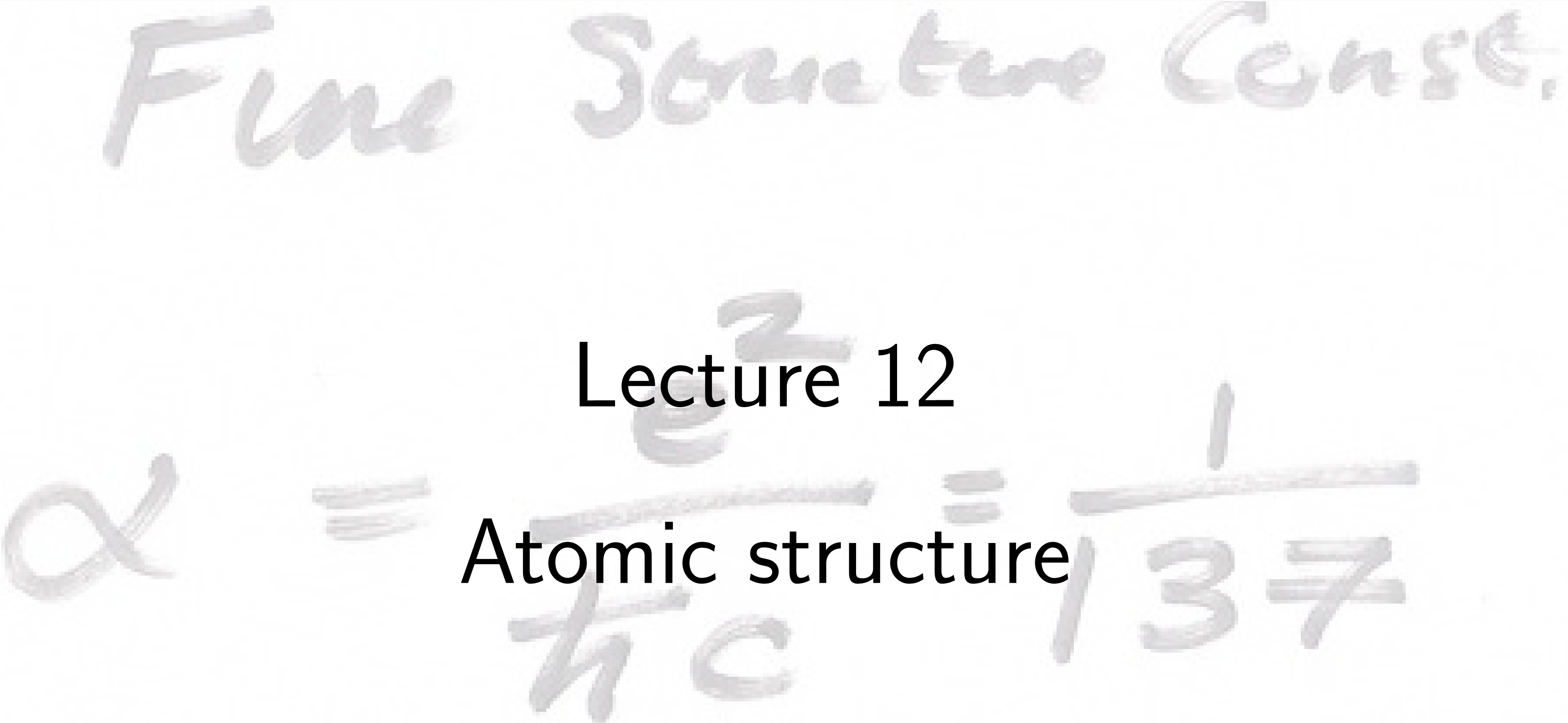

Lecture 12

Atomic structure

Atomic structure: background

- Our studies of atomic hydrogen, and hydrogen-like atoms reveal that the spectrum of the Hamiltonian,

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

  is characterized by large degeneracy with eigenvalues having 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: outline

- Relativistic (fine structure) corrections and spin-orbit coupling
- Signatures of quantum electrodynamics and the Lamb shift
- Nuclear spin and hyperfine structure of atoms

Atomic structure: hydrogen atom revisited

- As with any centrally symmetric potential, stationary solutions of the Schrödinger equation take form $\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)$.
- For atomic hydrogen, n^2-degenerate energy levels set by

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

  where m is reduced mass (ca. electron mass), and $a_0 = \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m}$.
- For higher single-electron ions (He^+, Li^{2+}, etc.), $E_n = -Z^2\frac{\mathrm{Ry}}{n^2}$.
- 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:

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

  is only the leading term in relativistic treatment (**Dirac theory**).
- Such relativistic corrections begin to impact when the electron becomes relativistic, i.e. $v \sim c$.
- With $\mathrm{Ry} = \frac{1}{2}mv^2$ (which follows from virial theorem for Coulomb potential, $2\langle\mathrm{k.e.}\rangle = -\langle p.e.\rangle$), and the identity,

  $$\boxed{Z^2\mathrm{Ry} = \frac{1}{2}mc^2(Z\alpha)^2, \qquad \alpha = \frac{e^2}{4\pi\epsilon_0}\frac{1}{\hbar c} \simeq \frac{1}{137}}$$

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

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The “real” hydrogen atom

- Terms of higher order in $\frac{v}{c} = Z\alpha$ provide relativistic corrections which lead to lifting of the degeneracy.
- Our discussion of these relativistic corrections will provide platform to describe multi-electron atoms.
- Relativistic corrections to spectrum of hydrogen-like atoms (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.

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  (c) and a contribution known as the Darwin term.

(a) Relativistic corrections to kinetic energy

- From the relativistic energy-momentum invariant,

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

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

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

- The relative scale of perturbation

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

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

- Similarly, since $[\hat{H}_1, \hat{L}_z] = 0$,

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

- Therefore, the off-diagonal matrix elements vanish:

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

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- Making use of the identity,

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

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

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

- Using the identities,

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

  resulting energy shift acquires angular momentum dependence:

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

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(b) Spin-orbit coupling

- Spin degree of freedom of the 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:

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

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

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(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,

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

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 derviation need only wait for Dirac formulation...

(b) Spin-orbit coupling

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

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

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- 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,

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

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

$$\boxed{\langle H_2\rangle_{n,j=\ell\pm1/2,m_j,\ell} = \frac{1}{2m^2c^2}\frac{\hbar^2}{2}\begin{pmatrix} \ell \\ -\ell - 1 \end{pmatrix}\frac{Ze^2}{4\pi\epsilon_0}\left\langle\frac{1}{r^3}\right\rangle_{n\ell}}$$

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

$$\boxed{\langle\hat{H}_2\rangle_{n,j=\ell\pm1/2,m_j,\ell} = \frac{1}{4}mc^2\left(\frac{Z\alpha}{n}\right)^4\frac{n}{j+1/2}\begin{cases}\frac{1}{j} & j=\ell+1/2 \\ -\frac{1}{j+1} & j=\ell-1/2\end{cases}}$$

- Rewriting expression for $\langle\hat{H}_1\rangle$ in new basis $|n,j=\ell\pm1/2,m_j,\ell\rangle$,

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

$$\boxed{\langle\hat{H}_1+\hat{H}_2\rangle_{n,j=\ell\pm1/2,m_j,\ell} = \frac{1}{2}mc^2\frac{(Z\alpha)^4}{n^4}\left(\frac{3}{4}-\frac{n}{j+1/2}\right)}$$

while for $\ell = 0$, we retain just $\langle\hat{H}_1\rangle$

(c) Darwin term

- Final contribution from relativistic effects arises from "Zwitterbewegung" of electron – giggling – which smears effective potential felt by electron,

$$\boxed{\hat{H}_3 = \frac{\hbar^2}{8m^2c^2}\nabla^2 V = -\frac{\hbar^2}{8m^2c^2}(4\pi e Q_{\rm nuclear}) = \frac{\pi\hbar^2 Ze^2}{2m^2c^2}\delta^{(3)}(\mathbf{r})}$$

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

$$\langle \hat{H}_3\rangle_{njm_j\ell} = \frac{\pi\hbar^2 Ze^2}{2m^2c^2}|\psi_{\ell n}(0)|^2 = \frac{mc^2(Z\alpha)^4}{2n^3}\delta_{\ell,0}$$

- 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,

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

independent of ℓ and m_j.

(c) Darwin term

- Final contribution from relativistic effects arises from "Zwitterbewegung" of electron – giggling – which smears effective potential felt by electron,

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

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

$$\langle \hat{H}_3 \rangle_{njm_j\ell} = \frac{\pi\hbar^2 Ze^2}{2m^2c^2}|\psi_{\ell n}(0)|^2 = \frac{mc^2(Z\alpha)^4}{2n^3}\delta_{\ell,0}$$

- 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,

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

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,

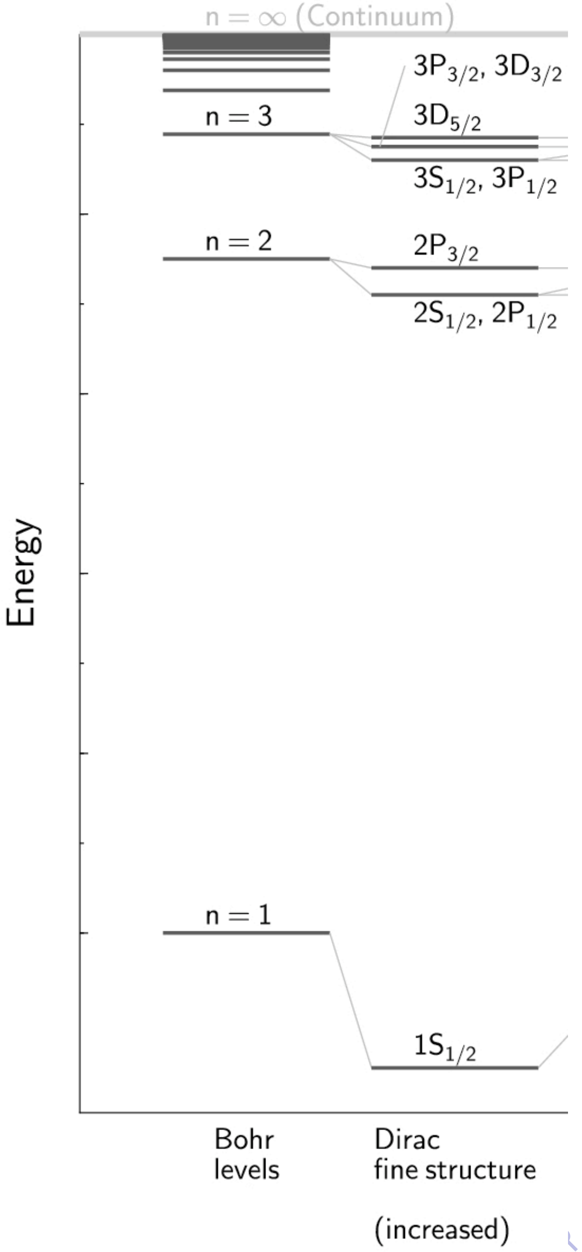
$$\boxed{n\,{}^{2s+1}L_j}$$

- 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

$$\boxed{\Delta E_{n,j=\ell\pm1/2,m_j,\ell} = \frac{1}{2}mc^2\left(\frac{\alpha Z}{n}\right)^4\left(\frac{3}{4}-\frac{n}{j+1/2}\right)}$$

- 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 $m_j=\pm1/2$, experience negative energy shift of $-\frac{1}{4}Z^4\alpha^2\,\mathrm{Ry}$.
- For $n=2$, $\ell=0,1$: With $j=1/2$, both $2S_{1/2}$ and $2P_{1/2}$ states have shift, $-\frac{5}{64}Z^4\alpha^2\,\mathrm{Ry}$, while $2P_{3/2}$ experiences a shift $-\frac{1}{64}Z^4\alpha^2\,\mathrm{Ry}$.



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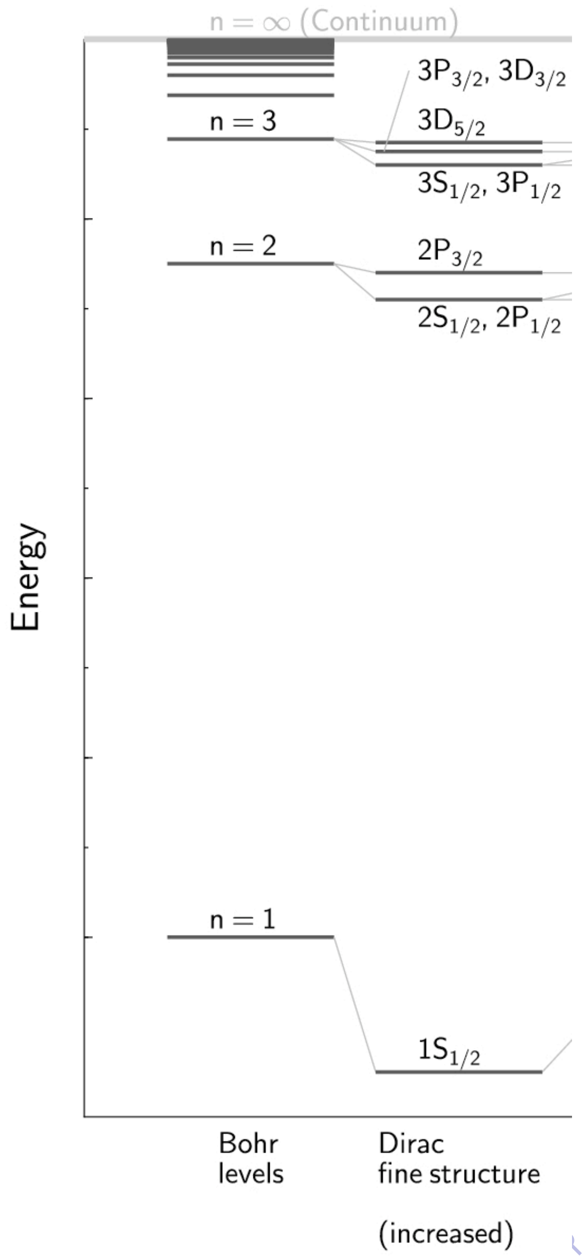

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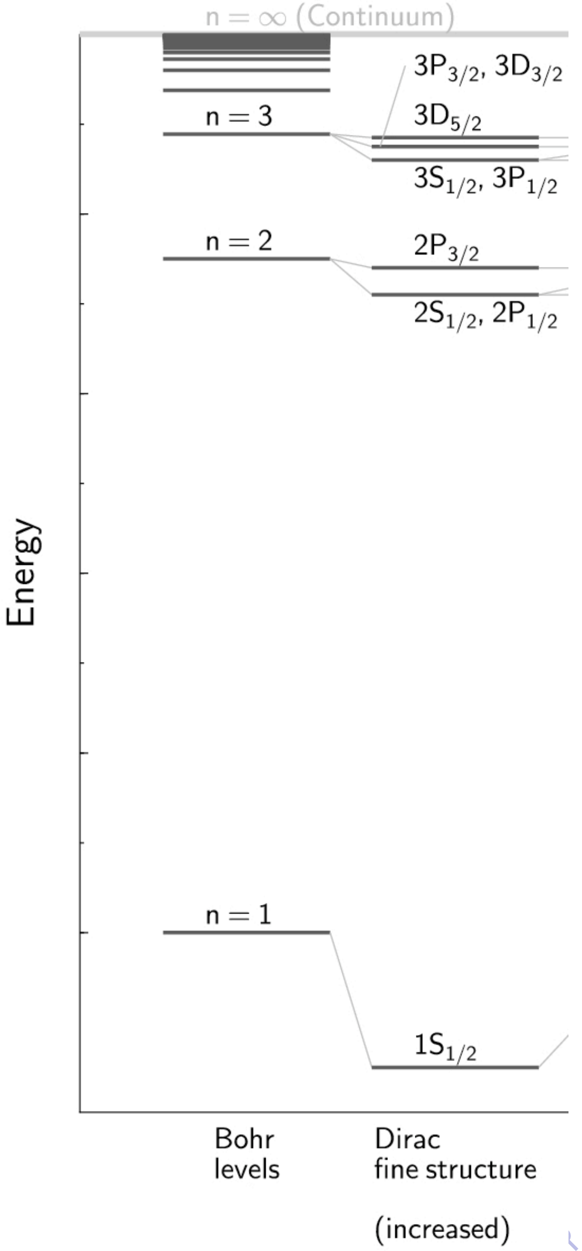
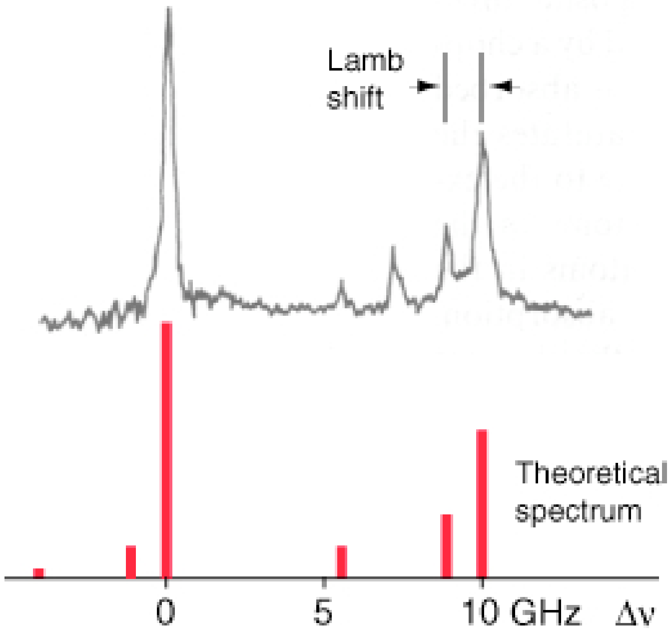


(Further) relativistic corrections: Lamb shift

- 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” ⇝ effective smearing of electron position,

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

- 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 $2s$ electron to be slightly higher in energy than the $2P_{1/2}$ electron.

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

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Hyperfine structure

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

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

  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, its gyromagnetic ratio is about $g_n \approx -3.83$.
- The magnetic moment generates a vector potential $\mathbf{A} = -\mathbf{M} \times \nabla(1/r)$ and a magnetic field

$$\boxed{\mathbf{B} = \nabla \times \mathbf{A} = -\left(\mathbf{M}\nabla^2 \frac{1}{r} - \nabla(\mathbf{M} \cdot \nabla)\frac{1}{r}\right)}$$

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- To explore the effect of field, consider for simplicity just s-electrons, i.e. $\ell = 0$.

  In this case, interaction of magnetic moment of electrons with field gives rise to hyperfine interaction,

  $$\hat{H}_{\mathrm{hyp}} = -\frac{e}{mc}\hat{\mathbf{S}}\cdot\mathbf{B}$$

- Making use of the identity, $\nabla^2(1/r) = \delta^{(3)}(\mathbf{r})$ and

  $$\int d^3r \left[\nabla(\mathbf{I}\cdot\nabla)\frac{1}{r}\right] |\psi_{n,0}(r)|^2 = \frac{\mathbf{I}}{3}\int d^3r \left(\nabla^2 \frac{1}{r}\right) |\psi_{n,0}(r)|^2 = \frac{\mathbf{I}}{3}|\psi_{n,0}(0)|^2$$

  to first order in perturbation theory

$$\boxed{\langle H_{\mathrm{hyp}}\rangle_{n,1/2,0} = \left(\frac{Z}{n}\right)^4 n\alpha^2\,\mathrm{Ry} \times \frac{8}{3} g_N \frac{m}{M_N}\frac{1}{\hbar^2}\mathbf{S}\cdot\mathbf{I}}$$

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- As with spin-orbit interaction, convenient to define the total spin $\mathbf{F} = \mathbf{I} + \mathbf{S}$,

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

Summary: atomic structure

- In non-relativistic quantum mechanics, the hydrogen atom is characterized by an n^2-fold degeneracy of states.
- Relativistic corrections lead to perturbations that split this degeneracy.
- Although (as we will see) all three key contributions emerge from a single consistent theory (due to Dirac), their physical origin can be ascribed to three sources:
  - **(a)** Relativistic corrections to the kinetic energy.
  - **(b)** Coupling between the spin and orbital degrees of freedom.
  - **(c)** Darwin contribution from the giggling of the electron.

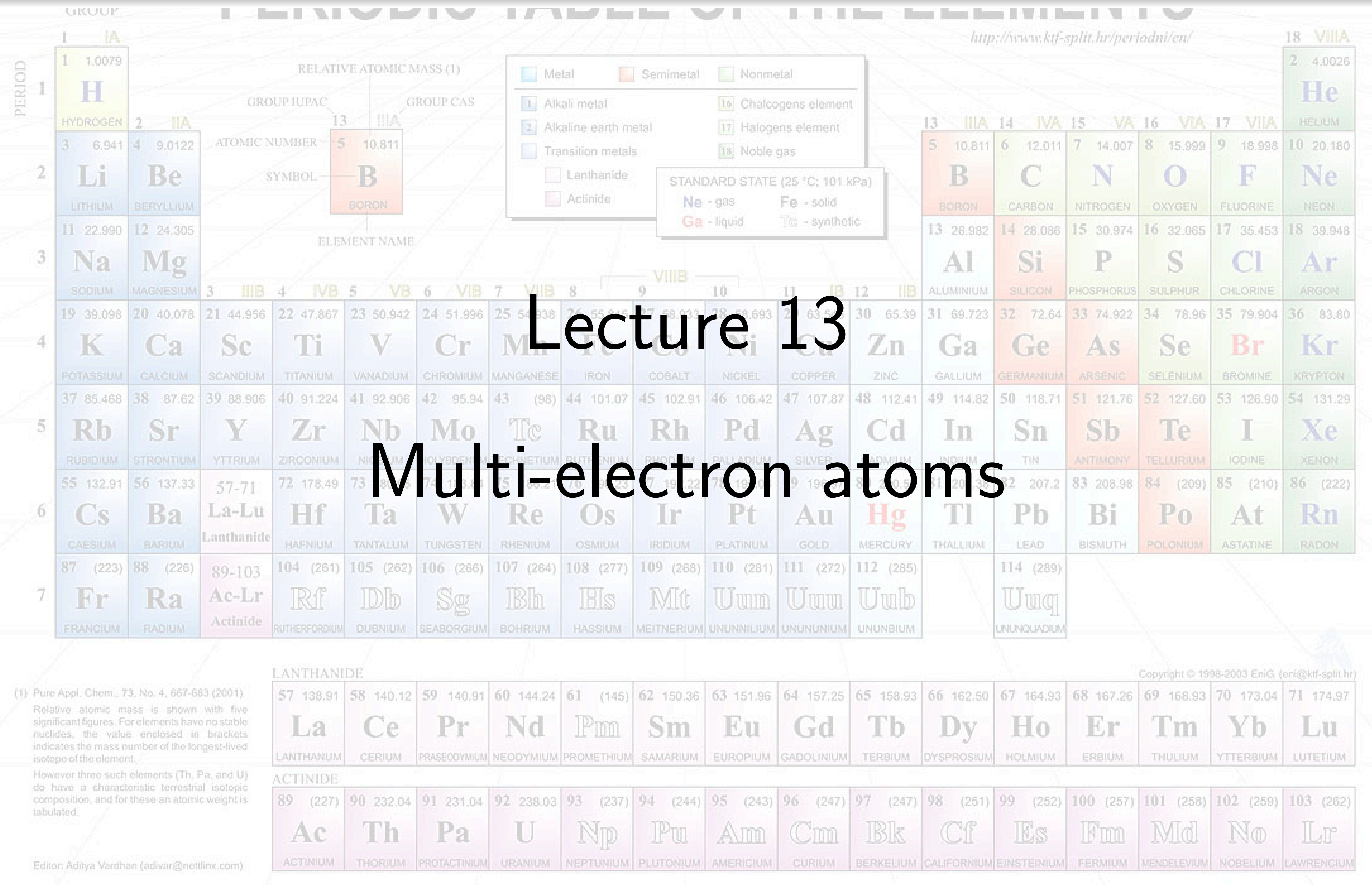
Summary: atomic structure

- Altogether, these contributions lead to a perturbative shift of the energy,

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

- Further spectroscopic corrections provide insight into quantum electrodynamics – Lamb shift.

- Finally, the spin degrees of freedom of the nucleus lead to further spin-orbit contributions which perturb the levels – hyperfine interactions.



Lecture 13

Multi-electron atoms

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.

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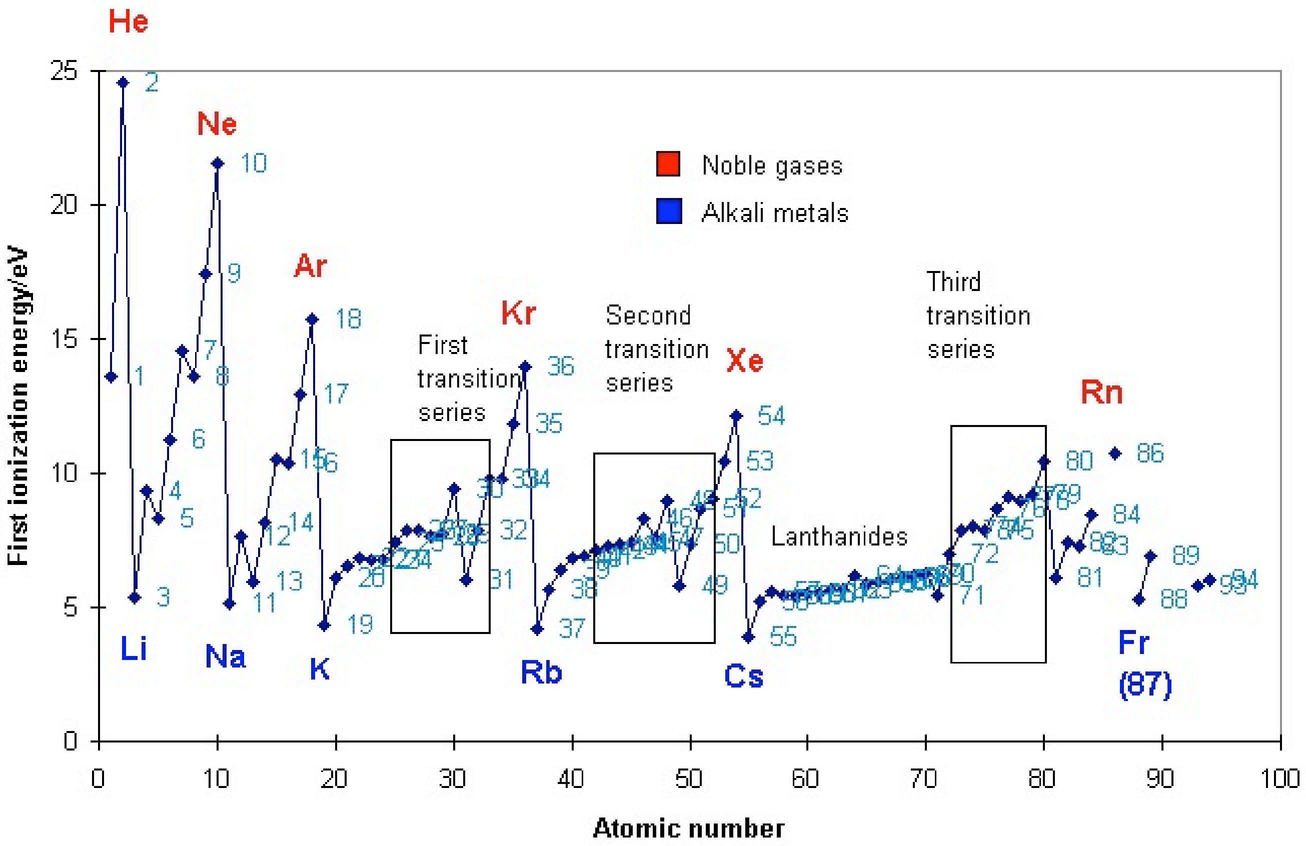
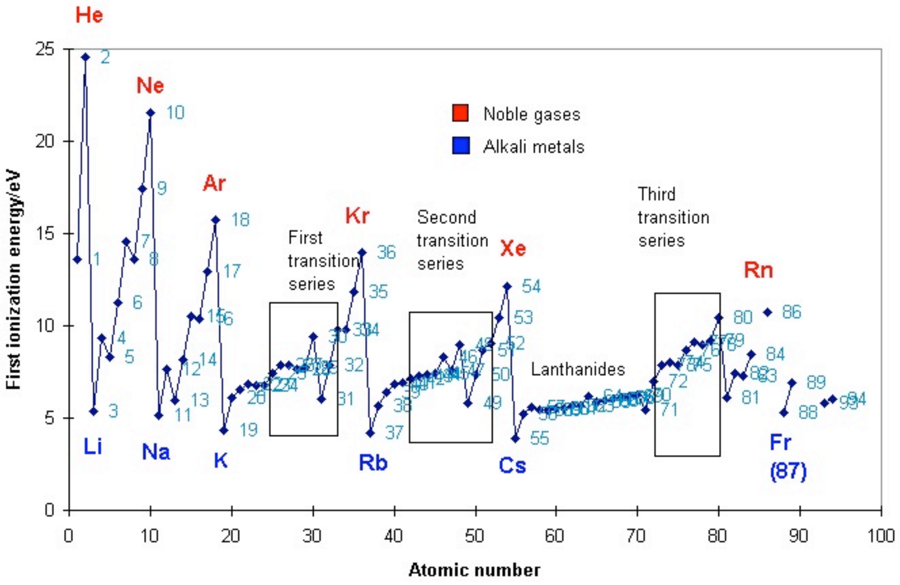
Background: ionization energies of elements



- Instead, find noble gases ($Z = 2, 10, 18, 36 \cdots$) 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

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

  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!).

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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

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

  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.

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- 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.
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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.

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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,

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

  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

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

- 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,

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

Self-consistent field method

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

- 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,

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

Self-consistent field method

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

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$$=\varepsilon_i\psi_i(\mathbf{r})$$

- 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, $U_i(r)=\int\frac{d\Omega}{4\pi}U_i(\mathbf{r})$.

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- From this result, we therefore find that

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

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Self-consistent field method

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

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

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

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- Once U_is are found, perturbation theory can be applied to

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Hartree method

Operationally, the Hartree method involves:

1. Intital guess for $U(r)$ – e.g. smooth function which interpolates between unscreened potential, $U(r) = 0$, as $r \to 0$ and $U(r) = \frac{1}{4\pi\epsilon_0}\frac{(Z-1)e^2}{r}$ as $r \to \infty$. Solution for this potential provides platform to seed self-consistent potentials, $U_i(r)$.
2. With these potentials, $U_i(r)$, determine new set of eigenstates for,
$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} + U_i(r)\right]\psi_i = \varepsilon_i\psi_i\,.$$
3. Estimate for ground state energy of atom found by filling levels, starting from lowest, and taking account of exclusion principle.
4. With revised $\psi_i(\mathbf{r})$, one can then make an improved estimate of $U_i(r_i)$ and return to step 2 iterating until convergence.

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Hartree-Fock method

- An improvement on this procedure can be developed which takes into account exchange interactions.
- This is achieved by introducting 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 $i = 1, 2 \cdots N$, denotes the single-particle wavefunction for electron i, and k is shorthand for the set of quantum numbers $(n\ell m_\ell m_s)$.

- The antisymmetry of the determinant ensures that the electrons obey fermi statistics.

Hartree-Fock method

- In this approximation, a variational analysis leads to the **Hartree-Fock equations**,

$$\varepsilon_i \psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{4\pi\epsilon r_i} \right] \psi_i(\mathbf{r})$$

$$+ \sum_{j\neq i} \int d^3 r_j \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \psi_j^*(\mathbf{r}') \left[\psi_j(\mathbf{r}')\psi_i(\mathbf{r}) - \psi_j(\mathbf{r})\psi_i(\mathbf{r}')\delta_{m_{s_i},m_{s_j}} \right]$$

- The first term translates to Hartree contribution and describes the influence of the charge density of the other electrons.
- The second term describes the non-local **exchange** contribution, a manifestation of particle statistics.

Central field approximation: conclusions

- Hartree-Fock calculations show eigenfunctions characterized by quantum numbers $n\ell m_\ell m_s$, with $\ell < n$, but states with different ℓ for given n non-degenerate; lower values of ℓ lie lower due to screening.
- 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	$1s$	$2s$	$2p$	$3s$	$3p$	$4s$	$3d$	$4p$	$5s$	$4d$	$\cdots$
$n =$	1	2	2	3	3	4	3	4	5	4	$\cdots$
$\ell =$	0	0	1	0	1	0	2	1	0	2	$\cdots$
Degeneracy	2	2	6	2	6	2	10	6	2	10	$\cdots$
Cumulative	2	4	10	12	18	20	30	36	38	48	$\cdots$

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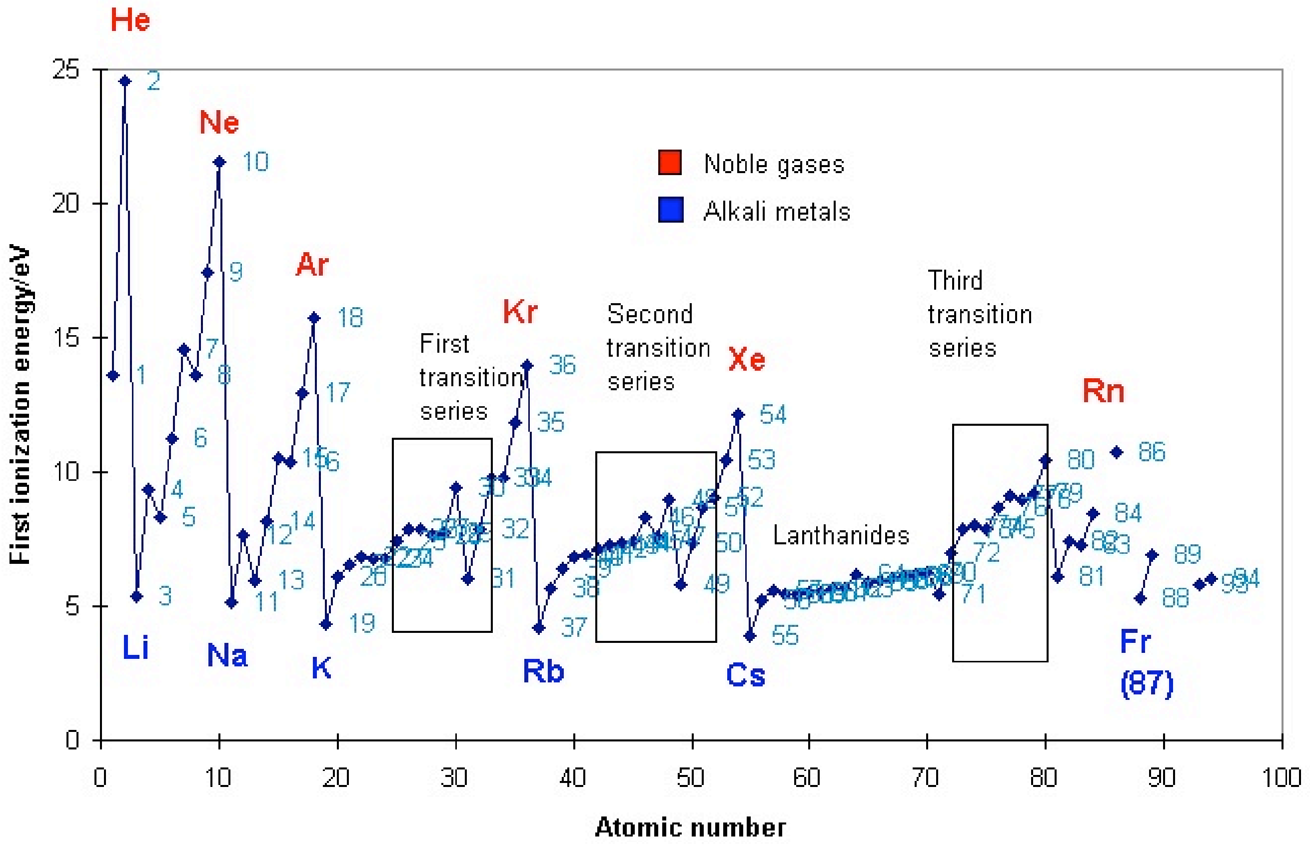

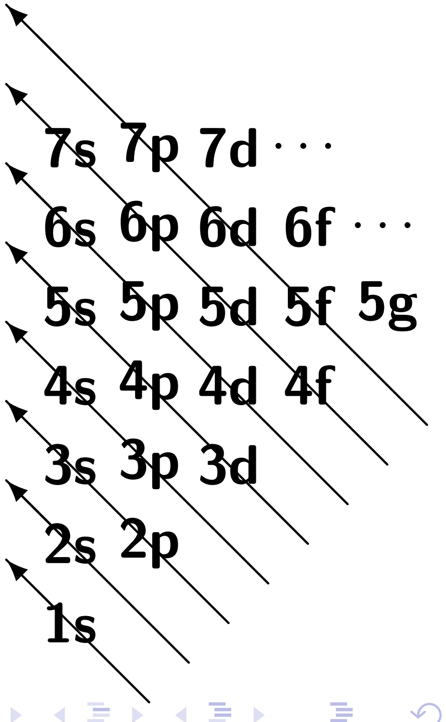
7s 7p 7d $\cdots$

6s 6p 6d 6f $\cdots$

5s 5p 5d 5f 5g

4s 4p 4d 4f

3s 3p 3d

2s 2p

1s

Periodic table

- We can use energy sequence to predict ground state electron configuration – fill levels accounting for exclusion **aufbau principle**.

Z	Element	Configuration	$^{2S+1}L_J$	Ioniz. Pot. (eV)
1	H	$(1s)$	$^2S_{1/2}$	13.6
2	He	$(1s)^2$	$^1S_0$	24.6
3	Li	He $(2s)$	$^2S_{1/2}$	5.4
4	Be	He $(2s)^2$	$^1S_0$	9.3
5	B	He $(2s)^2(2p)$	$^2P_{1/2}$	8.3
6	C	He $(2s)^2(2p)^2$	$^3P_0$	11.3
7	N	He $(2s)^2(2p)^3$	$^4S_{3/2}$	14.5
8	O	He $(2s)^2(2p)^4$	$^3P_2$	13.6
9	F	He $(2s)^2(2p)^5$	$^2P_{3/2}$	17.4
10	Ne	He $(2s)^2(2p)^6$	$^1S_0$	21.6
11	Na	Ne $(3s)$	$^2S_{1/2}$	5.1

- Sadly, there are exceptions to rule: e.g. Cu ($Z = 29$) expected to have configuration $\cdots (4s)^2(3d)^9$, actually has $\cdots (4s)^1(3d)^{10}$.

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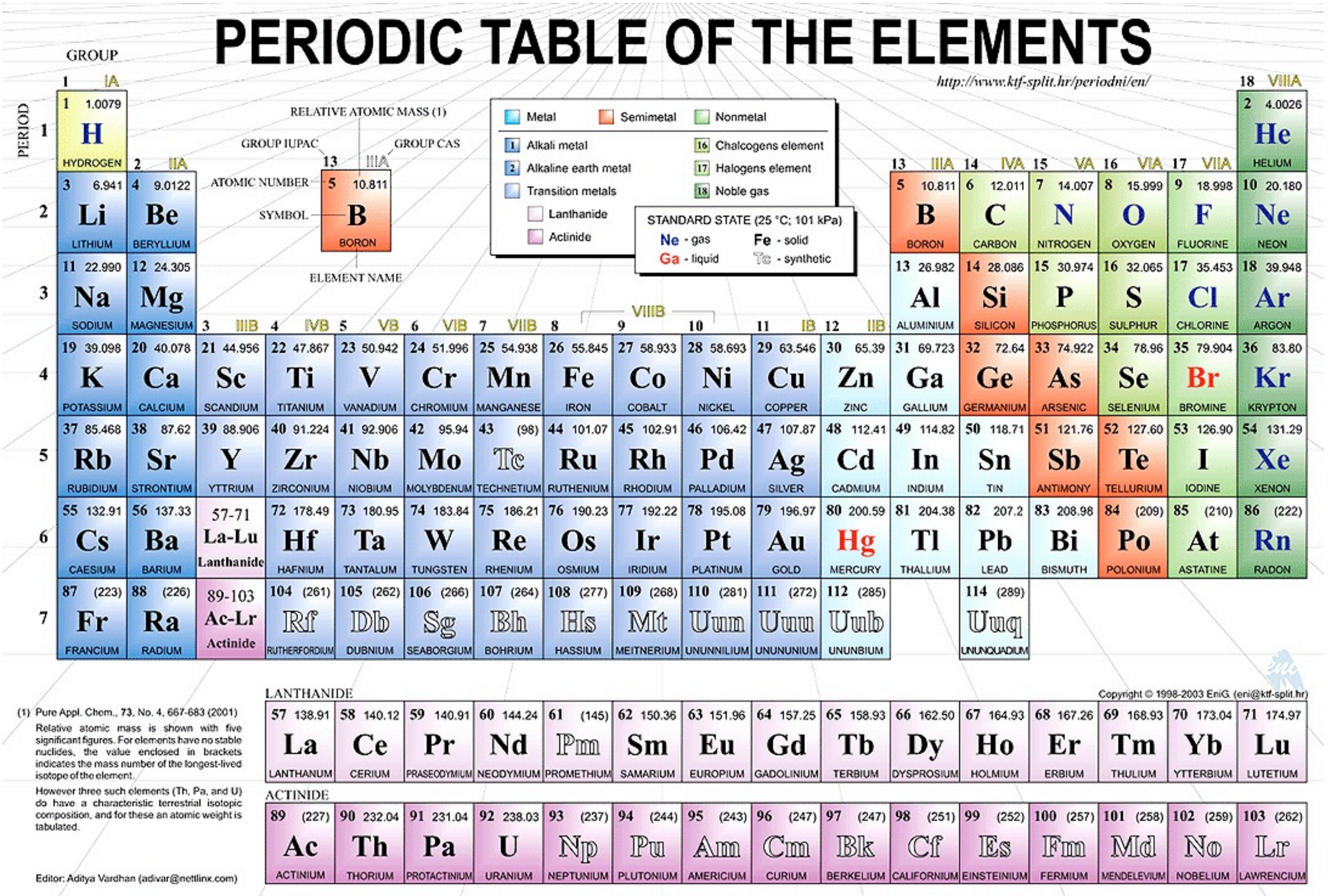
Periodic table

- 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/

GROUP

RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
13 IIIA
ATOMIC NUMBER 5
10.811
SYMBOL B
BORON
ELEMENT NAME

🟦 Metal 🟥 Semimetal 🟩 Nonmetal
1 Alkali metal
2 Alkaline earth metal
Transition metals
Lanthanide
Actinide
16 Chalcogens element
17 Halogens element
18 Noble gas

STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Ga - liquid
Fe - solid
Tc - synthetic

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
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 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 UNUNNILIUM	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 YTTERBIUM	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

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have 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.

Editor: Aditya Vardhan (adivar@netlinx.com)

Coupling schemes

- The aufbau principle allows prediction of the occupation of subshells in atomic ground state – but does not specify spins and orbital angular momenta of subshells.
- To deal with this problem, necessary to consider spin-orbit interaction 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

- The aufbau principle allows prediction of the occupation of subshells in atomic ground state – but does not specify spins and orbital angular momenta of subshells.
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- Their ordering in energy given by an empirical set of rules known as **Hund's rules**.

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   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).

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

   Separation of energies for states of different J arises from treating spin-orbit term $\hat{H}_2$ as a perturbation (fine structure),

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

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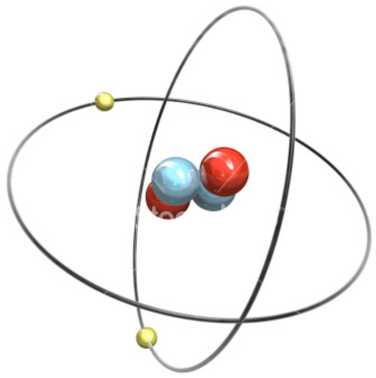
LS coupling – Example: helium



- 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 $J = 0$, since the total m_L and m_S must equal zero if all substates are occupied.

- For excited state of helium, e.g. $(1s)^1(2p)^1$, can now have $S = 1$ or $S = 0$, with the $S = 1$ state lying lower in energy according to Hund's rules.

- Combining orbital angular momenta gives $L = 1$ and thus, with $S = 0$, $J = 1$, while with $S = 1$, $J = 0, 1, 2$ with $J = 0$ lying lowest in energy.

- In spectroscopic notation ${}^{2S+1}L_J$, for the $(1s)^1(2p)^1$ state of helium, there are four possible states, ${}^3P_0$ ${}^3P_1$ ${}^3P_2$ and ${}^1P_1$ where the three ^{3}P states separated by spin-orbit interaction, and the singlet ^{1}P state lies much higher in energy owing to the Coulomb interaction.

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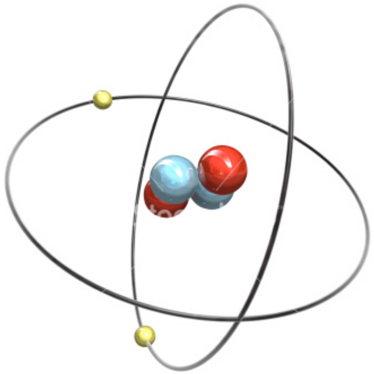

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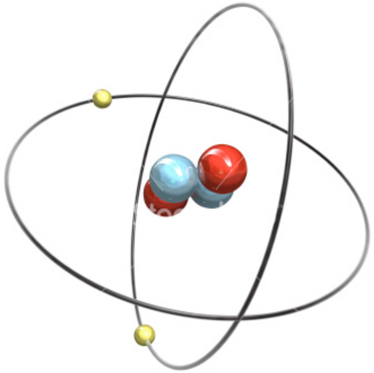

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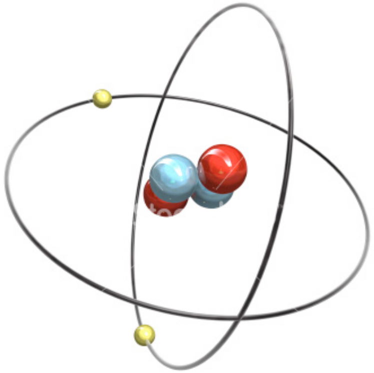

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Landé interval rule

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

$$\langle |J, m_J, L, S| \sum_i \xi_i(r_i)\hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i |J, m_J, L, S\rangle$$
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- Separation between pair of adjacent levels in a fine structure multiplet is proportional to the larger of the two J values involved.

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

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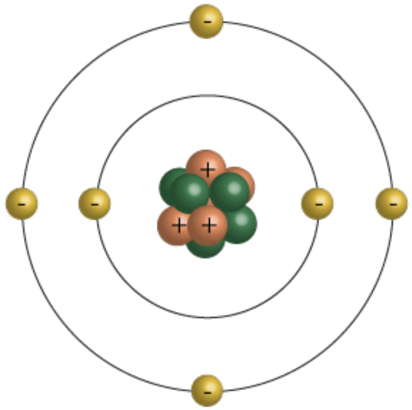

- Carbon has ground state electron configuration $(1s)^2(2s)^2(2p)^2$.
- Since we now have two *identical* electrons in same *unfilled* subshell, need to ensure that wavefunction is antisymmetric.
  - Total spin can either be singlet $S = 0$ state (antisymmetric) or one of the triplet $S = 1$ states (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
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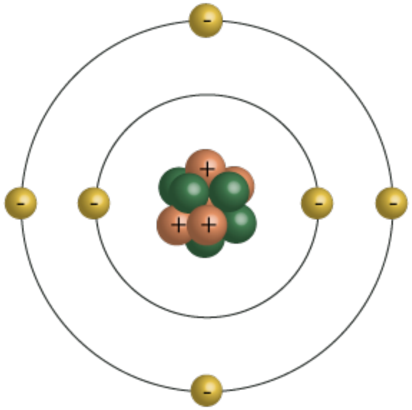

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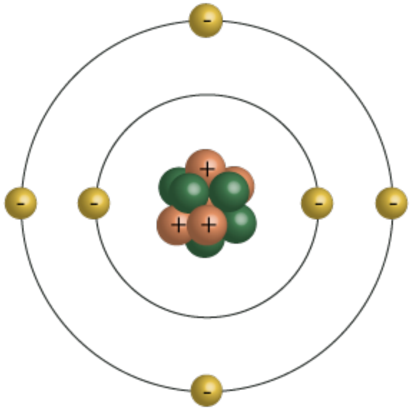

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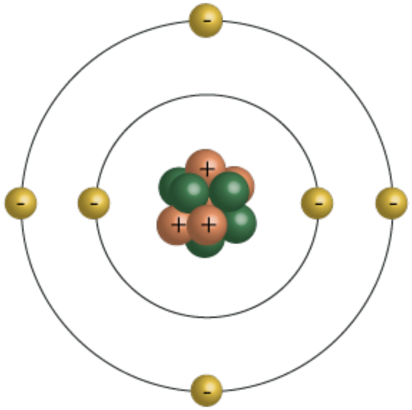

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$m_\ell^{(1)}$	$m_\ell^{(2)}$	m_L
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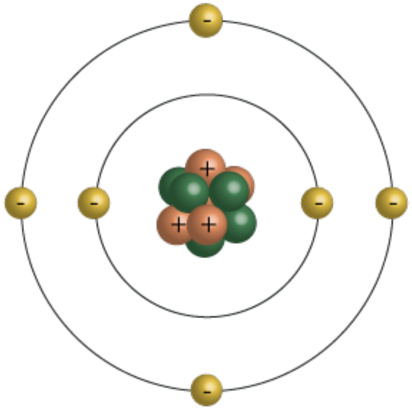

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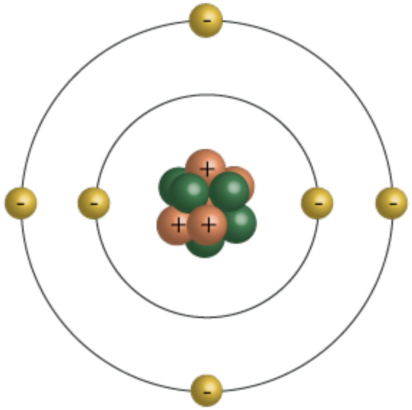

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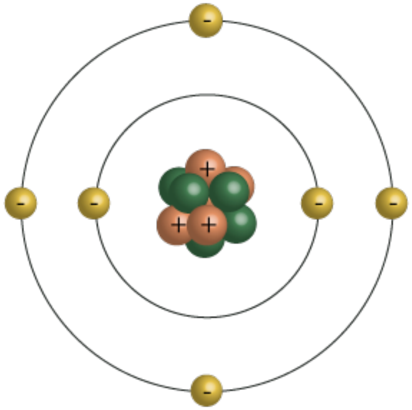

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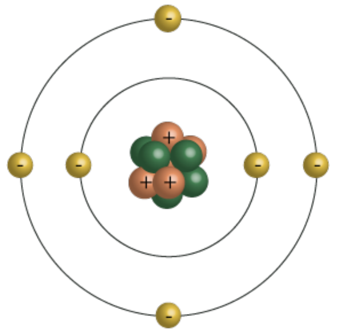
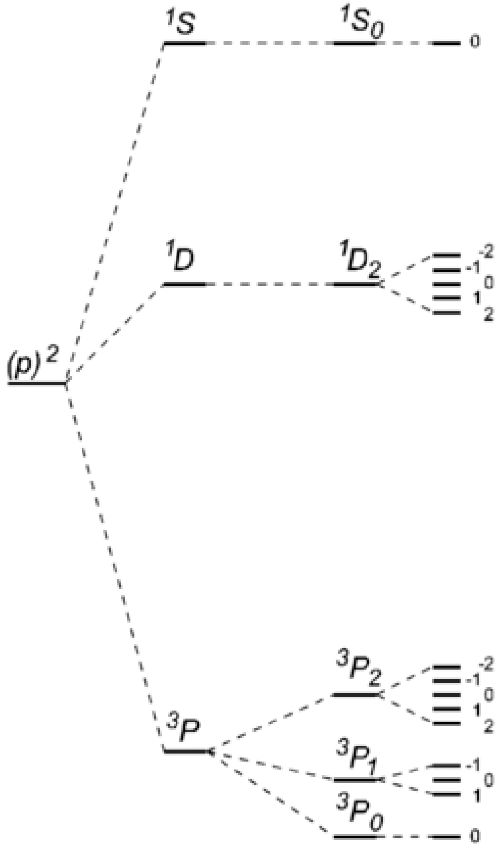


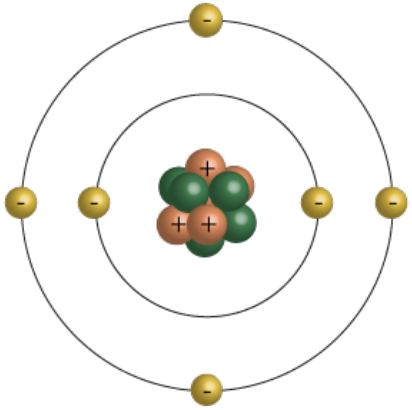
- Energy levels:

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



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

LS coupling – Example: carbon

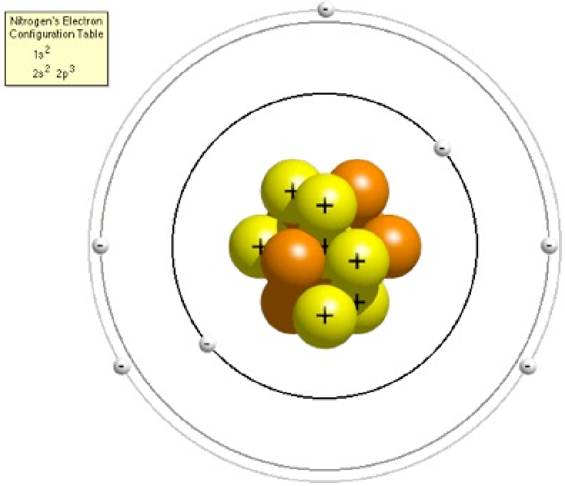


- For the excited states of carbon, e.g. $(2p)^1(3p)^1$, electrons are no longer equivalent, because they have different radial wavefunctions.
- So now one can combine any of $S = 0, 1$ with any of $L = 0, 1, 2$, yielding the following terms (in order of increasing energy, according to Hund's rules):

$$ {}^3\mathrm{D}_{1,2,3} \qquad {}^3\mathrm{P}_{0,1,2} \qquad {}^3\mathrm{S}_1 \qquad {}^1\mathrm{D}_2 \qquad {}^1\mathrm{P}_1 \qquad {}^1\mathrm{S}_0 $$

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

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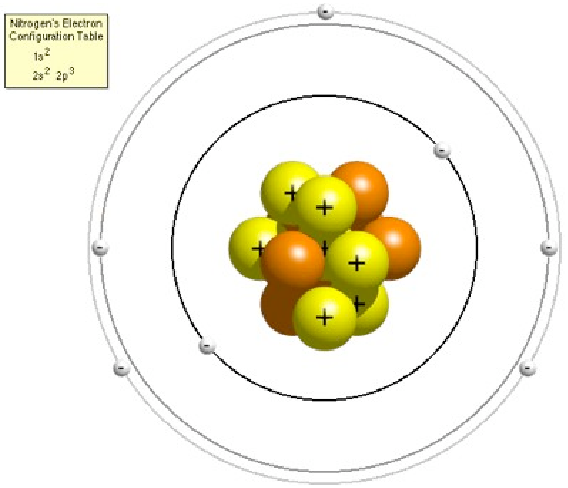

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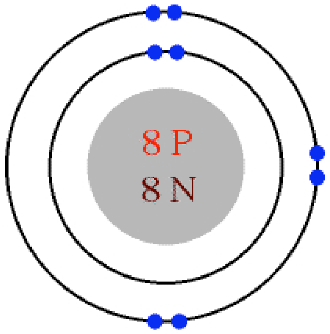
LS coupling – Example: oxygen



- Oxygen has the ground state electron configuration $(2p)^4$.

- Although there are four electrons in $(2p)$ subshell, maximum value of $S = 1$: there are only three available values of $m_\ell = \pm 1, 0$, and therefore one must contain two electrons with opposite spin.
- It follows that the maximum value of $m_S = 1$, achieved by having electrons with $m_s = +\frac{1}{2}$ in both the other m_ℓ states.
- By pursuing this argument, we may see that allowed values of L, S and J are the same as for carbon $(2p)^2$ – in fact this is a general result – allowed quantum numbers for a subshell with n electrons are the same as for that of a subshell with n "holes".
- Therefore, the energy levels for the oxygen ground state configuration are the same as for carbon, except that the fine structure multiplet is inverted, in accordance with Hund's third rule.

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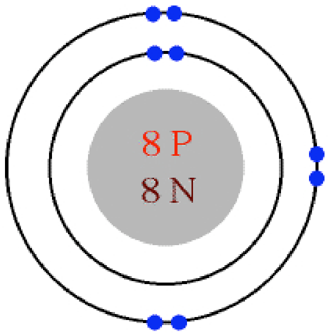

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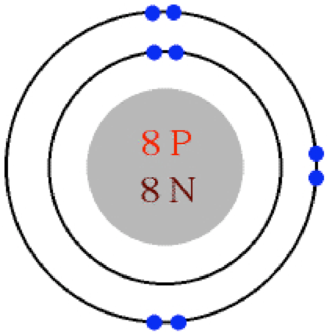

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jj coupling scheme

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

- When relativistic effects dominate over the residual electrostatic interaction, $\hat{H}_1$, (i.e. heavy elements) electrons move independently of each other in a central field, and subject to spin-orbit interaction,

$$\hat{H}_0 + \hat{H}_2 = \hat{H}_0 + \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$$

- In this limit, states are both eigenstates of $\hat{\mathbf{J}}^2$ (as before), because of overall rotational invariance, **and also of $\hat{\mathbf{J}}_i^2$ for each electron**.
- Coupling procedure involves first finding allowed j values of individual electrons, whose energies will be separated by spin-orbit, and then combining them to find allowed values of total J.
- The effect of the residual Coulomb interaction, $\hat{H}_1$, will then be to split the J values for a given set of js.

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- Sadly, in this case, there are no simple rules to parallel Hund's rules.
- In *jj* coupling, energy shifts can be estimated by first treating $\hat{H}_2$ in first order of perturbation theory,

$$\Delta E = \langle n_i\ell_i s_i j_i J m_J | \sum_i \xi(r_i)\hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i | n_i\ell_i s_i j_i J m_J\rangle = \sum_i \Delta E_i$$

where separate energy shifts are independent of total J and M_J

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

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

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jj coupling scheme: Examples

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

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- However, the pattern of levels is different; in LS coupling we found a triplet ($^3\mathrm{P}_0$, $^3\mathrm{P}_1$, and $^3\mathrm{P}_2$) and two singlets ($^1\mathrm{D}_2$ and $^1\mathrm{S}_0$), while in this ideal *jj* scenario, we have two doublets and a singlet.
- The sets of states in the two coupling schemes must be expressible as linear combinations of one another, and the physical states for a real atom are likely to differ from either approximation.
- In fact, this idealized form of *jj* coupling is not seen in the heaviest such atom in the periodic table, lead $(6p)^2$(!)
- But it is seen in highly ionized states, e.g. Cr^{18+} which has same electron configuration as carbon, $(2p)^2$, but where (because of large unscreened charge on nucleus), electrons move more relativistically.

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jj coupling scheme: Examples C-Si-Ge-Sn-Pb

- Classic example of transition from LS to *jj* coupling seen in excited states $(2p)(3s)$, $(3p)(4s), \cdots (6p)(7s)$ in series C-Si-Ge-Sn-Pb.
- Since electrons not in same subshell wavefunctions overlap less and Coulomb repulsion is reduced compared to spin-orbit interaction.
- In LS coupling, expect a triplet and a singlet:

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while in *jj* scheme expect two doublets:

$$\boxed{(1/2, 1/2)_{0,1} \qquad (1/2, 3/2)_{2,1}}$$

- Experimentally, C and Si conform to LS and Pb to *jj*, while Ge and Sn intermediate.

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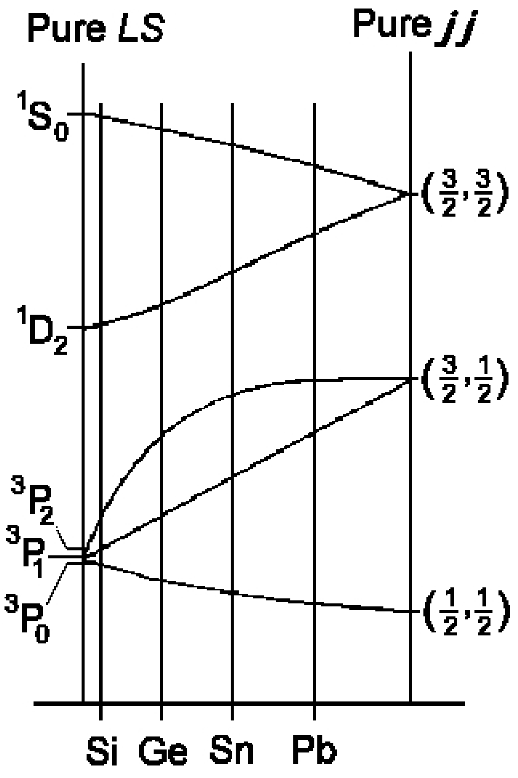

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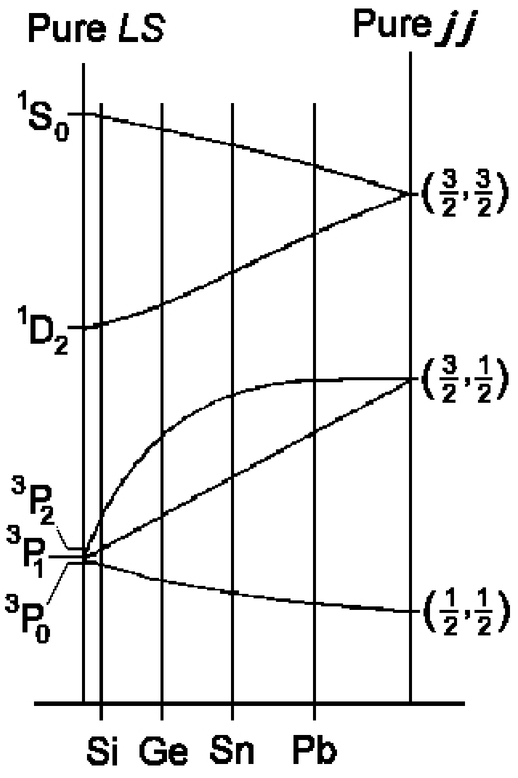
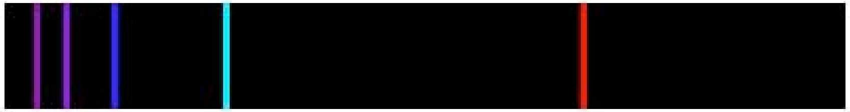
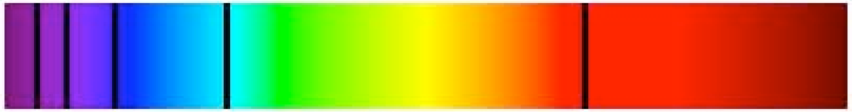


Atomic spectra

- 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, or by electric discharge), 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

The basic theory governing stimulated emission and absorption, and spontaneous emission of photons will be outlined in detail when we study radiative transitions. Here we anticipate some conclusions of this study.

- In **electric dipole approximation**, rate of transitions is proportional to the square of matrix element of electric dipole operator,

$$\boxed{|\langle\psi_{\rm f}|\hat{\mathbf{d}}|\psi_{\rm i}\rangle|^2}$$

- In addition, the rate of spontaneous transitions is proportional to ω^3, where $\omega = |E_{\rm f} - E_{\rm i}|$.
- The form of the dipole operator, $\hat{\mathbf{d}}$ means that some matrix elements vanish $\implies$ **selection rules**

Atomic spectra: selection rules

- For a transition to take place:
  - **(a)** Parity must change
  - **(b)** $\Delta J = \pm 1,\ 0$ (but $0 \rightarrow 0$ is not allowed) and $\Delta M_J = \pm 1,\ 0$
- Atomic states are always eigenstates of parity and of total angular momentum, $\hat{\mathbf{J}}^2$, so these selection rules can be regarded as absolutely valid in electric dipole transitions.
- It should be emphasized that the electric dipole approximation is an approximation, and higher order processes may occur, albeit at a slower rate, and have their own selection rules.

Atomic spectra: selection rules

- In specific coupling schemes, further selection rules apply. In the case of ideal LS coupling, we also require:
  - **(a)** $\Delta S = 0$ and $\Delta M_S = 0$
  - **(b)** $\Delta L = \pm 1,\ 0$ (but $0 \to 0$ is not allowed) and $\Delta M_L = \pm 1,\ 0$
  - **(c)** and $\Delta \ell_i = \pm 1$ if only electron i is involved in the transition
- In LS coupling, the states are eigenstates of total spin; since the dipole operator does not operate on the spin part of the wavefunction, the rules on ΔS and ΔM_S follow straightforwardly.
- This, and absolute rules relating to J, imply rules for L and M_L.
- The rule for $\Delta \ell_i$ follows from the parity change rule, since the parity of the atom is the product of the parities of the separate electron wavefunctions, given by $(-1)^{\ell_i}$.
- However, since LS coupling is only an approximation, these rules should themselves be regarded as approximate.

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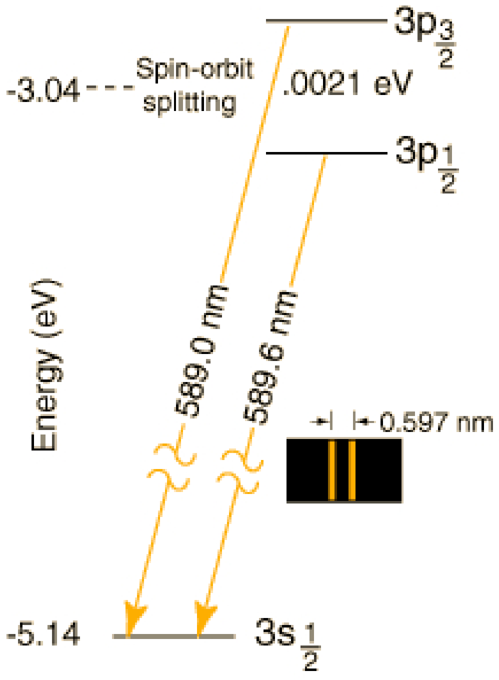
Atomic spectra: single electron atoms

- For “single electron atoms”, ground state consists of single electron in an s level, e.g. **alkali metals** such as sodium, and also hydrogen.
- For **sodium**, ground state configuration is $(3s)^1$:

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 is given by $(-1)^\ell$, allowed transitions involve $\Delta\ell = \pm 1$, i.e. $s \leftrightarrow p$, $p \leftrightarrow d$, etc. (Larger changes in ℓ contradict ΔJ rule.)

The $s \leftrightarrow p$ transitions are all doublets. Transition $3s \leftrightarrow 3p$ gives rise to the familiar yellow sodium “D-lines” at 589 nm.



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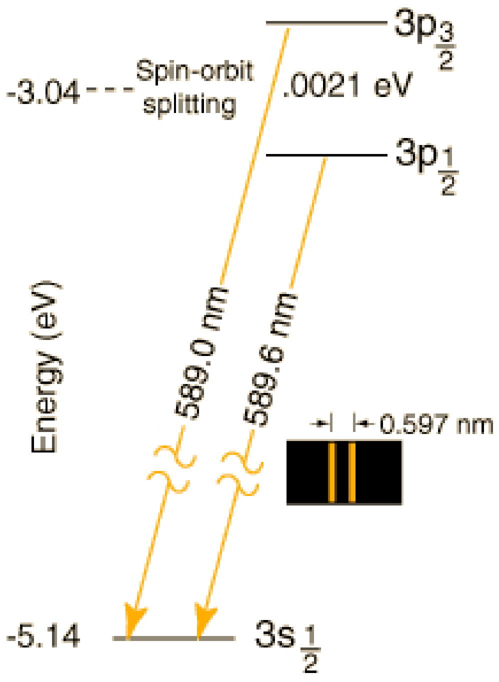

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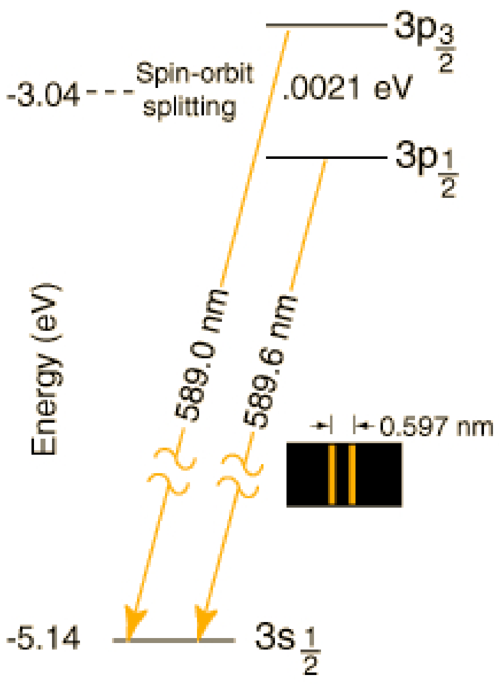

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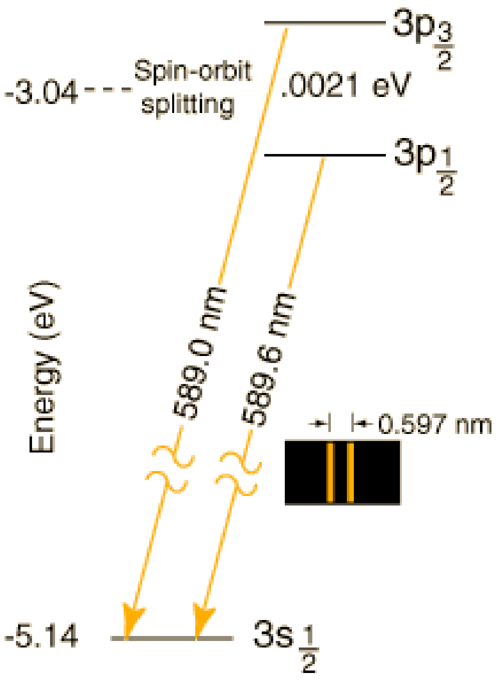

Atomic spectra: single electron atoms

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

Atomic spectra: helium

Consider now spectra of helium which has two electrons in an s level.

- The ground state has term $^1\mathrm{S}_0$. Low-lying excited states of form $(1s)(n\ell)$ (since energy required to excite both of electrons greater than first ionization energy). Excited states can have $S = 0$ or $S = 1$, with $S = 1$ lying lower in energy (Hund).
- The LS coupling approximation is sound for helium, so $\Delta S = 0$ selection rule implies that $S = 0$ and $S = 1$ states independent:
- Lines in $S = 0$ system all singlets and can be observed in emission, and those starting from the ground state in absorption. Lines in $S = 1$ system all multiplets: observed in emission only.
- Transitions of the form $^3\mathrm{S}_1 \leftrightarrow {}^3\mathrm{P}_{2,1,0}$ are observed as triplets, spaced according to the Landé interval rule.
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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, $\hat{H} = \hat{H}_0 + \hat{H}_{\rm rel.} + \hat{H}_{\rm Zeeman}$, where

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

  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 $\hat{H}_{\rm rel.}$ or the Zeeman term may dominate the spectrum of the atom.

Zeeman effect: revisited

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

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

  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 element of $\hat{H}_{\mathrm{Zeeman}}$ vanishes – avoids need for degenerate perturbation theory.

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

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

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

  $$\boxed{\Delta E^{\text{Zeeman}}_{j=\ell\pm1,m_j,\ell} = \ell \pm 1/2, m_j, \ell\rangle = \mu_{\text{B}} B m_j \left(1 \pm \frac{1}{2\ell + 1}\right)}$$

  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

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

- For a 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 $\langle\hat{S}_z\rangle$, a useful revision of the quantum mechanics of 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, $|J, M_J, L, S\rangle$.
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- As a result, we can deduce that, at first order in perturbation theory, the energy shift arising from the Zeeman term is given by

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

where effective **Landé g-factor**

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

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

Example: atomic spectra of sodium