

Fine Structure Const.

Lecture 12

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$$

Atomic structure

Atomic structure: background

- Our studies of hydrogen-like atoms revealed that the spectrum of the Hamiltonian,

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

is characterized by large n^2 -fold degeneracy.

- However, although the non-relativistic Schrödinger Hamiltonian provides a useful platform, the formulation is a little too naïve.
- The Hamiltonian is subject to several classes of “corrections”, which lead to important physical ramifications (which reach beyond the realm of atomic physics).
- In this lecture, we outline these effects, before moving on to discuss multi-electron atoms in the next.

Atomic structure: hydrogen atom revisited

- As with any centrally symmetric potential, stationary solutions of \hat{H}_0 index by quantum numbers $n\ell m$, $\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)$.
- For atomic hydrogen, n^2 -degenerate energy levels set by

$$E_n = -Ry \frac{1}{n^2}, \quad Ry = \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{2\hbar^2} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a_0}$$

where m is reduced mass (ca. electron mass), and $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m}$.

- For higher single-electron ions (He^+ , Li^{2+} , etc.), $E_n = -Z^2 \frac{Ry}{n^2}$.
- Allowed combinations of quantum numbers:

n	ℓ	Subshell(s)
1	0	1s
2	0, 1	2s 2p
3	0, 1, 2	3s 3p 3d
n	$0 \cdots (n-1)$	$ns \cdots$

Atomic structure: hydrogen atom revisited

- However, treatment of hydrogen atom inherently non-relativistic:

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

is only the leading term in relativistic treatment (**Dirac theory**).

- Such relativistic corrections begin to impact when the electron becomes relativistic, i.e. $v \sim c$.
- Since, for Coulomb potential, $2\langle\text{k.e.}\rangle = -\langle\text{p.e.}\rangle$ (virial theorem), $\frac{1}{2}mv^2 = \langle\text{k.e.}\rangle = -E_{000} = Z^2R_y$. Using identity,

$$Z^2R_y = \frac{1}{2}mc^2(Z\alpha)^2, \quad \alpha = \frac{e^2}{4\pi\epsilon_0} \frac{1}{\hbar c} \simeq \frac{1}{137}$$

where α denotes the **fine structure constant**, we find $\frac{v}{c} = Z\alpha$.

The “real” hydrogen atom: outline

- Terms of higher order in $\frac{v}{c} = Z\alpha$ provide relativistic corrections which lead to lifting of the degeneracy.
- These corrections (known as **fine-structure**) derive from three (superficially) different sources:
 - (a) relativistic corrections to the kinetic energy;
 - (b) coupling between spin and orbital degrees of freedom;
 - (c) and a contribution known as the Darwin term.

(a) Relativistic corrections to kinetic energy

- From the relativistic energy-momentum invariant,

$$E = \sqrt{\mathbf{p}^2 c^2 + m^2 c^4} = mc^2 + \frac{\mathbf{p}^2}{2m} - \frac{1}{8} \frac{(\mathbf{p}^2)^2}{m^3 c^2} + \dots,$$

we can anticipate the leading correction to the non-relativistic Hamiltonian is given by

$$\hat{H}_1 = -\frac{1}{8} \frac{(\hat{\mathbf{p}}^2)^2}{m^3 c^2}$$

- The relative scale of perturbation

$$\frac{\langle \hat{H}_1 \rangle}{\langle \hat{H}_0 \rangle} \simeq \frac{p^2}{m^2 c^2} = \frac{v^2}{c^2} \simeq (Z\alpha)^2$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0} \frac{1}{\hbar c} \simeq \frac{1}{137}$.

i.e. \hat{H}_1 is only a small perturbation for small atomic number, Z .

(a) Relativistic corrections to kinetic energy

$$\hat{H}_1 = -\frac{1}{8} \frac{(\hat{\mathbf{p}}^2)^2}{m^3 c^2}$$

- Since $[\hat{H}_1, \hat{\mathbf{L}}^2] = 0$ and $[\hat{H}_1, \hat{L}_z] = 0$,

$$\langle n\ell m | [\hat{H}_1, \hat{\mathbf{L}}^2] | n\ell' m' \rangle = \hbar^2 [\ell'(\ell' + 1) - \ell(\ell + 1)] \langle n\ell m | \hat{H}_1 | n\ell' m' \rangle = 0$$

$$\langle n\ell m | [\hat{H}_1, \hat{L}_z] | n\ell' m' \rangle = \hbar(m' - m) \langle n\ell m | \hat{H}_1 | n\ell' m' \rangle = 0$$

- Therefore, the off-diagonal matrix elements vanish:

$$\langle n\ell m | \hat{H}_1 | n\ell' m' \rangle = 0 \quad \text{for } \ell \neq \ell' \quad \text{or} \quad m \neq m'$$

and we can estimate energy shift without having to invoke degenerate perturbation theory.

(a) Relativistic corrections to kinetic energy

- Making use of the identity,

$$\hat{H}_1 = -\frac{1}{8} \frac{(\hat{\mathbf{p}}^2)^2}{m^3 c^2} = -\frac{1}{2mc^2} \left[\hat{H}_0 - V(r) \right]^2, \quad V(r) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}$$

scale of resulting energy shift can be obtained from first order perturbation theory,

$$\langle n\ell m | \hat{H}_1 | n\ell m \rangle = -\frac{1}{2mc^2} \left(E_n^2 - 2E_n \langle V(r) \rangle_{n\ell} + \langle V^2(r) \rangle_{n\ell} \right)$$

- Using the identities,

$$\left\langle \frac{1}{r} \right\rangle_{n\ell} = \frac{Z}{a_0 n^2}, \quad \left\langle \frac{1}{r^2} \right\rangle_{n\ell} = \frac{Z^2}{a_0^2 n^3 (\ell + 1/2)}.$$

resulting energy shift acquires angular momentum dependence:

$$\langle \hat{H}_1 \rangle_{n\ell m} = -\frac{mc^2}{2} \left(\frac{Z\alpha}{n} \right)^4 \left(\frac{n}{\ell + 1/2} - \frac{3}{4} \right)$$

(b) Spin-orbit coupling

- Spin degree of freedom of electron emerges naturally from relativistic formulation of quantum mechanics. Alongside the spin, this formulation leads to a further relativistic correction which involves coupling between spin and orbital degrees of freedom.
- For a general potential $V(r)$, this spin-orbit coupling is given by:

$$\hat{H}_2 = \frac{1}{2m^2c^2} \frac{1}{r} (\partial_r V) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

- For a hydrogen-like atom, $V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$ and

$$\hat{H}_2 = \frac{1}{2m^2c^2} \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

(b) Spin-orbit coupling: physical origin

- Physically, as electron moves through electric field of nucleus, $\mathbf{E} = -\nabla V(r) = -\hat{\mathbf{e}}_r(\partial_r V)$, in its rest frame it will experience a magnetic field, $\mathbf{B} = \frac{1}{c^2} \mathbf{v} \times \mathbf{E}$.
- In this field, the spin magnetic moment of the electron, $\boldsymbol{\mu}_s = -\frac{e}{m} \mathbf{S}$, leads to an additional interaction energy,

$$-\boldsymbol{\mu}_s \cdot \mathbf{B} = -\frac{e}{(mc)^2} \mathbf{S} \cdot (\mathbf{p} \times \hat{\mathbf{e}}_r(\partial_r V)) = \frac{e}{(mc)^2} \frac{1}{r} (\partial_r V) \mathbf{L} \cdot \mathbf{S}$$

where we have used the relation $\mathbf{p} \times \hat{\mathbf{e}}_r = -\frac{1}{r} \mathbf{L}$.

- Additional factor of 1/2 derives from further relativistic effect known as **Thomas precession**.
- Those discontent with heuristic derivation need only wait for Dirac formulation...

(b) Spin-orbit coupling

$$\hat{H}_2 = \frac{1}{2m^2c^2} \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

- Without spin-orbit interaction, eigenstates of hydrogen-like atoms can be expressed in basis of mutually commuting operators, \hat{H}_0 , $\hat{\mathbf{L}}^2$, \hat{L}_z , $\hat{\mathbf{S}}^2$, and \hat{S}_z .
- However, with spin-orbit, total Hamiltonian no longer commutes with \hat{L}_z or \hat{S}_z – useful to exploit degeneracy of \hat{H}_0 to switch to new basis in which $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ is diagonal.
- Achieved by turning to basis of eigenstates of the operators, \hat{H}_0 , $\hat{\mathbf{J}}^2$, \hat{J}_z , $\hat{\mathbf{L}}^2$, and $\hat{\mathbf{S}}^2$, where $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. Since $\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, it follows that,

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2) = \frac{1}{2}(j(j+1) - \ell(\ell+1) - s(s+1))$$

(b) Spin-orbit coupling

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2) = \frac{1}{2}(j(j+1) - \ell(\ell+1) - s(s+1))$$

$$\hat{H}_2 = \frac{1}{2m^2c^2} \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$$

- Combining spin 1/2 with angular momentum ℓ , total angular momentum can take values $j = \ell \pm 1/2$. Corresponding basis states $|j = \ell \pm 1/2, m_j, \ell\rangle$ diagonalize operator,

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} |j = \ell \pm 1/2, m_j, \ell\rangle = \frac{\hbar^2}{2} \begin{pmatrix} \ell \\ -\ell - 1 \end{pmatrix} |\ell \pm 1/2, m_j, \ell\rangle$$

- Once again, off-diagonal matrix elements of \hat{H}_2 vanish allowing correction to be computed in first order perturbation theory.

$$\langle H_2 \rangle_{n,j=\ell\pm 1/2,m_j,\ell} = \frac{1}{2m^2c^2} \frac{\hbar^2}{2} \begin{pmatrix} \ell \\ -\ell - 1 \end{pmatrix} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r^3} \right\rangle_{n\ell}$$

(b) Spin-orbit coupling

$$\langle H_2 \rangle_{n,j=\ell\pm 1/2,m_j,\ell} = \frac{1}{2m^2c^2} \frac{\hbar^2}{2} \begin{pmatrix} \ell \\ -\ell - 1 \end{pmatrix} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r^3} \right\rangle_{n\ell}$$

- Making use of identity,

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \left(\frac{mc\alpha Z}{\hbar n} \right)^3 \frac{1}{\ell(\ell + 1/2)(\ell + 1)}, \quad \ell > 0$$

$$\langle \hat{H}_2 \rangle_{n,j=\ell\pm 1/2,m_j,\ell} = \frac{1}{4} mc^2 \left(\frac{Z\alpha}{n} \right)^4 \frac{n}{j + 1/2} \begin{cases} \frac{1}{j} & j = \ell + 1/2 \\ -\frac{1}{j+1} & j = \ell - 1/2 \end{cases}$$

- Rewriting expression for $\langle \hat{H}_1 \rangle$ in new basis $|n, j = \ell \pm 1/2, m_j, \ell\rangle$,

$$\langle \hat{H}_1 \rangle_{n,j=\ell\pm 1/2,m_j,\ell} = -\frac{1}{2} mc^2 \left(\frac{Z\alpha}{n} \right)^4 n \begin{cases} \frac{1}{j} & j = \ell + 1/2 \\ \frac{1}{j+1} & j = \ell - 1/2 \end{cases} .$$

- Combining these expressions, for $\ell > 0$, we have

(c) Darwin term

- Final relativistic correction arises from “Zitterbewegung” of electron – giggling – which smears effective potential felt by electron,

$$\hat{H}_3 = \frac{\hbar^2}{8m^2c^2} \nabla^2 V = \frac{\hbar^2}{8m^2c^2} \frac{eQ_{\text{nuclear}}(\mathbf{r})}{\epsilon_0} = \frac{\pi\hbar^2}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \delta^{(3)}(\mathbf{r})$$

- Since perturbation acts only at origin, it effects only $\ell = 0$ states,

$$\langle \hat{H}_3 \rangle_{nj=1/2, m_j \ell=0} = \frac{\pi\hbar^2}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} |\psi_{n00}(0)|^2 = \frac{1}{2} mc^2 \frac{(Z\alpha)^4}{n^3}$$

- This term is formally identical to that which would be obtained from $\langle \hat{H}_2 \rangle$ at $\ell = 0$. As a result, combining all three contributions,

$$\Delta E_{n, j=\ell \pm 1/2, m_j, \ell} = \frac{1}{2} mc^2 \left(\frac{\alpha Z}{n} \right)^4 \left(\frac{3}{4} - \frac{n}{j + 1/2} \right)$$

independent of ℓ and m_j .

Spectroscopic notation

- To discuss energy shifts for particular states, it is helpful to introduce some nomenclature from atomic physics.
- For a state with principal quantum number n , total spin s , orbital angular momentum ℓ , and total angular momentum j , one may define the state by the spectroscopic notation,

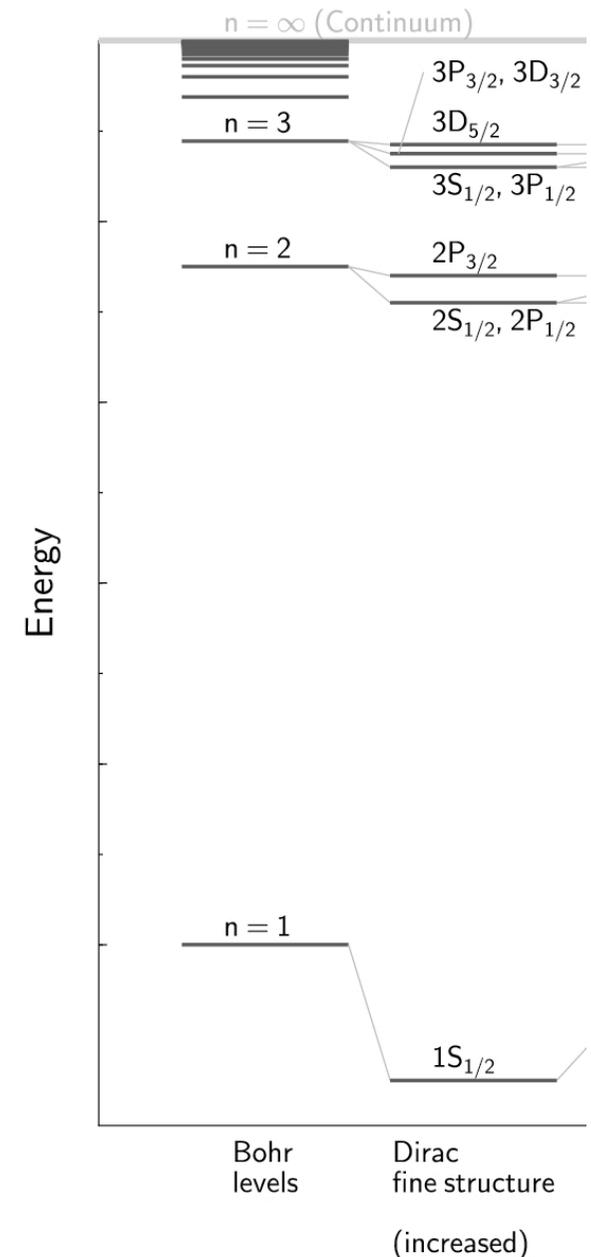
$$n^{2s+1} L_j$$

- For a hydrogen-like atom, with just a single electron, $2s + 1 = 2$. In this case, the factor $2s + 1$ is often just dropped for brevity.

Relativistic corrections

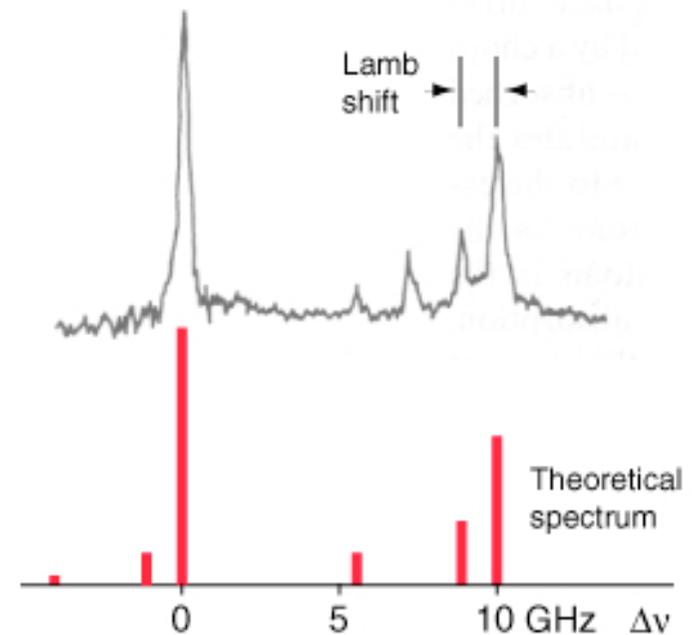
$$\Delta E_{n,j=l\pm 1/2,m_j,l} = \frac{1}{2}mc^2 \left(\frac{\alpha Z}{n}\right)^4 \left(\frac{3}{4} - \frac{n}{j+1/2}\right)$$

- For a given n , relativistic corrections depend only on j and n .
- For $n = 1$, $\ell = 0$ and $j = 1/2$: Both $1S_{1/2}$ states, with $m_j = \pm 1/2$, experience negative energy shift of $-\frac{1}{4}Z^4\alpha^2 R_y$.
- For $n = 2$, $\ell = 0, 1$: With $j = 1/2$, both $2S_{1/2}$ and $2P_{1/2}$ states have shift, $-\frac{5}{64}Z^4\alpha^2 R_y$, while $2P_{3/2}$ experiences a shift $-\frac{1}{64}Z^4\alpha^2 R_y$.



(Further) relativistic corrections: Lamb shift

- Perturbative corrections predicted by Dirac theory predict that, for hydrogen, the $2S_{1/2}$ and $2P_{1/2}$ states should remain degenerate.
- However, in 1951, an experimental study by Willis Lamb discovered that $2P_{1/2}$ state is slightly lower than the $2S_{1/2}$ state – Lamb shift.
- Might seem that such a tiny effect would be insignificant, but shift provided considerable insight into **quantum electrodynamics**.



Lamb shift

- Within framework of quantum electrodynamics, Coulomb interaction is mediated by exchange of photons – “gauge particles”.
- Interaction of electron with electromagnetic field can induce a “self-interaction” \rightsquigarrow effective smearing of electron position,

$$\langle (\delta \mathbf{r})^2 \rangle \simeq \frac{2\alpha}{\pi} \left(\frac{\hbar}{mc} \right)^2 \ln \frac{1}{\alpha Z}, \quad \delta r \sim 10^{-5} a_0$$

- Causes electron spin g -factor to be slightly different from 2.
- There is also a slight weakening of the force on the electron when it is very close to the nucleus, causing $2S_{1/2}$ state to be slightly higher in energy than the $2P_{1/2}$ state.

$$\Delta E_{\text{Lamb}} \simeq \frac{1}{2} mc^2 \left(\frac{\alpha Z}{n} \right)^4 n \times \left(\frac{8}{3\pi} \alpha \ln \frac{1}{\alpha Z} \right) \delta_{\ell,0}$$

Hyperfine structure

- Finally, we should address the potential influence of the nuclear spin, \mathbf{I} , which leads to a nuclear magnetic moment,

$$\mathbf{M} = g_N \frac{e}{2M_N} \mathbf{I}$$

where nucleus has mass M_N and gyromagnetic ratio g_N .

- Since nucleus has internal structure, g_N is not simply 2. For proton, sole nuclear constituent of atomic hydrogen, $g_p \approx 5.56$. Even though neutron is charge neutral, $g_n \approx -3.83$.
- Magnetic moment generates vector potential $\mathbf{A} = -\frac{\mu_0}{4\pi} \mathbf{M} \times \nabla(1/r)$ and magnetic field

$$\mathbf{B} = \nabla \times \mathbf{A} = \frac{\mu_0}{4\pi} \left[\frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{M}) - r^2 \mathbf{M}}{r^5} + \frac{8\pi}{3} \mathbf{M} \delta^{(3)}(\mathbf{r}) \right]$$

Hyperfine interaction

$$\mathbf{B} = \nabla \times \mathbf{A} = \frac{\mu_0}{4\pi} \left[\frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{M}) - r^2\mathbf{M}}{r^5} + \frac{8\pi}{3} \mathbf{M} \delta^{(3)}(\mathbf{r}) \right]$$

- As a result, we obtain hyperfine interaction with orbital and spin degrees of freedom of electron,

$$\hat{H}_{hyp} = \frac{e}{2m} (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B}$$

- Energy level shift of the ground state can be estimated using perturbation theory. If we consider (for simplicity) just the $\ell = 0$ states, only last term in \mathbf{B} contributes at lowest order, and leads to

$$\langle \hat{H}_{hyp} \rangle_{n,1/2,0} = \frac{\mu_0}{4\pi} \frac{g_N e}{2M_N} \frac{e}{m} \frac{8\pi}{3} |\psi_{n00}(0)|^2 \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} / \hbar^2$$

Hyperfine interaction

$$\langle \hat{H}_{\text{hyp}} \rangle_{n,1/2,0} = \frac{\mu_0}{4\pi} \frac{g_N e}{2M_N} \frac{e}{m} \frac{8\pi}{3} |\psi_{n00}(0)|^2 \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} / \hbar^2$$

- With $|\psi_{n00}(0)|^2 = \frac{1}{\pi n^3} \left(\frac{Z\alpha mc}{\hbar} \right)^3$, we obtain

$$\langle \hat{H}_{\text{hyp}} \rangle_{n,1/2,0} = \frac{1}{2} mc^2 \left(\frac{Z\alpha}{n} \right)^4 n \times \frac{8}{3} g_N \frac{m}{M_N} \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} / \hbar^2$$

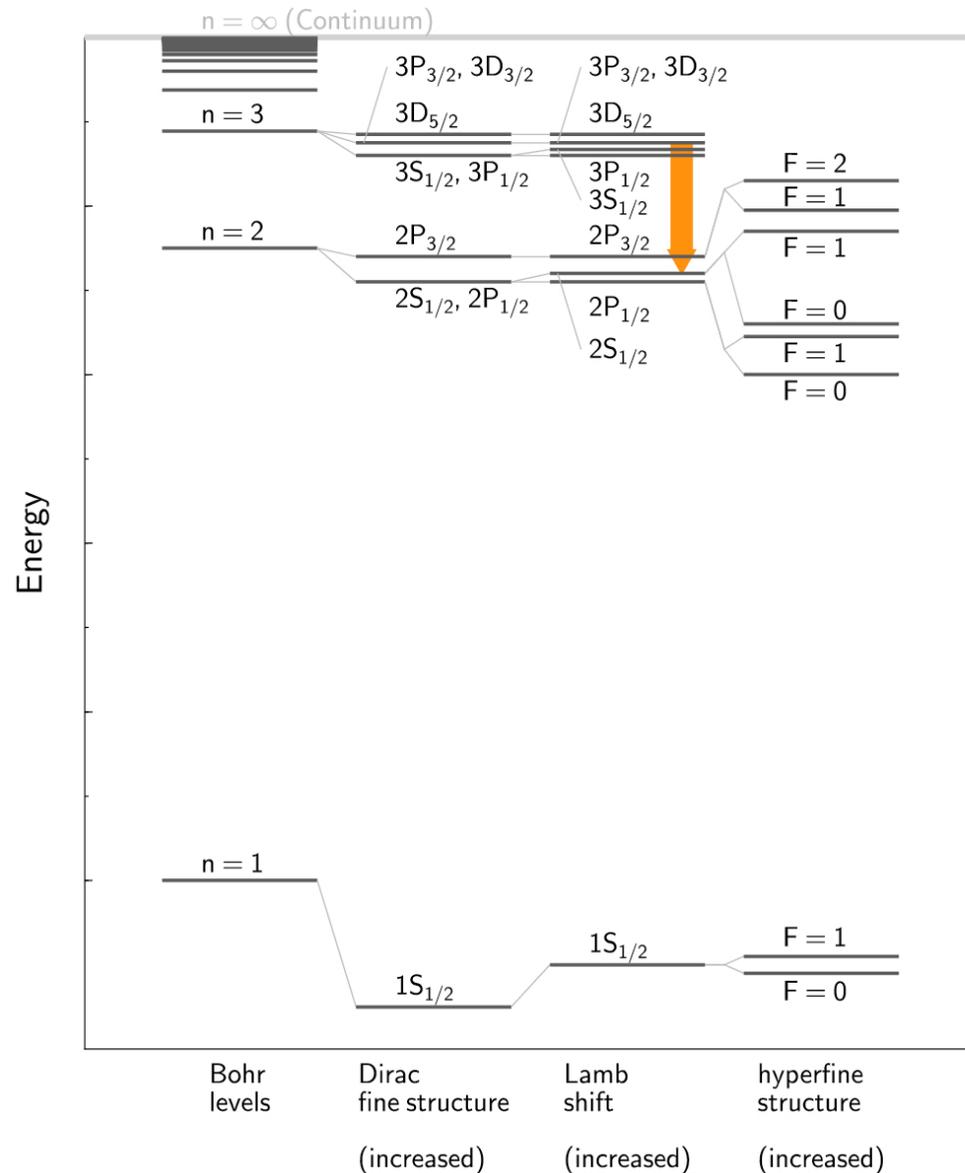
showing scale of perturbation suppressed over fine structure by factor $m/M_N \sim 10^{-3}$.

- Finally, as with spin-orbit interaction, if we set $\mathbf{F} = \mathbf{I} + \mathbf{S}$,

$$\begin{aligned} \frac{1}{\hbar^2} \mathbf{S} \cdot \mathbf{I} &= \frac{1}{2\hbar^2} (\mathbf{F}^2 - \mathbf{S}^2 - \mathbf{I}^2) = \frac{1}{2} (F(F+1) - 3/4 - I(I+1)) \\ &= \frac{1}{2} \begin{cases} I & F = I + 1/2 \\ -I - 1 & F = I - 1/2 \end{cases} \end{aligned}$$

Summary of atomic energy scales

- **Gross structure:** Dictated by orbital kinetic and potential energies, ca. 1 – 10 eV.
- **Fine structure:** Relativistic corrections (spin-orbit, etc.) split degenerate multiplets leading to small shift in energy, ca. 10^{-4} – 10^{-5} eV.
- **Hyperfine structure:** Interaction of electron magnetic moment with field generated by nuclear spin leads to further splitting of multiplets, ca. 10^{-7} – 10^{-8} eV



PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

PERIOD	GROUP I IA		GROUP IUPAC										GROUP CAS						18 VIIIA
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM	
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM			5 10.811 B BORON								6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON		
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON	
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON	
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON	
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON	
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uuu UNUNNIUM	111 (272) Uub UNUNUNIUM	112 (285) Uuq UNUNQUADIUM	114 (289) Uuq UNUNQUADIUM						

Lecture 13-14

Multi-electron atoms

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERIUM	71 174.97 Lu LUTETIUM
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ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM
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(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001). Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

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Background

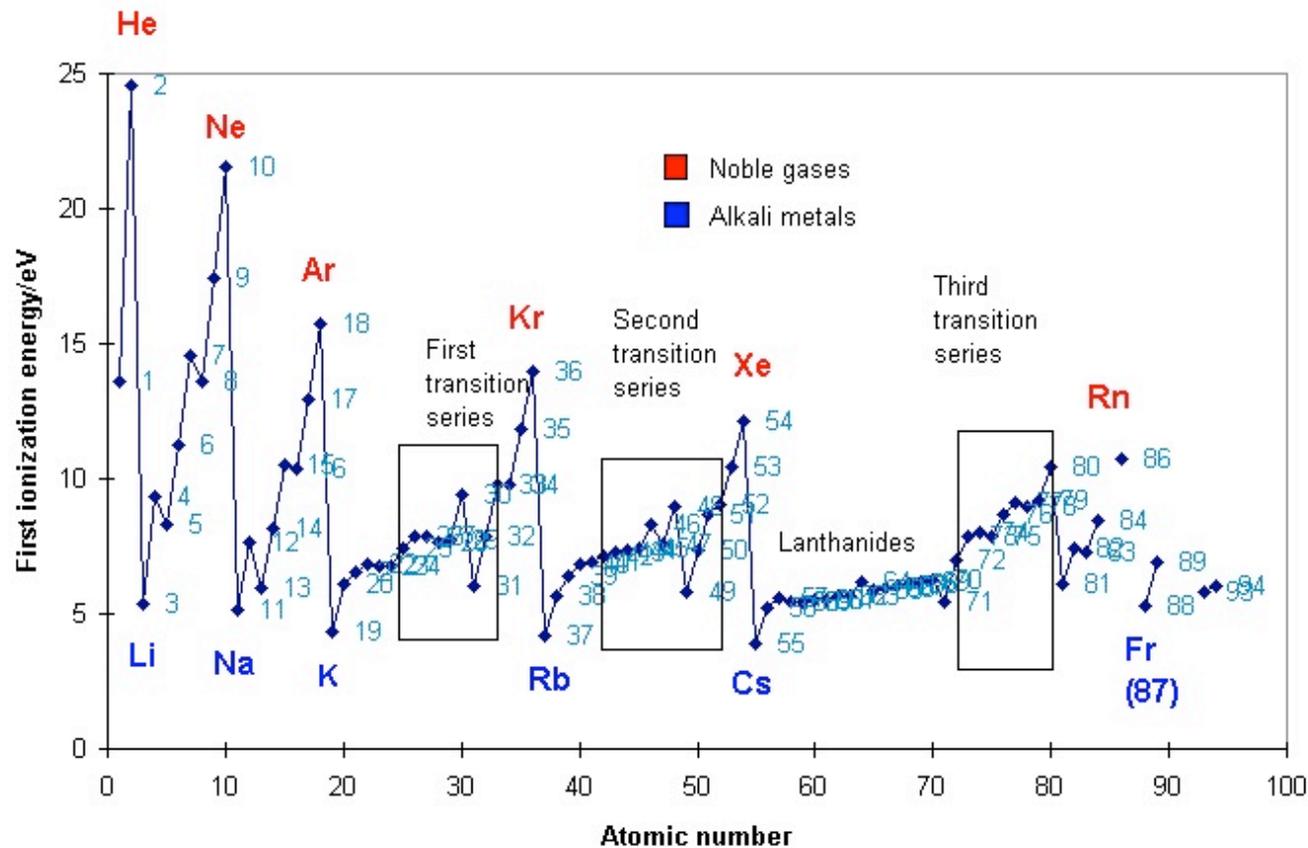
How can we determine energy levels of a multi-electron atom?

- We could start with hydrogenic energy levels for atom of nuclear charge Z , and start filling electrons from lowest levels, accounting for Pauli exclusion.
- Degeneracy for quantum numbers (n, ℓ) is $2 \times (2\ell + 1)$. Each energy level, n , accommodates $2 \times n^2$ electrons:

n	ℓ	Degeneracy in shell	Cumulative total
1	0	2	2
2	0, 1	$(1 + 3) \times 2 = 8$	10
3	0, 1, 2	$(1 + 3 + 5) \times 2 = 18$	28
4	0, 1, 2, 3	$(1 + 3 + 5 + 7) \times 2 = 32$	60

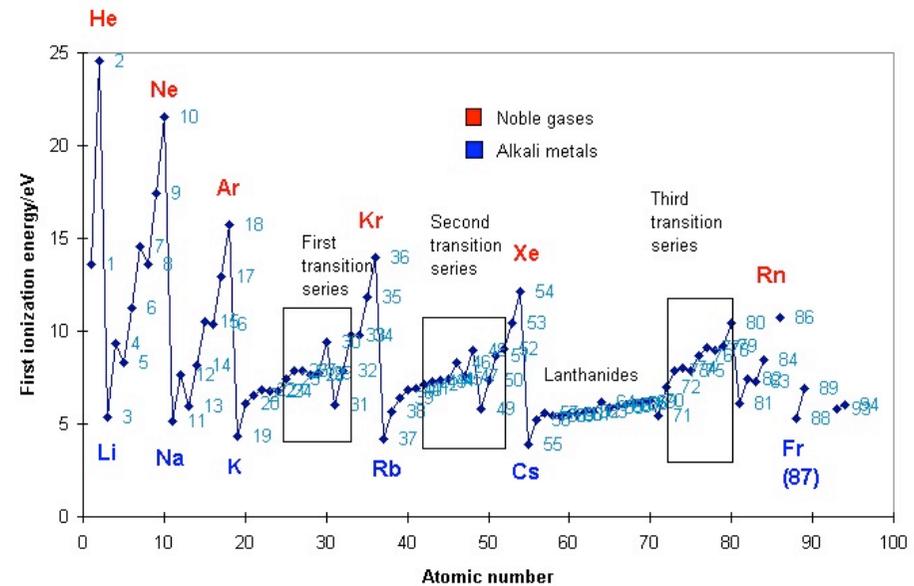
- Expect atoms containing 2, 10, 28 or 60 electrons would be especially stable and that, in atoms containing one more electron, outermost electron would be less tightly bound.

Background: ionization energies of elements



- Instead, find noble gases ($Z = 2, 10, 18, 36 \dots$) are especially stable, and elements containing one more electron (alkali metals) significantly less tightly bound.

Background



- Failure to predict stable electron configurations reflects omission of electron-electron interaction (cf. our discussion of helium).
- In fact, first ionization energies of atoms show only a weak dependence on Z – outermost electrons are almost completely **shielded** from nuclear charge:

Effective nuclear charge varies as $Z_{\text{eff}} \sim (1 + \gamma)^Z$ where $\gamma > 0$ characterizes “ineffectiveness of screening”; i.e. ionization energy $I_Z = -E_Z \sim Z_{\text{eff}}^2 \sim (1 + 2\gamma Z)$ (cf. experiment).

Multi-electron atoms

- Leaving aside (for now) relativistic effects, Hamiltonian for multi-electron atom given by

$$\hat{H} = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} \right] + \sum_{i<j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}}$$

where $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$.

- In addition to nuclear binding potential, there is a further Coulomb interaction between electrons.
As we have seen with helium, this contribution can have important consequences on spectra and spin structure of wavefunction.
- However, electron-electron interaction makes problem “many-body” in character and analytically intractable – we must develop some approximation scheme (even though effects may not be small!).

Multi-electron atoms: outline

- Central field approximation
- Self-consistent field method – **Hartree approximation**
- Structure of the periodic table
- Coupling schemes:
 - ① LS coupling and Hund's rules
 - ② jj coupling
- Atomic spectra: selection rules
- Zeeman effect revisited

Central field approximation

- Electron interaction contains large spherically symmetric component arising from “core electrons”. Since

$$\sum_{m=-\ell}^{\ell} |Y_{lm}(\theta, \phi)|^2 = \text{const.}$$

closed shell has spherically symmetric charge distribution.

- This suggests a “partitioning” of the Hamiltonian, $\hat{H} = \hat{H}_0 + \hat{H}_1$, with

$$\hat{H}_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} + U_i(r_i) \right]$$

$$\hat{H}_1 = \sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r_i)$$

where the radially-symmetric “single-electron potentials”, $U_i(r)$, accommodate “average effect” of other electrons, i.e. \hat{H}_1 is small.

Central field approximation

$$\hat{H}_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} + U_i(r_i) \right]$$

$$\hat{H}_1 = \sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r_i)$$

- Since single-particle Hamiltonian \hat{H}_0 continues to commute with the angular momentum operator, $[\hat{H}_0, \hat{\mathbf{L}}] = 0$, its eigenfunctions remain indexed by quantum numbers (n, ℓ, m_ℓ, m_s) .
- However, since effective potential, $V(r) + U_i(r)$, is no longer Coulomb-like, ℓ values for a given n need not be degenerate.
- But how do we fix $U_i(r)$; the potential energy experienced by each electron depends on the wavefunction of all the other electrons, which is only known after the Schrödinger equation has been solved.
- This suggests an **iterative approach** to solving the problem.

Self-consistent field method

Before embarking on this programme, we should first consider our ambitions:

- The development of computation schemes to address quantum mechanics of many-particle systems is a specialist (and challenging) topic common to physics and chemistry.
- Our interest here is merely in the **outcome** of such investigations, and their ramifications for atomic physics.
- We will therefore discuss (general) principles of the methodology, but the detailed technical aspects of the approach need not be committed to memory!



Self-consistent field method

- To understand how the potentials $U_i(r)$ can be estimated, we will follow a **variational approach due to Hartree**:

If electrons are (for now) considered distinguishable, wavefunction can be factorized into (normalized) product state,

$$\Psi(\{\mathbf{r}_i\}) = \psi_{i_1}(\mathbf{r}_1)\psi_{i_2}(\mathbf{r}_2)\cdots\psi_{i_N}(\mathbf{r}_N)$$

where the quantum numbers, $i \equiv n\ell m_\ell m_s$, index individual state occupancies.

- Note that $\Psi(\{\mathbf{r}_i\})$ is not a properly antisymmetrized Slater determinant – exclusion principle taken into account only insofar that we have assigned different quantum numbers, $n\ell m_\ell m_s$.
- In this approximation, if $U_i(r) = 0$, the ground state would involve filling the lowest shells with electrons.

Self-consistent field method

$$\Psi(\{\mathbf{r}_i\}) = \psi_{i_1}(\mathbf{r}_1)\psi_{i_2}(\mathbf{r}_2)\cdots\psi_{i_N}(\mathbf{r}_N)$$

- Variational ground state energy:

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_i \int d^3r \psi_i^* \left(-\frac{\hbar^2 \nabla^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i \\ + \frac{1}{4\pi\epsilon_0} \sum_{i < j} \int d^3r \int d^3r' \psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_j(\mathbf{r}') \psi_i(\mathbf{r})$$

- According to variational principle, we must minimize energy by varying $E[\{\psi_i\}]$, subject to normalization condition, $\langle \psi_i | \psi_i \rangle = 1$.
- Latter imposed by set of Lagrange multipliers, ϵ_i ,

$$\frac{\delta}{\delta \psi_i^*} \left[E - \epsilon_i \left(\int d^3r |\psi_i(\mathbf{r})|^2 - 1 \right) \right] = 0$$

Self-consistent field method

$$\frac{\delta}{\delta\psi_i^*} \left[E - \varepsilon_i \left(\int d^3r |\psi_i(\mathbf{r})|^2 - 1 \right) \right] = 0$$

- Following variation, obtain **Hartree equations**,

$$\left(-\frac{\hbar^2 \nabla^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- Amongst all possible trial functions ψ_i , set that minimizes energy determined by effective potential,

$$U_i(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

- To simplify procedure, useful to engineer radial symmetry by replacing $U_i(\mathbf{r})$ by spherical average, $U_i(r) = \int \frac{d\Omega}{4\pi} U_i(\mathbf{r})$.

Self-consistent field method

$$\left(-\frac{\hbar^2 \nabla^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3 r' |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

- To fix Lagrange multipliers, ϵ_i , we can multiply Hartree equations by $\psi_i^*(\mathbf{r})$ and integrate,

$$\epsilon_i = \int d^3 r \psi_i^* \left(-\frac{\hbar^2 \nabla^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right) \psi_i + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3 r' d^3 r |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2$$

- From this result, we find

$$E = \sum_i \epsilon_i - \frac{1}{4\pi\epsilon_0} \sum_{i < j} \int d^3 r' d^3 r |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2$$

Self-consistent field method

- In summary, within the Hartree framework, the multi-electron Hamiltonian is replaced by the effective single-particle Hamiltonian,

$$\hat{H}_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} + U_i(r_i) \right]$$

where the central potentials U_i depend self-consistently on the single-particle wavefunctions,

$$U_i(r) = \int \frac{d\Omega}{4\pi} \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \int d^3r' |\psi_j(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

- Once U_i s are found, perturbation theory can be applied to residual Coulomb interaction,

$$\hat{H}_1 = \sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r_i)$$

Hartree-Fock method

- An improvement on this procedure can be achieved by introducing a trial variational state wavefunction involving a Slater determinant,

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \psi_1(\mathbf{r}_3) & \cdots \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \psi_2(\mathbf{r}_3) & \cdots \\ \psi_3(\mathbf{r}_1) & \psi_3(\mathbf{r}_2) & \psi_3(\mathbf{r}_3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}$$

where $\psi_k(\mathbf{r}_i)$, with $i = 1, 2, \dots, N$, denote the single-particle wavefunctions for electron i , and $k = (n\ell m_\ell m_s)$

- A variational analysis leads to **Hartree-Fock equations** with additional **exchange contribution**,

$$\begin{aligned} \varepsilon_i \psi_i(\mathbf{r}) = & \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i} \right] \psi_i(\mathbf{r}) \\ & + \sum_{j \neq i} \int d^3 r'_j \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{r}'_j|} \psi_j^*(\mathbf{r}'_j) \left[\psi_j(\mathbf{r}'_j) \psi_i(\mathbf{r}) - \psi_j(\mathbf{r}) \psi_i(\mathbf{r}'_j) \delta_{m_{s_i}, m_{s_j}} \right] \end{aligned}$$

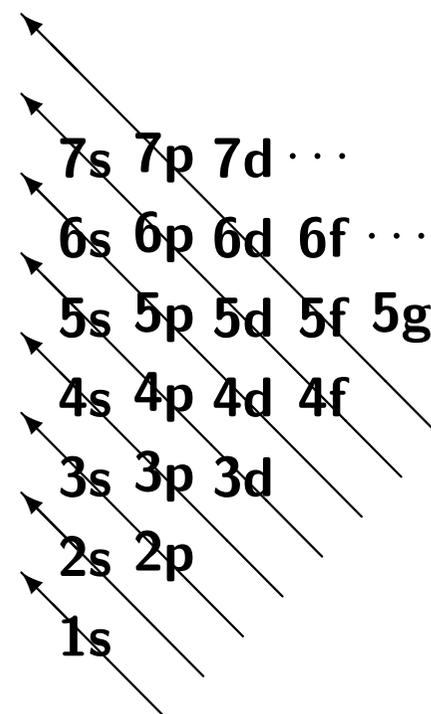
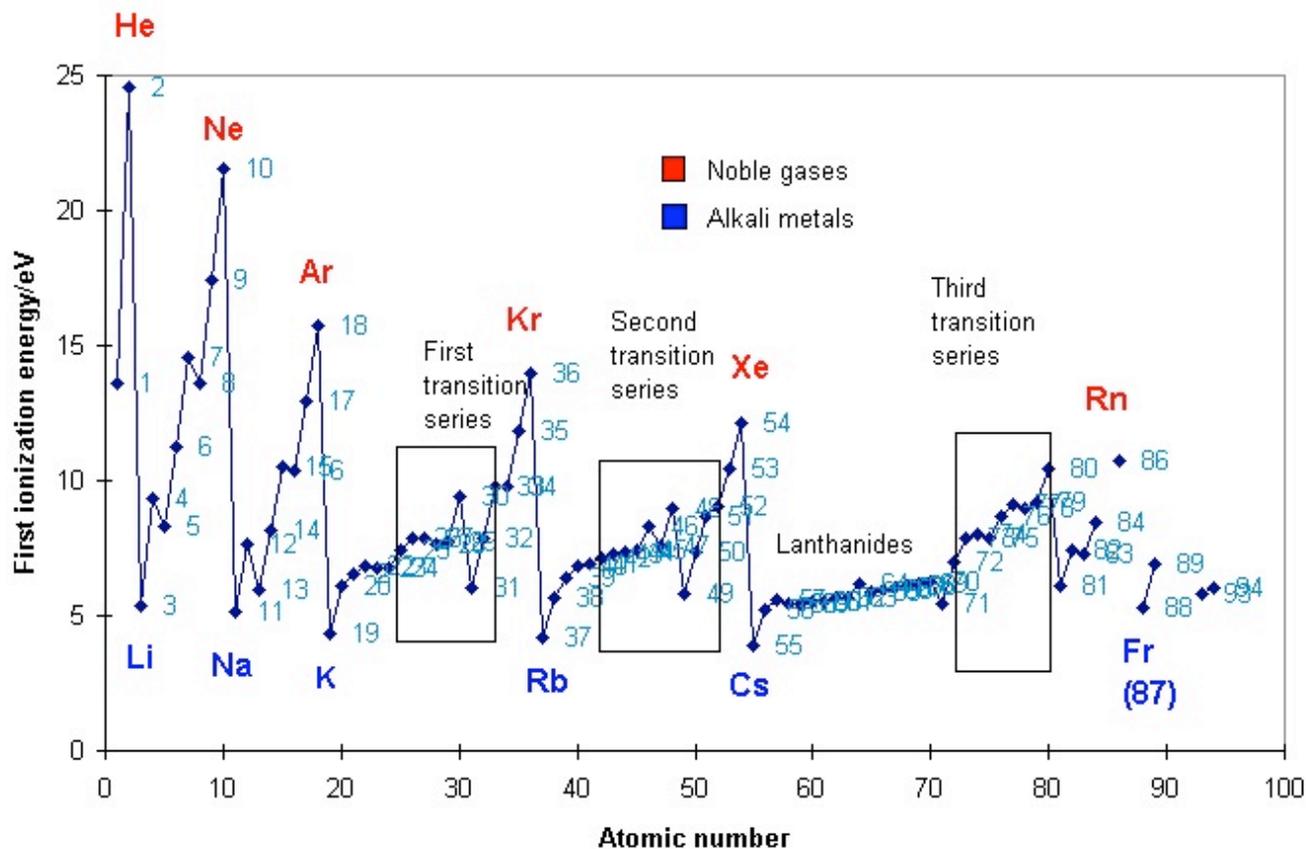
Central field approximation: conclusions

- Although states characterized by quantum numbers $n\ell m_\ell m_s$, Hartree-Fock calculations show that those with different ℓ for given n are now non-degenerate – large ℓ values more effectively screened and lie higher in energy.
- States corresponding to particular n referred to as a **shell**, and those belonging to n, ℓ are a **subshell**. Energy levels ordered as

Subshell name	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	...
$n =$	1	2	2	3	3	4	3	4	5	4	...
$\ell =$	0	0	1	0	1	0	2	1	0	2	...
Degeneracy	2	2	6	2	6	2	10	6	2	10	...
Cumulative	2	4	10	12	18	20	30	36	38	48	...

Central field approximation: conclusions

Subshell name	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	...
Cumulative	2	4	10	12	18	20	30	36	38	48	...



Periodic table

- Can use energy sequence to predict ground state electron configuration – fill levels accounting for exclusion **aufbau principle**.
- Sadly, there are exceptions to rule: e.g. Cu ($Z = 29$) expected to have configuration $(\text{Ar})(4s)^2(3d)^9$, actually has $(\text{Ar})(4s)^1(3d)^{10}$.

1	H	(1s)	13.6
2	He	(1s) ²	24.6
3	Li	He (2s)	5.4
4	Be	He (2s) ²	9.3
5	B	He (2s) ² (2p)	8.3
6	C	He (2s) ² (2p) ²	11.3
7	N	He (2s) ² (2p) ³	14.5
8	O	He (2s) ² (2p) ⁴	13.6
9	F	He (2s) ² (2p) ⁵	17.4
10	Ne	He (2s) ² (2p) ⁶	21.6
11	Na	Ne (3s)	5.1
12	Mg	Ne (3s) ²	7.6
14	Si	Ne (3s) ² (3p) ²	8.1
16	S	Ne (3s) ² (3p) ⁴	10.4
18	Ar	Ne (3s) ² (3p) ⁶	15.8
19	K	Ar (4s)	4.3

Periodic table

- Aufbau principle forms basis of **Periodic table of elements**: elements with similar electron configurations in outermost shells have similar chemical properties.

PERIODIC TABLE OF THE ELEMENTS
<http://www.ktf-split.hr/periodni/en/>

PERIOD	GROUP																		
	1 IA	2 IIA											13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA	
1	1.0079 H HYDROGEN																		4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON	
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON	
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON	
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON	
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON	
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM	114 (289) Uuq UNUNQUADIUM						

LANTHANIDE														
57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERIUM	71 174.97 Lu LUTETIUM

ACTINIDE														
89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

Editor: Aditya Vardhan (advvar@netlinx.com)

Coupling schemes

- The aufbau principle predicts ground state occupation of subshells – but does not specify spin and orbital angular momenta of subshells.
- To deal with this question, we must consider spin-orbit and residual Coulomb interaction between outer electrons.
- Hamiltonian for multi-electron atom can be written as,

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

where \hat{H}_0 includes central field terms, \hat{H}_1 is residual Coulomb interaction, and \hat{H}_2 is spin-orbit interaction.

Coupling schemes

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- For light atoms, $\hat{H}_1 \gg \hat{H}_2$, can treat \hat{H}_2 as a perturbation on $\hat{H}_0 + \hat{H}_1$ – known as **LS** (or **Russell-Saunders**) **coupling**.
- For heavy atoms (or ionized light atoms), $\hat{H}_2 \gg \hat{H}_1$, electrons become relativistic and spin-orbit interaction dominates – **jj coupling**.

Both scenarios are approximations – real atoms do not always conform to this “comparatively simple” picture.

Coupling schemes: LS coupling

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- Since \hat{H} commutes with set of total angular momenta, $\hat{\mathbf{J}}^2$, $\hat{\mathbf{L}}^2$, and $\hat{\mathbf{S}}^2$, energy levels of multi-electron atoms are characterized by quantum numbers L, S, J .
- Their ordering in energy set by **Hund's rules**.
- As rules empirical, there are exceptions. Moreover, as atomic mass increases and electrons become relativistic, spin-orbit interactions become increasingly important further undermining rules.

Coupling schemes: LS coupling and Hund's rules

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- 1 Combine spins to obtain possible values of total spin S . (Remember that closed shells contribute zero spin.)

The largest permitted value of S lies lowest in energy.

Physically: maximising S makes spin wavefunction as symmetric as possible: tends to make spatial wavefunction antisymmetric, reduces Coulomb repulsion (cf. helium).

Coupling schemes: LS coupling and Hund's rules

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- 2 For each value of S , find the possible values of total angular momentum L . (Remember that closed shells contribute zero orbital angular momentum.)

The largest permitted value of L lies lowest in energy.

Physically: maximising L also tends to keep the electrons apart.

- In deciding on permitted values of L and S , we also have to ensure that both quantum statistics and the exclusion principle is respected, i.e. total electron wavefunction must be antisymmetric under particle exchange.

Coupling schemes: LS coupling and Hund's rules

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- 3 Couple **L** and **S** to obtain values of J (hence name of scheme).
(Remember that closed shells contribute zero angular momentum.)

If subshell is less than half full, smallest value of J lies lowest in energy; otherwise, largest value lies lowest.

Energy separation for different J arises from treating spin-orbit term as a perturbation (fine structure),

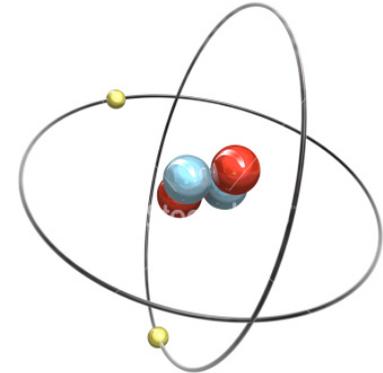
$$\begin{aligned} \langle Jm_J LS | \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i | Jm_J LS \rangle &= \zeta(L, S) \langle Jm_J LS | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | Jm_J LS \rangle \\ &= \zeta(L, S) [J(J+1) - L(L+1) - S(S+1)]/2 \end{aligned}$$

Since sign of $\zeta(L, S)$ changes according to whether the subshell is more or less than half-filled, the third Hund's rule is established.

LS coupling – Example: helium

- Helium has ground state electron configuration $(1s)^2$, i.e. $L = S = J = 0$.

N.B. For any completely filled subshell,
 $L = S = 0$ and hence $J = 0$.



- For excited state, e.g. $(1s)^1(2p)^1$, can have $S = 1$ or $S = 0$, with $S = 1$ state lying lower in energy according to Hund's rules.
- Combining orbital angular momenta gives $L = 1$ and, with $S = 0$, $J = 1$, while with $S = 1$, $J = 0, 1, 2$ with $J = 0$ lowest in energy.
- In spectroscopic notation $^{2S+1}L_J$, four possible states, 3P_0 3P_1 3P_2 and 1P_1 where three 3P states separated by spin-orbit interaction, and singlet 1P state lies much higher in energy due to Coulomb.

Landé interval rule

- Since separation of energies for states of different J arises from spin-orbit term contribution \hat{H}_2 (fine structure),

$$\begin{aligned} & \langle |J, m_J, L, S\rangle \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i |J, m_J, L, S\rangle \\ &= \frac{\zeta(L, S)}{2} [J(J+1) - L(L+1) - S(S+1)] \end{aligned}$$

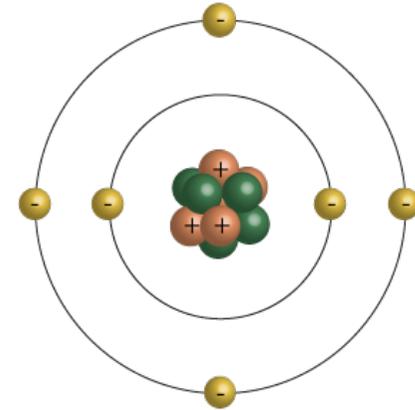
separation between pair of adjacent levels in a fine structure multiplet is proportional to larger of two J values,

$$\Delta_J \propto J(J+1) - (J-1)J = 2J$$

e.g. separation between 3P_2 and 3P_1 , and 3P_1 and 3P_0 should be in ratio 2:1.

LS coupling – Example: carbon

- Carbon has ground state electron configuration $(1s)^2(2s)^2(2p)^2$.
- With two *identical* electrons in same *unfilled* subshell, wavefunction must be antisymmetric.
- Total spin can either be singlet $S = 0$ (antisymmetric) or one of the triplet $S = 1$ states (symmetric).



- To form **antisymmetric** total angular momentum state, two electrons must have different values of m_ℓ
- Inspecting the values of m_L we can deduce that $L = 1$.

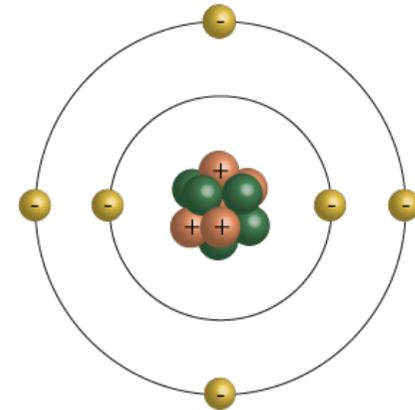
$m_\ell^{(1)}$	$m_\ell^{(2)}$	m_L
1	0	1
1	-1	0
0	-1	-1

- To form **symmetric** total angular

$m_\ell^{(1)}$	$m_\ell^{(2)}$	m_L
1	1	2

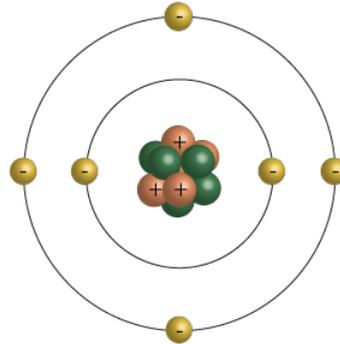
LS coupling – Example: carbon

- Carbon has ground state electron configuration $(1s)^2(2s)^2(2p)^2$.
- With two *identical* electrons in same *unfilled* subshell, wavefunction must be antisymmetric.



- To ensure antisymmetry of wavefunction, we must therefore take $S = 1$ with $L = 1$ and $S = 0$ with $L = 2$ or 0 .
- To account for fine structure, states with $S = 1$ and $L = 1$ can be combined into single $J = 0$ state, three $J = 1$ states, and five $J = 2$ states leading to terms 3P_0 , 3P_1 , and 3P_2 respectively.
- Similarly the $S = 0$, $L = 2$ state can be combined to give five $J = 2$ states, 1D_2 , while $S = 0$, $L = 0$ state gives single $J = 0$ state, 1S_0 .

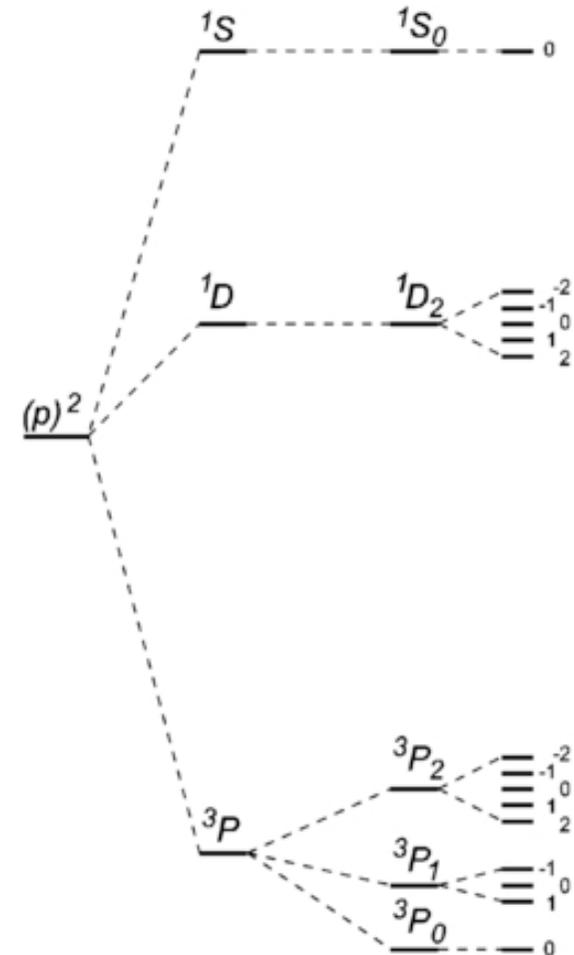
LS coupling – Example: carbon



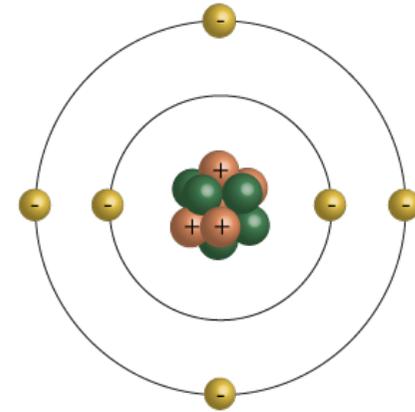
- Measured energy levels:

	E / cm^{-1}
1S_0	20649
1D_2	10195
3P_2	43
3P_1	16
3P_0	0

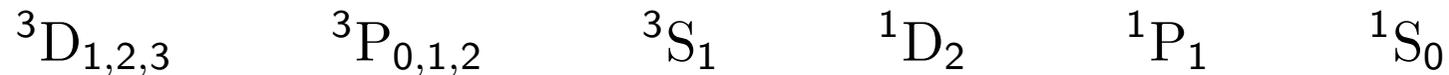
- Landé interval rule approximately obeyed by fine structure triplet, and separation between L and S values caused by Coulomb repulsion is *much* greater than spin-orbit effect.



LS coupling – Example: carbon



- For excited states of carbon, e.g. $(2p)^1(3p)^1$, electrons are no longer equivalent because they have different radial wavefunctions.
- We can now combine any of $S = 0, 1$ with any of $L = 0, 1, 2$, yielding the following terms (in order of increasing energy, according to Hund's rules):



Recap: atomic structure

- Our studies of the energy spectrum of atomic hydrogen using the non-relativistic Schrödinger equation showed that states are organised in a shell structure, indexed by a principle quantum number n and characterised by an n^2 -fold degeneracy.
- To address the electronic structure of multielectron atoms, we have to accommodate two classes of additional effects:
 - ① Even hydrogenic (i.e. single-electron) atoms are subject to corrections from relativistic effects (spin-orbit coupling, etc.) – **fine structure**, vacuum fluctuations of EM field – **Lamb shift**, and interaction with nuclear spin – **hyperfine structure** which together conspire to lift state degeneracy.
 - ② In addition, in multielectron atoms, the direct Coulomb interaction between electrons lead to screening of the nuclear charge, and rearrange the ordering of the shell structure.

Recap: atomic structure

- Although electron-electron interactions make the multielectron system formally intractable, the spherical symmetry of filled core electron states justifies **central field approximation** in which the principle effect of interactions is captured by a single-particle potential,

$$\hat{H}_0 = \sum_i \left[-\frac{\hbar^2 \nabla_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} + U_i(r_i) \right], \quad \hat{H}_1 = \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i U_i(r_i)$$

- Numerical studies (based on self-consistent Hartree-Fock scheme) provide a simple phenomenology to describe energy ordering of core subshells – **aufbau principle**
- Influence of residual electron interaction, \hat{H}_1 , and relativistic spin-orbit corrections

$$\hat{H}_2 = \sum_i \xi(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$$

on valence states can then be addressed within perturbation theory.

Recap: atomic structure

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- For light atoms, $\hat{H}_1 \gg \hat{H}_2$, can treat \hat{H}_2 as a perturbation on $\hat{H}_0 + \hat{H}_1$ – known as **LS** (or **Russell-Saunders**) **coupling**.
- For heavy atoms (or ionized light atoms), $\hat{H}_2 \gg \hat{H}_1$, electrons become relativistic and spin-orbit interaction dominates – ***jj*** **coupling**.

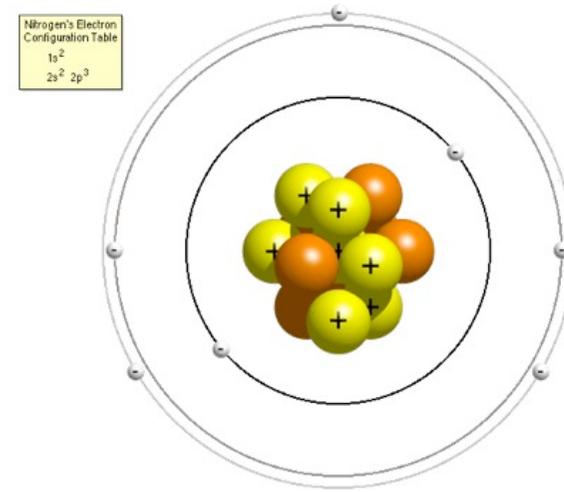
Recap: atomic structure

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- In LS coupling, the ground state electron configuration is specified by an empirical set of rules known as **Hund's rules**. Subject to Pauli exclusion:
 - 1 The largest permitted value of total S lies lowest in energy.
 - 2 The largest permitted value of total L lies lowest in energy.
 - 3 If subshell is less than half full, smallest value of total J lies lowest in energy; otherwise largest value lies lowest.

LS coupling – Example: nitrogen

- Nitrogen has ground state electron configuration $(1s)^2(2s)^2(2p)^3$.
- The maximal value of spin is $S = 3/2$ while L can take values 3, 2, 1 and 0.



- Since spin wavefunction (being maximal) is symmetric, spatial wavefunction must be antisymmetric – all three states with $m_\ell = 1, 0, -1$ must be involved.
- We must therefore have $L = 0$ and $J = 3/2$ with the term, ${}^4S_{3/2}$.

jj coupling scheme

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_i U_i(r)}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- When relativistic effects dominate residual electrostatic interaction, \hat{H}_1 , (i.e. heavy elements) electrons move independently in central field, subject to spin-orbit interaction. In this limit, states are both eigenstates of $\hat{\mathbf{J}}^2$ (as before), **and also of $\hat{\mathbf{J}}_i^2$ for each electron.**
- In *jj* coupling, separate energy shifts independent of total J and M_J , $\Delta E = \langle n_i \ell_i s_i j_i J m_J | \sum_i \xi(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i | n_i \ell_i s_i j_i J m_J \rangle = \sum_i \Delta E_i$ where

$$\Delta E_i = \zeta(n_i, \ell_i) [j_i(j_i + 1) - \ell_i(\ell_i + 1) - s_i(s_i + 1)] / 2$$

- The degeneracy with respect to J is then lifted by the small electrostatic interaction between electrons, \hat{H}_1 .

jj coupling scheme: Example

- Consider configuration $(np)^2$ (cf. carbon in LS scheme): Combining $s = 1/2$ with $\ell = 1$, each electron can have $j = 1/2$ or $3/2$.
- If electrons have same j value, they are equivalent, so we have to take care of symmetry:
 - (a) $j_1 = j_2 = 3/2 \Rightarrow J = 3, 2, 1, 0$, of which $J = 2, 0$ are antisymmetric.
 - (b) $j_1 = j_2 = 1/2 \Rightarrow J = 1, 0$, of which $J = 0$ is antisymmetric.
 - (c) $j_1 = 1/2, j_2 = 3/2 \Rightarrow J = 2, 1$.
- Taking into account Pauli exclusion, in jj coupling (where the term is written $(j_1, j_2)_J$), we have the following terms:

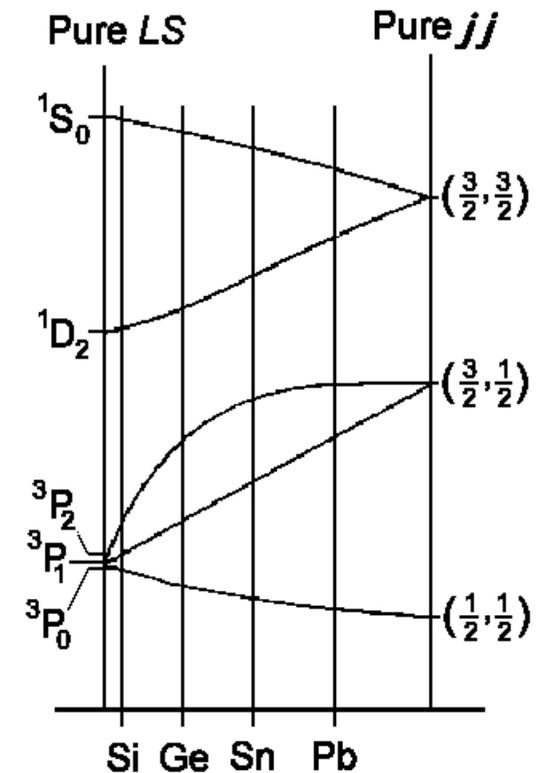
$$(1/2, 1/2)_0 \quad (3/2, 1/2)_1 \quad (3/2, 1/2)_2 \quad (3/2, 3/2)_2 \quad (3/2, 3/2)_0$$

in order of increasing energy.

jj coupling scheme: Example

$(1/2, 1/2)_0$ $(3/2, 1/2)_1$ $(3/2, 1/2)_2$ $(3/2, 3/2)_2$ $(3/2, 3/2)_0$

- Both LS and *jj* coupling give same J values (two states with $J = 0$, two with $J = 2$ and one with $J = 1$) and in same order.
- However, pattern of levels different: in LS coupling we found a triplet ($^3P_0, ^3P_1, ^3P_2$) and two singlets (1D_2 and 1S_0), while in ideal *jj* scenario, we have two doublets and a singlet.
- The sets of states in two schemes must be expressible as linear combinations of one another, and physical states for real atom likely to differ from either approximation – e.g. *jj* coupling not seen in $\text{Pb}(6p)^2$ but is seen in Cr^{18+} which has same configuration as carbon, $(2p)^2$.



Atomic spectra

- Atomic spectra result from transitions between different electronic states of an atom via emission or absorption of photons.
- In **emission spectra**, atom is excited by some means (e.g. thermally through collisions), and one observes discrete spectral lines in light emitted as atoms relax.



- In **absorption spectra**, one illuminates atoms using a broad waveband source, and observes dark absorption lines in the spectrum of transmitted light.



- Atoms excited in this process subsequently decay by emitting photons in random directions – **fluorescence**.

Atomic spectra: selection rules

Basic theory governing emission and absorption will be outlined in detail when we study radiative transitions. Here we anticipate some results:

- In **electric dipole approximation**, rate of transitions is proportional to matrix elements of electric dipole operator, $\hat{\mathbf{d}} = -e \sum_i \mathbf{r}_i$,

$$\Gamma \propto \omega^3 |\langle \psi_f | \hat{\mathbf{d}} | \psi_i \rangle|^2, \quad \omega = |E_f - E_i|$$

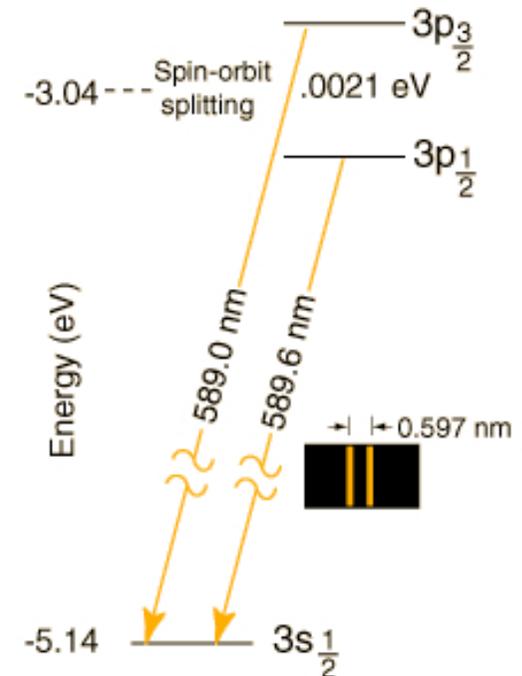
- Form of dipole operator, $\hat{\mathbf{d}}$ means that some matrix elements vanish \rightsquigarrow **selection rules**. For a transition to take place:
 - 1 Parity must change
 - 2 $\Delta J = \pm 1, 0$ (but $0 \rightarrow 0$ is not allowed) and $\Delta M_J = \pm 1, 0$
- Atomic states always eigenstates of parity and $\hat{\mathbf{J}}^2$, so selection rules can be regarded as absolutely valid in electric dipole transitions.

Atomic spectra: selection rules

- In specific coupling schemes, further selection rules apply. In the case of ideal LS coupling, we also require:
 - ① $\Delta S = 0$ and $\Delta M_S = 0$
Follows from conservation of total spin in transition.
 - ② $\Delta L = \pm 1, 0$ (but $0 \rightarrow 0$ is not allowed) and $\Delta M_L = \pm 1, 0$
Follows from 1. and rules relating to J .
 - ③ $\Delta \ell_i = \pm 1$ if only electron i is involved in transition.
Follows from parity change rule since the parity of atom is product of parities of separate electron wavefunctions, $(-1)^{\ell_i}$.
- However, since LS coupling is only an approximation, these rules should themselves be regarded as approximate.

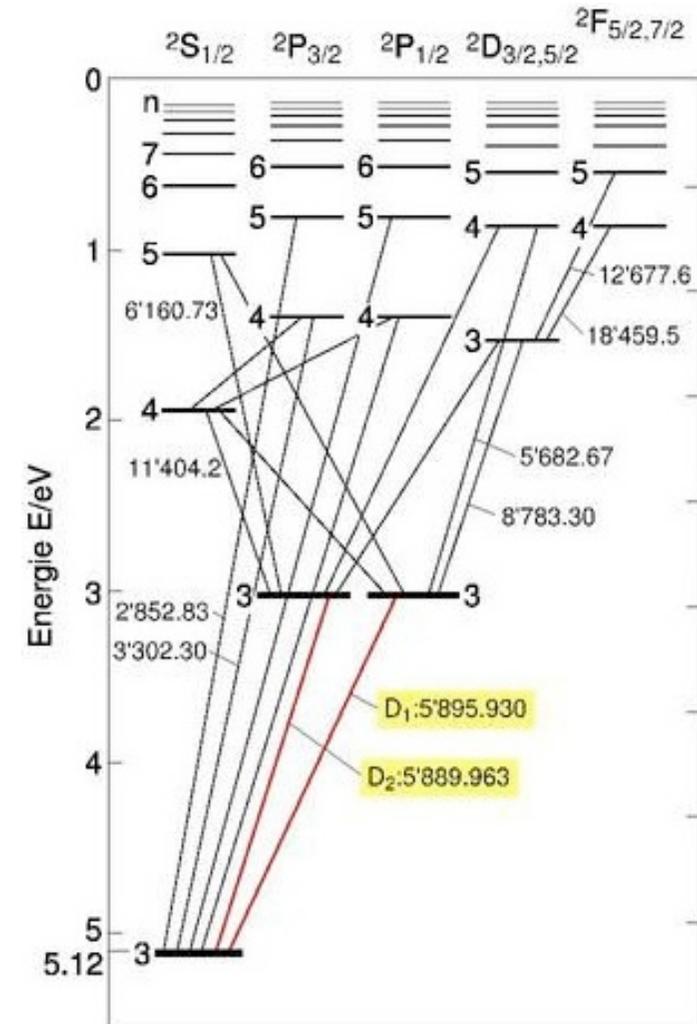
Atomic spectra: single electron atoms

- For “single electron atoms”, e.g. **alkali metals** such as **sodium**, and also hydrogen, ground state is $(ns)^1$.
- Ground state has term $^2S_{1/2}$ while excited states all doublets with $J = L \pm 1/2$ (except for s states which have $J = 1/2$).
- Since parity given by $(-1)^\ell$, allowed transitions involve $\Delta\ell = \pm 1$, i.e. $s \leftrightarrow p$, $p \leftrightarrow d$, etc. (Larger changes in ℓ contravene ΔJ rule.)
- The $s \leftrightarrow p$ transitions are all doublets. In sodium, transition $3s \leftrightarrow 3p$ gives rise to familiar yellow sodium “D-lines” at 589 nm.



Atomic spectra: single electron atoms

- $p \leftrightarrow d$ transitions involve two doublets, ${}^2P_{1/2,3/2}$ and ${}^2D_{3/2,5/2}$. However, the ${}^2P_{1/2} \leftrightarrow {}^2D_{5/2}$ transition is forbidden by ΔJ rule, so line is actually a triplet.
- As n increases, levels approach those for hydrogen, as nuclear charge is increasingly screened by inner electrons.
- In an absorption spectrum, atoms start from ground state, so only $ns \rightarrow n'p$ lines are seen. In emission, atoms are excited into essentially all their excited levels, so many more lines will be seen in the spectrum.



Zeeman effect: revisited

To conclude survey of atomic structure, we now return to consider how atomic spectra are influenced by a magnetic field?

- Begin with hydrogen-like atoms involving just a single electron. In a magnetic field, $\hat{H} = \hat{H}_0 + \hat{H}_{\text{rel.}} + \hat{H}_{\text{Zeeman}}$, where

$$\hat{H}_{\text{Zeeman}} = -\frac{e}{2mc} B(\hat{L}_z + 2\hat{S}_z) = -\mu_B B(\hat{L}_z + 2\hat{S}_z)/\hbar$$

denotes Zeeman term.

- Since we are dealing with confined electrons, we have neglected the diamagnetic contribution to the Hamiltonian.
- Depending on scale of magnetic field, the spin-orbit term in $\hat{H}_{\text{rel.}}$ or the Zeeman term may dominate the spectrum of the atom.

Zeeman effect: revisited

$$\hat{H}_{\text{Zeeman}} = -\frac{e}{2mc} B(\hat{L}_z + 2\hat{S}_z) = -\mu_B B(\hat{L}_z + 2\hat{S}_z)/\hbar$$

- Previously we have seen that, to leading order, relativistic corrections lead to fine-structure energy shift,

$$\Delta E_{n,j}^{\text{rel.}} = \frac{1}{2} mc^2 \left(\frac{Z\alpha}{n} \right)^4 \left(\frac{3}{4} - \frac{n}{j + 1/2} \right)$$

for states $|n, j = \ell \pm 1/2, m_j, \ell\rangle$.

- For weak magnetic fields, we can also treat Zeeman energy in framework of perturbation theory:

Although states with common j (e.g. $2S_{1/2}$ and $2P_{1/2}$) are degenerate, spatial wavefunctions have different parity, and off-diagonal matrix elements of \hat{H}_{Zeeman} vanish – avoids need for degenerate perturbation theory.

Zeeman effect: revisited

$$\hat{H}_{\text{Zeeman}} = -\frac{e}{2mc} B(\hat{L}_z + 2\hat{S}_z) = -\mu_B B(\hat{L}_z + 2\hat{S}_z)/\hbar = -\mu_B B(\hat{J}_z + \hat{S}_z)/\hbar$$

- Making use of identity, (exercise – refer back to addition of angular momentum and spin)

$$\langle n, j = \ell \pm 1/2, m_j, \ell | \hat{S}_z | n, j = \ell \pm 1/2, m_j, \ell \rangle = \pm \frac{\hbar m_j}{2\ell + 1}$$

we obtain the following expression for the first order energy shift,

$$\Delta E_{j=\ell\pm 1, m_j, \ell}^{\text{Zeeman}} = \mu_B B m_j \left(1 \pm \frac{1}{2\ell + 1} \right)$$

i.e. all degenerate levels split by field.

- In contrast to the “normal” Zeeman effect, the magnitude of the splitting now depends on ℓ .

Zeeman effect: revisited

$$\hat{H}_{\text{Zeeman}} = -\frac{e}{2mc} B(\hat{L}_z + 2\hat{S}_z) = -\mu_B B(\hat{L}_z + 2\hat{S}_z)/\hbar = -\mu_B B(\hat{J}_z + \hat{S}_z)/\hbar$$

- For **multi-electron atom** in weak field, unperturbed states given by $|J, M_J, L, S\rangle$, where J, L, S refer to total angular momenta.
 - To determine Zeeman shift, need to determine $\langle \hat{S}_z \rangle$, presenting an opportunity to revise angular momenta:
- 1 First we note that the operator $2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2$ is diagonal in the basis of states, $|J, M_J, L, S\rangle$.
 - 2 Therefore, recalling that $[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k$ and $[\hat{L}_i, \hat{S}_k] = 0$, it follows that the matrix element of the following operator vanishes,

$$\hat{\mathbf{S}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) - (\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})\hat{\mathbf{S}} = \hat{L}_j[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{L}_j\hat{S}_k \equiv -i\hbar\hat{\mathbf{S}} \times \hat{\mathbf{L}}$$

Zeeman effect: revisited

$$-i\hbar\hat{\mathbf{S}} \times \hat{\mathbf{L}} \equiv \hat{\mathbf{S}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) - (\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})\hat{\mathbf{S}}$$

- 3 Moreover, since $[\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \hat{\mathbf{J}}] = 0$, it follows that the matrix element of the following operator also vanishes,

$$-i\hbar(\hat{\mathbf{S}} \times \hat{\mathbf{L}}) \times \hat{\mathbf{J}} = \hat{\mathbf{S}} \times \hat{\mathbf{J}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) - (\hat{\mathbf{L}} \cdot \hat{\mathbf{S}})\hat{\mathbf{S}} \times \hat{\mathbf{J}}$$

- 4 If we expand left hand side, we thus find that the matrix element of the following operator also vanishes,

$$(\hat{\mathbf{S}} \times \hat{\mathbf{L}}) \times \hat{\mathbf{J}} = \hat{\mathbf{L}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) - \hat{\mathbf{S}}(\hat{\mathbf{L}} \cdot \hat{\mathbf{J}}) \stackrel{\hat{\mathbf{L}}=\hat{\mathbf{J}}-\hat{\mathbf{S}}}{=} \hat{\mathbf{J}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) - \hat{\mathbf{S}}\hat{\mathbf{J}}^2$$

- 5 Therefore, it follows that $\langle \hat{\mathbf{S}}\hat{\mathbf{J}}^2 \rangle = \langle \hat{\mathbf{J}}(\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}) \rangle$. With $\hat{\mathbf{S}} \cdot \hat{\mathbf{J}} = \frac{1}{2}(\hat{\mathbf{J}}^2 + \hat{\mathbf{S}}^2 - \hat{\mathbf{L}}^2)$, we have $\langle \hat{S}_z \rangle \langle \hat{\mathbf{J}}^2 \rangle = \langle \hat{J}_z \rangle \langle \hat{\mathbf{S}} \cdot \hat{\mathbf{J}} \rangle$, i.e.

$$\langle \hat{S}_z \rangle = \langle \hat{J}_z \rangle \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Zeeman effect: revisited

$$\langle \hat{S}_z \rangle = \langle \hat{J}_z \rangle \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

- As a result, we can deduce that, at first order in perturbation theory, the energy shift arising from the Zeeman term is given by

$$\Delta E_{J,M_J,L,S} = \mu_B B \langle (\hat{J}_z + \hat{S}_z) \rangle / \hbar = \mu_B g_J M_J B$$

where effective **Landé g-factor**

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

N.B. for hydrogen ($S = 1/2$ and $J = L \pm 1/2$), we recover previous result.

Example: atomic spectra of sodium

$$\Delta E_{J,M_J,L,S} = \mu_B g_J M_J B$$

