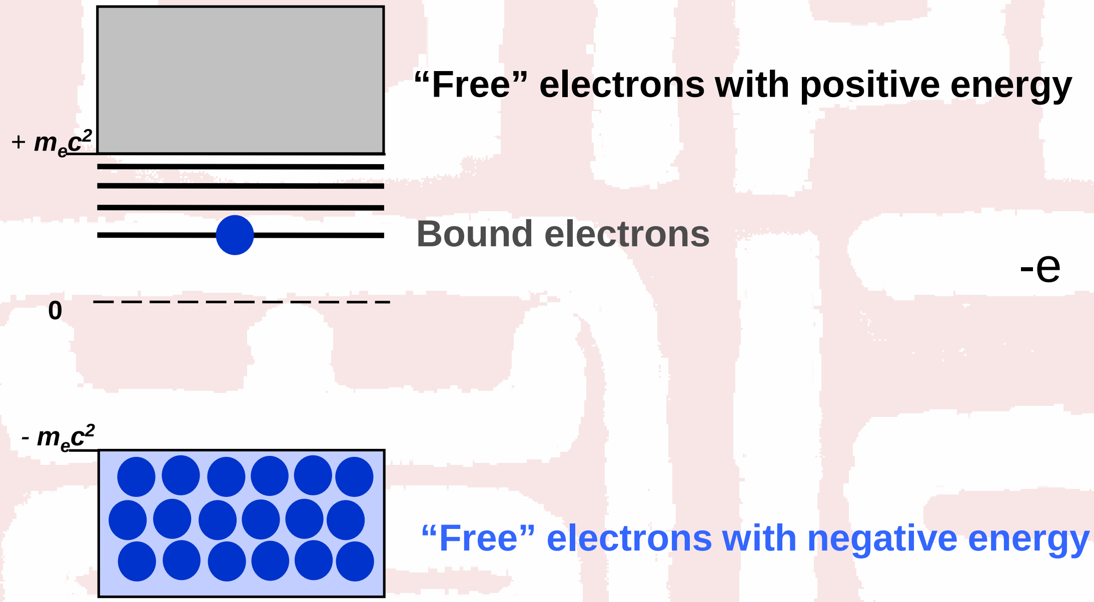
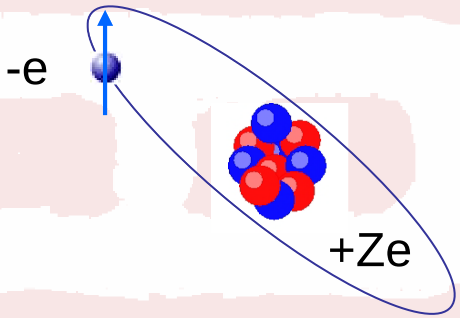
Dirac方程

$$\left(-i\hbar c\boldsymbol{\alpha}\cdot\nabla-\frac{Ze^2}{4\pi\varepsilon_0 r}+m_e c^2\alpha_0\right)\psi(\mathbf{r})=E\psi(\mathbf{r})$$





在非相对论近似下，狄拉克方程近似为

$$\left[\frac{\hat{\boldsymbol{p}}^2}{2m}+V(r)-\frac{\hat{\boldsymbol{p}}^4}{8m^3c^2}+\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}-\frac{\hbar^2}{2m^2c^2}\frac{dV}{dr}\cdot\frac{d}{dr}\right]\psi=E\psi$$

$$\left[\hat{H}_0+\hat{H}_m+\hat{H}_{ls}+\hat{H}_d\right]\psi=E\psi$$

$$V(r)=-\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$\hat{H}_m$ 是相对论动能修正项,

$\hat{H}_{ls}$ 是自旋轨道相互作用项,

$\hat{H}_d$ 是势能修正项，又称达尔文项。

未受扰动的方程为

$$\hat{H}_0 \psi_{nlm_l m_s} = E_n \psi_{nlm_l m_s}$$

零级近似的波函数 $\psi_{nlm_l m_s}$ 为Pauli波函数或“自旋-轨道”：

$$\psi_{nlm_l m_s}(q) = \psi_{nlm_l}(\mathbf{r}) \chi_{1/2, m_s}$$

空间波函数：

$$\hat{H}_0 \psi_{nlm_l}(\mathbf{r}) = E_n \psi_{nlm_l}(\mathbf{r})$$

$$\psi_{nlm_l}(\mathbf{r}) = R_{nl}(r) Y_{lm_l}(\theta, \phi)$$

$$\hat{H}_m = -\frac{\hat{\boldsymbol{p}}^4}{8m^3c^2}$$ **(动能的相对论修正)**

未受扰动能级E_n是$2n^2$重简并的，应用简并微扰论。

由对易关系可知，$\psi_{nlm_lm_s}$ 是$\hat{H}_m$的本征函数，$\hat{H}_m$在以$\psi_{nlm_lm_s}$ 为基矢的表象中是对角化的，相应简并微扰论中久期方程的系数矩阵也是对角化的，由对角元可以得到能量的修正值

$$\begin{aligned}
\Delta E_1 &= \left\langle \psi_{nlm_lm_s} \middle| \hat{H}_m \middle| \psi_{nlm_lm_s} \right\rangle \\
&= \left\langle \psi_{nlm_lm_s} \middle| -\frac{\hat{\boldsymbol{p}}^4}{8m^3c^2} \middle| \psi_{nlm_lm_s} \right\rangle \\
&= \left\langle \psi_{nlm_l} \middle| -\frac{\hat{\boldsymbol{p}}^4}{8m^3c^2} \middle| \psi_{nlm_l} \right\rangle \\
&= -\frac{1}{2mc^2} \left\langle \psi_{nlm_l} \middle| \hat{T}^2 \middle| \psi_{nlm_l} \right\rangle
\end{aligned}$$

$$\hat{T} = \hat{H}_0 - \left(-\frac{Ze^2}{4\pi\varepsilon_0 r} \right)$$

$$\Delta E_1 = -\frac{1}{2mc^2} \langle nlm_l | \left(H_0 + \frac{Ze^2}{4\pi\varepsilon_0 r} \right) \left(H_0 + \frac{Ze^2}{4\pi\varepsilon_0 r} \right) | nlm_l \rangle$$

$$= -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{Ze^2}{4\pi\varepsilon_0} \right) \left\langle \frac{1}{r} \right\rangle_{nlm_l} + \left(\frac{Ze^2}{4\pi\varepsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle_{nlm_l} \right]$$

$$\left\langle \frac{1}{r} \right\rangle_{nlm_l} = \frac{Z}{a_0 n^2} \qquad \left\langle \frac{1}{r^2} \right\rangle_{nlm_l} = \frac{Z^2}{a_0^2 n^3 (l + \frac{1}{2})}$$

$$\Delta E_1 = -\frac{1}{2mc^2}\left\{\left[\frac{mc^2(Z\alpha)^2}{2n^2}\right]^2 - 2\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{mc^2(Z\alpha)^2}{2n^2}\frac{Z}{a_0 n^2} + \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{Z^2}{a_0^2 n^3(l+\frac{1}{2})}\right\}$$

$$= \frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}\frac{(Z\alpha)^2}{n^2}\left[\frac{3}{4} - \frac{n}{l+\frac{1}{2}}\right]$$

$$= -E_n\frac{(Z\alpha)^2}{n^2}\left[\frac{3}{4} - \frac{n}{l+\frac{1}{2}}\right]$$

$$\hat{H}_d = -\frac{\hbar^2}{2m^2c^2}\frac{dV}{dr}\cdot\frac{d}{dr} = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\delta(r)$$ **(达尔文项)**

$\hat{H}_d$ 在以 $\psi_{nlm_lm_s}$ 为基矢的表象中也是对角化的

$l=0$

$$\Delta E_3 = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\langle n00|\delta(r)|n00\rangle$$

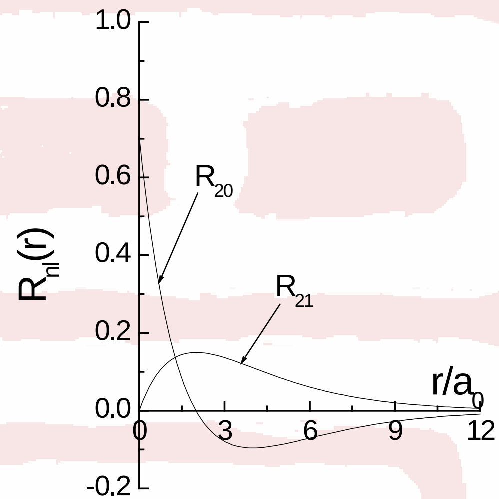
$$= \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\left|\psi_{n00}(0)\right|^2$$

$$= \frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}\frac{(Z\alpha)^2}{n}$$

$$= -E_n\frac{(Z\alpha)^2}{n}$$

$l\neq 0$

$$\Delta E_3 = 0$$



$$\hat{H}_{ls} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}$$ **(自旋-轨道相互作用项)**

在以 $\psi_{nlm_lm_s}$ 为基矢的表象中不是对角化的。

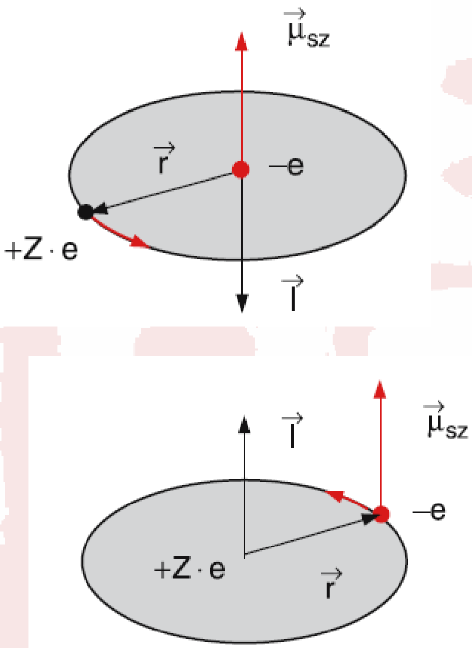
§ 2.1　单电子(H)原子　氢原子的精细结构

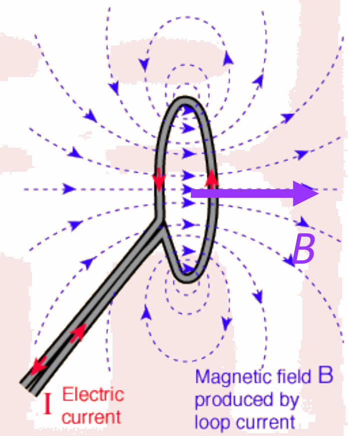
$$\mathbf{B}' = \frac{Ze\boldsymbol{l}}{4\pi\varepsilon_0 mc^2 r^3} = \xi'(r)\boldsymbol{l}$$

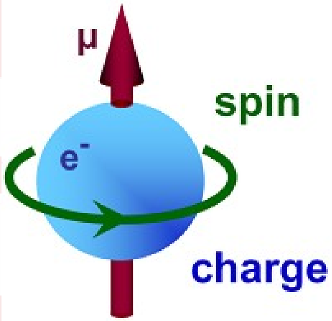
$$\mathbf{B} = \frac{1}{2}\frac{Ze\boldsymbol{l}}{4\pi\varepsilon_0 mc^2 r^3} = \xi(r)\boldsymbol{l}$$

$$\hat{\boldsymbol{\mu}}_s = -g_s\mu_B\mathbf{s}/\hbar$$

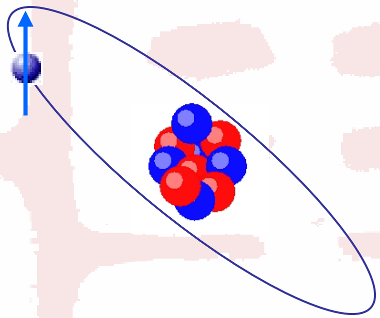
$$\hat{H}_{ls} = -\hat{\boldsymbol{\mu}}_s \cdot \mathbf{B} = \zeta(r)\hat{\boldsymbol{l}}\cdot\hat{\boldsymbol{s}}$$







◆ 不考虑自旋-轨道耦合



$$\psi_{nlm_l sm_s}(\mathbf{r}) = R_{nl}(r) Y_{lm_l}(\theta,\phi)\chi_{sm_s}(\sigma)$$

$$[\hat{\boldsymbol{l}}^2, \hat{H}_0] = 0,\ [\hat{l}_z, \hat{H}_0] = 0$$

$$[\hat{\boldsymbol{s}}^2, \hat{H}_0] = 0,\ [\hat{s}_z, \hat{H}_0] = 0$$

$\psi_{nlm_l sm_s}(\mathbf{r})$ 是 $\hat{H}_0, \hat{\boldsymbol{l}}^2, \hat{l}_z, \hat{\boldsymbol{s}}^2, \hat{s}_z$ 的共同本征态，

n, l, m_l, s, m_s为好量子数。

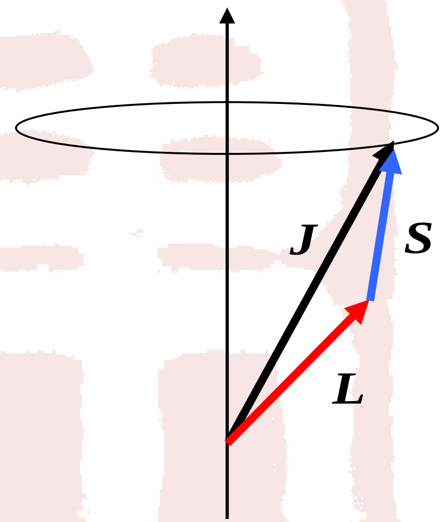
◆ 考虑自旋-轨道耦合

$$\hat{H}_{ls} = -\hat{\boldsymbol{\mu}}_s \cdot \mathbf{B} = \zeta(r)\hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}}$$

$\hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}}$ 与 $\hat{l}_z, \hat{s}_z$ 不对易，m_l, m_s不是好量子数。

- 引入总角动量

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



- 算符 $\boldsymbol{j}^2$ 和 j_z 与 $\boldsymbol{l}\cdot\boldsymbol{s}$ 以及 $\hat{H} = \hat{H}_0 + \hat{H}_m + \hat{H}_{ls} + \hat{H}_d$ 对易。

⇒ $\hat{\boldsymbol{j}}$ 是“正确的”可观测量

$$\hat{\boldsymbol{j}}^2 \Omega_{jm_j} = j(j+1)\hbar^2 \Omega_{jm_j} \qquad \hat{j}_z \Omega_{jm_j} = m_j \hbar \Omega_{jm_j}$$

$$\Omega_{jm_j} = \sum_{m_l, m_s} \langle lsm_l m_s | jm_j \rangle Y_{lm_l}(\theta,\phi)\, \chi_{sm_s}(\sigma)$$

$\langle lsm_l m_s | jm_j \rangle$ C-G(Clebsch-Gordan)系数

$$j = l + \frac{1}{2}, \left| l - \frac{1}{2} \right| \qquad m_j = j, j-1, \ldots, -(j-1), -j$$

在新的耦合表象中　$\Omega_{jm_j} = \left| nlsjm_j \right\rangle$

$\hat{H}_{ls}$ 是对角化的，对角元给出了相应的能量修正

$l \neq 0$

$$\Delta E_2 = \left\langle nlsjm_j \middle| \hat{H}_{ls} \middle| nlsjm_j \right\rangle$$
$$= \left\langle nlsjm_j \middle| \zeta(r) \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}} \middle| nlsjm_j \right\rangle$$
$$= \left\langle nl \middle| \zeta(r) \middle| nl \right\rangle \left\langle nlsjm_j \middle| \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}} \middle| nlsjm_j \right\rangle$$

其中

$$\left\langle nl \middle| \zeta(r) \middle| nl \right\rangle = \frac{1}{2m^2c^2} \left(\frac{Ze^2}{4\pi\varepsilon_0} \right) \left\langle \frac{1}{r^3} \right\rangle_{nl}$$
$$= \frac{1}{2m^2c^2} \left(\frac{Ze^2}{4\pi\varepsilon_0} \right) \frac{Z^3}{a_0^3 n^3 l(l+\frac{1}{2})(l+1)}$$

$$\langle nlsjm_j | \hat{\boldsymbol{l}} \cdot \hat{\boldsymbol{s}} | nlsjm_j \rangle = \langle nlsjm_j | \tfrac{1}{2}(\hat{\boldsymbol{j}}^2 - \hat{\boldsymbol{l}}^2 - \hat{\boldsymbol{s}}^2) | nlsjm_j \rangle$$

$$= \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - s(s+1) \right]$$

$$= \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4} \right]$$

$$\Rightarrow \quad \Delta E_2 = -E_n \frac{(Z\alpha)^2}{2nl(l+\frac{1}{2})(l+1)} \times \begin{cases} l, & j = l + \frac{1}{2} \\ -(l+1), & j = l - \frac{1}{2} \end{cases}$$

$l = 0$

$$\Delta E_2 = 0$$

类氢单电子原子的相对论能量修正为

$$\Delta E_{nj} = -\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}\frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)$$

$$= E_n\frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)$$

修正后的总能量为

$$E_{nj} = E_n\left[1+\frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)\right]$$

Dirac方程的精确解为

$$E_{nj}^{Dirac} = mc^2\Bigg/\sqrt{1+\left(\frac{Z\alpha}{n-|j+1/2|+\sqrt{(j+1/2)^2-(Z\alpha)^2}}\right)^2}$$

非相对论近似:

$$E_{nj}^{Dirac} = mc^2 \Bigg/ \sqrt{1 + \left(\frac{Z\alpha}{n - |j+1/2| + \sqrt{(j+1/2)^2 - (Z\alpha)^2}} \right)^2}$$

$$\approx mc^2 \left(1 - \frac{1}{2}\frac{(\alpha Z)^2}{n^2} - \frac{1}{2}\frac{(\alpha Z)^4}{n^3}\left(\frac{1}{j+1/2} - \frac{3}{4n} \right) - \dots \right)$$

Rest mass term **Nonrelativistic energy** **First relativistic correction**

不计静止质量:

$$E_{nj} = E_n \left[1 + \frac{(Z\alpha)^2}{n^2} \left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right) \right]$$

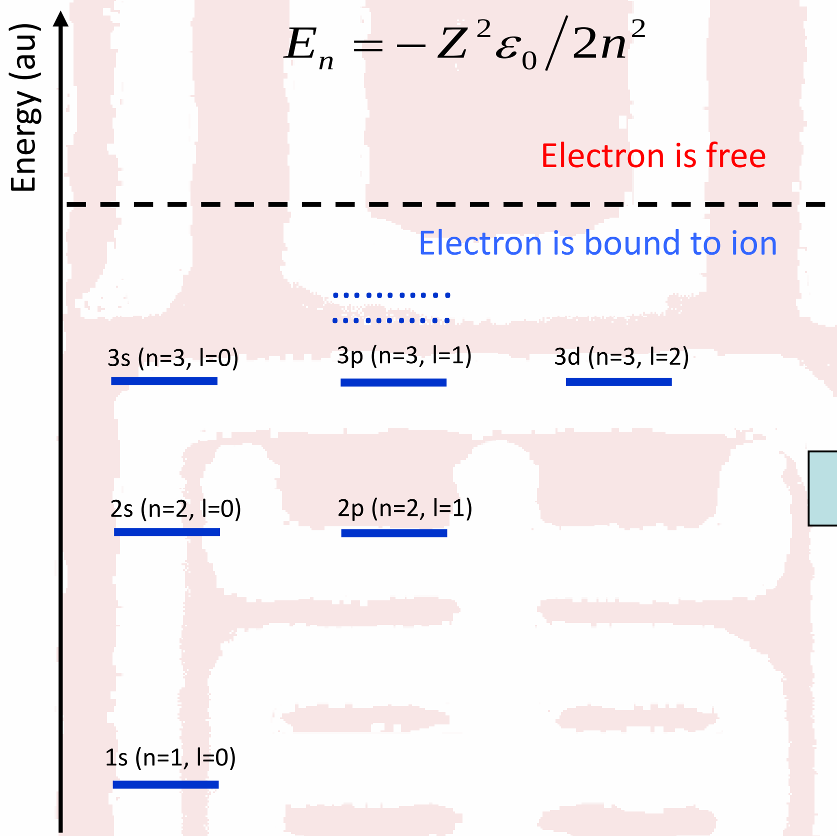
$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

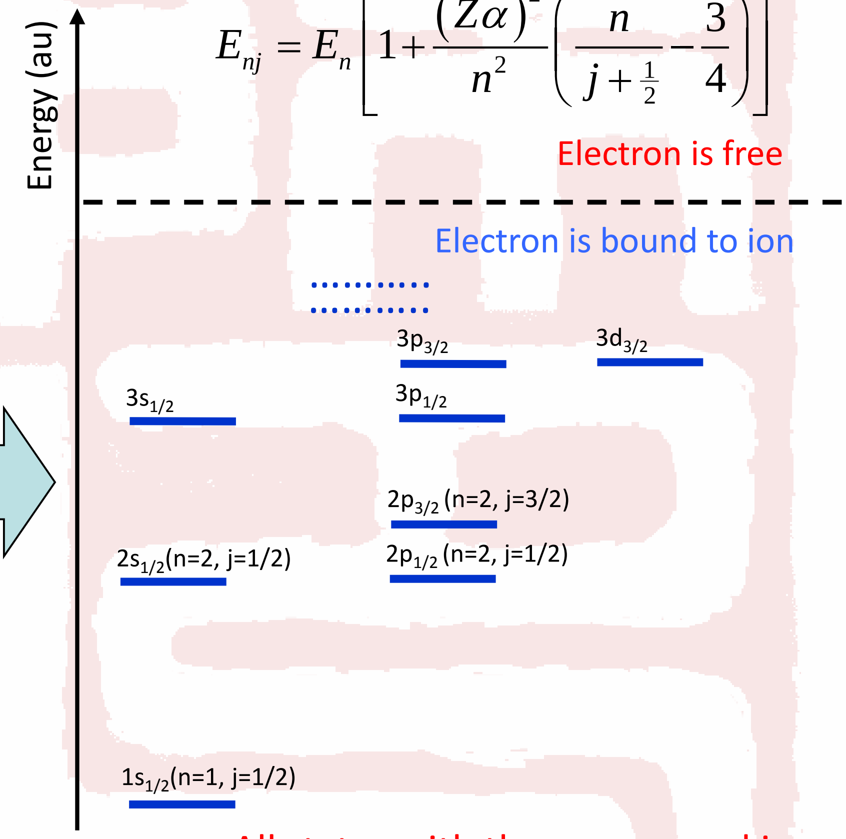
$$\hat{H} = \hat{H}_0 + \hat{H}_m + \hat{H}_{ls} + \hat{H}_d$$

$$\psi_{nlm_l}(\mathbf{r}) = R_{nl}(r)Y_{lm_l}(\theta,\phi) \Longrightarrow \psi_{nlm_l sm_s}(\mathbf{r}) = R_{nl}(r)Y_{lm_l}(\theta,\phi)\chi_{sm_s}(\sigma) \Longrightarrow \psi_{nlsjm_j}(\mathbf{r}) = R_{nl}(r)\sum_{m_l,m_s}\langle lsm_l m_s | jm_j\rangle Y_{lm_l}(\theta,\phi)\chi_{sm_s}(\sigma)$$

$$E_n = -Z^2\varepsilon_0/2n^2$$

$$E_{nj} = E_n\left[1 + \frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

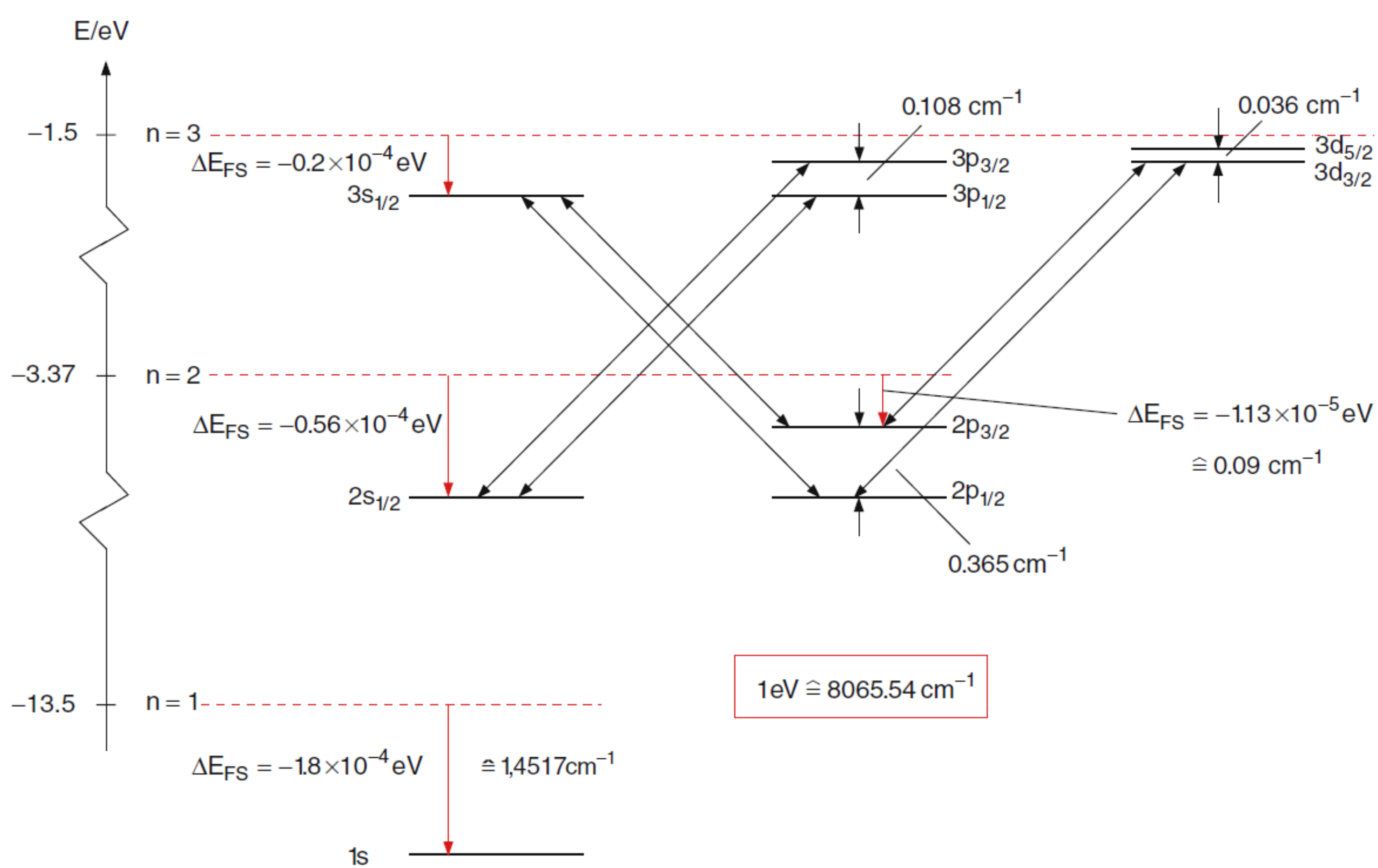




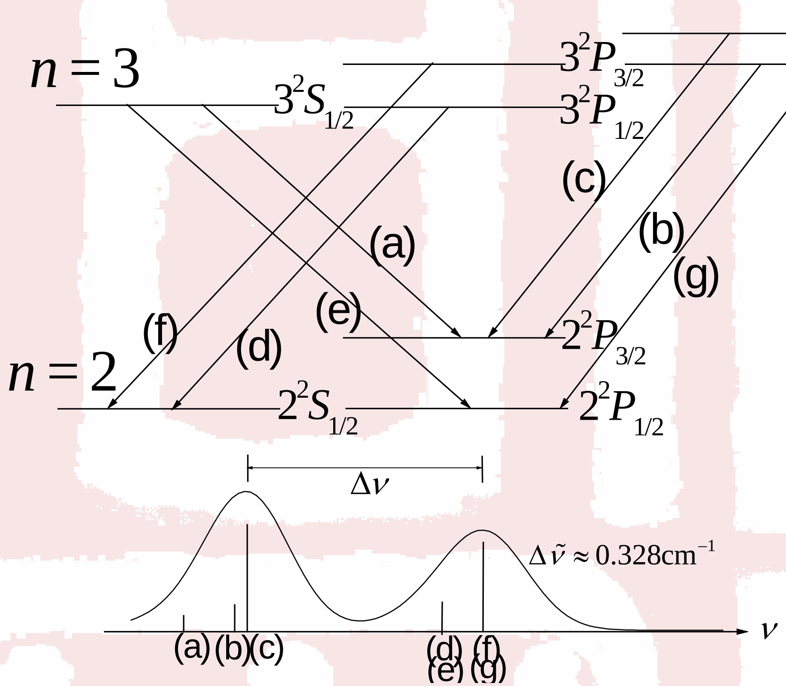
All states with the same n are degenerated!

All states with the same n and j are degenerated!

§ 2.1 单电子(H)原子 氢原子的精细结构



§2.1 单电子(H)原子 氢原子的精细结构



电偶极跃迁的选择定则

$$\left.\begin{aligned}\Delta l &= \pm 1\\ \Delta j &= 0, \pm 1\end{aligned}\right\}$$

(a) $3^2S_{1/2} \to 2^2P_{3/2}$，(b) $3^2D_{3/2} \to 2^2P_{3/2}$，(c) $3^2D_{5/2} \to 2^2P_{3/2}$

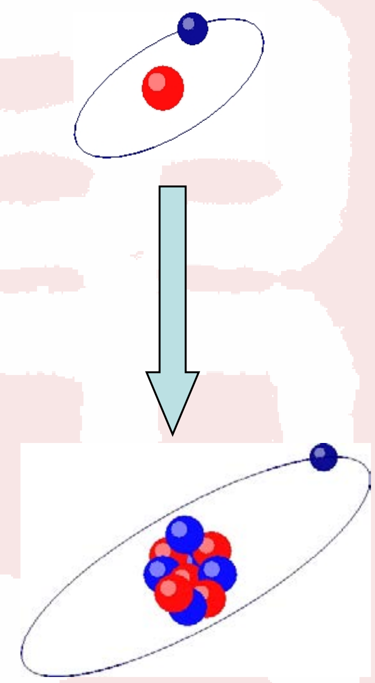
(d) $3^2S_{1/2} \to 2^2P_{1/2}$，(e) $3^2P_{1/2} \to 2^2S_{1/2}$，

(f) $3^2P_{3/2} \to 2^2S_{1/2}$，(g) $3^2D_{3/2} \to 2^2P_{1/2}$

作业2.3：计算光谱测量到的氢原子H_α的双线间隔。

$$\Delta\tilde{\nu} \approx 0.328\text{cm}^{-1}$$

§ 2.1 单电子(H)原子 氢原子的精细结构



- 对于重的类氢离子体系(Z >> 1)，从简单的Bohr模型可以估算出基态电子的速度：

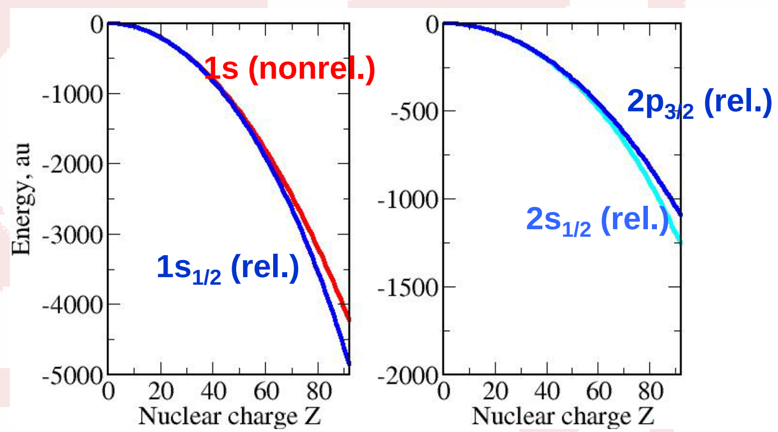
$$v = (\alpha Z)\,c$$

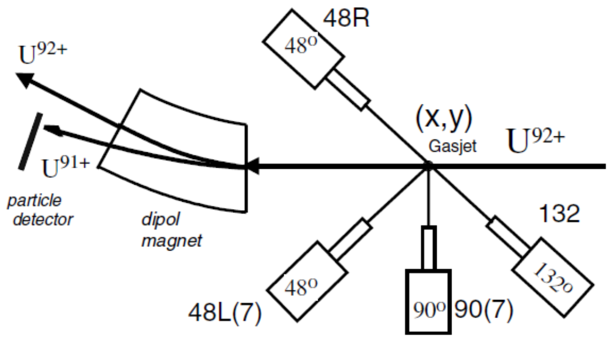
光速

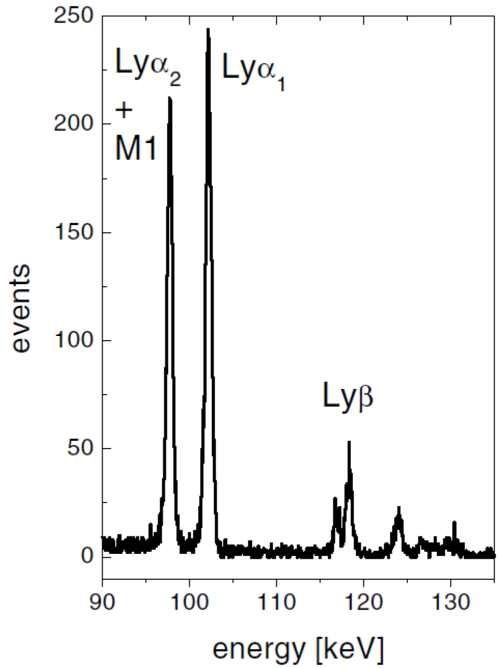
- 对于氢原子： $\alpha Z \approx 1/137 \approx 0.00729$

- 对于类氢铀离子(Z=92): $\alpha Z \approx 0.67$

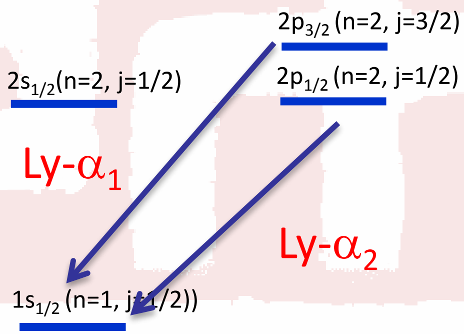
电子的运动速度接近光速！必须考虑相对论效应！







- Example: Fine-structure splitting in H-like uranium ion.



	Experiment (eV)
Ly α_1	102 209 ± 63
Ly $\alpha_2 + M1$	97 706 ± 61

作业2.4：计算类氢铀离子Ly-α_1 和 Ly-α_2 线的能量，并和实验结果比较。

§2.1 单电子(H)原子 氢原子的精细结构

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Direct Observations of Relativistic Effects in Single-Electron Momentum Distributions in Xenon Outer Shells

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(Received 11 January 1984)

The $5p_{3/2}$ and $5p_{1/2}$ one-electron momentum probability distributions in xenon, measured by means of the noncoplanar symmetric $(e, 2e)$ reaction, show clear and direct manifestations of relativistic effects. The momentum densities and branching ratios cannot be described by nonrelativistic wave functions, but they are in very good agreement with those given by Dirac-Fock wave functions.

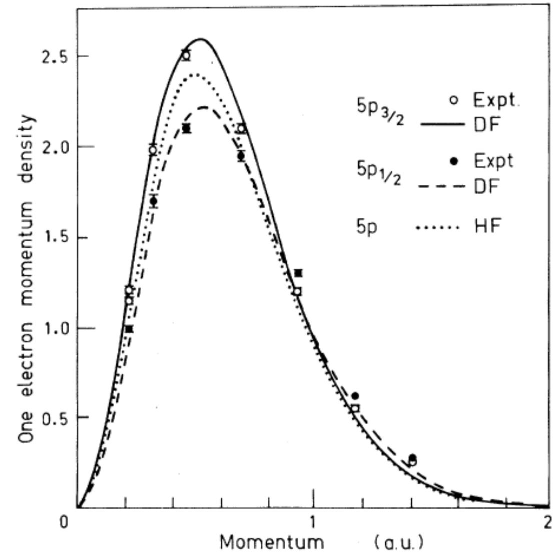

FIG. 1. The one-electron momentum probability distributions for the $5p_{3/2,1/2}$ orbitals in xenon compared with DF (solid line and dashed line) and HF (dotted line) wave functions.

$$\psi_{nlm_l}(\mathbf{r}) = R_{nl}(r)Y_{lm_l}(\theta,\phi)$$

傅里叶变换

$$\phi_{nlm}(\mathbf{p}) = N_{nlm}P_{nl}(p)Y_{lm}(\Omega_p)$$

$$F_i(p) = \int d\Omega_p \left|\psi_i(p)\right|^2$$

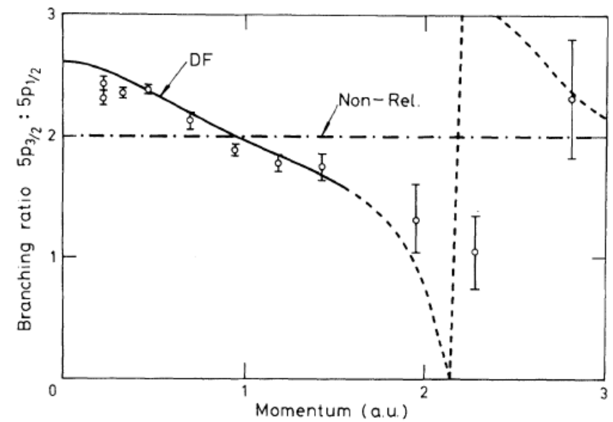

FIG. 2. The 1200-eV noncoplanar symmetric $(e, 2e)$ branching ratios plotted as a function of the momentum.