Chapter 14 自旋的發現及其描述 (3rd edition, Chapter 10)

角動量與磁偶極 (magnetic dipole)

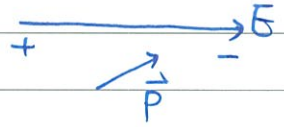
(1) 电偶極與磁偶極
(electric dipole)

這二個當初所引入的觀念十分相似，但實際上差異很大：

electric dipole $\quad \overset{\vec{p}}{- \longrightarrow +} \quad$ $\vec{p}=q\vec{d}$ $\quad$ d = − + 之間之距離

magnetic dipole ○ i (電流線圈) $\quad \vec{\mu}=\frac{i\vec{a}}{c}$

在 $\vec{E}$ 下，

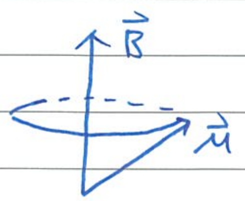


$\left\{ \begin{array}{l} \vec{\tau}=\vec{p}\times\vec{E} \\ U=-\vec{p}\cdot\vec{E} \end{array} \right.$ ∴ $\vec{p}$ 之運動轉成與 $\vec{E}$ 平行

在 $\vec{B}$ 下，$\vec{\mu}$ 之運動呢？ $\quad \vec{\tau}=\vec{\mu}\times\vec{B}$, $U=-\vec{\mu}\cdot\vec{B}$ 仍成立

∴若將 $\vec{\mu}$ 想成 $\boxed{S\ N}$ 小磁鐵，則 $\vec{\mu}$ 似乎應該作與 $\vec{p}$ 在 $\vec{E}$ 下之運動一般，但答案是否定的！

真正之運動：



$\vec{\mu}$ 會作 precession，正如陀螺作 precession 一般！

Why?

(ii) 仔細思考，我們發現：

① 一般 magnetic dipole 和 electric dipole 不同，並不是因為"單極"之分佈不均造成的！

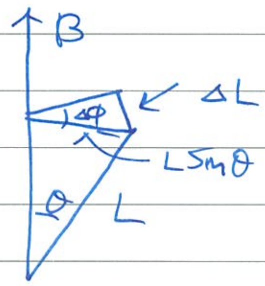
② magnetic dipole 是由於電荷圓周繞行運動造成的！

而因為電荷也帶質量，∴ 繞行也帶角動量！

∴ expect: $\vec{\mu} \propto \vec{L}$! ，設 $\vec{\mu} = \gamma \vec{L}$

$$\therefore \ \vec{\tau} = \frac{d\vec{L}}{dt} = \vec{\mu} \times \vec{B} = \gamma \vec{L} \times \vec{B}$$

$$\therefore \ \vec{L}\cdot\frac{d\vec{L}}{dt} = 0, \quad \frac{dL^2}{dt} = 0, \quad \Delta L = \gamma L B \sin\theta \, \Delta t = L \sin\theta \, \Delta\phi$$



$$\therefore \ \Delta\phi = \gamma B \Delta t$$

$\omega = \gamma B$ 為 precession 之角頻率 $= \frac{|e|B}{2mc}$

≡ Larmor frequency

$\gamma = ?$ 古典：

$$\mu = \frac{i \cdot \pi r^2}{c}, \quad i = \frac{q}{T}, \quad T = \frac{2\pi}{\omega}$$

$$\therefore \ \mu = \frac{\omega q}{2c} r^2$$

$$L = r m v = m r^2 \omega$$

$$\therefore \ \mu = \frac{q}{2mc} L, \quad \gamma = \frac{q}{2mc}$$

由於電子之 $q=-|e|$，且 $[L]=\hbar$

∴ 常記作： $\vec{\mu} = -\frac{|e|\hbar}{2mc}\frac{\vec{L}}{\hbar}$

$$\equiv -g\frac{\mu_b}{\hbar}\vec{L} \quad —— ①$$

g = gyromagnetic ratio，$\vec{L}$ = orbital angular，則 $g=g_e=1$

$\mu_b = \frac{|e|\hbar}{2mc}$ ≡ Bohr magneton $= 0.927\times10^{-23}$ amp-m^2

量子：$\underbrace{\frac{1}{2m}\left(\vec{p}-\frac{q}{c}\vec{A}\right)^2}_{\text{如 Chapter 13 所述}}$ $\quad \vec{A} = \frac{1}{2}\vec{r}\times\vec{B}$

很小可被忽略

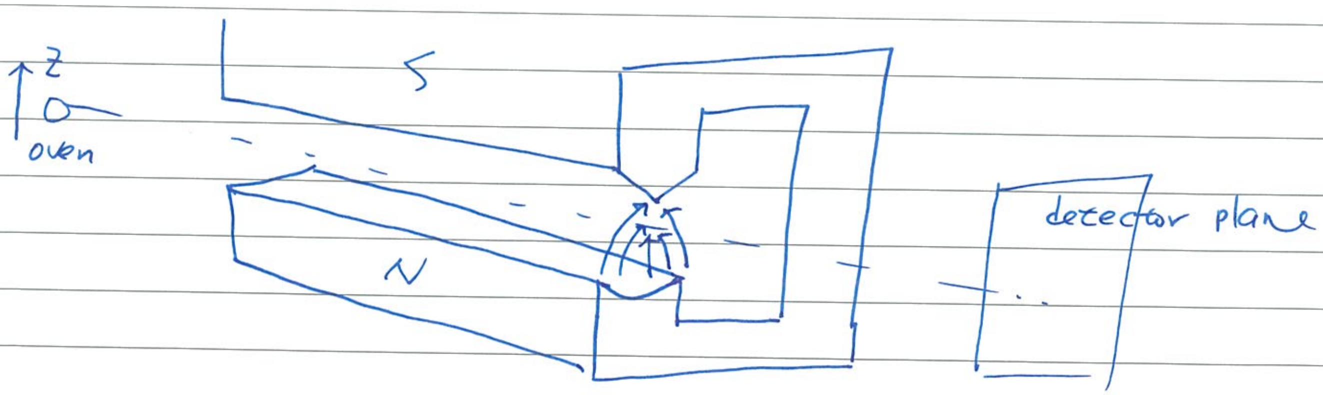
$\Rightarrow \frac{p^2}{2m} - \vec{\mu}\cdot\vec{B} + O(B^2)$ $\quad \vec{\mu} = -g_e\frac{\mu_b}{\hbar}\vec{L}$ 之關係因

也可以建立！

Stern-Gerlach expt. (自旋的發現)

利用 $U=-\vec{\mu}\cdot\vec{B}$，Stern 和 Gerlach 設計以下實驗用以

直接觀測 space quantization：



$\vec{F} = -\nabla\vec{\mu}\cdot\vec{B} = -\mu_z \nabla B$, $\frac{dB}{dz} > 0$

$\therefore F = -\mu_z \frac{dB}{dz}$

Classical: 由 oven 出，束之 $\vec{\mu}$ 之方向是任意的

∴應該看到 

但 expt. 如：

因 $\mu_z = -g_\ell \mu_b m$

$F = g_\ell \mu_b \frac{dB}{dz} m$ $m = 0, \pm1, \pm2 \ldots$

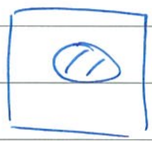
吻合！

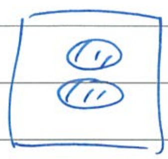
Confirm space quantization!

Suprises:

的軌域
取 neuclues $s=0$

send in $\ell = 0$ atoms (如 H atom, silver)

should see 

但看到  ?

Why? 如何將其納入角動量理論？

仔細測量發現：對應的 splitting 之 → 事實上 $g_s = 2.0023192$.

$\vec{\mu}_s = -g_s \frac{\mu_b}{\hbar} \vec{S}$, $g_s \approx 2$, $S_z = \pm\hbar/2$

∠ ②

自旋(spin)有古典對應嗎?

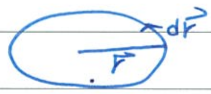
當上述現象被發現時,很自然會聯想到這可能是由於電子的自轉造成的,因此稱之為 spin!

這個想法其實不對,因為若是自轉造成的,則 g_s 應該為 1:(假設電荷及質量分佈一致)

若視電子為一帶電小球,則

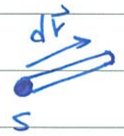
均勻 自轉

$\vec{S} = \int d^3r\, \vec{r}\times\rho_m\vec{v}$, 要計算 $\vec{\mu}$, 必須推廣 $\mu = ia/c$



$\vec{a} = \frac{1}{2}\oint \vec{r}\times d\vec{r}$

$\vec{\mu} = \frac{1}{2c}\oint \vec{r}\times d\vec{r}$



$i\,d\vec{r} = \vec{j}\,s\,dr$

$= \vec{j}_e\,d\tau$

$\vec{j}_e \parallel d\vec{r}$, $d\tau = s\,dr$ = 沿著線之體積

$\therefore \vec{\mu} = \frac{1}{2c}\int \vec{r}\times\vec{j}_e\, d^3r$

$= \frac{1}{2c}\int \vec{r}\times\rho_e\vec{v}\, d^3r$

若 $\rho_e, \rho_m = \text{const}$, 則 $\frac{\rho_e}{\rho_m} = \frac{-|e|}{m}$

$\therefore \vec{\mu} = \frac{-|e|}{2mc}\vec{S} = -g_s\frac{\mu_B}{\hbar}\vec{S}$ $\quad\therefore g_s$ 應為 1!

(若要 $g_s \neq 1$, charge 與 mass 分佈要不同, 見 Homework)

自旋的量子描述

(i) 真正讓我們了解到 $\vec{S}$ 稱為自旋仍有一些道理是從下的考慮:

① 它無法用粒子之座標描述 (∵ 不是 orbital angular moment)

② 因此，它就像粒子之 m, e 一樣，為內在的性質 (intrinsic)

如果我們嘗試"以座標來描述"，則最好的 candidate 為之前尚未考慮之情形：$c = 1/2$

$\therefore\ m = \quad -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \ldots$

此時 ∵ 只看到 (对电子而言) $\pm 1/2$，∴ l 只能是 $\frac{1}{2}$，

否則 $L_\pm$ 可以將 m 帶到 $\pm 3/2$，而 l 必須 $\geq m_{max}$

($-l \leq m \leq l$ 仍成立) $\hat{L}_+ = \hbar e^{i\phi}\left(\frac{d}{d\theta} + i\cot\theta \frac{d}{d\phi}\right)$

$\because Y_{ll} \propto \sin^l\theta\, e^{il\phi}$ $\quad \left(\frac{d}{d\theta} - \frac{1}{2}\cot\theta\right) f(\theta) = 0$

$f(\theta) = \sqrt{\sin\theta}$

$\therefore Y_{\frac{1}{2},\pm\frac{1}{2}} = C_\pm \sqrt{\sin\theta}\ e^{\pm i\phi/2}$

但這顯然会

$Y_{1/2,-1/2} \propto L_- Y_{1/2,1/2}$ 矛盾！

$\because L_- Y_{1/2,1/2} = \hbar\, e^{-i\phi}\left(-\frac{d}{d\theta} + i\cot\theta \frac{d}{d\phi}\right) C_+ \sqrt{\sin\theta}\, e^{i\phi/2}$

$\propto \left[-\frac{1}{2}\frac{\cos\theta}{\sqrt{\sin\theta}} - \frac{\cot\theta}{2}\sqrt{\sin\theta}\right] e^{-i\phi/2}$

$\propto \frac{\cos\theta}{\sqrt{\sin\theta}}\, e^{-i\phi/2} \not\propto Y_{1/2,-1/2}$

由此可見，S 無法納入 orbital angular moment！

(ii) 角動量的推廣及矩陣表示法的必要

由以上的討論，可知 $\vec{S}$ 與 (x,y,z) 無關，所以它並不能用 $\vec{r}, \vec{p}, \cdots$ 等 orbital 量表示，為一像 $m, e, \cdots$ 等之內在特性。

所以，它的表現雖然與 $\vec{L}=\vec{r}\times\vec{p}$ 相似，但並不完全可以由 $\vec{r}\times\vec{p}$ 定義而得到.

那麼如何定它呢？

從現象的角度來說，我們只能承認：

給定 $\vec{r}$，粒子之波函數有二個分量：(即 Schrödinger 方程式不完整) $\begin{cases}\psi_\uparrow(\vec{r})\\ \psi_\downarrow(\vec{r})\end{cases}$

此處，我們暫定 quantization axis 為 z 軸.

所以，$\psi_\uparrow(\vec{r})$ 之 $S_z=\hbar/2$，$\psi_\downarrow(\vec{r})$ 之 $S_z=\hbar/2$.

換句話說，$\psi(\vec{r})$ 應該以一個向量 $\begin{pmatrix}\psi_\uparrow(\vec{r})\\ \psi_\downarrow(\vec{r})\end{pmatrix}$ 表示，

(向量場對大家而言，並不陌生，如水流之流場，電場，磁場…皆是！)

即 $\psi(\vec{r}) = \begin{pmatrix}\psi_\uparrow(\vec{r})\\ \psi_\downarrow(\vec{r})\end{pmatrix} = \psi_\uparrow(\vec{r})\underbrace{\begin{pmatrix}1\\0\end{pmatrix}}_{\chi_+} + \psi_\downarrow\underbrace{\begin{pmatrix}0\\1\end{pmatrix}}_{\chi_-}$

註：$|\psi_\uparrow(\vec{r})|^2$ 為在 $\vec{r}$ 處找到自旋向上之機率，$|\psi_\downarrow(\vec{r})|^2$ 為…自旋向下之機率

這裏二個分量所形成之空間與 $\vec{r}$ 無關： $\boxed{\int d\vec{r}\,(|\psi_\uparrow|^2+|\psi_\downarrow|^2)=1}$

每一點 $\vec{r}$，都可以有二個互相垂直之 χ_+ 及 χ_-

∴ χ_+ 及 χ_- 形式一個基底，∵ 且 $\chi_\pm$ 為 S_z 的 eigenstates：

$$S_z \chi_+ = \frac{\hbar}{2} \chi_+ \quad \text{—— ③}$$
$$S_z \chi_- = -\frac{\hbar}{2} \chi_- \quad \text{—— ④}$$

一般的波函數 $= \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \alpha \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \beta \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

這樣的推論，使我們推廣角動量之定義：

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

可以驗証 ③ & ④ 是滿足的！

這樣還不夠，因為 S_x 及 S_y 仍不知道。

為了找到 S_x 及 S_y 之表示，我們想到所对應的 $L_\pm = L_x \pm i L_y$，　$L_\pm Y_{\ell,m} = \hbar\sqrt{(\ell \mp m)(\ell \pm m + 1)}\, Y_{\ell, m\pm1}$ —— ⑤

這裏，$S_\pm = S_x \pm i S_y$，且由之前的討論，$S_\pm \neq \hbar e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$

但這只是表示 $\hbar e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$ 並非 $S_\pm$ 之形式，

⑤式仍可以是正確的。

☆ 一旦⑤式是正確的，則角動量的結果 $m = -j, -j+1, \ldots, j-1, j$ 自動成立（這正是實驗所看到的）而⑤式的建立完全依據於角動量之commutation relation

如果假設⑤式是对的，則 $S_+ \chi_+ = 0$

設 $s = 1/2$　$S_+ \underset{m=-1/2}{\chi_-} = \hbar\sqrt{\left(\frac{1}{2}-\left(-\frac{1}{2}\right)\right)\left(\frac{1}{2}-\frac{1}{2}+1\right)}\, \chi_+ = \hbar \chi_+$

$$S_- \chi_- = 0$$

$$S_- \chi_+ = \hbar\sqrt{\left(\frac{1}{2}+\frac{1}{2}\right)\left(\frac{1}{2}-\frac{1}{2}+1\right)}\, \chi_- = \hbar \chi_-$$

這表示 $S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$，$S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

check: $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$$S_+\chi_+ = S_+\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$$

$$S_+\chi_- = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hbar\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar\chi_+$$

$$S_-\chi_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0$$

$$S_-\chi_+ = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hbar\chi_-$$

由此，$S_x = \frac{1}{2}(S_+ + S_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

$$S_y = \frac{1}{2i}(S_+ - S_-) = \frac{\hbar}{2i}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

从上的建構，告訴我們 $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$

$\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$，$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$，$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$，$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

為所謂的 Pauli matrices.

(以矩陣來表示 operators)

如此的建構，事實上，為最小 (minimum) 且保有角動量(量子)基本構造的一個建構：

(a) Commutation relation 仍一樣：

如：$[S_x, S_y] = (\frac{\hbar}{2})^2 [\sigma_x, \sigma_y]$

$$\because \sigma_x\sigma_y - \sigma_y\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = 2i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 2i\sigma_z$$

$\therefore\ [S_x, S_y] = \frac{\hbar^2}{4} 2i\sigma_z = i\hbar(\frac{\hbar}{2}\sigma_z) = i\hbar S_z$

同理，$\left.\begin{array}{l}[\sigma_y, \sigma_z] = 2i\sigma_x \\ [\sigma_z, \sigma_x] = 2i\sigma_y\end{array}\right\} \Rightarrow \begin{array}{l}[S_y, S_z] = i\hbar S_x \\ [S_z, S_x] = i\hbar S_y.\end{array}$

注意：(b)式之來源為 commutation relation 與 $L_\pm = \hbar e^{\pm i\varphi}(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi})$ 無關

(b) $S^2 = \frac{3\hbar^2}{4}\mathbb{I} = \hbar^2\frac{1}{2}(\frac{1}{2}+1)\mathbb{I}$

$\sigma_x^2 = \begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix} = \mathbb{I}$

$\sigma_y^2 = \begin{pmatrix}0&-i\\i&0\end{pmatrix}\begin{pmatrix}0&-i\\i&0\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix} = \mathbb{I}$

$\sigma_z^2 = \begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix} = \mathbb{I}$

$\therefore\ S^2 = \frac{\hbar^2}{4}(\sigma_x^2 + \sigma_y^2 + \sigma_z^2) = \frac{3\hbar^2}{4}\mathbb{I}$

(c) 平均值：任一波函數 $= \begin{pmatrix}\alpha\\\beta\end{pmatrix}$

$|\alpha|^2 + |\beta|^2 = 1$

$\langle S_x\rangle = (\alpha^*, \beta^*) S_x \begin{pmatrix}\alpha\\\beta\end{pmatrix}$

$\langle S_y\rangle = (\alpha^*, \beta^*) S_y \begin{pmatrix}\alpha\\\beta\end{pmatrix}$

$\langle S_z\rangle = \ \cdots\ S_z \begin{pmatrix}\alpha\\\beta\end{pmatrix}$

$= |\alpha|^2\frac{\hbar}{2} - |\beta|^2\frac{\hbar}{2}$

由此可以得知 經驗：① 量子物理中算符的 commutation relations 才是定義算符的基本關係，實際的表示式 (如 $\vec{r}\times\vec{p}$) 並不是決定 eigenvalues (如 $m\hbar$) 之重點

② 所有的 operators，在一個基底下，皆可以以矩陣表示，如 $l=1$ 之 $Y_{1,1}, Y_{1,-1}, Y_{1,0}$ 可以用 $\begin{pmatrix}1\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\1\end{pmatrix}\begin{pmatrix}0\\1\\0\end{pmatrix}$ 來表示了！ $\Rightarrow$ 則 平均值之計算要小心。

⇒見 page 14-16

注意：以上為自旋為 $\frac{1}{2}$ 之例，真實的粒子其自旋 $s = \frac{1}{2}, 1, \frac{3}{2}, \ldots$ 可以

$\left.\begin{array}{l}\text{電子}\\\text{質子}\\\text{中子}\end{array}\right\} s = \frac{1}{2},\quad s = \frac{3}{2}\ \vdots \Bigg\} \Rightarrow$ 費米子， $s = 1, 2, 3. \Rightarrow$ 波色子

Paper House

不同 quantization axis 間的轉換

以上用 z 為 quantization axis 為表示式.

我們也可以用 x 軸為 quantization axis.

此時 $S_x = \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}$ 之 eigenvalues 也是 $\pm\hbar/2$

(這表示 $\pm\hbar/2$ 和軸之選取無關)

但若以 z 軸之 eigenstate $\chi_+ = \begin{pmatrix}1\\0\end{pmatrix}$, $\chi_- = \begin{pmatrix}0\\1\end{pmatrix}$

來表示:

$$S_x = \hbar/2 \text{ 之 eigenstate} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \equiv \tilde{\chi}_+$$

$$S_x = -\hbar/2 \quad '' \quad = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} \equiv \tilde{\chi}_-$$

Check:

$$S_x\left[\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}\right] = \frac{1}{\sqrt{2}}\cdot\frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1\\1\end{pmatrix} = \frac{\hbar}{2}\left[\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}\right]$$

$$S_x\left[\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}\right] = \frac{1}{\sqrt{2}}\frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1\\-1\end{pmatrix} = -\frac{\hbar}{2}\left[\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}\right]$$

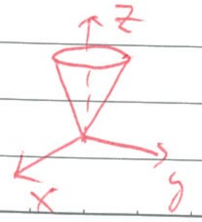
因此, $\chi_+ = \frac{1}{\sqrt{2}}(\tilde{\chi}_+ + \tilde{\chi}_-)$

$\chi_- = \frac{1}{\sqrt{2}}(\tilde{\chi}_+ - \tilde{\chi}_-)$

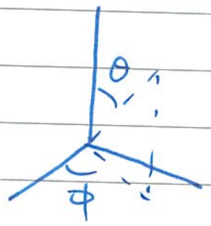
物理意義:

z 軸之 spin ↑, 對 x 軸而言, 有 $\left|\frac{1}{\sqrt{2}}\right|^2$ 機率 為 ←

$\left(\frac{1}{\sqrt{2}}\right)^2$ .. 為 →



例：我們可以用 $\hat{n}=(\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)$ 為任意方向 quantization axis. 此時 spin ↑，指得是 spin 基本上朝 $\hat{n}$ 之方向.



設其狀態為 $\begin{pmatrix} u \\ v \end{pmatrix}$（還是以z軸之 $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$，及 $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ 為 reference）

則 $\vec{S}\cdot\hat{n}\begin{pmatrix} u \\ v \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} u \\ v \end{pmatrix}$ —— ⑥

書上：$\theta=\pi/2$, $\hat{n}=(\cos\phi,\ \sin\phi,\ 0)$

$$\therefore\ \vec{S}\cdot\hat{n} = S_x\cos\phi + S_y\sin\phi = \frac{\hbar}{2}\sigma_x\cos\phi + \frac{\hbar}{2}\sigma_y\sin\phi$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & \cos\phi - i\sin\phi \\ \cos\phi + i\sin\phi & 0 \end{pmatrix}$$

$$\therefore\ ⑥式 \Rightarrow \underbrace{\begin{pmatrix} 0 & \overset{e^{-i\phi}}{\cos\phi - i\sin\phi} \\ \underset{e^{i\phi}}{\cos\phi + i\sin\phi} & 0 \end{pmatrix}}\begin{pmatrix} u \\ v \end{pmatrix} = \lambda\begin{pmatrix} u \\ v \end{pmatrix}$$

此矩陣之 eigenvalue, λ

滿足 $\lambda^2 = (\cos\phi - i\sin\phi)(\cos\phi + i\sin\phi) = 1$

$\therefore\ \lambda = \pm 1$，$\lambda = 1 \Rightarrow$ $e^{-i\phi}v = u$
$e^{i\phi}u = v$

取 $u = \frac{e^{-i\phi/2}}{\sqrt{2}}$，$v = \frac{e^{i\phi/2}}{\sqrt{2}}$，$\therefore \begin{pmatrix} u \\ v \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\phi/2} \\ e^{i\phi/2} \end{pmatrix}$

（也可以取 $\begin{pmatrix} u \\ v \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{i\phi} \end{pmatrix}$）

自旋與旋進(pression)與其奇特的含意

*2個分量在自旋空間之Schrödinger方程式

$$\vec{\mu}_s = -\frac{|e|g_s}{2mc}\vec{s} = -g_s\frac{\mu_b}{\hbar}\vec{s}$$ ，在外加磁場 $\vec{B}$ 下，

$$\therefore\ \hat{H}_s = -\vec{\mu}_s\cdot\vec{B} = g_s\frac{\mu_b}{\hbar}\vec{s}\cdot\vec{B}$$

$$= \frac{1}{2}g_s\mu_b\vec{\sigma}\cdot\vec{B}$$

討論 $\hat{H} = (\frac{p^2}{2m}+V)\mathbb{I} + H_s$
separable
$\Psi = \psi_0(\vec{r})\chi$ ← ψ_s

取 $\vec{B}=B\hat{z}$ ，$\therefore\ \hat{H}_s = \frac{1}{2}g_s\mu_b\sigma_z B = \frac{1}{2}g_s\mu_b\begin{pmatrix}1&0\\0&-1\end{pmatrix}B$ $\quad \frac{\psi_{s1}}{\psi_{s2}}=\frac{a}{b}$

設自旋 $\psi_s = \begin{pmatrix}a(t)\\b(t)\end{pmatrix}$ ，則 $i\hbar\frac{d\psi_s}{dt} = \hat{H}_s\psi_s$

$$= \frac{1}{2}g_s\mu_b\vec{\sigma}\cdot\vec{B}\,\psi_s \quad — (7)$$

在 $\vec{B}=B\hat{z}$ 下，

$$i\hbar\begin{pmatrix}\frac{da}{dt}\\ \frac{db}{dt}\end{pmatrix} = \frac{1}{2}g_s\mu_b\begin{pmatrix}1&0\\0&-1\end{pmatrix}B\begin{pmatrix}a\\b\end{pmatrix}$$

$$= \begin{pmatrix}\frac{1}{2}g_s\mu_b B a(t)\\ -\frac{1}{2}g_s\mu_b B b(t)\end{pmatrix}$$

因此， $i\hbar\frac{da(t)}{dt} = \frac{1}{2}g_s\mu_b B a(t)$ ， $i\hbar\frac{db(t)}{dt} = -\frac{1}{2}g_s\mu_b B b(t)$

$$a(t) = e^{-\frac{ig_s\mu_b B}{2\hbar}t}a(0) \rightarrow a_0$$

$\mu=\gamma L \Rightarrow \vec{\mu}_s=\gamma\vec{s}$
$\gamma = g_s\frac{\mu_b}{\hbar}$ ， $\omega_L=\gamma B=\frac{|e|Bg_s}{2mc}$

$$b(t) = e^{\frac{ig_s\mu_b B}{2\hbar}t}b(0) \rightarrow b_0$$

$F = \frac{4.8\times10^{-10}\times10^4}{9\times10^{-28}g\cdot3\times10^{10}} = 1.8\times10^{11}\,\text{rad/sec}$ ← 1 Tesla T

$\because g_s\simeq2$ ， $\therefore\ \frac{g_s\mu_b B}{2\hbar}\simeq\frac{|e|B}{2mc}$ ~~ω_c~~ = cyclotron frequency
$=\frac{1}{2}\times$ Larmor frequency 當 $g_s=2$ $\quad T\simeq10^{-11}\,\text{sec}$

$$\therefore \psi_s(t) = \begin{pmatrix} a_0 e^{-\frac{i\omega_L t}{2}} \\ b_0 e^{\frac{i\omega_L t}{2}} \end{pmatrix}$$

例： $\begin{pmatrix} a_0 \\ b_0 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$，即 $t=0$ 時 $\begin{pmatrix} a_0 \\ b_0 \end{pmatrix}$ 為

S_x 之 eigenstate，即 spin 朝 $\leftarrow$ (正x方向)

此時 $\langle S_x \rangle = \frac{\hbar}{2} \cdot \frac{1}{\sqrt{2}} (1,1) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$，平均值的定義 ⇒ 見後

$= \frac{\hbar}{2} \cdot \frac{1}{2} (1,1) \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \hbar/2$

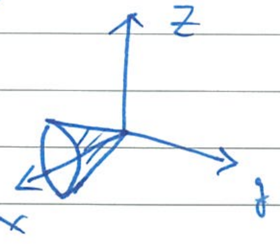
但 $\langle S_y \rangle = \frac{1}{\sqrt{2}} (1,1) \cdot \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$= \frac{\hbar}{4} (1,1) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{\hbar}{4} (1,1) \begin{pmatrix} -i \\ i \end{pmatrix} = 0$

$\langle S_z \rangle = \frac{1}{\sqrt{2}} (1,1) \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$= \frac{\hbar}{4} (1,1) \begin{pmatrix} 1 \\ -1 \end{pmatrix} = 0$

此與 "cone" 之圖像吻合



$\therefore t=0,\ \langle \vec{S} \rangle = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$

$\because t>0$ 時，$\psi(t) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-\frac{i\omega_L t}{2}} \\ e^{\frac{i\omega_L t}{2}} \end{pmatrix}$

此時

$$\langle S_x\rangle = \frac{\hbar}{2}\frac{1}{2}\left(e^{\frac{i\omega_L t}{2}},\ e^{\frac{-i\omega_L t}{2}}\right)\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}e^{\frac{-i\omega_L t}{2}}\\ e^{\frac{i\omega_L t}{2}}\end{pmatrix}$$

$$= \frac{\hbar}{4}\left(e^{\frac{i\omega_L t}{2}},\ e^{\frac{-i\omega_L t}{2}}\right)\begin{pmatrix}e^{\frac{i\omega_L t}{2}}\\ e^{\frac{-i\omega_L t}{2}}\end{pmatrix}$$

$$= \frac{\hbar}{2}\cos\omega_L t$$

$$\langle S_y\rangle = \frac{\hbar}{2}\frac{1}{2}\left(e^{\frac{i\omega_L t}{2}},\ e^{\frac{-i\omega_L t}{2}}\right)\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}e^{\frac{-i\omega_L t}{2}}\\ e^{\frac{i\omega_L t}{2}}\end{pmatrix}$$

$$= \frac{\hbar}{4}\left(e^{\frac{i\omega_L t}{2}},\ e^{\frac{-i\omega_L t}{2}}\right)\begin{pmatrix}-ie^{\frac{i\omega_L t}{2}}\\ ie^{\frac{-i\omega_L t}{2}}\end{pmatrix}$$

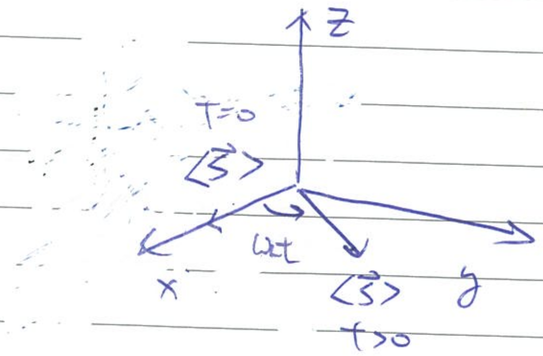
$$= \frac{\hbar i}{4}\left(-e^{i\omega_L t} + e^{-i\omega_L t}\right)$$

$$= \frac{\hbar}{2}\sin\omega_L t$$

$$\langle S_z\rangle = \frac{\hbar}{4}\left(e^{\frac{i\omega_L t}{2}},\ e^{\frac{-i\omega_L t}{2}}\right)\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}e^{\frac{-i\omega_L t}{2}}\\ e^{\frac{i\omega_L t}{2}}\end{pmatrix}$$

$$= 0$$

所以，$\langle\vec{S}\rangle = (\langle S_x\rangle, \langle S_y\rangle, \langle S_z\rangle)$ 在做 precession



∴ precession 以 ω_c (cyclotron frequency) 進行！
$= \omega_L$

在 $t = \frac{2\pi}{\omega_c} \equiv T$ 時，$\langle \vec{S} \rangle$ 轉一圈回到原來的方向。

但如果我們看波函數 $\psi(t) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-\frac{i\omega_L t}{2}} \\ e^{\frac{i\omega_L t}{2}} \end{pmatrix}$

$\because \frac{\omega_L T}{2} = \frac{1}{2}\omega_c T = \pi$

$\therefore$ $\langle \vec{S} \rangle$ 轉一圈時，$\psi(T) = -\psi(0)$!! (轉一圈"變臉"了！仍看到背後)

這個奇特的現象是因為 $s=1/2$ 之故！

(remember, for orbital angular momentum,

$Y_{\ell,m} \propto e^{im\phi}$, $m=$ 整數

$\therefore e^{im(\phi+2\pi)} = e^{im\phi}$!

此處相當於 $m=1/2$, $\therefore e^{im(\phi+2\pi)} = -e^{im\phi}$!)

這個現象可以由干涉實驗加以驗證：

$B \neq 0$ (讓 $\langle \vec{S} \rangle$ 正好轉一圈)

干涉 (利用 neutron)

NO.

DATE: NMR I

Introduction to

Nuclear magnetic resonance (NMR & MRI)

Chapt. 26. §26.6.

magnetic resonance imaging

{ identification of types of atoms & their positions, enviroments } ⇒ obtain 3 dimensional structures of molecules

unlike X-ray where molecules have to be in the state of crystals. many biological molecules of interest don't have crystal structure however

also molecules in crystal states are different than that in solutions.

basics

* quantization of angular momentum

$\vec{J} = \vec{L} + \vec{S}$

(orbital: $\vec{L}$, spin: $\vec{S}$)

$L = \sqrt{l(l+1)}\hbar$ $\quad l = 0, 1, 2, \ldots, n-1$

$S = \sqrt{s(s+1)}\hbar$ $\quad s = \frac{1}{2}, \frac{3}{2}, \ldots$ or $0, 1, 2, \ldots$

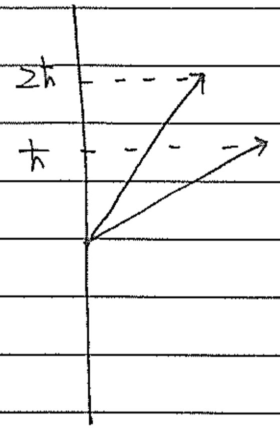
$J = \sqrt{j(j+1)}\hbar$. $\quad |l-s| \le j \le l+s$

Z component

$S_z = m\hbar$, $\quad m = -s, -s+1, \ldots, s-1, s$

$L_z = m_z\hbar$, $\quad m_z = -l, \ldots, l$

e.g. $L = \sqrt{6}\,\hbar$



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DATE:

NMR 2.

* $\vec{\mu} = 2.79 \frac{e}{m_p} \vec{S}$ (proton) $\Rightarrow$ reason to choose nucleus

$\because$ heavy, no orbital motion.

(associated with $\vec{S}/\vec{I} \Rightarrow \vec{\mu}$)

$\therefore \; U = -\vec{\mu}\cdot\vec{B} = -2.79 \frac{e}{m_p} S_z B$

$S_z = \pm\frac{\hbar}{2}$ define $\mu_N = \frac{e\hbar}{2m_p} = 5.05\times10^{-27}\,Am^2$

— nuclear magneton

$U = \pm 2.79\,\mu_N B$

example. $B = 1.4T$

$\Delta U = 2\times2.79\times5.05\times10^{-27}\,Am^2\times1.4\,T$

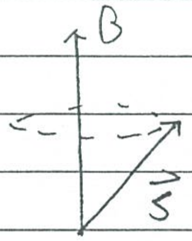
$= 3.94\times10^{-26}\,J = 2.47\times10^{-7}\,eV$

* As we mentioned, $\vec{\mu}$ will precess in $\vec{B}$ field.

— for e

$\frac{d\vec{S}}{dt} = \vec{\tau} = \vec{\mu}\times\vec{B}$ $\quad -\gamma\vec{S} = \vec{\mu}$

$\frac{d\vec{\mu}}{dt} = \gamma\,\cancel{\vec{\mu}\times}\vec{B}\times\vec{\mu}$ $\quad \Omega = \gamma B = 2\pi f_p$



$f_p = \frac{\gamma B}{2\pi}$ $\quad \gamma = 2.79\frac{e}{m_p}$

$= 0.444\frac{e}{m_p}B$

$B = 1.5T$ (most often used in MRI), $f_p = 63.8\times10^{7}\,Hz$

It is important to note that $B \neq B_{ext}$.

$\therefore$ The measurement of $\underline{\Delta f = f_p - f_e}$ $(f_e = 0.444 \frac{e}{m_p} B_e)$
(shift)
is the goal of NMR expts.

* Forced precession : & NMR

Recall that if $\vec{B} = (0, 0, B)$

$\frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B}$ can be reduced to

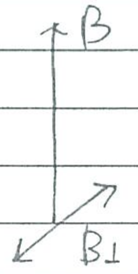
$$\frac{d^2\vec{\mu}}{dt^2} = \gamma^2 (\vec{\mu} \times \vec{B}) \times \vec{B} = -\gamma^2 \vec{B} \times (\vec{\mu} \times \vec{B}) = -\gamma^2 (B^2 \vec{\mu} - \underbrace{(\vec{B} \cdot \vec{\mu})}_{B^2 \cos\theta_\mu \hat{z}} \vec{B})$$

$$\frac{d^2\mu_x}{dt^2} = -(\gamma B)^2 \mu_x$$

$$\mu_x = \mu_\perp \cos(\gamma B t)$$

$\frac{d\mu_z}{dt} = 0. \quad \frac{d^2\mu_z}{dt^2} = \cdots$

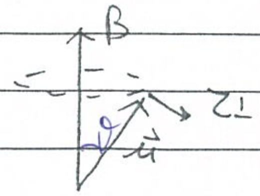
if we apply a $\vec{B}_\perp = B_\perp (\cos\omega t, \quad 0 \quad , \quad - \quad)$



it becomes a driven harmonic oscillator

When $\omega = \Omega$, it responds most largely!

What will happen is as following :



$\vec{B}_\perp$ tries to rotate $\vec{\mu}$ down!

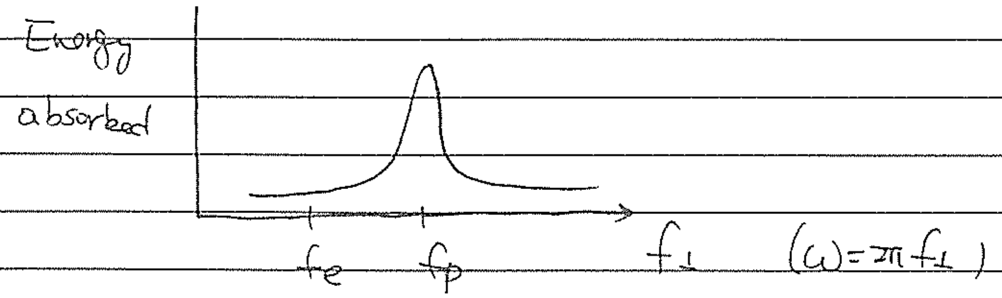
$\because S_z = \pm \frac{\hbar}{2}$, there are two states $\therefore$

$\vec{\mu}$ will flip from $-2.79 \frac{e}{m_p} \frac{\hbar}{2}$ to $+2.79 \frac{e}{m_p} \left(-\frac{\hbar}{2}\right)$

$\Delta U = 2 \times 2.79 \times \frac{e}{m_p} \frac{\hbar}{2} \times B$

$= 2.41 \times 10^{-7}\,eV$ for $B = 1.4\,T$

which is the energy absorbed by $\vec{\mu}$:



(if $B > B_e$, $f_p > f_e$!)

<u>NMR apparatus</u>

1. a permanent magnet / electromagnet $\Rightarrow B_e$ (1.4T)

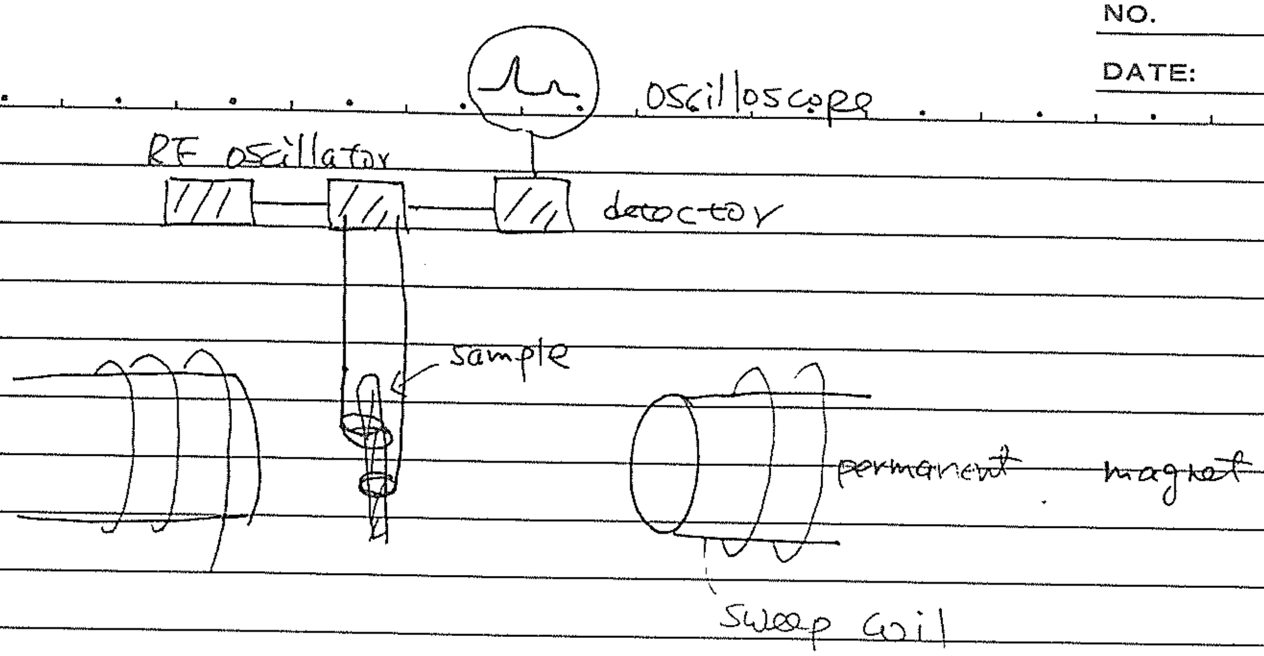
   uniformity : $1/10^8$

2. Sweep coil : change B_e over a small range

3. radio frequency (R.F.) oscillator

   $\Rightarrow B_1$ $f_1 = 6 \times 10^7$ Hz $\Rightarrow$ μ_x rotates oppositely

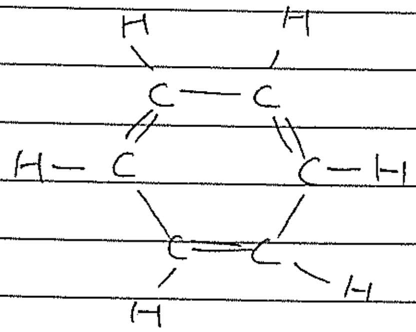
4. When energy is absorbed, an EMF (slightly out of phase with the oscillator voltage) is induced in the oscillator: and can be detected!

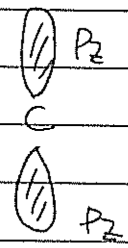


$\boxed{\text{Chemical shift}}$

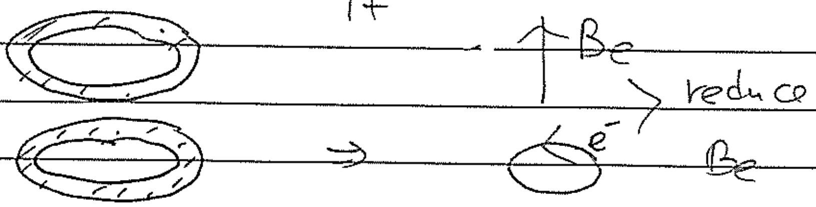
the local field B around a proton. varies a lot. $\therefore B \neq B_e$

example1: benzene

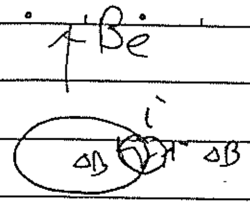




$\because$ electrons in C move in two rings

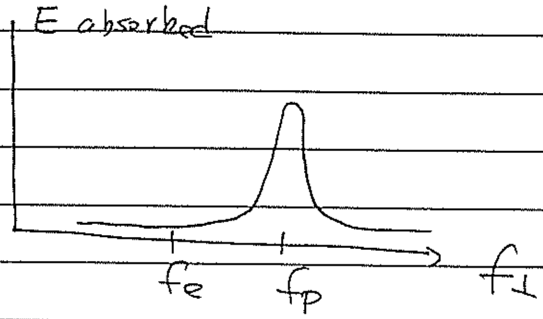


$\therefore B < B_e$ inside, however, $B > B_e$ outside



$B_e + \Delta B > B_e$ (outside)

$\therefore f_p > f_e$



two information confirmed { exist a close path for e^-
Hs are outside this path.

example 2.

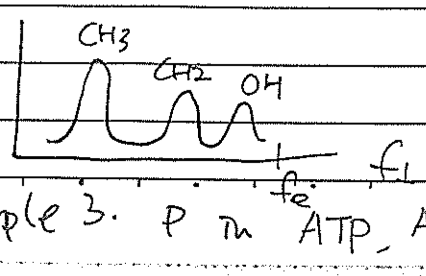
neutral H + Be $f_p < f_e$ ∵ diamagnetic effect
⇑
for s-wave e^-

ethanol (酒精) $CH_3 - CH_2 - OH$

OH group. O strongly attracts e^- from H
∴ less symmetric
∴ the ability to reduce Be is reduced. $f_p \downarrow$

CH_2 " e^-s are more closer to H
∴ f_p is larger than OH's

CH_3 even larger ⇒



also, height ∝ intensity, ∴ 3 : 2 : 1

example 3. P in ATP, ADP!

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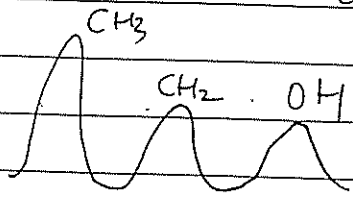
NMR 7

Effect of spins

· Spin also generates magnetic field.

example: · photon : spin = 1/2 ↑ or ↓

$CH_3 - CH_2 - OH$

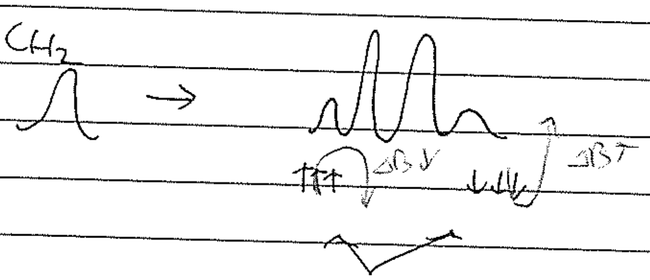


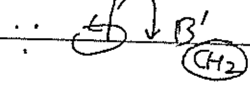
↙

photon spins

			net	ratio
↑↑↑			3/2	1
↑↑↓	↑↓↑	↓↑↑	1/2	3
↓↓↑	↓↑↓	↑↓↓	-1/2	3
↓↓↓			3/2	1

∴ due to its field



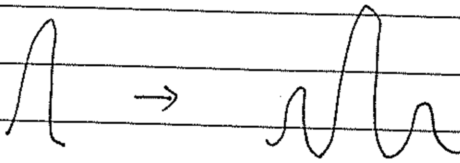


Similarly, CH_2 ⇒ ↑↑ 1

↑↓ or ↓↑ 2

↓↓ 1

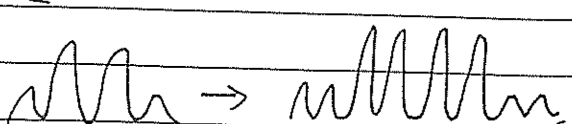
∴ cause CH_3



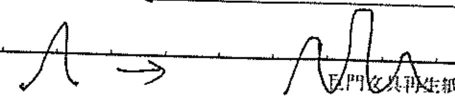
effect of OH on CH_2

↓

↑ or ↓



effect of CH_2 on OH.



→ see over

NO.
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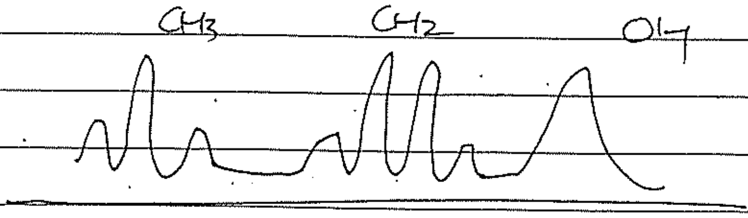
Room temperature



⇐ OH moves quickly wash out the effect

lower temperature