# *Your questions/comments*

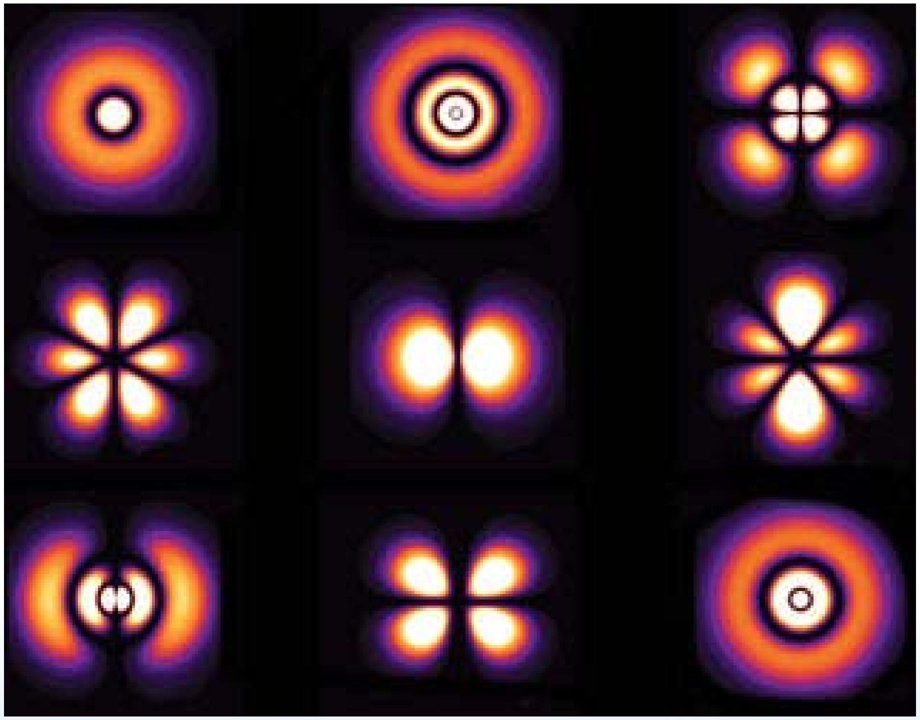
**ANNOUNCEMENTS:** EXAM 3 mean was 76%, no scaling necessary
End of semester coming very soon!
Check your gradebook NOW; ICES course evaluation
James Scholar Credit projects due Friday, Dec. 5

"It's been a long time since I calculated the number of electrons based on quantum numbers so I need some practice with that."

"totally didn't get this in chemistry, so i'm excited to re-learn it now with a legit professor. welcome back everyone :)"

"Quick review on shortcuts for determining the number of electrons, shell configurations, etc. when given a set of quantum numbers?"

"I'm finding this material, especially the material from checkpoint 3, to be very confusing. I'm hoping to see a lot of clarification in lecture."

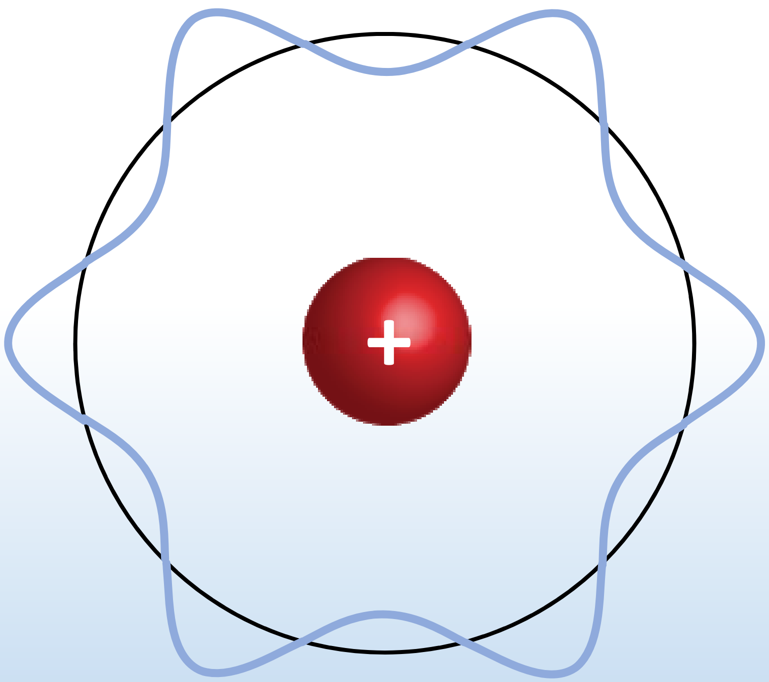


# Phys 102 – Lecture 26

**The quantum numbers and spin**

# *Recall: the Bohr model*

Only orbits that fit *n* e⁻ wavelengths are allowed



e⁻ wave

**SUCCESSES** H atom + single e⁻ atoms

Correct energy quantization & atomic spectra

$$E_n = -\frac{m_e k^2 e^4}{2\hbar^2} \cdot \frac{\cancel{1}\, Z^2}{n^2} \qquad n = 1, 2, 3, \ldots$$

**FAILURES**

Radius & momentum quantization violates Heisenberg Uncertainty Principle

$$r_n = \frac{n^2 \hbar^2}{m_e k e^2} \equiv n^2 a_0 \qquad \Delta r \cdot \Delta p_r \geq \frac{\hbar}{2}$$

Electron orbits cannot have zero *L*

$$L_n = n\hbar$$

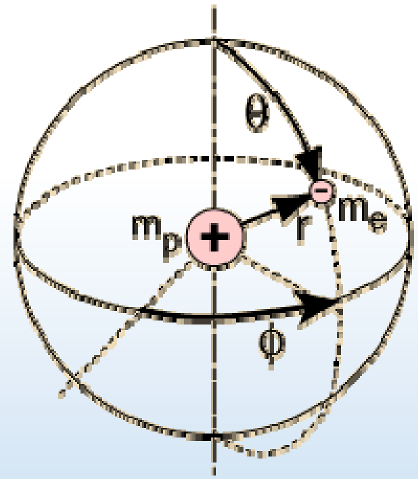
Orbits can hold any number of electrons

# Quantum Mechanical Atom

Schrödinger's equation determines e⁻ "wavefunction"

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{ke^2}{r}\right)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \quad \Rightarrow \quad \psi_{n,\ell,m_\ell}$$

3 quantum numbers determine e⁻ state




"SHELL"

"Principal Quantum Number" $n$ = 1, 2, 3, …

$$E_n = -\frac{m_e k^2 e^4}{2\hbar^2}\frac{1}{n^2}$$

Energy

Same as Bohr

*s, p, d, f* "SUBSHELL"

"Orbital Quantum Number" $\ell$ = 0, 1, 2, 3 …, $n$–1

$$L = \sqrt{\ell(\ell+1)}\hbar$$

Magnitude of angular momentum

"Magnetic Quantum Number" $m_\ell = -\ell, \ldots -1, 0, +1 \ldots, \ell$

$$L_z = m_\ell \hbar$$

Orientation of angular momentum

# ACT: CheckPoint 3.1 & more

For which state is the angular momentum *required* to be 0?

A. $n = 3$

B. $n = 2$

C. $n = 1$

$\ell = 0, 1, 2, 3 \ldots, n-1$
so for $n = 1$, $\ell = 0$

How many values for $m_\ell$ are possible for the $f$ subshell ($\ell = 3$)?

A. 3

B. 5

C. 7

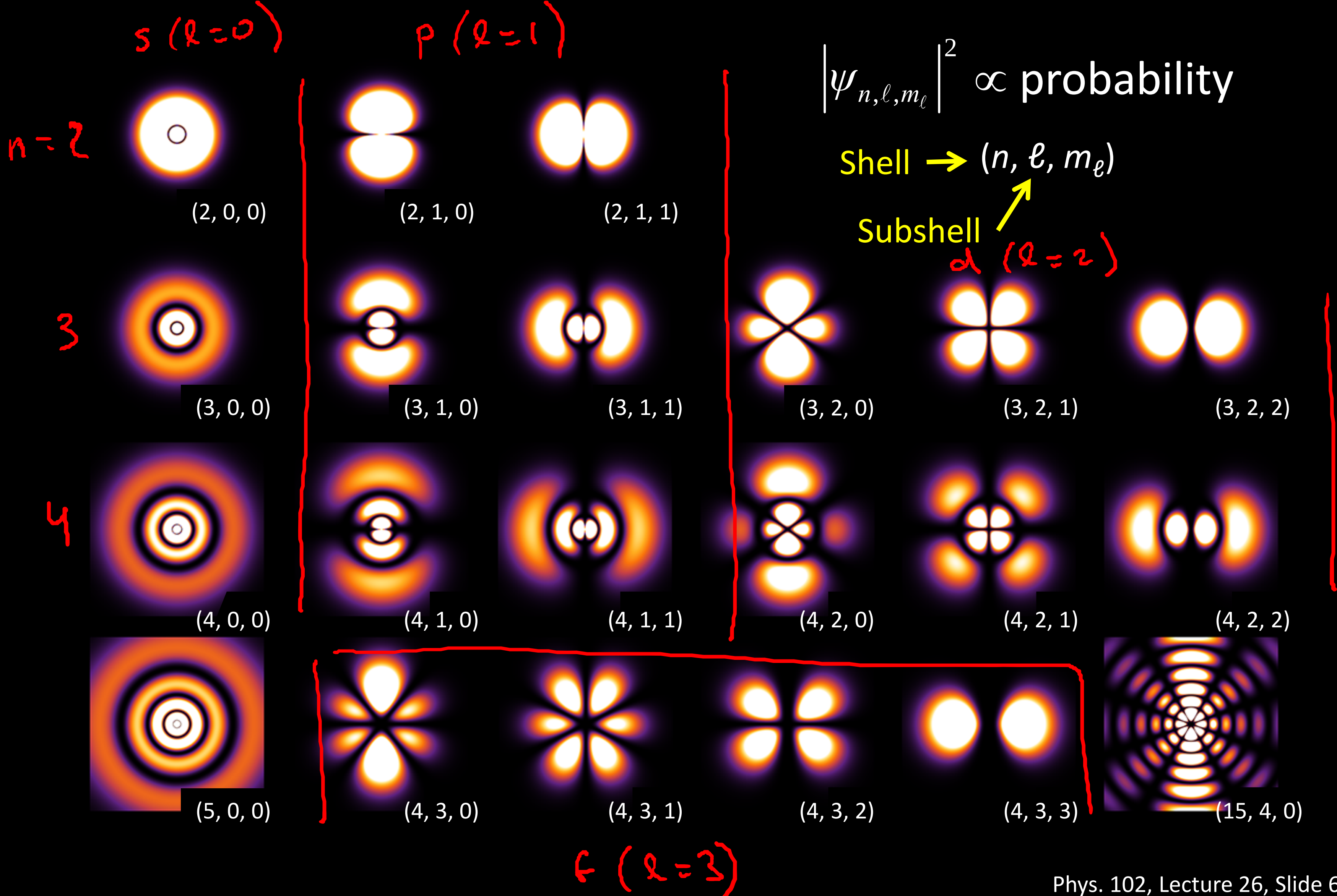
$m_\ell = -\ell, \ldots -1, 0, +1 \ldots, \ell$
so for $\ell = 3$, $m_\ell = \underbrace{-3, -2, -1, 0, +1, +2, +3}_{2\ell+1 \text{ terms}}$

# *Hydrogen electron orbitals*

$$\left|\psi_{n,\ell,m_\ell}\right|^2 \propto \text{probability}$$

Shell → $(n, \ell, m_\ell)$

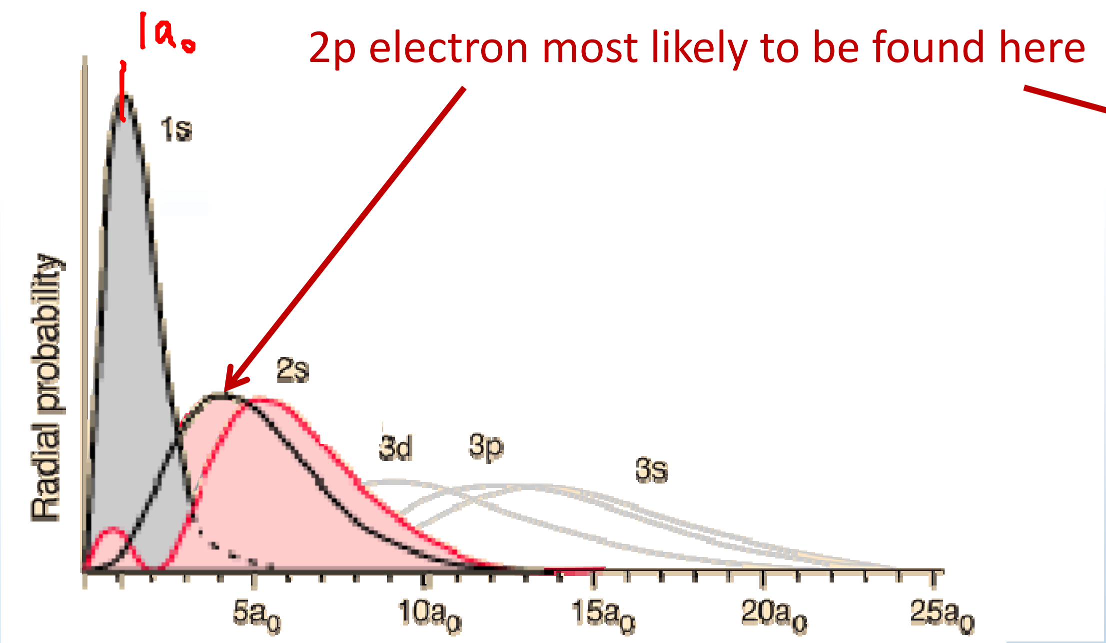
Subshell ↗

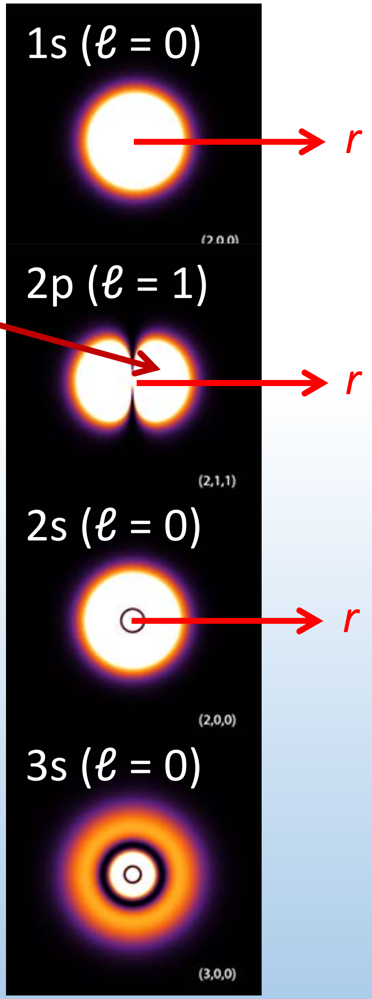


# *CheckPoint 2: orbitals*

Orbitals represent *probability* of electron being at particular location

2p electron most likely to be found here

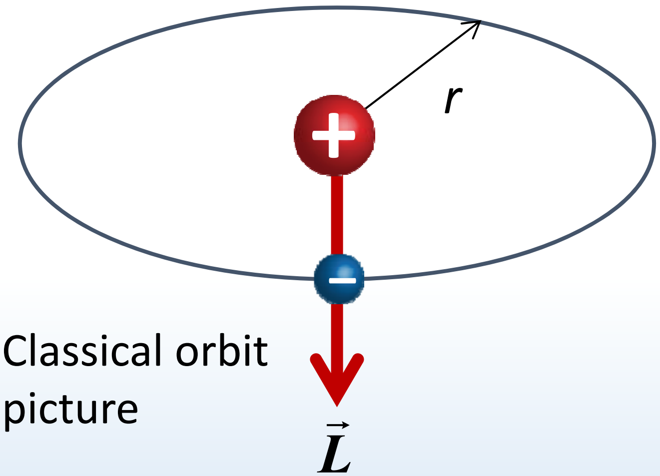



Bohr radius $a_0 \equiv \dfrac{\hbar^2}{m_e k e^2}$

# *Angular momentum*

What do the quantum numbers $\ell$ and $m_\ell$ represent?




Classical orbit picture

Magnitude of angular momentum vector quantized

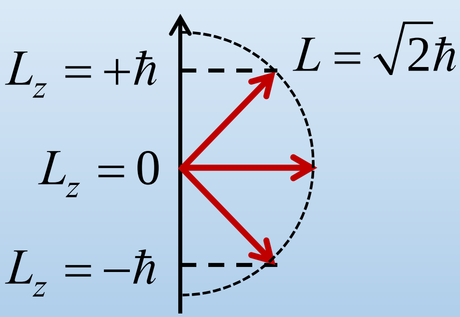
$$\left|\vec{L}\right| = L = \sqrt{\ell(\ell+1)}\hbar \qquad \ell = 0, 1, 2 \cdots n-1$$

Only *one* component of *L* quantized

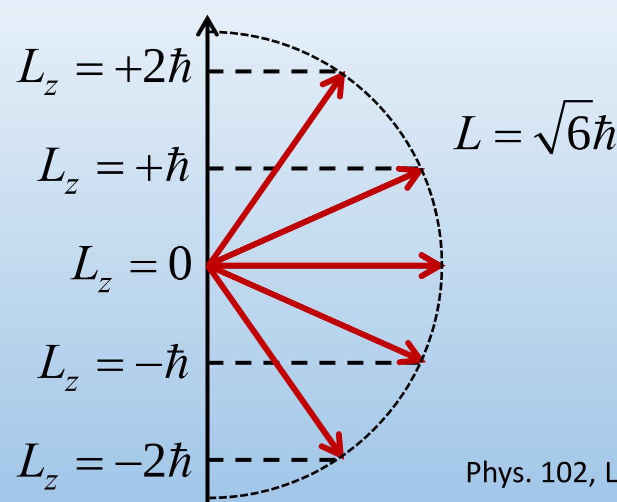
$$L_z = m_\ell \hbar \qquad m_\ell = -\ell, \cdots -1, 0, 1, \cdots \ell$$

Other components $L_x$, $L_y$ are not quantized

$\ell = 1$

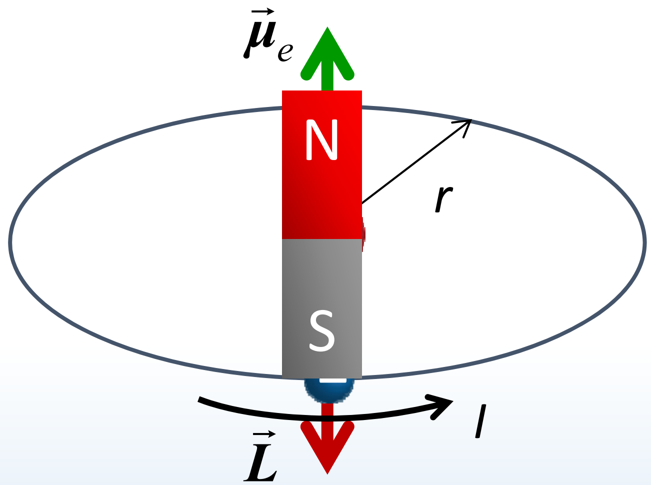



$\ell = 2$



# *Orbital magnetic dipole*

Electron orbit is a current loop and a magnetic dipole




$$\mu_e = IA = \frac{\Delta q}{\Delta t}\pi r^2 = \frac{ev}{2\pi r}\pi r^2 = \frac{e}{2m_e} m_e v r$$

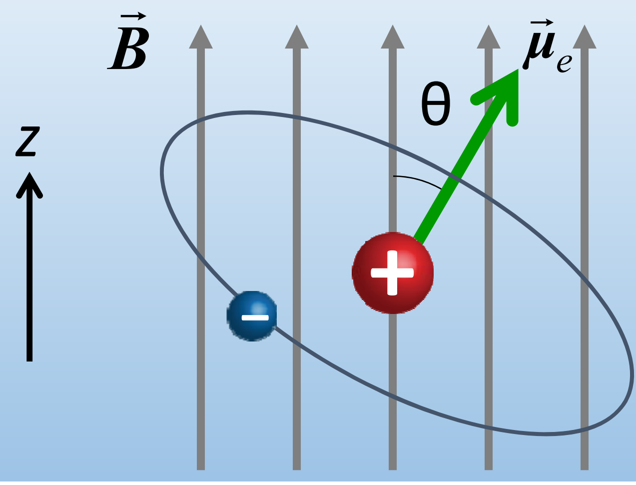
Recall Lect. 12

$$\boxed{\vec{\mu}_e = -\frac{e}{2m_e}\vec{L}}$$

Dipole moment is quantized

What happens in a *B* field?

Recall Lect. 11




$$U = -\mu_e B\cos\theta = \frac{eB}{2m_e} L_z$$

Orbitals with different *L* have different quantized energies in a *B* field

# *ACT: Hydrogen atom dipole*

What is the magnetic dipole moment of hydrogen in its ground state due to the orbital motion of electrons?

$$\boxed{\vec{\boldsymbol{\mu}}_e = -\frac{e}{2m_e}\vec{\boldsymbol{L}}}$$

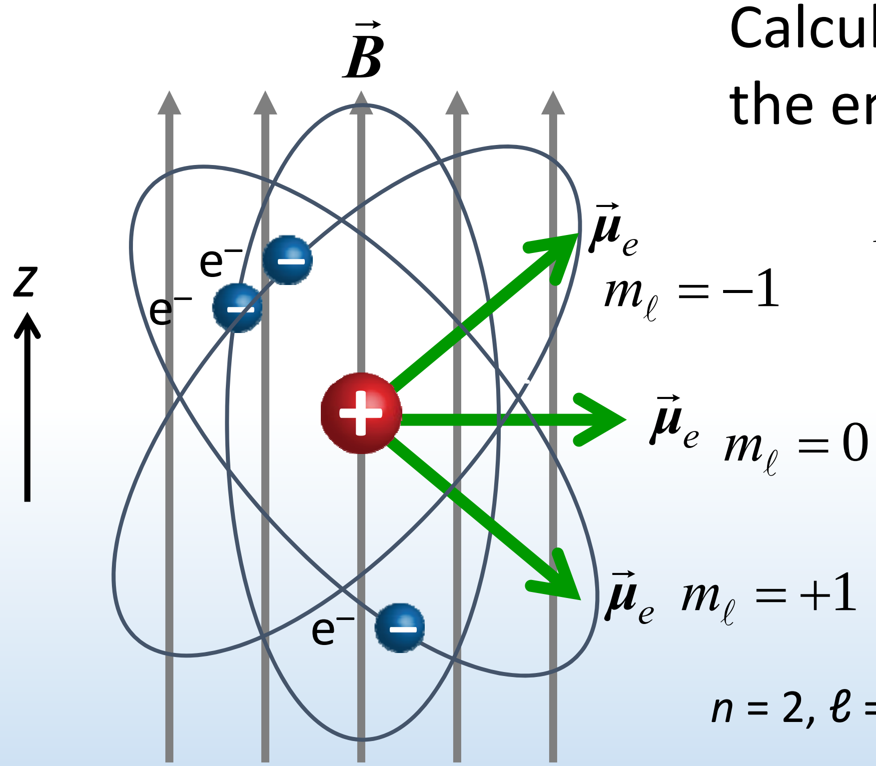
A. $\mu_H = -\dfrac{e\hbar}{2m_e}$

B. $\mu_H = 0$

C. $\mu_H = +\dfrac{e\hbar}{2m_e}$

***CheckPoint 3.1.*** In ground state, $n$ = 1 and $\ell$ = 0, so $\mu_e$ = 0

# *Calculation: Zeeman effect*




Calculate the effect of a 1 T *B* field on the energy of the 2p ($n$ = 2, $\ell$ = 1) level

$$E_{tot} = E_{n=2} - \mu_e B\cos\theta$$
$$= E_{n=2} + \frac{e\hbar}{2m_e} B m_\ell$$

For $\ell$ = 1,
$m_\ell$ = −1, 0, +1

$\vec{B} = 0$ $\quad\quad$ $\vec{B} > 0$

$m_\ell = +1$

$n$ = 2, $\ell$ = 1 $\quad$ $m_\ell = 0$

$m_\ell = -1$

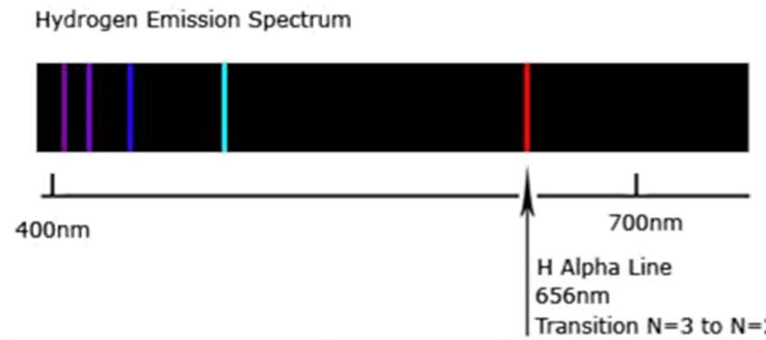
Energy level splits into 3, with energy splitting

$$\Delta E \equiv \frac{e\hbar B}{2m_e} = 5.8\times10^{-5}\,\mathrm{eV} \qquad \mu_B \equiv \frac{e\hbar}{2m_e} = 5.8\times10^{-5}\,\frac{\mathrm{eV}}{\mathrm{T}}$$

"Bohr magneton"

# ACT: Atomic dipole

The H α spectral line is due to e⁻ transition between the $n$ = 3, $\ell$ = 2 and the $n$ = 2, $\ell$ = 1 sub-shells.

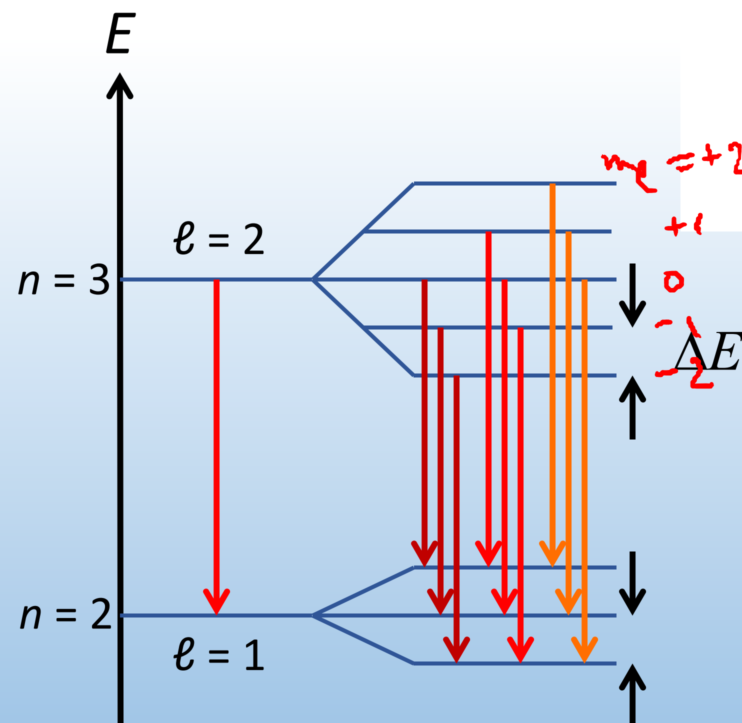


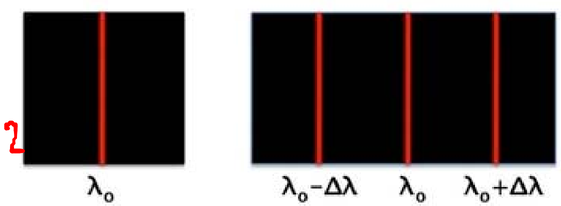

How many levels should the $n$ = 3, $\ell$ = 2 state split into?

A. 1

B. 3

C. 5




$$\Delta E = \frac{e\hbar}{2m_e}B$$

# *Intrinsic angular momentum*

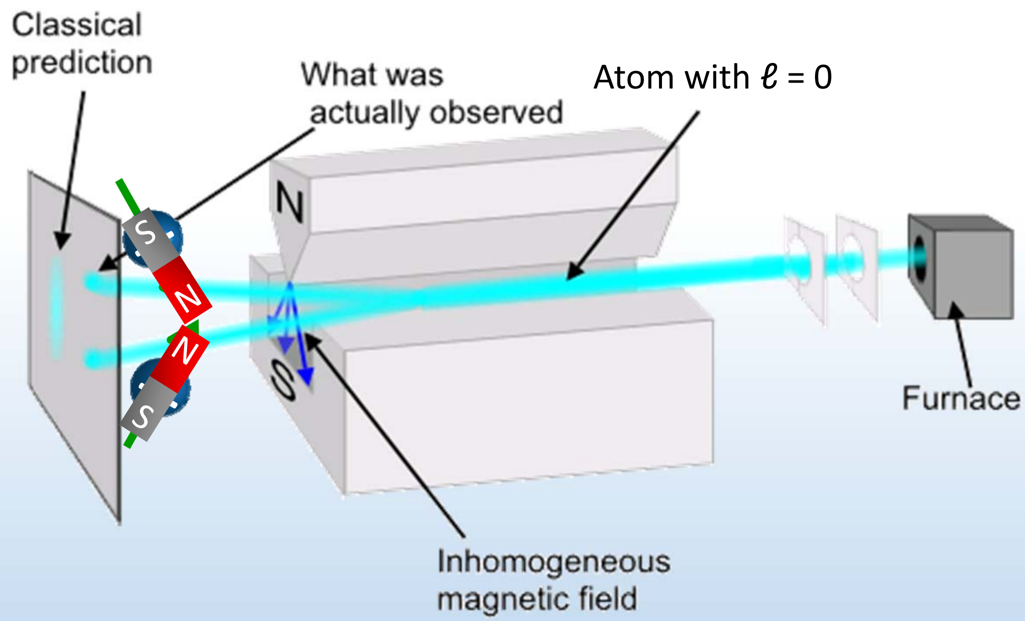
A beam of H atoms in ground state passes through a *B* field

$n = 1$, so $\ell = 0$ and expect NO effect from *B* field

Instead, observe beam split in two!

Since we expect $2\ell + 1$ values for magnetic dipole moment, $e^-$ must have *intrinsic* angular momentum with $\ell = ½$.

"Spin" *s*



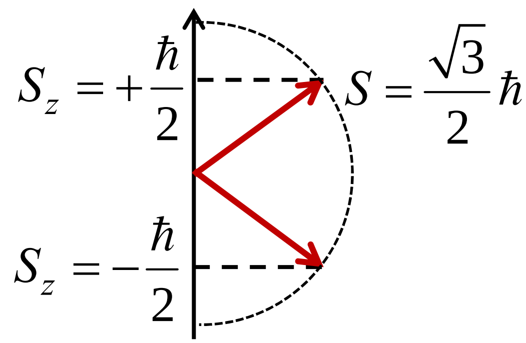

"Stern-Gerlach experiment"

# *Spin angular momentum*

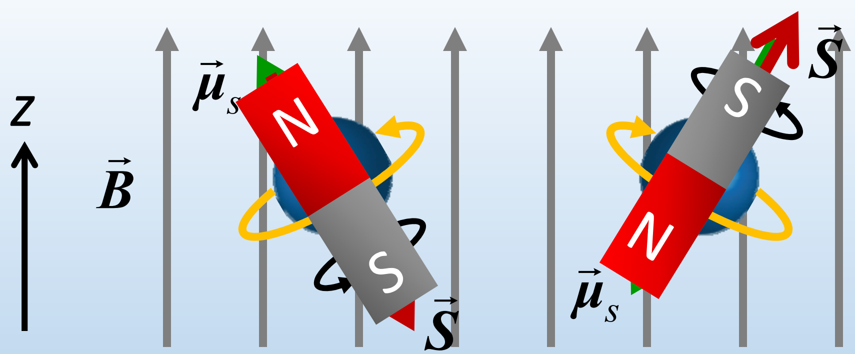
Electrons have an intrinsic angular momentum called “spin”

$$\left|\vec{S}\right| = S = \sqrt{s(s+1)}\hbar$$ with $s$ = ½

$$S_z = m_s\hbar \qquad m_s = -\tfrac{1}{2}, +\tfrac{1}{2}$$




Spin also generates *magnetic* dipole moment




Spin DOWN (–½) Spin UP (+½)

$$\boxed{\vec{\mu}_s = -\frac{e}{2m_e} g\vec{S}}$$ with g ≈ 2

$$U = -\mu_s B\cos\theta = \frac{ge\hbar}{2m_e} B m_s \cos\theta$$

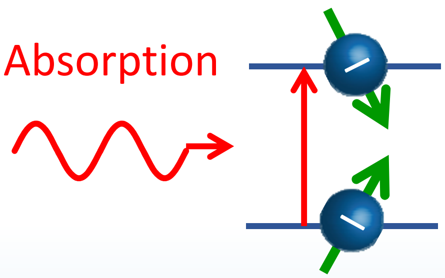
$m_s = +\frac{1}{2}$

$\vec{B} > 0$

$m_s = -\frac{1}{2}$

# *Spin resonance*

$e^-$ in B field absorbs photon with energy equal to splitting of energy levels




$m_s = +\frac{1}{2}$

$m_s = -\frac{1}{2}$

$$hf = \Delta E$$
$$= \frac{ge\hbar}{2m_e} B$$
$$= g\mu_B B \approx 2 \cdot 5.8 \times 10^{-5}\,\frac{\text{eV}}{\text{T}} \cdot 1\text{T} \approx \underbrace{11.6 \times 10^{-5}\,\text{eV}}_{28\text{ GHz}}$$

"Electron spin resonance (ESR)"

Typically microwave EM wave

Protons & neutrons also have spin ½

$$\vec{\boldsymbol{\mu}}_{prot} = +\frac{e}{2m_p} g_p \vec{\boldsymbol{S}} << \vec{\boldsymbol{\mu}}_s \qquad \text{since } m_p >> m_e$$

"Nuclear magnetic resonance (NMR)"

Typically radio EM wave

For B = 1 T, *f* = 43 MHz

Sensitive probe for local chemical environment: Local B fields (ex: from $e^-$ orbitals) change energy splitting slightly "Chemical shift"

# Quantum number summary

"Principal Quantum Number", $n$ = 1, 2, 3, …

$$E_n = -\frac{m_e k^2 e^4}{2\hbar^2}\frac{1}{n^2}$$ Energy

"Orbital Quantum Number", $\ell$ = 0, 1, 2, …, $n$–1

$$L = \sqrt{\ell(\ell+1)}\hbar$$ Magnitude of angular momentum

"Magnetic Quantum Number", $m_l = -\ell, \ldots -1, 0, +1 \ldots, \ell$

$$L_z = m_\ell \hbar$$ Orientation of angular momentum

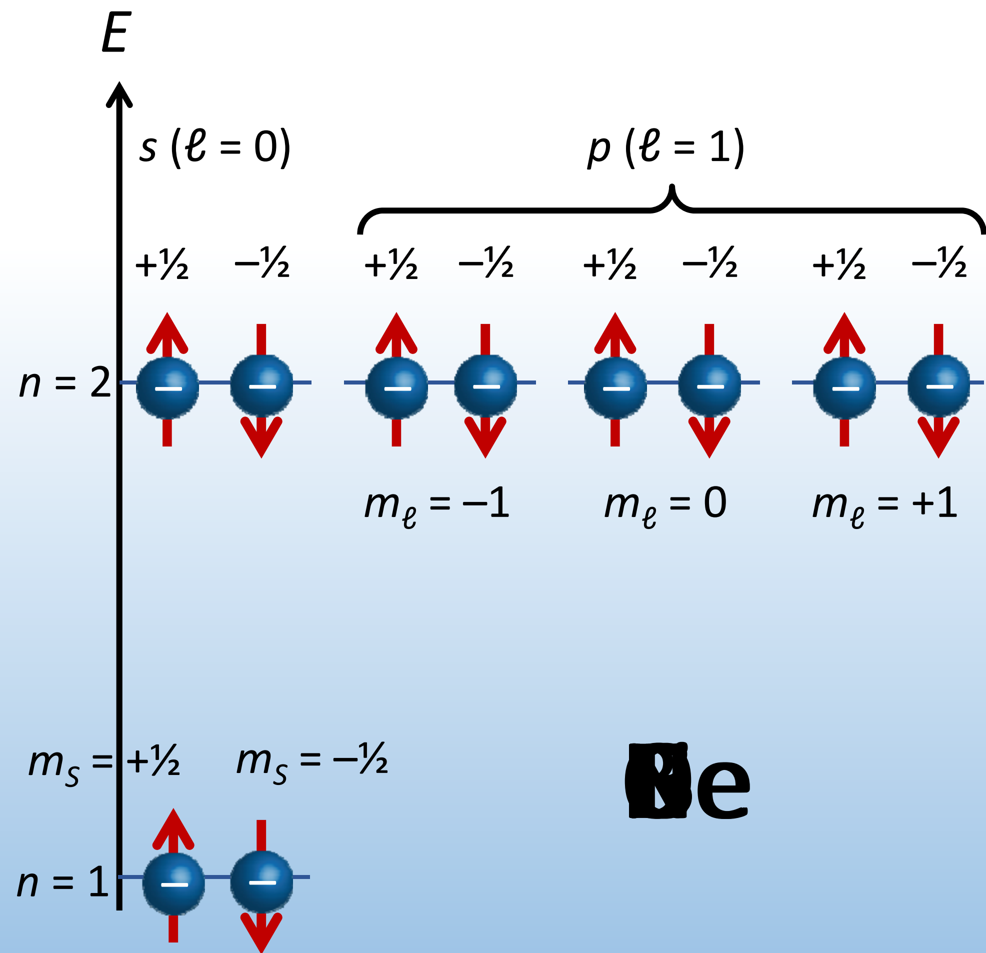
"Spin Quantum Number", $m_s$ = –½, +½

$$S_z = m_s \hbar$$ Orientation of spin

# *Electronic states*

spin ½

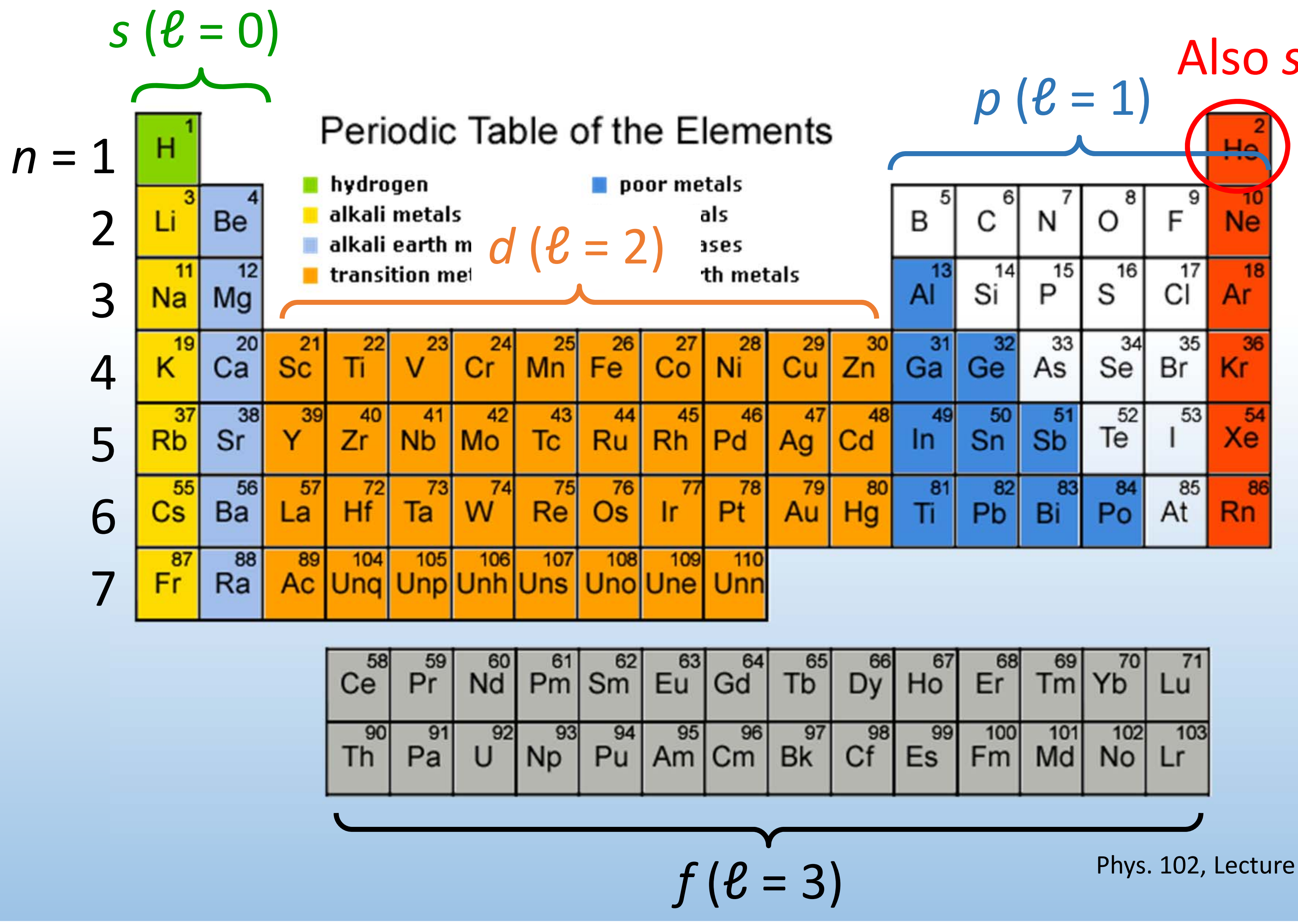
*Pauli Exclusion Principle*: no two $e^-$ can have the same set of quantum numbers $n$, $\ell$, $m_\ell$, $m_s$




As $e^-$ are added, they must occupy higher energy levels

# The Periodic Table

Pauli exclusion & energies determine sequence



# *CheckPoint 3.2*

How many electrons can there be in a 5g ($n$ = 5, $\ell$ = 4) sub-shell of an atom?

$$2\ell+1 \left\{ \begin{array}{lll} m_\ell = +4 & m_s = +½, -½ & \text{2 states} \\ m_\ell = +3 & m_s = +½, -½ & \text{2 states} \\ m_\ell = +2 & m_s = +½, -½ & \text{2 states} \\ m_\ell = +1 & m_s = +½, -½ & \text{2 states} \\ m_\ell = 0 & m_s = +½, -½ & \text{2 states} \\ m_\ell = -1 & m_s = +½, -½ & \text{2 states} \\ m_\ell = -2 & m_s = +½, -½ & \text{2 states} \\ m_\ell = -3 & m_s = +½, -½ & \text{2 states} \\ m_\ell = -4 & m_s = +½, -½ & \text{2 states} \end{array} \right.$$

There are a total of

$$2(2\ell+1) = 18$$

states within one subshell

# *ACT: Quantum numbers*

How many total electron states exist with $n$ = 2?

A. 2

B. 4

C. 8

$\ell = 0$ ($s$ sub-shell)

| | | | |
|---|---|---|---|
| 1 | $m_\ell = 0$ | $m_s = +½, –½$ | 2 states |

$\ell = 1$ ($p$ sub-shell)

| | | | |
|---|---|---|---|
| 3 | $m_\ell = +1$ | $m_s = +½, –½$ | 2 states |
| | $m_\ell = 0$ | $m_s = +½, –½$ | 2 states |
| | $m_\ell = -1$ | $m_s = +½, –½$ | 2 states |

There are a total of

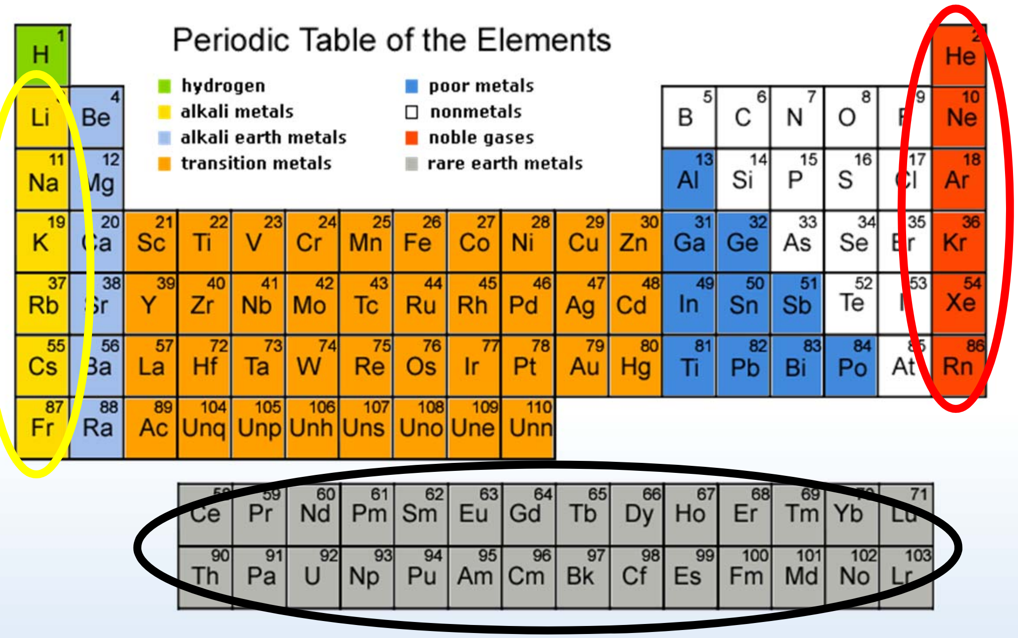
$2n^2 = 8$

states in one shell

For general $n$, there are a total of: $2\times(1 + 3 + 5 + ...(2n+1)) = 2n^2$ states

# ACT: Magnetic elements

Where would you expect the most *magnetic* elements to be in the periodic table?




A. Alkali metals ($s$, $\ell = 0$)

B. Noble gases ($p$, $\ell = 1$)

C. Rare earth metals ($f$, $\ell = 3$)

Magnets are made from elements in the *d* and *f* subshells.
High $\ell$ means high dipole moment Ex: Fe, Co, Nd, Sm

# *Summary of today's lecture*

- Quantum numbers
  - Principal quantum number $E = -13.6\,eV / n^2$
  - Orbital quantum number $L = \sqrt{\ell(\ell+1)}\hbar, \quad \ell = 0, 1, n-1$
  - Magnetic quantum number $L_z = m_z\hbar, \quad m_\ell = -\ell, \ldots, 0, \ldots \ell$
- Spin angular momentum
  - $e^-$ has intrinsic angular momentum $S_z = m_s\hbar \quad m_s = -\frac{1}{2}, \frac{1}{2}$
- Magnetic properties
  - Orbital & spin angular momentum generate magnetic dipole moment
- Pauli Exclusion Principle
  - No two $e^-$ can have the same quantum numbers