# Atomic structure and spectra

2F4Y

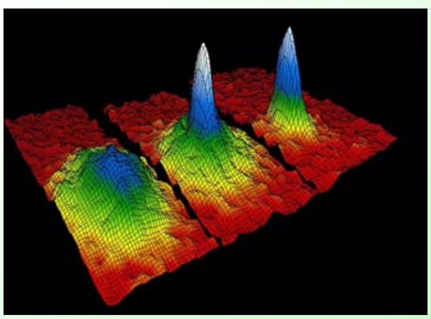
## Atomic Structure and Spectra

**Why?**
- Teaching
- Bose - Einstein condensate
- Timekeeping
- Thermometer
- Molecular spectra

**How?**
- Remind ourselves of relevant information
- Develop a qualitative understanding of effects which influence spectra

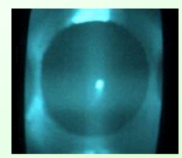


## Bose-Einstein condensate



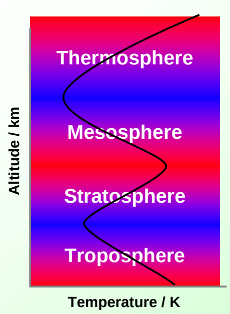


## Timekeeping



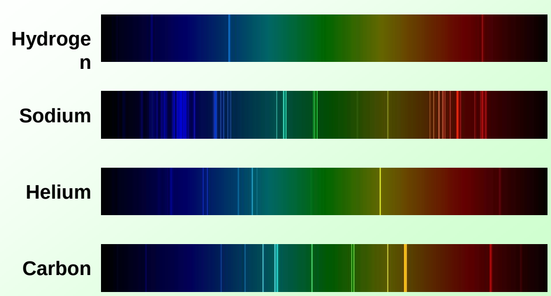


## Thermometer






## Atomic spectra



## What do we know already? (1)

- Hydrogen atom
  - Lyman, Balmer, Paschen, Brackett

$$\Re_{\mathrm{H}} = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c} \qquad \mu = \frac{m_e m_p}{\left(m_e + m_p\right)}$$

$$E_n = -\frac{1}{n^2} hc\Re \qquad \Re_\infty = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} = 109,737.31\,\mathrm{cm}^{-1}$$

$$\Re_{\mathrm{H}} = \Re_\infty \Big/ \left(1 + m_e / m_p\right)$$

- Bohr model



## What do we know already? (2)

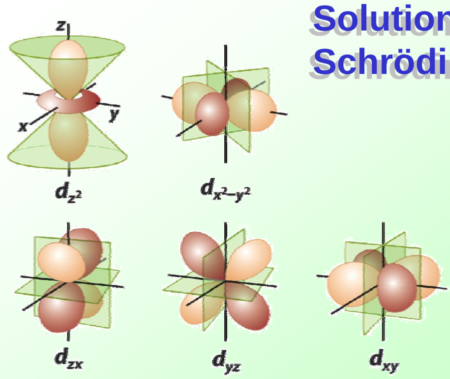
- One electron solutions to the Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

- The angular parts



## Solutions to Schrödinger

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## What do we know already? (2)

- One electron solutions to the Schrödinger equation

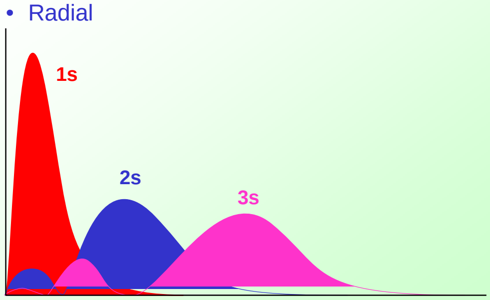
$$\hat{H}\Psi = E\Psi$$

- The angular parts
  - … are the familiar pictures of orbitals we know (and love).
- The radial parts
  - … less familiar



## The one electron wavefunctions

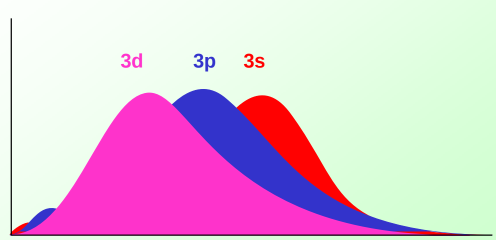
- Radial





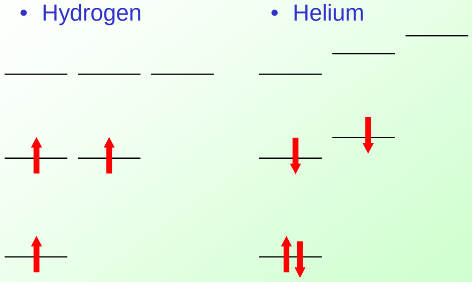

## The one electron wavefunctions

- Radial



## Effect on energy levels

- Hydrogen
- Helium





## Multi-electron atoms

- The Coulomb integral
  - Effect of electron-electron repulsion



## Structure components so far:

- Configurations
  - e.g. 1s2s vs 1s2p



## A note on electronic configurations

- May be written
  - $1s^2 2s^2 2p^6 3s^2 3p^4$
- This is equivalent to:
  - [He] $2s^2 2p^6 3s^2 3p^4$
  - [Ne] $3s^2 3p^4$

The reasons for this will become apparent...



## Configurations are split into terms

- Helium



## Quantum effects

- The Exchange integral
  - Pure quantum mechanical effect
  - Parallel spins avoid one another
  - Effects average repulsion energy
  - Persists even if electrons uncharged

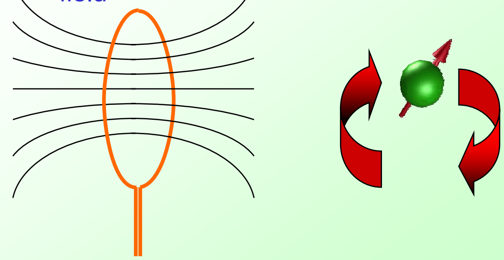
## Structure components so far:

- Configurations
  - e.g. 1s2s vs 1s2p
- Terms
  - 1s2p (↑↓) compared to (↑↑)



## There's more...

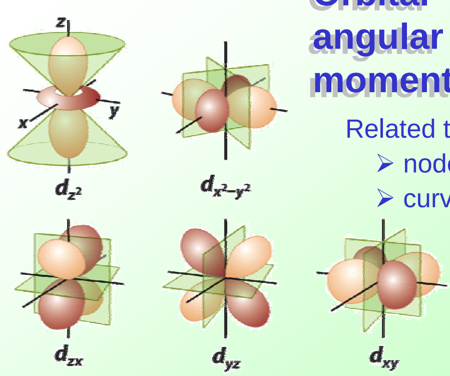
- Circulating charge creates magnetic field





## Orbital angular momentum

Related to
- nodes
- curvature



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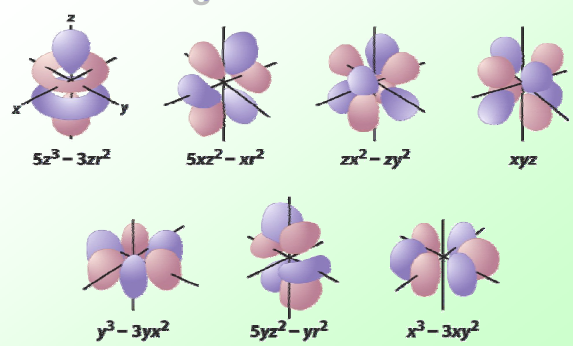
## Orbital angular momentum



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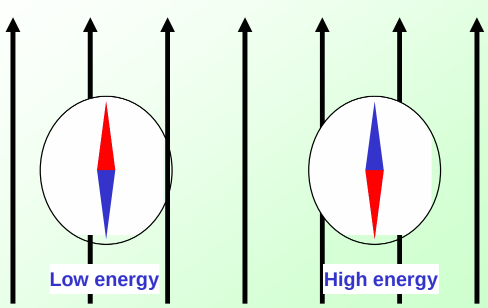
## Macroscopic example






## So what?

- An electron has an associated magnetic field
- An electron with orbital angular momentum induces a magnetic field
- The two fields can be aligned or opposed

**This gives rise to two different energy states for an individual electron**

## Spin-orbit coupling

- The magnetic moment of the electron due to its **spin** may interact with the magnetic field created by virtue of the **orbit**al angular momentum of the electron.

**This is known as**

**spin - orbit coupling**



## Structure components so far:

- Configurations
  - e.g. 1s2s vs 1s2p
- Terms
  - 1s2p (↑↓) compared to (↑↑)
- Levels
  - Fine structure due to spin-orbit coupling



## External field

- Levels split up once again: **states**
- Known as the Zeeman effect

## Internal field

- Nucleus can also have magnetic dipole
- Produces very small splitting: **hyperfine splitting**



## Structure components so far:

- Configurations
  - e.g. 1s2s vs 1s2p
- Terms
  - 1s2p (↑↓) compared to (↑↑)
- Levels
  - Fine structure due to spin-orbit coupling
- States
  - External field splits levels into states



## Quantum description

- Solve the Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

- Replace the operator

$$\hat{H} = \hat{H}_0 + \hat{H}^a_{rep} + \hat{H}^b_{rep} + \hat{H}_{S.O.} \left(+\hat{H}_B\right)$$

Spin-orbit coupling

Repulsion/screening

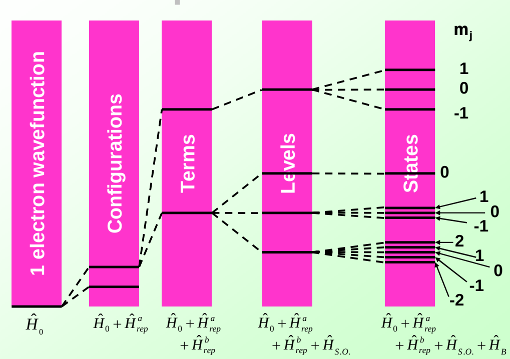
1 electron (hydrogenic) wavefunction

Singlet/triplet

Zeeman



## Pictorial representation

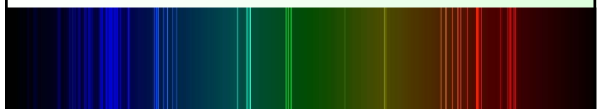


## Summary

- Qualitative view of atomic structure
  - Configurations, terms, levels and states
- Energy shifts caused by magnetic interactions
  - Fine and hyperfine structure
  - Zeeman effect
- First steps in quantum treatment



## Atomic spectra



- How to
  - predict a spectrum
  - get information on atomic interactions



## Things to remember

- Electron quantum numbers lower case
- Total quantum numbers upper case
- Orbital angular momentum
  - l = 0 (s - orbital)
  - l = 1 (p - orbital)
  - l = 2 (d - orbital) etc.



## Spectroscopists shorthand

$$^{(2S+1)}L_J$$

**Term symbol**



## Spectroscopists shorthand

**Term symbol**

$$^{(2S+1)}L_J$$

Orbital angular momentum

Electron spin

Total angular momentum



## Examples of term symbols

$^2P_{3/2}$ $^1S_0$

$^3P_2,\ ^3P_1,\ ^3P_0$ $^3P_{2,1,0}$

## Shorthand

- How to determine the values of the components of the term symbol
- Quantum mechanical restrictions on the values

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## Restrictions

- The orbital angular momentum is not allowed to take any value.
  - First define some axis ( *z* )
  - *l* may only have certain components in the *z* direction

$$\mathbf{l} = \sqrt{l\left(l+1\right)}$$

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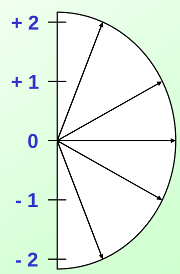
## Restrictions (2)

- d-electron
- *l* = 2
- z-axis projections
  - 0
  - ± 1
  - ± 2




$$\left|\mathbf{l}\right| = \sqrt{2\left(2+1\right)} = \sqrt{6}$$

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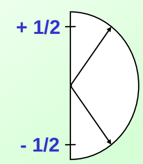
## Electron spin

- Half-integral z-projections




$$\left|\mathbf{s}\right| = \sqrt{1/2\left(1/2+1\right)} = \sqrt{3/4} = 1/2\sqrt{3}$$

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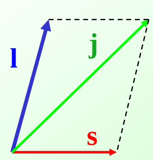
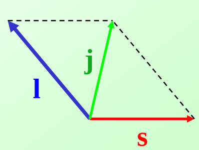
## Coupling

- Magnetic effects are said to "couple" spin and orbital angular momenta
- Do vector addition of spin and orbital parts




$$\left|\mathbf{l}+\mathbf{s}\right| = \mathbf{j}$$




$$\left|\mathbf{l}+\mathbf{s}\right| = \mathbf{j}$$

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## How to find S, L and J

- Vector addition (last slide)
- Clebsch-Gordan series
- Addition of z-components

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## Vector addition

- Not very user friendly

## Clebsh-Gordan series

Recommended

- Easy to implement
- Only ***fails*** for ***equivalent electrons***

## Z-component addition

- Not very user friendly
- Always correct



## Doing the Clebsch-Gordan… (1)

- $l$ and $s$ combine to give total angular momentum j

$$\mathbf{j} = \mathbf{l} + \mathbf{s}$$

$$|\mathbf{j}| = \left[ j(j+1) \right]^{1/2}$$

$$j_z = \pm j, \pm(j-1), \ldots, 1/2$$

… for a single electron



## Doing the Clebsh-Gordan… (2)

- The Clebsh-Gordan series tells us:

$$j_z = l + s, l + s - 1, \ldots, |l - s|$$

… which is what we need to know to find j

- For the whole atom

$$J = \sum_i j_i$$



## Doing the Clebsh-Gordan… (3)

- In addition:

$$J = L + S, L + S - 1, \ldots, |L - S|$$

… which is another way to find $J$

- Where:

$$L_z = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$$

$$S_z = N/2, N/2 - 1, \ldots, 1/2 \quad \text{for odd N}$$

$$S_z = N/2, N/2 - 1, \ldots, 0 \quad \text{for even N}$$



## Coupling schemes

- There are two (equally valid) ways to find J
- Different coupling schemes
- Best applied in different situations
- Russell-Saunders coupling

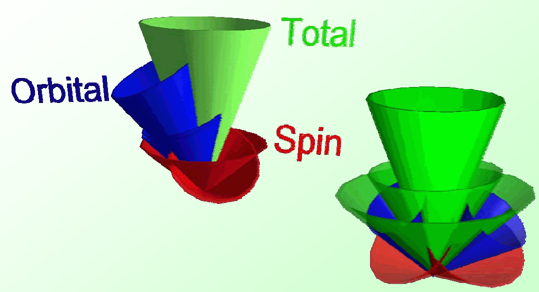
$$L = \sum_i l_i \quad S = \sum_i s_i \quad J = L + S$$

- *jj* - coupling

$$j_i = l_i + s_i \quad J = \sum_i j_i$$



## Coupling schemes

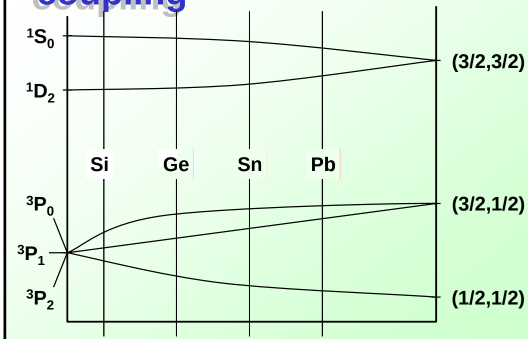


## Comparison of coupling schemes

| | RS | jj |
|---|---|---|
| Light | Good | BAD |
| Heavy | BAD | Good |



## Correlation of RS and jj coupling






## Spectroscopists shorthand

$$^{(2S+1)}L_J$$

**Term symbol**



## Use Russell-Saunders

- Example: He - $1s^1 2s^1$

$$L = l_1 + l_2 = 0 + 0$$

$$S = s_1 + s_2, \ldots, |s_1 - s_2| = N/2, \ldots, 0$$

$$= 1/2 + 1/2, 1/2 + 1/2 - 1 = 1, 0$$

$$J = L + S, \ldots, |L - S|$$

$L = 0, S = 0, J = 0$ → $^1S_0$

$L = 0, S = 1, J = 1$ → $^3S_1$



## Use Russell-Saunders

- Example: He - $1s^1 2p^1$

$$L = l_1 + l_2 = 1 + 0$$

$$S = s_1 + s_2, \ldots, |s_1 - s_2| = N/2, \ldots, 0 = 1, 0$$

$$J = L + S, \ldots, |L - S|$$

$L = 1, S = 1, J = 2, 1, 0$ → $^3P_2, {}^3P_1, {}^3P_0$

$L = 1, S = 0, J = 1$ → $^1P_1$



## Selection Rules

- Shorthand is convenient as selection rules are:

$$\Delta S = 0$$

$$\Delta L = \pm 1$$

$$\Delta J = 0, \pm 1$$

$$(\text{not } J = 0 \rightarrow J = 0)$$

## Examples of selection rules

| | $\Delta S = 0$ | $\Delta L = \pm 1$ | $\Delta J = 0, \pm 1$ |
|---|---|---|---|
| $^3S_1 \nrightarrow {}^3P_1$ | ✓ | ✓ | ✓ |
| $^1S_0 \nrightarrow {}^1D_2$ | ✓ | ✗ | ✓ |
| $^3S_1 \nrightarrow {}^1P_2$ | ✗ | ✓ | ✓ |
| $^3P_1 \nrightarrow {}^3D_2$ | ✓ | ✓ | ✓ |

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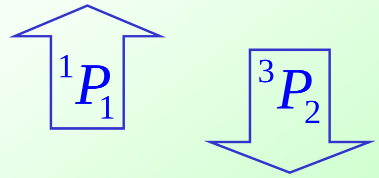
## Hund's Rules

- Rule 1: The state with the maximum multiplicity lies lowest in energy

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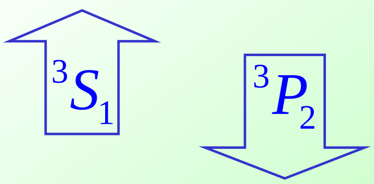
## Hund's Rules

- Rule 2: For a given multiplicity, the term with the largest value of L lies lowest in energy.

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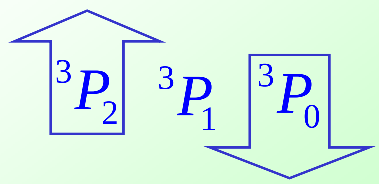
## Hund's Rules

- Rule 3: For atoms with less than half filled shells, the level with the lowest value of J lies lowest in energy.

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## Hund's Rules

- Rule 1: The state with the maximum multiplicity lies lowest in energy
- Rule 2: For a given multiplicity, the term with the largest value of L lies lowest in energy.
- Rule 3: For atoms with less than half filled shells, the level with the lowest value of J lies lowest in energy.

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## Spin Orbit Coupling

- Spin-orbit coupling constant defined by

$$E_{L,J,S} = \frac{1}{2} hcA\left[J\left(J+1\right) - L\left(L+1\right) - S\left(S+1\right)\right]$$

- Note that this refers to isolated levels and not transition energies

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## The Zeeman effect

- The magnetic moment of electrons:

$$\mu = -\left(\frac{ge}{2m}\right)\mathbf{J} = -\left(\frac{ge}{2m}\right)\left[J(J+1)\right]^{1/2}\frac{h}{2\pi}$$

- Depends on where the electrons are:

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

- Single s electron g = 2 (2.00023)



## The Zeeman effect (2)

- Of course we are interested in the z component

$$\mu_z = -\left(\frac{geh}{4\pi m}\right)J_z$$

- Now the z-direction defined by the field

$$E = \mu_z B_z$$

$$J_Z = m_J = J, J-1, J-2, \cdots, -J$$



## The Zeeman effect (3)

- The *extra* energy each level gets is:

$$E_{\text{Extra}} = g_J \mu_B B m_J$$

- With J = 1 three states are observed:

$$E + g_J\mu_B B(1) \quad E + g_J\mu_B B(0) \quad E + g_J\mu_B B(-1)$$

- The splitting between states is obviously $\Delta E = g_J \mu_B B$



## The Zeeman effect (4)

- Impose the extra selection rules:

$$\Delta m_J = 0, \pm 1$$



## The end

Thank you for your attention