \tag{228}$$

where $E_{\mathrm{rel.}}$ is same as before, i.e. $E_{\mathrm{rel.}} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{\ell+1/2} - 3\right]$
for SO-interaction we need

$$\langle \vec{S} \cdot \vec{L} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle = \hbar^2 m_\ell m_s \tag{229}$$

(because $\langle S_x \rangle = \langle S_y \rangle = \langle L_x \rangle = \langle L_y \rangle = 0$ for eigenstates of S_z and L_z)
therefore

$$E_{\mathrm{fs}} = \frac{13.6\,\mathrm{eV}}{n^3}\alpha^2 \left(\frac{3}{4n} - \left[\frac{\ell(\ell+1) - m_\ell m_s}{\ell(\ell+1/2)(\ell+1)} \right] \right) \tag{230}$$

and total energy is $E_{\mathrm{fs}} + E_{n m_\ell m_s}$
Note: square bracketed term in Eq. 230 indeterminate for $\ell = 0$,

Zeeman effect in QM IX

but then $j = s$, $m_j = m_s$, so

$$E_Z = \frac{e}{2m}\vec{B}_\text{ext} \cdot \langle \vec{L} + 2\vec{S} \rangle = \frac{e}{2m} B_\text{ext} 2 m_s \hbar = 2 m_s \mu_\text{B} B_\text{ext} \tag{231}$$

and fine-structure energies (includingn relativistic correction)

$$E_{nj} = -\frac{13.6\,\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(n - \frac{3}{4}\right)\right] \tag{232}$$

as $j = 1/2$, so total energy

$$E = -\frac{13.6\,\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(n - \frac{3}{4}\right)\right] + 2 m_s \mu_\text{B} B_\text{ext} \tag{233}$$

and fine-structure is α^2 term:

$$E_\text{fs} = -\frac{13.6\,\text{eV}}{n^4}\alpha^2\left(n - \frac{3}{4}\right) = \frac{13.6\,\text{eV}}{n^3}\alpha^2\left(\frac{3}{4n} - 1\right) \tag{234}$$

→ square bracketed term is 1 for $\ell = 0$

Zeeman effect in QM X

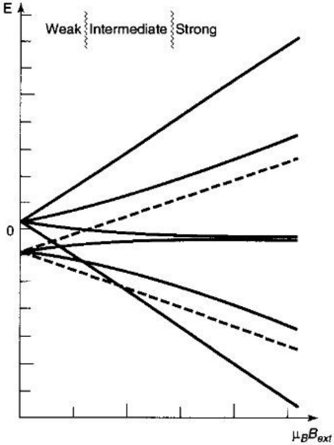
Intermediate-field Zeeman effect

- as neither H_Z nor H_fs dominates, both are equal perturbations to Bohr Hamiltonian $H' = H_\mathrm{fs} + H_\mathrm{Z}$
- consider case $n = 2 \rightarrow \ell = 0, 1$, express basis $|jm_j\rangle$ (makes matrix elements of H_fs easier) by linear combination of $|\ell m_\ell\rangle|sm_s\rangle$

Zeeman effect in QM XI

- …eigenvalues are with $\gamma \equiv 13.6\,\mathrm{eV}(\alpha/8)^2$ and $\beta \equiv \mu_\mathrm{B} B_\mathrm{ext}$ for $n = 2$:

$$\epsilon_1 = E_2 - 5\gamma + \beta$$
$$\epsilon_2 = E_2 - 5\gamma - \beta$$
$$\epsilon_3 = E_2 - \gamma + 2\beta$$
$$\epsilon_4 = E_2 - \gamma - 2\beta$$
$$\epsilon_5 = E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$$
$$\epsilon_6 = E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$$
$$\epsilon_7 = E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$$
$$\epsilon_8 = E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4}$$

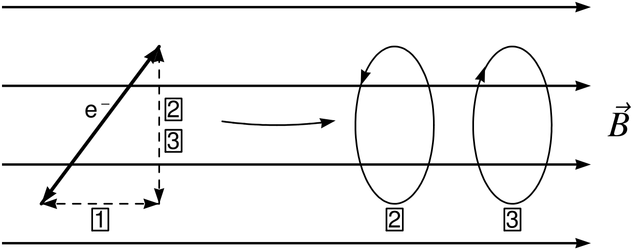


for $\beta = 0$ (zero-field limit) → fine-structure energies
for $\beta \ll \gamma$ (weak-field) → as in weak-field treatment
for $\beta \gg \gamma$ (strong-field) → as in strong-field case

Classical description of Zeeman effect I

Normal Zeeman effect

- classical description (w/o QM) by Lorentz:



emission by bound electron (circular orbit) → projection into one direction → linear oscillator, split into $\boxed{1}$ and $\boxed{2}$ + $\boxed{3}$
no force on $\boxed{1} \to \delta\omega = 0$, linearly polarized light

Classical description of Zeeman effect II

- consider only *orbital* angular momentum of electron $\vec{\ell}$
  → magnetic moment $\vec{\mu} = \frac{e}{2m}\vec{\ell} = \gamma\vec{\ell}$:

$$E_\mathrm{Z} = -(\vec{\mu}\cdot\vec{B}_\mathrm{ext}) = -\mu_z B_\mathrm{ext} = -\gamma\ell_z B_\mathrm{ext} \tag{235}$$

→ "Larmor precession" (but with $g = 1$, because of orbit instead of spin) around z-axis with constant ℓ_z and frequency

$$\omega_\mathrm{L} = \gamma B = \frac{e}{2m}B \tag{236}$$

→ perturbation of electron orbit (with Bohr frequency ω_0), especially component perpendicular to $\vec{B}$
without external magnetic field → frequency ω_0 for $\boxed{2}$, $\boxed{3}$

$$m\omega_0^2\vec{r} = \frac{Ze^2}{4\pi\epsilon_0 r^3}\vec{r} \tag{237}$$

Classical description of Zeeman effect III

now *with* additional external field → Lorentz force, e.g. in cartesian coordinates

$$m\ddot{x} + m\omega_0^2 x - e\dot{y}\vec{B}_0 = 0 \tag{238}$$

$$m\ddot{y} + m\omega_0^2 y - e\dot{x}\vec{B}_0 = 0 \tag{239}$$

$$m\ddot{x} + m\omega_0^2 z = 0 \tag{240}$$

→ equations of motion for electron
with $u = x + \imath y$ and $v = x - \imath y$:

$$u = u_0 \exp[\imath(\omega_0 - \frac{e}{2m}B)t] \tag{241}$$

$$v = v_0 \exp[\imath(\omega_0 + \frac{e}{2m}B)t] \tag{242}$$

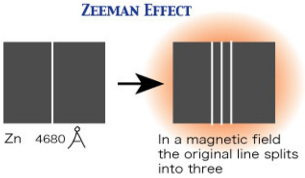
→ left- and right-circular oscillation with $\omega_0 \pm \frac{e}{2m}B$
→ emission / absorption of circular polarized light of frequency $\omega_0 \pm \frac{e}{2m}B$ (Lorentz, Nobel prize 1902)

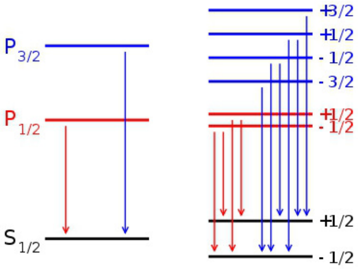
Classical description of Zeeman effect IV

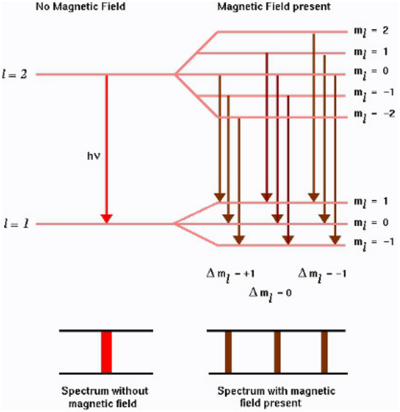
- frequency shift $\delta\omega = \frac{e}{2m}B$ of spectral lines does not depend on frequency ω_0
- circular polarization along $\vec{B}$, linear polarization perpendicular to $\vec{B}$ $\rightarrow \sigma^+$ (right-handed circularly pol.*, $+\delta\omega$) and σ^- (left-handed circularly pol.*, $-\delta\omega$) radiation
  *relative to $\vec{B}$
- no emission of unshifted line π *along* $\vec{B}$

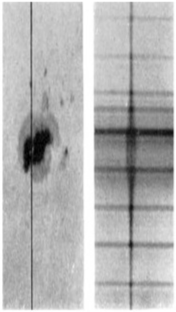
→ only triple splitting of lines explained

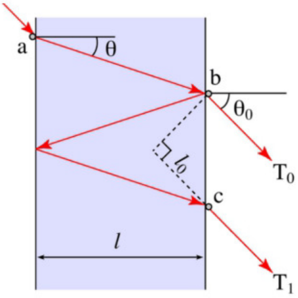
S6 Zeeman Effect











Application of Zeeman effect I

Astrophysics

- consider only weak fields where g_J is good quantum number
- interaction energy (we already know), aligned with z-axis:

$$V = \vec{\mu} \cdot \vec{B} \quad \rightarrow \quad V = -\mu_z B = m_J g_J \mu_B B \tag{243}$$

$$m_J = -J, -J+1, \ldots, J \quad \text{and} \quad \mu_B = \frac{e\hbar}{2m_e} \tag{244}$$

- compare two Zeeman components with $\Delta m_J = \pm 1$ and λ_1, λ_2:

$$\Delta E = g_J \mu_B B \quad \rightarrow \quad B = \frac{4\pi mc}{eg_J}(\lambda_2^{-1} - \lambda_1^{-1}) \tag{245}$$

$$\rightarrow B \approx \frac{4\pi mc}{eg_J}\frac{\Delta\lambda}{\lambda_1^2} \tag{246}$$

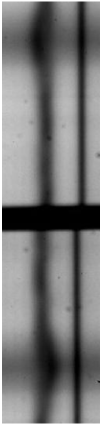
Application of Zeeman effect II

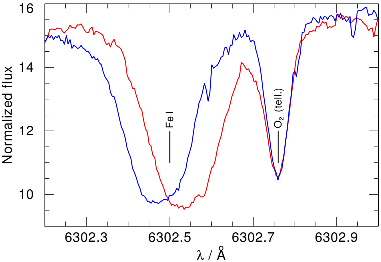
- e.g. for *single* electron above filled shell (e.g. H, Li, ...), $s = 1/2 \rightarrow\ g_s = g_S = 2$ and $j = \ell \pm s$:

$$g_J = g_j = 1 \pm \frac{g_S - 1}{2\ell + 1} \tag{247}$$

Application of Zeeman effect III

Magnetic field of a sunspot





Spectrum of a sun spot: right-hand circularly polarized (σ^+, blue) and left-hand circularly polarized (σ^-, red) light of a Fe I line ($g_J = 5/2$)

$$B \approx 0.02141 \cdot \frac{\Delta\lambda}{g_J \lambda_0^2}\,\mathrm{T\,\AA} \approx 0.2\,\mathrm{T} \tag{248}$$

Application of Zeeman effect IV

Weak stellar magnetic fields

- line splitting (π and σ components) approximately:

$$\Delta\lambda_B = g_J \frac{eB\lambda^2}{4\pi mc^2} \tag{249}$$

  assume that Zeeman line splitting $\Delta\lambda_B \ll \Delta\lambda_{\text{Doppler, Stark}}$
  $\rightarrow$ individual line shifts in subpixel regime

- measure so-called stokes parameter I, V:

$$I = P_{0^\circ} + P_{90^\circ} = \langle E_x^2 + E_y^2 \rangle \quad \rightarrow \quad \text{unpolarized} \tag{250}$$

$$V = P_{\text{rc}} - P_{\text{lc}} \tag{251}$$

$$\frac{V}{I} = \frac{1}{2}\left[\left(\frac{f^{\text{o}} - f^{\text{e}}}{f^{\text{o}} + f^{\text{e}}}\right)_{\alpha=-45^\circ} - \left(\frac{f^{\text{o}} - f^{\text{e}}}{f^{\text{o}} + f^{\text{e}}}\right)_{\alpha=+45^\circ}\right] \tag{252}$$

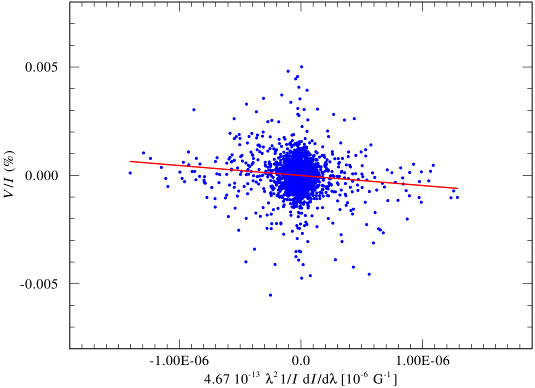
  where f is flux measured from ordinary and extraordinary beam, α is angle of polarisator

Application of Zeeman effect V

- in weak field regime (Landstreet 1982), ensemble of spectral lines:

$$\frac{V}{I} = -\frac{g_{\mathrm{eff}} e \lambda^2}{4\pi m c^2} \frac{1}{I} \frac{dI}{d\lambda} \langle B_z \rangle \tag{253}$$

- e.g. FORS2 of NGC 1514 → slope gives magnetic field of $-250\,$G



Selection rules for radiative line transitions

Selection rule for multiplicity

From helium atom we already learnt a *selection rule*:

- considering time evolution of the position-space wave function, then
- transitions between different multiplicities are forbidden:

$$\Delta S = 0 \tag{254}$$

→ radiative line transitions only within singlet *or* triplet states

- small modification of the this rule are possible (why?)

Fermi's Golden Rule

So far, only stationary states ("pure" Hamiltonian H_0). How to consider transitions?

→ perturbation theory ($H = H_0 + H'$), especially:

→ Fermi's Golden Rule:

- gives transition rate $T_{i \to f}$ from one energy eigenstate $|i\rangle$ into another energy eigenstate $|f\rangle$, due to a perturbation H' (perturbing Hamiltonian)

Fermi's Golden Rule

$$T_{i \to f} = \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 \varrho(E_f) \tag{255}$$

where $\varrho(E_f)$ is the *space density* of the final states

- $\langle f|H'|i\rangle$ is called matrix element (in bra–ket notation) of the perturbation H'

Interaction of a two-level atom with coherent light I

Let us consider the time-dependent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\Delta + V + V_\mathrm{S}\right)\psi(\vec{r},t) = \imath\hbar\frac{d\psi(\vec{r},t)}{dt} \tag{256}$$

with potential of the nucleus, V; V_S corresponds to potential of "light field" with electric field (plane wave)

$$\vec{F} = \vec{F}_0\cos(kx - \omega t) \tag{257}$$

Atom is placed at $\vec{r} = 0$, consider only light with $2\pi/k = \lambda \gg d_\mathrm{atom}$, so $x = 0$ in Eq. (257), i.e. spatially constant light field

$$\vec{F} = \vec{F}_0\cos(\omega t) \tag{258}$$

with polarization in z-direction: $\vec{F}_0 = (0, 0, F_0)$

Interaction of a two-level atom with coherent light II

Then, force of electric field $\vec{F}$ on electron: $-e\vec{F}$, therefore (why?)

$$V_\mathrm{S} = eF_0 z \cos\omega t \tag{259}$$

Assumption: already solved unperturbed Schrödinger eq. ($V_\mathrm{S} = 0$), found φ_i, φ_j with energies E_i, E_j.
Now: wave function ψ of perturbed system as superposition of φ_i, φ_j
Hence matrix element for coherent light:

$$H_{ij}^\mathrm{S} = \int \varphi_i^*(\vec{r})\, eF_0 z\, \varphi_j(\vec{r}) dV \cos\omega t \tag{260}$$

Hamiltonian of EM field I

Hamiltonian for electromagnetic field with generalized momentum

$$H = \frac{(\vec{p} - e\vec{A})^2}{2m} + e\Phi(\vec{r}) \qquad \approx \frac{\vec{p}^{\,2}}{2m} - \frac{e}{m}\vec{A}\cdot\vec{p} + e\Phi(\vec{r}) \tag{261}$$

with not too strong vector potential $\vec{A}$ and electrostatic potential Φ, i.e. time-dependent perturbation $\frac{e}{m}\vec{A}(\vec{r},t)\cdot\vec{p}$

- irradiated light as plane wave with polarization vector $\vec{\epsilon}$:

$$\vec{A}(\vec{r},t) \sim \vec{\epsilon}\cos(\vec{k}\cdot\vec{r} - \omega t) \sim \vec{\epsilon} e^{\imath\vec{k}\cdot\vec{r}} \tag{262}$$

- hence the perturbation term

$$e\vec{p}\cdot\vec{A} \sim e\vec{p}\cdot\vec{\epsilon} e^{\imath\vec{k}\cdot\vec{r}} \tag{263}$$

  and the matrix element

$$e\int \varphi_n^*(\vec{r})\vec{p}\cdot\vec{\epsilon} e^{\imath\vec{k}\cdot\vec{r}}\varphi_m(\vec{r})dV \tag{264}$$

Hamiltonian of EM field II

- approximation for large λ, i.e. $\vec{k} \cdot \vec{r} = 2\pi r/\lambda \ll 1$ compared to extent r of φ, series expansion of e:

$$e^{\imath \vec{k} \cdot \vec{r}} \approx 1 + \imath \vec{k} \cdot \vec{r} + \ldots \approx 1 \tag{265}$$

- matrix element, lowest order

$$\int \varphi_n^*(\vec{r}) e \vec{p} \cdot \vec{\epsilon} \varphi_m(\vec{r}) dV \tag{266}$$

- because of $\frac{\hbar}{\imath} \frac{\vec{p}}{m} = [H, \vec{r}]$, matrix element (266) is (proof!)

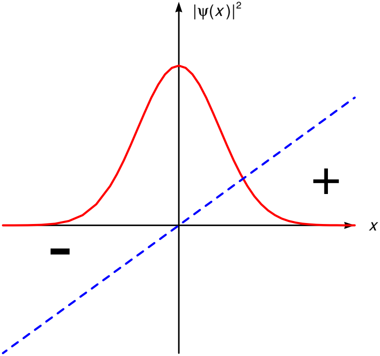
$$-\vec{\epsilon} \imath m \frac{E_n - E_m}{\hbar} \int \varphi_n^*(\vec{r}) e \vec{r} \varphi_m(\vec{r}) dV \tag{267}$$

→ contains term $e\vec{r}$ → electric dipole moment

Matrix elements by symmetry considerations I

In one dimension, e.g. for $\vec{\epsilon} \parallel x$-axis matrix element $I = \langle\psi|x|\psi\rangle$

$$\begin{aligned} I &= \int_{-\infty}^{+\infty} \psi^*(x)\, x\, \psi(x) dx \quad |x \to -x \\ &= \int_{+\infty}^{-\infty} \psi^*(-x)\,(-x)\psi(-x) d(-x) \\ &= \int_{-\infty}^{+\infty} \psi^*(-x)\,(-x)\psi(-x) d(x) \end{aligned}$$



because symmetry of wavefunction $\psi(-x) = \pm\psi(x)$, $\to \psi^*\psi$ invariant under P transformation, so without detailed calculation:

$$\Rightarrow \quad I = -I \quad \Rightarrow I = 0 \tag{268}$$

Selection rule for the magnetic quantum number I

Electric dipole matrix element between two *different* hydrogen wave functions

$$I_z = \int \psi^*_{n',\ell',m'}(\vec{r})\, z\, \psi_{n,\ell,m}(\vec{r}) dV \tag{269}$$

$$= \int dV \psi^*_{n',\ell',m'}(r,\theta,\phi)\, r\cos\theta\, \psi_{n,\ell,m}(r,\theta,\phi) \tag{270}$$

because of $\psi(r,\phi) = e^{\imath m\phi}\psi(r,0)$ (with integer m), for rotations ϕ_0 around z-axis:

$$I_z = e^{-\imath(m-m')\phi_0} I_z \tag{271}$$

Therefore: either $I_z = 0$, or, if $I_z \neq 0 \rightarrow m = m'$

Selection rule for the magnetic quantum number II

Now for x- and y-component:

$$I_x = \int dV \, \psi^*_{n',\ell',m'}(r,\theta,\phi) \, x \, \psi_{n,\ell,m}(r,\theta,\phi) \tag{272}$$

$$I_y = \int dV \, \psi^*_{n',\ell',m'}(r,\theta,\phi) \, y \, \psi_{n,\ell,m}(r,\theta,\phi) \tag{273}$$

multiply I_y with $\imath \rightarrow x + \imath y = r \sin\theta \cos\phi + r \sin\theta \, \imath \sin\phi$

$$I_x + \imath I_y = \int dV \, \psi^*_{n,\ell,m}(r,\theta,\phi) \, r \sin\theta e^{\imath\phi} \, \psi_{n',\ell',m'}(r,\theta,\phi) \tag{274}$$

again, rotation around z-axis by angle ϕ_0

$$I_x + \imath I_y = e^{-\imath(m-1-m')\phi_0}(I_x + \imath I_y) \tag{275}$$

Selection rule for the magnetic quantum number III

Therefore:

$$I_x + \imath I_y = 0 \quad \text{if} \quad m \neq m' + 1 \tag{276}$$

$$I_x - \imath I_y = 0 \quad \text{if} \quad m \neq m' - 1 \tag{277}$$

Or summarized: if $m \neq m' + 1$ and $m \neq m' - 1$ then

$$I_x = 0, \quad I_y = 0 \tag{278}$$

Selection rules for magnetic quantum number of one-electron systems

For light polarized in z-direction:

$$\Delta m = 0 \tag{279}$$

For light polarized in x- or y-direction:

$$\Delta m = \pm 1 \tag{280}$$

→ corresponds to π (linearly pol.) and σ (circularly pol.) transitions

General selection rules I

In general, use *spherical components* of dipole moment (for one e$^-$)

$$r^{(\pm)} = \frac{1}{\sqrt{2}}(x \pm \imath y)\,, \quad r^{(0)} = z \tag{281}$$

hence the product of $\vec{r}$ and polarization vector $\vec{\epsilon}$

$$\vec{r} \cdot \vec{\epsilon} = r^{(+)}\epsilon^{(-)} + r^{(-)}\epsilon^{(+)} + r^{(0)}\epsilon^{(0)} = \sum_{\nu=-1}^{1} r^{\nu}\epsilon^{(-\nu)} \tag{282}$$

trick → write spherical components of $\vec{r}$ with help of spherical harmonics and $r = \sqrt{x^2 + y^2 + z^2}$ (why?):

$$r^{(\pm)} = \sqrt{\frac{4\pi}{3}} r Y_{1,\pm 1}(\theta, \phi)\,, \quad r^{(0)} = \sqrt{\frac{4\pi}{3}} r Y_{1,0}(\theta) \quad \text{with} \tag{283}$$

$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm \imath \phi}\,, \quad Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta \tag{284}$$

General selection rules II

For one-electron wave function (w/o spin)

$$\psi_i(\vec{r}) = \frac{\varphi_\ell}{r} Y_{\ell,m}(\theta,\phi)\,, \quad \psi_f(\vec{r}) = \frac{\varphi_{\ell'}}{r} Y_{\ell',m'}(\theta,\phi) \tag{285}$$

matrix elements of spherical components $r_{fi}^{(\nu)}$ can be written as integral over three spherical harmonics, which be reduced to an integral over radial wavefunctions with help of Wigner-Eckart theorem:

$$r_{fi}^{(\nu)} = \int_0^\infty \varphi_{\ell'}^* \, r \, \varphi_\ell(r) dr \sqrt{\frac{4\pi}{3}} \int d\Omega \, Y_{\ell',m'}^* \, Y_{1,\nu} \, Y_{\ell,m} \tag{286}$$

$$= \int_0^\infty \varphi_{\ell'}^* \, r \, \varphi_\ell(r) dr \, F(\ell',\ell) \langle \ell', m' | 1, \nu, \ell, m \rangle \tag{287}$$

with Clebsch-Gordan coefficient (CG) $\langle \ell', m' | 1, \nu, \ell, m \rangle$ for coupling of initial angular momentum ℓ, m with angular momentum $1, \nu$ of spherical component of $\vec{r}$ to the final state ℓ', m'

General selection rules III

quantum numbers ℓ', 1, ℓ must satisfy triangular condition for CG coefficients (selection rule for CG coefficients):

$$|\ell - 1| \leq \ell' \leq \ell + 1 \tag{288}$$

→ implies $\Delta\ell \leq 1$, moreover from parity of spherical harmonics

$$P Y_{\ell,m}(\theta, \phi) = (-1)^{\ell} Y_{\ell,m}(\theta, \phi) \tag{289}$$

follows that $\ell + 1 + \ell'$ must be even, otherwise *parity* of integrand $Y^*_{\ell',m'} Y_{1,\nu} Y_{\ell,m}$ would be negative → integral $\int d\Omega$ would vanish

another selection rule for CG coefficients states that

$$m + \nu = m' \tag{290}$$

General selection rules IV

Selection rules for angular momentum of one-electron systems

$$\Delta\ell = \ell_f - \ell_i = \pm 1\,, \quad \Delta m = m_f - m_i = 0, \pm 1 \tag{291}$$

transitions $\psi_i \rightarrow \psi_i$ which do not satisfy (291) are *forbidden* (in dipole approximation)

Addition: factor $F(\ell', \ell)$ is in this case

$$F(\ell', \ell) = \begin{cases} \sqrt{\ell'/(2\ell'+1)} & \text{if } \ell' = \ell + 1, \\ -\sqrt{\ell/(2\ell'+1)} & \text{if } \ell' = \ell - 1 \end{cases} \tag{292}$$

One-electron wave functions with spin:

$$r_{fi}^{(\nu)} = \langle \Phi_f | r^{(\nu)} | \Phi_i \rangle = \langle j' || \vec{r} || j \rangle \langle j', m' | 1, \nu, j, m \rangle \tag{293}$$

General selection rules V

where m corresponds to eigenvalues of z-component of total angular momentum $\vec{J} = \vec{L} + \vec{S}$
again: used Wigner-Eckart theorem (WE) to get *reduced matrix element* $\langle j' || \vec{r} || j \rangle$ (independent of m and ν) → in general, WE theorem states that for matrix elements of operators in eigenstates of angular momentum operator m and ν dependence is only via CG coefficients of coupling between initial state and component of operator to final state

→ from selection rules for CG coefficients:

Selection rules for total angular momentum of one-electron systems

$$\Delta j = j_f - j_i = 0, \pm 1\,, \quad \Delta m_j = m_j^f - m_j^i = 0, \pm 1 \qquad (294)$$

$$j = 0 \not\leftrightarrow 0\,, \quad m_j = 0 \not\leftrightarrow 0 \text{ if } \Delta j = 0 \qquad (295)$$

→ Interpretation: EM field (photon) carries angular momentum (spin ±1)
→ angular momentum conservation

Selection rules of multi-electron systems I

Multi-electron wave functions with spin: by applying WE theorem:

Selections rules for total angular momentum of multi-electron systems

For quantum numbers J, M_J of total angular momentum $\vec{J} = \vec{L} + \vec{S}$

$$\Delta J = J_f - J_i = 0, \pm 1\,, \quad \Delta M_J = M_J^f - M_J^i = 0, \pm 1 \tag{296}$$

$$J = 0 \not\leftrightarrow 0\,, \quad M_J = 0 \not\leftrightarrow 0 \text{ if } \Delta J = 0 \tag{297}$$

for *LS* coupling: total orbital angular momentum $\vec{L} = \sum \vec{\ell}$ and total spin $\vec{S} = \sum \vec{s}$ are "good" quantum numbers, selections rules for L, M_L

$$\Delta L = L_f - L_i = 0, \pm 1\,, \quad \Delta M_L = M_L^f - M_L^i = 0, \pm 1 \tag{298}$$

$$L = 0 \not\leftrightarrow 0\,, \quad M_L = 0 \not\leftrightarrow 0 \text{ if } \Delta L = 0 \tag{299}$$

Selection rules of multi-electron systems II

Selection rules for spin, as the dipole operator $e\vec{r}$ doesn't act on spins:

Selections rules for total spin of multi-electron systems

$$\Delta S = 0\,, \quad \Delta M_S = 0 \tag{300}$$

holds exact only for weak spin-orbit interaction → LS-coupling of light atoms

→ already derived for helium: no transition between singlet and triplet system

However, for heavy atoms, e.g. with jj-coupling → intercombination possible

Intercombination transition for strong spin-orbit interaction

$$\Delta S = \pm 1\,, \quad \Delta L = 0, \pm 1, \pm 2 \tag{301}$$

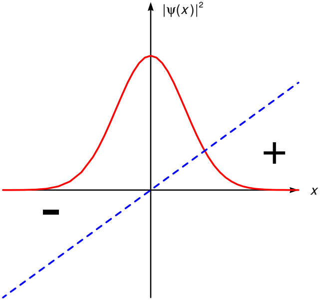
Selection rules of multi-electron systems III

Selection rule for parity → remember example in one dimension,

$$I = \int_{-\infty}^{+\infty} \psi^*(x)\, x\, \psi(x) dx \quad |x \to -x \tag{302}$$

$$= \int_{+\infty}^{-\infty} \psi^*(-x)\,(-x)\psi(-x) d(-x) \tag{303}$$

$$= \int_{-\infty}^{+\infty} \psi^*(-x)\,(-x)\psi(-x) d(x) \tag{304}$$



we used symmetry of wavefunction $\psi(-x) = \pm\psi(x)$, especially equal parity of ψ^* and ψ to show that $\psi^*\psi$ invariant under P transformation and therefore ⇒ $I = -I$ $\Rightarrow I = 0$

Selection rules of multi-electron systems IV

Selection rule for parity of electric dipole transitions

$$P_i\,P_f = -1 \quad \rightarrow \quad \text{change of parity} \tag{305}$$

Selection rules of multi-electron systems V

However, transitions which are forbidden for electric dipole operator (E1) may be allowed by electric 2^k pole operator (e.g. E2 electric quadrupole) or Mk magnetic 2^k pole operator (e.g. M1 magnetic dipole, M3 magnetic octupole)

Selection rule for E2, E4, ... and M1, M3, ... radiation

$$P_i\,P_f = 1 \quad \rightarrow \quad \text{same parity of intial and final state} \tag{306}$$

for even electric and odd magnetic multipole

Selection rule for E1, E3, ... and M2, M4, ... radiation

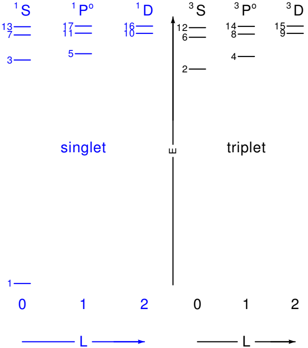
$$P_i\,P_f = -1 \quad \rightarrow \quad \text{change of parity} \tag{307}$$

for odd electric and even magnetic multipole

Collisions

Collisional transitions not restricted by selection rules

States for which the radiative transition to any lower state is forbidden are called *meta stable*.



- e.g. 1st excited state of He I: triplet (configuration?)
- transition to ground state (singlet) forbidden (by which rule?)
- but: level is depopulated by collisions

If collisional deexcitation negligible (low density) → forbidden lines can be observed, e.g. in planetary nebulae, solar corona

Oscillator strengths

Oscillator strengths I

Characterization of electric dipole transitions between Ψ_i and Ψ_f by dimensionless quantity from *Fermi's Golden Rule*

$$f_\mathrm{fi}^{(x)} = \frac{2m}{\hbar^2}\hbar\omega |\langle\Psi_\mathrm{f}| \sum_{j=1}^{N} x_j |\Psi_\mathrm{i}\rangle|^2 \tag{308}$$

in cartesian coordinates for N-electron atom, where $\omega = E_f - E_i$, by summing up over all three components

$$f_\mathrm{fi} = f_\mathrm{fi}^{(x)} + f_\mathrm{fi}^{(y)} + f_\mathrm{fi}^{(z)} = \frac{2m}{\hbar}\omega |\langle\Psi_\mathrm{f}|\vec{r}|\Psi_\mathrm{i}\rangle|^2 \tag{309}$$

$\rightarrow f$ is called oscillator strength of the corresponding electric dipole line transition

Oscillator strengths II

Example: Cross section of line transition

Absorption $\sigma(E)$ of x-polarized photons ($\vec{\epsilon} = \vec{e}_x$) by $\Psi_i \rightarrow \Psi_f$ line transition (of energy E)

$$\sigma = 4\pi^2 \frac{e^2}{\hbar c} \frac{\hbar^2}{2m} f_{\mathrm{fi}}^{(x)} \delta(E_f - E_i - E) \tag{310}$$

Oscillator strengths III

From commutator relation of position and momentum follows *sum rule* for oscillator strengths over all final states n:

$$\sum_n f_{ni}^{(x)} = N \tag{311}$$

By summing up over x, y, z →

Thomas-Reiche-Kuhn sum rule

$$\sum_n f_{ni} = \sum_n \left(f_{ni}^{(x)} + f_{ni}^{(y)} + f_{ni}^{(z)} \right) = 3N \tag{312}$$

→ typical values of allowed transitions $0.1 < f < 1$

→ f values of multi-electron systems may be larger than 1

→ f values of E2, M1, etc. usually $\ll 1$

Oscillator strengths IV

f-values of Lyman lines

Analytic expression (Menzel & Pekeris 1935):

$$g_1 f_{n'1} = \frac{2^9 n'^5 (n'-1)^{2n'-4}}{3(n'+1)^{2n'+4}} \tag{313}$$

What is value of g_1?

For Lyα ($1 \rightarrow 2$): $f = 0.4162$

What is the detailed transition of Lyα (angular momentum)?

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