Quantum Mechanics

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Lesson X
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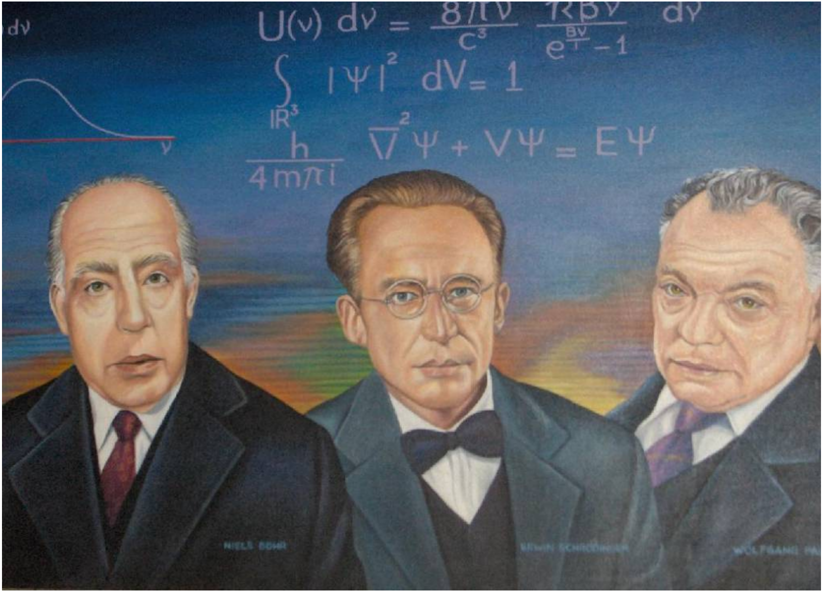
∫_{IR³} |Ψ|² dV = 1
h/4mπi ∇²Ψ + VΨ = EΨ

- Until now we have focused on quantum mechanics of particles which are “featureless” ☞ carrying no internal degrees of freedom

- A relativistic formulation of quantum mechanics due to Dirac (not covered in this course) reveals that quantum particles can exhibit an intrinsic angular momentum component known as spin

- However ☞ the discovery of quantum mechanical spin predates its theoretical understanding and appeared as a result of an ingeneous experiment due to Stern and Gerlach that we will discuss in this lesson

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We have seen that...

- In addition to quantized energy (specified by principle quantum number n) ☞ solutions subject to physical boundary conditions also have quantized orbital angular momentum L
- Magnitude of L is required to obey ☞ $L\, Y_l^m = \sqrt{l(l+1)}\hbar\, Y_l^m$ with $(l = 0, 1, 2, \cdots, n-1)$ ☞ $l \equiv$ orbital quantum number
- Bohr model of H atom also has quantized angular momentum $L = n\hbar$ ☞ but lowest energy state $n = 1$ would have $L = \hbar$
- Schrödinger equation shows that lowest state has $L = 0$
- This lowest energy-state wave function is a perfectly symmetric sphere
- For higher energy states ☞ vector L has in addition only certain allowed directions such that z-component is quantized as $L_z\, Y_l^m = m_l\hbar\, Y_l^m$ ☞ $(m_l = 0, \pm1, \pm2, \cdots, \pm l)$

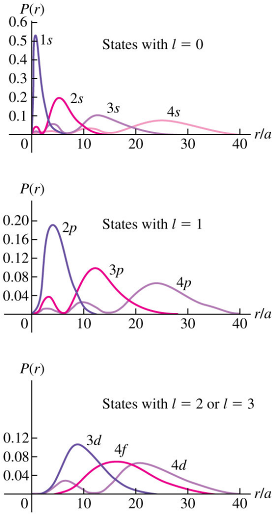
The hydrogen atom: Degeneracy

- States with different quantum numbers l and n are often referred to with letters as follows:

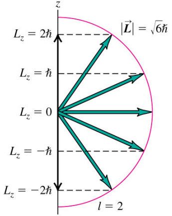
l value	letter
0	s
1	p
2	d
3	f
4	g
5	h

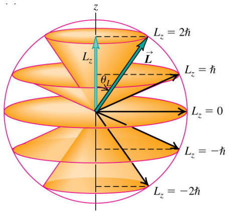
n value	shell
1	K
2	L
3	M
4	N

- Hydrogen atom states with the same value of n but different values of l and m_l are degenerate (have the same energy).
- Figure at right shows radial probability distribution for states with $l = 0, 1, 2, 3$ and different values of $n = 1, 2, 3, 4$.



Quantum states of hydrogen atom





- For each value of the quantum number n there are n possible values of the quantum number l
- For each value of l there are $2l + 1$ values of the quantum number m_l

n	*l*	m_l	Spectroscopic Notation	Shell
1	0	0	1*s*	*K*
2	0	0	2*s*	*L*
2	1	−1, 0, 1	2*p*	
3	0	0	3*s*	*M*
3	1	−1, 0, 1	3*p*	
3	2	−2, −1, 0, 1, 2	3*d*	
4	0	0	4*s*	*N*
and so on				

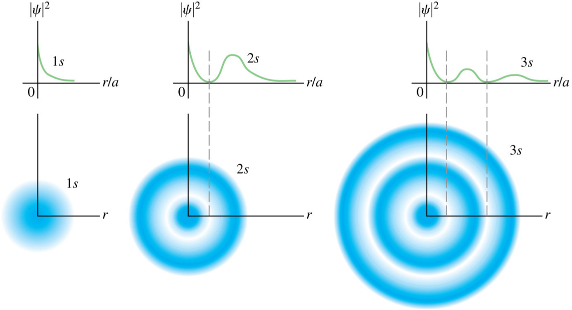
Example

- How many distinct states of the hydrogen atom (n, l, m_l) are there for the $n = 3$ state?
- What are their energies?
- The $n = 3$ state has possible l values $0, 1, 2$
- Each l has m_l possible values ☞ (0), $(-1, 0, 1)$, $(-2, -1, 0, 1, 2)$
- The total number of states is then $1 + 3 + 5 = 9$
- There is another quantum number $s = \pm\frac{1}{2}$ for electron spin so there are 18 possible states for $n = 3$ (more on this later)
- Each of these states have same n ☞ so they all have same energy

The hydrogen atom: Probability distributions I

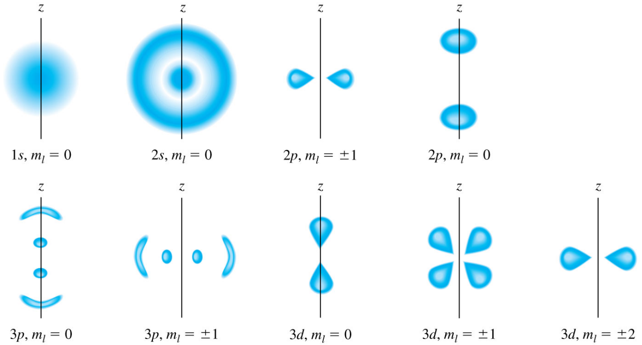
- States of the hydrogen atom with $l = 0$ (zero orbital angular momentum) have spherically symmetric wave functions that depend on r but not on θ or ϕ. These are called s states.

- electron probability distributions for three of these states.



The hydrogen atom: Probability distributions II

- States of the hydrogen atom with nonzero orbital angular momentum, such as p states ($l = 1$) and d states ($l = 2$), have wave functions that are *not* spherically symmetric.
  electron probability distributions for several of these states, as well as for two spherically symmetric s states.



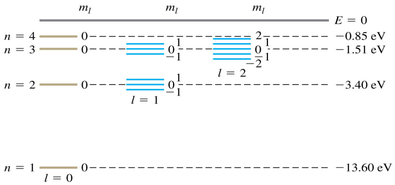
Ground-state electron configurations

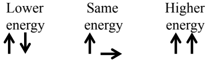
Element	Symbol	Atomic Number (Z)	Electron Configuration
Hydrogen	H	1	$1s$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	Al	13	$1s^2 2s^2 2p^6 3s^2 3p$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^5$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^{10}$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

- e-states with nonzero orbital angular momentum $(l = 1, 2, 3, \cdots)$ carry magnetic dipole moment due to electron motion
- These states are affected if atom is placed in magnetic field $\vec{B}$

$$\boldsymbol{\mu} = -\frac{e}{2m_e}\hat{\mathbf{L}} \equiv -\mu_B \hat{\mathbf{L}}/\hbar, \qquad H_{\rm int} = -\boldsymbol{\mu}\cdot\mathbf{B}$$

- Zeeman effect ☞ shift in energy of states with nonzero m_l





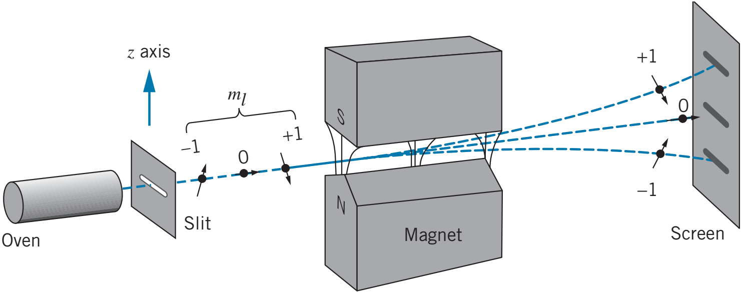
- Think of magnets, which like to be anti-aligned. This is a lower energy state.

- When beam of atoms are passed through inhomogeneous (but aligned) magnetic field where they experience force

$$\mathbf{F} = \nabla(\boldsymbol{\mu}\cdot\mathbf{B}) \simeq \mu_z(\partial_z B_z)\hat{\mathbf{e}}_z$$

we expect splitting into **odd integer** $(2l+1)$ number of beams

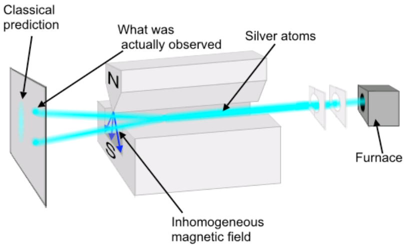
Stern-Gerlach apparatus



- Beam of atoms passes through a region where there is nonuniform $\vec{B}$-field
- Atoms with their magnetic dipole moments in opposite directions experience forces in opposite directions

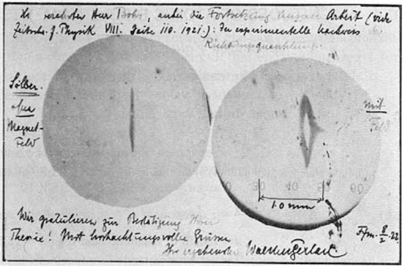
Stern-Gerlach experiment

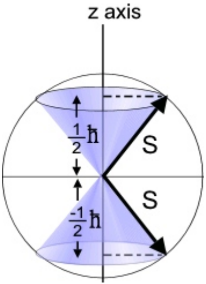
- In experiment, a beam of silver atoms were passed through inhomogeneous magnetic field and collected on photographic plate.
- Since silver involves spherically symmetric charge distribution plus one $5s$ electron, total angular momentum of ground state has $L = 0$.
- If outer electron in $5p$ state, $L = 1$ and the beam should split in 3.



Stern-Gerlach experiment

- However, experiment showed a bifurcation of beam!

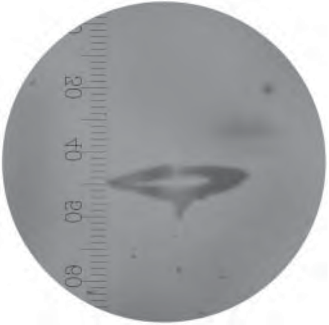




Gerlach's postcard, dated 8th February 1922, to Niels Bohr

- Since orbital angular momentum can take only integer values, this observation suggests electron possesses an additional intrinsic $s = \frac{1}{2}$ component known as **spin**.

Results of Stern-Gerlach experiment



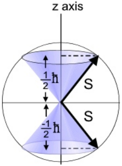
- Image of slit with field turned off (left)
- With the field on ☞ two images of slit appear
- Small divisions in the scale represent 0.05 mm

Quantum mechanical spin

- Later, it was understood that elementary quantum particles can be divided into two classes, **fermions** and **bosons**.
- Fermions (e.g. electron, proton, neutron) possess half-integer spin.
- Bosons (e.g. mesons, photon) possess integral spin (including zero).

Spinors

- Space of angular momentum states for spin $s = 1/2$ is two-dimensional:



$$|s = 1/2, m_s = 1/2\rangle = |\uparrow\rangle, \qquad |1/2, -1/2\rangle = |\downarrow\rangle$$

- General **spinor** state of spin can be written as linear combination,

$$\alpha|\uparrow\rangle + \beta|\downarrow\rangle = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \qquad |\alpha|^2 + |\beta|^2 = 1$$

- Operators acting on spinors are 2×2 matrices. From definition of spinor, z-component of spin represented as,

$$S_z = \frac{1}{2}\hbar\sigma_z, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

i.e. S_z has eigenvalues $\pm\hbar/2$ corresponding to $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

Uhlenbeck-Goudsmit-Pauli hypothesis

- Magnetic moment ☞ connected via intrinsic angular momentum

$$\vec{\mu}_S = -\frac{e}{2m_e} g_e \vec{S} \tag{1}$$

- For intrinsic spin ☞ only matrix representation is possible
  - Spin up $|\uparrow\rangle$ and down $|\downarrow\rangle$ are defined by

$$\text{spin up} \quad \Leftrightarrow \left(\begin{array}{c} 1 \\ 0 \end{array}\right) \qquad \text{spin down} \quad \Leftrightarrow \left(\begin{array}{c} 0 \\ 1 \end{array}\right) . \tag{2}$$

  - $\hat{S}_z$ spin operator is defined by

$$\hat{S}_z = \frac{\hbar}{2} \left(\begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array}\right) \tag{3}$$

- $\hat{S}_z$ acts on up and down states by ordinary matrix multiplication

$$\hat{S}_z|\uparrow\rangle = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}|\uparrow\rangle \qquad (4)$$

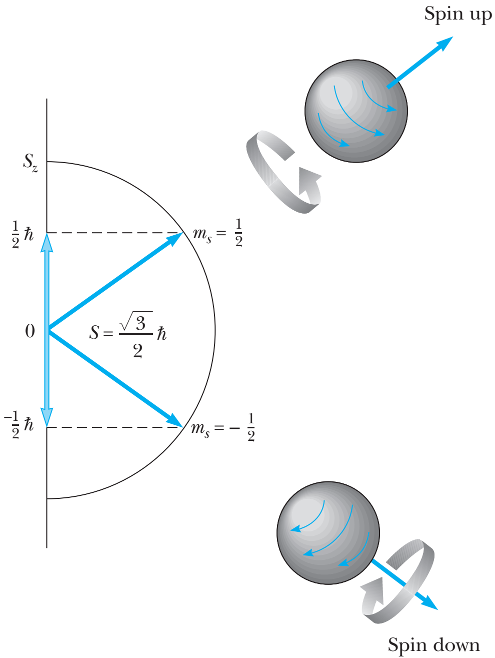
$$\hat{S}_z|\downarrow\rangle = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2}|\uparrow\rangle \qquad (5)$$

- As for orbital angular momentum $[\hat{S}_i, \hat{S}_j] = i\hbar\,\epsilon_{ijk}\hat{S}_k$

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad \hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad (6)$$

- Only 4 hermitian 2-by-2 matrices ☞ indentity + Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (7)$$


Spin up
S_z
$\frac{1}{2}\hbar$
$m_s = \frac{1}{2}$
0
$S = \frac{\sqrt{3}}{2}\hbar$
$-\frac{1}{2}\hbar$
$m_s = -\frac{1}{2}$
Spin down

Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- Pauli spin matrices are Hermitian, traceless, and obey defining relations (cf. general angular momentum operators):

$$\sigma_i^2 = \mathbb{I}, \qquad [\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$$

- Total spin

$$\mathbf{S}^2 = \frac{1}{4}\hbar^2\boldsymbol{\sigma}^2 = \frac{1}{4}\hbar^2\sum_i \sigma_i^2 = \frac{3}{4}\hbar^2\,\mathbb{I} = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\,\mathbb{I}$$

i.e. $s(s+1)\hbar^2$, as expected for spin $s = 1/2$.

Spatial degrees of freedom and spin

- Spin represents additional internal degree of freedom, independent of spatial degrees of freedom, i.e. $[\hat{\mathbf{S}}, \mathbf{x}] = [\hat{\mathbf{S}}, \hat{\mathbf{p}}] = [\hat{\mathbf{S}}, \hat{\mathbf{L}}] = 0$.
- Total state is constructed from **direct product**,

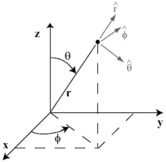
$$|\psi\rangle = \int d^3x \, (\psi_+(\mathbf{x})|\mathbf{x}\rangle \otimes |\uparrow\rangle + \psi_-(\mathbf{x})|\mathbf{x}\rangle \otimes |\downarrow\rangle) \equiv \begin{pmatrix} |\psi_+\rangle \\ |\psi_-\rangle \end{pmatrix}$$

- In a weak magnetic field, the electron Hamiltonian can then be written as

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(r) + \mu_{\rm B} \left(\hat{\mathbf{L}}/\hbar + \boldsymbol{\sigma} \right) \cdot \mathbf{B}$$

Relating spinor to spin direction

For a general state $\alpha|\uparrow\rangle + \beta|\downarrow\rangle$, how do α, β relate to orientation of spin?



- Let us assume that spin is pointing along the unit vector $\hat{\mathbf{n}} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, i.e. in direction (θ, φ).
- Spin must be eigenstate of $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}$ with eigenvalue unity, i.e.

$$\begin{pmatrix} n_z & n_x - in_y \\ n_x + in_y & -n_z \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

- With normalization, $|\alpha|^2 + |\beta|^2 = 1$, (up to arbitrary phase),

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} e^{-i\varphi/2}\cos(\theta/2) \\ e^{i\varphi/2}\sin(\theta/2) \end{pmatrix}$$

Spin symmetry

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} e^{-i\varphi/2}\cos(\theta/2) \\ e^{i\varphi/2}\sin(\theta/2) \end{pmatrix}$$

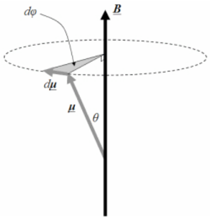
- Note that under 2π rotation,

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \mapsto -\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

- In order to make a transformation that returns spin to starting point, necessary to make two complete revolutions, (cf. spin 1 which requires 2π and spin 2 which requires only π!).

(Classical) spin precession in a magnetic field

Consider magnetized object spinning about centre of mass, with angular momentum $\mathbf{L}$ and magnetic moment $\boldsymbol{\mu} = \gamma \mathbf{L}$ with γ gyromagnetic ratio.



- A magnetic field $\mathbf{B}$ will then impose a torque

$$\mathbf{T} = \boldsymbol{\mu} \times \mathbf{B} = \gamma \mathbf{L} \times \mathbf{B} = \partial_t \mathbf{L}$$

- With $\mathbf{B} = B\hat{\mathbf{e}}_z$, and $L_+ = L_x + iL_y$, $\partial_t L_+ = -i\gamma B L_+$, with the solution $L_+ = L_+^0 e^{-i\gamma B t}$ while $\partial_t L_z = 0$.
  - Angular momentum vector $\mathbf{L}$ precesses about magnetic field direction with angular velocity $\boldsymbol{\omega}_0 = -\gamma \mathbf{B}$ (independent of angle).
  - We will now show that precisely the same result appears in the study of the quantum mechanics of an electron spin in a magnetic field.

(Quantum) spin precession in a magnetic field

- Last lecture, we saw that the electron had a magnetic moment, $\boldsymbol{\mu}_{\rm orbit} = -\frac{e}{2m_e}\hat{\mathbf{L}}$, due to orbital degrees of freedom.
- The intrinsic electron spin imparts an additional contribution, $\boldsymbol{\mu}_{\rm spin} = \gamma\hat{\mathbf{S}}$, where the **gyromagnetic ratio**,

$$\gamma = -g\frac{e}{2m_e}$$

  and g (known as the **Landé g-factor**) is very close to 2.
- These components combine to give the total magnetic moment,

$$\boldsymbol{\mu} = -\frac{e}{2m_e}(\hat{\mathbf{L}} + g\hat{\mathbf{S}})$$

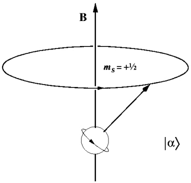
- In a magnetic field, the interaction of the dipole moment is given by

$$\hat{H}_{\rm int} = -\boldsymbol{\mu}\cdot\mathbf{B}$$

(Quantum) spin precession in a magnetic field

- Focusing on the spin contribution alone,

$$\hat{H}_{\rm int} = -\gamma \hat{\mathbf{S}} \cdot \mathbf{B} = -\frac{\gamma}{2}\hbar \boldsymbol{\sigma} \cdot \mathbf{B}$$



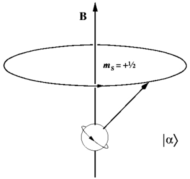
- The spin dynamics can then be inferred from the time-evolution operator, $|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle$, where

$$\hat{U}(t) = e^{-i\hat{H}_{\rm int}t/\hbar} = \exp\left[\frac{i}{2}\gamma \boldsymbol{\sigma} \cdot \mathbf{B} t\right]$$

- However, we have seen that the operator $\hat{U}(\theta) = \exp[-\frac{i}{\hbar}\theta \hat{\mathbf{e}}_n \cdot \hat{\mathbf{L}}]$ generates spatial rotations by an angle θ about $\hat{\mathbf{e}}_n$.
- In the same way, $\hat{U}(t)$ effects a spin rotation by an angle $-\gamma Bt$ about the direction of $\mathbf{B}$!

(Quantum) spin precession in a magnetic field

$$\hat{U}(t) = e^{-i\hat{H}_{\rm int}t/\hbar} = \exp\left[\frac{i}{2}\gamma\boldsymbol{\sigma}\cdot\mathbf{B}t\right]$$



- Therefore, for initial spin configuration,

$$\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = \begin{pmatrix} e^{-i\varphi/2}\cos(\theta/2)\\ e^{i\varphi/2}\sin(\theta/2)\end{pmatrix}$$

- With $\mathbf{B} = B\hat{\mathbf{e}}_z$, $\hat{U}(t) = \exp[\frac{i}{2}\gamma Bt\sigma_z]$, $|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle$,

$$\begin{pmatrix}\alpha(t)\\ \beta(t)\end{pmatrix} = \begin{pmatrix} e^{-\frac{i}{2}\omega_0 t} & 0\\ 0 & e^{\frac{i}{2}\omega_0 t}\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = \begin{pmatrix} e^{-\frac{i}{2}(\varphi+\omega_0 t)}\cos(\theta/2)\\ e^{\frac{i}{2}(\varphi+\omega_0 t)}\sin(\theta/2)\end{pmatrix}$$

- i.e. spin precesses with angular frequency $\boldsymbol{\omega}_0 = -\gamma\mathbf{B} = -g\omega_c\hat{\mathbf{e}}_z$, where $\omega_c = \frac{eB}{2m_e}$ is **cyclotron frequency**, ($\frac{\omega_c}{B} \simeq 10^{11}\,\text{rad}\,\text{s}^{-1}\text{T}^{-1}$).