Lecture 3 Chapter 3.

Monday, May 27, 2024 10:01 AM

Quantum Mechanics of Spin

3.1 New vs old quantum theories (q. th)

(a) 1920 th: old quantum theory was gradually superseded by new one

- Cornerstone of old q. th: Bohr's model of hydrogen atom:
  - orbits of electrons are quantized, only certain sizes, shapes and magnetic properties are allowed;
  - principal quantum number n: allowed radii of the orbits;
  - orbital q.n. l: allowed shapes;
  - magnetic q.n. m: magnetic behavior
  - q.n. s: self-rotation of e around its own axis (?)
- Achievements of old q. th
  - infers existence of discrete energy levels of atoms;
  - calculates energy spacing between these levels;
  - allows to interpret atomic spectra

(b) New q. th.

- triggered by
  - Heisenberg's matrix mechanics &
  - Schrödinger's wave mechanics
- both formalisms
  - predict quantization of energy;
  - provide prescription to determine the energy difference between the levels
  - probabilities of transitions between

- the energy difference between the levels
- probabilities of transitions between quantized energy states

- Schrödinger & Eckart: two theories are mathematically equivalent
- Dirac (1926) unified two theories
- Schrödinger eq for a single particle

$$i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = H\psi(\vec{r},t) \qquad (1)$$

No spin $H = \frac{\vec{p}^{\,2}}{2m} + U(\vec{r})$

$$\vec{p} = -i\hbar \nabla_{\vec{r}} \; , \quad \vec{r} = x\vec{e}_x + y\vec{e}_y + z\vec{e}_z$$

How to include spin in (1)?

<u>Digression</u>. Orbital angular momentum

- classical mechanics

$$\vec{L} = (\vec{r} \times \vec{p})$$

- q. mech $\hat{\vec{L}} = (\vec{r} \times \hat{\vec{p}}) =$

$$= \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ x & y & z \\ -i\hbar\frac{\partial}{\partial x} & -i\hbar\frac{\partial}{\partial y} & -i\hbar\frac{\partial}{\partial z} \end{vmatrix} = \vec{e}_x i\hbar\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right) + \vec{e}_y i\hbar\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right) + \vec{e}_z i\hbar\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)$$

$\Downarrow$ easy exercise

$$\hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y = i\hbar\hat{L}_x$$
$$\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z = i\hbar\hat{L}_y$$
$$\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = i\hbar\hat{L}_z$$

$$L_x L_y - L_y L_x = i\hbar L_z$$

end of digression

(3.2) Pauli spin matrices

q. th.: any physical observable $\Rightarrow$ operator $\rightarrow$ linop (Sch) / $\rightarrow$ matrix (Heis)

Eigenvalues: expectation values of the phys. quantity

Spin: physical observable

Known: operators (matrices) for orbital angular momentum (see digression)

Pauli: the same for spin angular momentum

$$S_y S_z - S_z S_y = i\hbar S_x$$
$$S_z S_x - S_x S_z = i\hbar S_y \qquad (2)$$
$$S_x S_y - S_y S_x = i\hbar S_z$$

- Stern-Gerlach experiment

  z axis joined south and north poles of the magnet

  S_z has two values $\pm \frac{\hbar}{2}$

  $\Downarrow$

- Pauli: S_z matrix operator must be

  (i) 2×2 matrix (such matrix has 2 eigenvalues)

  (ii) these eigenvalues $\pm \frac{\hbar}{2}$

$$M_{2\times 2} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (3)$$

not unique choice

<u>Digression</u>. Matrix A $\quad \underbrace{A\vec{v}}_{\text{eigenvector}} = \underbrace{\lambda}_{\text{eigenvalue}}\vec{v} = \lambda \underbrace{I}_{\text{identity matrix}}\vec{v}$

$$(A - \lambda I)\vec{v} = 0$$ nonzero solution iff $\det(A - \lambda I) = 0 \Rightarrow$ find λ

Exercise $A = \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix}$ $\lambda_1 = 1$, $\lambda_2 = 3$ $\vec{v}_{\lambda=1} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$, $\vec{v}_{\lambda=3} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

and any nonzero scalar multiplies

--- end of digression ---

- Pauli realized: choice of z-axis in S-G experiment is completely arbitrary $\Rightarrow$ expectation values of S_x and S_y (eigenvalues) should also be $\pm \hbar/2$.

- Pauli defined $\sigma_{x,y,z}$

$$S_x = \frac{\hbar}{2}\sigma_x, \ldots \qquad (*)$$

σ-matrices must have eigenvalues ± 1.

Eq. (2)

$$\begin{aligned} \sigma_y\sigma_z - \sigma_z\sigma_y &= 2i\sigma_x \\ \sigma_z\sigma_x - \sigma_x\sigma_z &= 2i\sigma_y \\ \sigma_x\sigma_y - \sigma_y\sigma_x &= 2i\sigma_z \end{aligned} \qquad (4)$$

and

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (5)$$

- How to find σ_x and σ_y having eigenvalues ± 1 AND obeying Eq. (4) ?

<u>Digression</u>. Hermitian matrix (self-adjoint)

$$A = \overline{A^T} \iff \underset{\substack{\parallel \\ a+ib}}{a_{ij}} = \underset{\substack{\parallel \\ a-ib}}{a_{ji}^*} \Rightarrow A = A^H$$

Example $\begin{pmatrix} 0 & a-ib & c-id \\ a+ib & 1 & m-in \\ c+id & m+in & 2 \end{pmatrix}$ diagonal elements always real

Spectral Theorem:

(i) Eigenvalues of Hermitian matrix are real

(ii) Eigenvectors corresponding ~~to~~ ~~dis~~tinct eigenvalues are orthogonal

--- end of digression ---

- start search for σ_x and σ_y with

$$\sigma_x = \begin{pmatrix} 0 & a \\ a^* & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & b \\ b^* & 0 \end{pmatrix}$$

Remember: eigenvalues ± 1!

$$\Downarrow$$

$$|a|^2 = |b|^2 = 1$$

$$\Downarrow$$

$$a, b = \pm 1 \text{ or } \pm i$$

- Satisfy Eq (4) $\sigma_x \sigma_y - \sigma_y \sigma_x = 2i\sigma_z$

$$\begin{pmatrix} 0 & a \\ a^* & 0 \end{pmatrix}\begin{pmatrix} 0 & b \\ b^* & 0 \end{pmatrix} - \begin{pmatrix} 0 & b \\ b^* & 0 \end{pmatrix}\begin{pmatrix} 0 & a \\ a^* & 0 \end{pmatrix} = 2i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\begin{pmatrix} ab^* & 0 \\ 0 & a^*b \end{pmatrix} - \begin{pmatrix} ba^* & 0 \\ 0 & b^*a \end{pmatrix} = 2i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$ab^* - ba^* = 2i \Rightarrow ab^* - (ab^*)^* = 2i$$

$$\Downarrow$$

$$\boxed{\mathrm{Im}(ab^*) = 1} \Rightarrow$$

$\Rightarrow$ if to select $a = +1 \Rightarrow b = -i \Rightarrow$

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

Pauli spin matrices:
serve as operators for spin components, see (*)

__Remark 1__ Pauli's choice is by no means unique (take $a = -i, b = +1$), but now historically and universally adopted

__Remark 2__. $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ unit matrix

$$S^2 = S_x^2 + S_y^2 + S_z^2 \underset{\substack{\uparrow \\ (*)}}{=} \frac{3}{4}\hbar^2 I = \bar{s}(\bar{s}+1)\hbar^2 I$$

with $\bar{s} = 1/2$

Compare with orbital angular momentum operator
$$L^2 = l(l+1)\hbar^2 I, \quad l = 1, 2, 3, \ldots$$

__Properties of the Pauli spin matrices__ (shown by direct computation)

1. $\det(\sigma_j) = -1, \quad j = x, y, z$
2. $\mathrm{Tr}(\sigma_j) = 0$
3. $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I$
4. $\sigma_x \sigma_y \sigma_z = iI$
5. $\sigma_x \sigma_y = -\sigma_y \sigma_x = i\sigma_z$
6. $\sigma_y \sigma_z = -\sigma_z \sigma_y = i\sigma_x$
7. $\sigma_z \sigma_x = -\sigma_x \sigma_z = i\sigma_y$
8. $\sigma_p \sigma_q + \sigma_q \sigma_p = 0 \quad (p \neq q;\ p, q = x, y, z)$

3.2 Eigenvectors of the Pauli matrices. Spinors.

Eigenvalues ± 1. $|\pm\rangle = ?$

- unit norm AND orthonormality

σ_z) $\sigma_z |\pm\rangle = \pm 1 |\pm\rangle_z$ go to (**)

$$\boxed{|+\rangle_z = \begin{pmatrix} 1 \\ 0 \end{pmatrix}}, \quad \boxed{|-\rangle_z = \begin{pmatrix} 0 \\ 1 \end{pmatrix}} \qquad (6a,b)$$

σ_x) $\sigma_x |\pm\rangle_x = \pm 1 |\pm\rangle_x$

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} |\pm\rangle_x = \pm 1 |\pm\rangle_x$$

1) $$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} = \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} \Rightarrow V_1 = V_2 \Rightarrow$$

norm AND orth.

$$\Rightarrow \boxed{|+\rangle_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}} \qquad (7a)$$

2) $$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} = - \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} \Rightarrow V_2 = -V_1 \Rightarrow$$

$$\Rightarrow \boxed{|-\rangle_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}} \qquad (7b)$$

$$|\pm\rangle_x = \frac{1}{\sqrt{2}} \left[|+\rangle_z \pm |-\rangle_z \right] \qquad (7c)$$

σ_y) $\sigma_y |\pm\rangle_y = \pm 1 |\pm\rangle_y$

$$(**) \Rightarrow \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} = \pm \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} \Rightarrow$$

$$\Rightarrow \boxed{|+\rangle_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}}, \quad \boxed{|-\rangle_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}} \qquad (8a,b)$$

$$\Rightarrow \boxed{|+\rangle_y = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ i\end{pmatrix}}, \quad \boxed{|-\rangle_y = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -i\end{pmatrix}} \qquad (8a, b)$$

$$|\pm\rangle_y = \frac{1}{\sqrt{2}}\left[|+\rangle_z \pm i |-\rangle_z \right] \qquad (8c)$$

Remark 1 Eigenvectors of Pauli spin matrices are examples of spinors
2×1 column vectors representing the spin state of electron

Know spinor $\rightarrow \langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle$ expectation values,
i.e. electron's spin orientation

(3.3) Pauli equation and spinors

- Absorb space-time dependent part of electron's wavefunction in spinor

$$[\psi(\vec{r}, t)] = \begin{pmatrix} \phi_1(\vec{r}, t) \\ \phi_2(\vec{r}, t) \end{pmatrix} \quad \text{general form of a spinor}$$

ϕ_1, ϕ_2 : two components of spinor wavefunction (normalized)

- Schrödinger eq Pauli eq

$$\left\{ [H] + \frac{\hbar}{i}\frac{\partial}{\partial t}[I] \right\} [\psi(\vec{r}, t)] = [0] \qquad (9)$$

$[H]$: 2×2 matrix (may contain 2×2 Pauli matrices)

$[I]$: 2×2 unit matrix

set of two diff. eqs for ϕ_1, ϕ_2

- Expected value along n-th coordinate axis

$$[\psi(\vec{r}, t)]^\dagger [S_n][\psi(\vec{r}, t)], \quad S_n = \frac{\hbar}{2}\sigma_n, \; n = x, y, z$$

$\dagger$ dagger Hermitian conjugate

Go to (**)

$$\underbrace{\langle S_x(\vec{r},t)\rangle} = \frac{\hbar}{2}\left[\psi(\vec{r},t)\right]^{\dagger}\left[\sigma_x\right]\left[\psi(\vec{r},t)\right] =$$

$$= \frac{\hbar}{2}\left[\phi_1^*(\vec{r},t), \phi_2^*(\vec{r},t)\right]\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} \phi_1(\vec{r},t) \\ \phi_2(\vec{r},t) \end{bmatrix} =$$

Associativity $(AB)C = A(BC)$

$$= \frac{\hbar}{2}\left[\phi_1^* \ , \ \phi_2^*\right]\begin{bmatrix} \phi_2 \\ \phi_1 \end{bmatrix} = \frac{\hbar}{2}\left(\phi_1^*\phi_2 + \phi_1\phi_2^*\right) =$$

$$= \frac{\hbar}{2}\left(\phi_1^*\phi_2 + c.c.\right) = \underbrace{\hbar\, Re\left(\phi_1^*(\vec{r},t)\,\phi_2(\vec{r},t)\right)} \quad (10a)$$

$$\underbrace{\langle S_y(\vec{r},t)\rangle} = \frac{\hbar}{2}\left[\psi(\vec{r},t)\right]^{\dagger}\left[\sigma_y\right]\left[\psi(\vec{r},t)\right] =$$

$$= \frac{\hbar}{2}\left[\phi_1^*(\vec{r},t) \ , \ \phi_2^*(\vec{r},t)\right]\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{bmatrix} \phi_1(\vec{r},t) \\ \phi_2(\vec{r},t) \end{bmatrix} =$$

$$[1\times 2][2\times 2] = [1\times 2]$$

$$= \frac{\hbar}{2}\left[i\phi_2^* \ , \ -i\phi_1^*\right]\begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} = \frac{\hbar}{2}\left(i\phi_2^*\phi_1 - i\phi_1^*\phi_2\right) =$$

$$= \frac{\hbar}{2}\left\{-i\left(Re(\phi_1^*\phi_2) + i\,Im(\phi_1^*\phi_2)\right) + i\left(Re(\phi_1^*\phi_2) - i\,I(\phi_1^*\phi_2)\right)\right\} =$$

$$= \underbrace{\hbar\, Im\left(\phi_1^*\phi_2\right)} \quad (10b)$$

$$\langle S_z(\vec{r},t)\rangle = \frac{\hbar}{2}\left[\psi(\vec{r},t)\right]^{\dagger}\left[\sigma_z\right]\left[\psi(\vec{r},t)\right] =$$

$$= \frac{\hbar}{2}\left[\phi_1^* \ , \ \phi_2^*\right]\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} =$$

$$= \frac{\hbar}{2}\left[\phi_1^* \ \ \phi_2^*\right]\begin{bmatrix} \phi_1 \\ -\phi_2 \end{bmatrix} = \frac{\hbar}{2}\left(\left|\phi_1(\vec{r},t)\right|^2 - \left|\phi_2(\vec{r},t)\right|^2\right) \quad (10c)$$

<u>Conclusion</u> Solve Pauli eq (9) =>

=> find 3 components of the expected

$\Rightarrow$ find 3 components of the expected value of spin angular momentum at any $(\vec{r}, t)$.

Exercise. If 2-component spinor is the state $|+\rangle_z$, then show $\langle S_x \rangle = \langle S_y \rangle = 0$ and $\langle S_z \rangle = \frac{\hbar}{2}$

Also, if spinor is $|-\rangle_z \Rightarrow \langle S_x \rangle = \langle S_y \rangle = 0$ and $\langle S_z \rangle = \frac{\hbar}{2}$

Solution. Go to Eqs. (10) and (6)

For state $|+\rangle_z$ $\phi_1 = 1$, $\phi_2 = 0$

$$\langle S_x \rangle = \hbar \operatorname{Re}(\phi_1^* \phi_2) = 0$$

$$\langle S_y \rangle = \hbar \operatorname{Im}(\phi_1^* \phi_2) = 0$$

$$\langle S_z \rangle = \frac{\hbar}{2}\left(|\phi_1|^2 - |\phi_2|^2\right) = \frac{\hbar}{2}$$

For state $|-\rangle_z$ $\phi_1 = 0$, $\phi_2 = 1$

$$\langle S_x \rangle = \langle S_y \rangle = 0, \quad \langle S_z \rangle = -\frac{\hbar}{2}$$

$\Rightarrow$ State $|+\rangle_z$ $+z$-polarized state

$|-\rangle_z$ $-z$-polarized state

Spin polarized along $+z$

— " — $-z$

3.4. More on Pauli equation (9)

Normally, 3 types of terms in $[H]$

$$[H] = H_0 [I] + [H_B] + [H_{so}] \qquad (11)$$

- H_0 spin-independent H_0
- spin-dependent matrices 2×2 $[H_B]$, $[H_{so}]$

(a) $[H_B]$: self-rotation of charge →

→ magnetic moment $\vec{\mu}_e$

Energy of interaction of $\vec{\mu}_e$ with external magnetic field

$$E_{int} = -\vec{\mu}_e \vec{B}$$

$$\Updownarrow$$

$$[H_B] = -\frac{g}{2}\mu_B \vec{B}\cdot\vec{\sigma} \quad \text{(Lande)}$$

Zeeman Hamiltonian (Zeeman interaction term),

g gyromagnetic factor

$$\vec{S} = \frac{\hbar}{2}\vec{\sigma}, \quad \vec{\sigma} = \sigma_x \vec{e}_x + \sigma_y \vec{e}_y + \sigma_z \vec{e}_z$$

μ_B Bohr magneton μ_B

Digression. Bohr magneton

Bohr theory:

- electron equivalent to circular current with magnetic moment

$$\mu_e = \frac{eS}{T} \quad \text{square } S, \text{ period of rotation } T$$

- Remind Bohr quantization role for orbital momentum

$$m_e v_e r = n\hbar, \quad n = 1, 2, \ldots$$

1st orbit $r_0 = \dfrac{\hbar}{m_e v_e}$

• magnetic moment of electron on the 1st Bohr orbit μ_B

$$\mu_B = \frac{e \cdot \pi r_0^2}{\dfrac{2\pi r_0}{v_e}} = \frac{e}{2} v_e r_0 = \frac{e\hbar}{2m_e}$$

$$\mu_B \sim 10^{-23}\ A \cdot m^2$$

(b) back to (11)

$[H_{SO}]$ spin - orbit interaction

$$\boxed{\left\{ H_0 [I] + [H_B] + [H_{SO}] + \frac{\hbar}{i}\frac{\partial}{\partial t}[I] \right\} [\psi(\vec{r},t)] = [0]} \quad (12)$$

Solution of (12): 2-component wavefunction ψ

=> spin components (10)

Remark Dirac: relativistic generalization of the Pauli eq.