§1.5.2 H原子光谱和Bohr原子模型—氢原子光谱线系



Ritz 公式 Rydberg-Ritz combination principle

D

$$\tilde{v} = R_H \left[\frac{1}{m^2} - \frac{1}{n^2} \right] = T(m) - T(n)$$

$$T(m) = \frac{\pi_H}{m^2}$$
称为光谱项





W. Ritz (1878-1909)



Bohr原子模型三部曲



Niels Bohr (1913). "<u>On the Constitution of</u> <u>Atoms and Molecules, Part I</u>". *Philosophical Magazine* 26: 1–24. Niels Bohr (1913). <u>"On the Constitution of</u>

Atoms and Molecules, Part II Systems Containing Only a Single Nucleus". Philosophical Magazine 26: 476–502. http://web.ihep.su/dbserv/compas/src/bohr1 3b/eng.pdf.

Niels Bohr (1913). "On the Constitution of Atoms and Molecules, Part III Systems containing several nuclei". *Philosophical Magazine* 26: 857–875.



Niels Bohr

7 October 1885 – 18 November 1962 The Nobel Prize in Physics 1922

"for his services in the investigation of the structure of atoms and of the radiation emanating from them"







经典轨道:H原子中的电子围绕原子核作圆周运动 (Rutherford原子核式模型)。

定态条件:为了避免"原子塌缩",借鉴了Planck的能量量子化观点。



 $E_n = -\frac{1}{2} \frac{e^2}{4\pi\varepsilon_0 r_n}$

Max Planck (1<mark>858-19</mark>47)



 $24\pi\varepsilon_0 r$ 假设H原子的能量也是量子化的。

H原子核外电子只能在一系列具有确定能量的分立的圆周轨道上运动。

定态条件: 并且假设在这些轨道上运动时不辐射电磁波。

Bohr将这样一些稳定的轨道称为定态。









(3)角动量量子化(H原子)

$$L = L_n = n\hbar = n\frac{h}{2\pi}, \quad n = 1, 2, 3, \dots$$



N. Bohr (1885-19<mark>62)</mark>



Bohr对应原理

经典规律和量子规律虽然在形式上和内容 上均有不同之处,看起来似乎是矛盾的。但这 种矛盾只是它们应用在不同条件和场合下才出 现,它们在各自的应用领域中均是正确的,因 此,经典的和量子的物理量之间应该有一一对 应的关系,在极限条件下,彼此趋于一致,即 量子规律转化为经典规律,这叫做对应原理。



Hydrogen Atom

proton

electron 🧲

H原子辐射频率

经典理论
$$f = \frac{e}{2\pi} \sqrt{\frac{1}{4\pi\varepsilon_0 m_e r^3}}$$

Bohr量子理论

从Rydberg经验公式出发,结合定态假设

H原子定态能量

$$E_n = -hcT(n) = -hc\frac{R_H}{n^2}$$
 $r_n = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{2R_Hhc}n^2$

H原子的定态能量和轨道半径都是正整数n的函数,即是量子化的 n=1,2,3,... 称为量子数



Bohr频率规则

$$v = |E_m - E_n| / h = \left[\left(-hc \frac{R_H}{n^2} \right) - \left(-hc \frac{R_H}{m^2} \right) \right] / h \qquad (\forall R < n)$$
$$= R_H c \left(\frac{1}{m^2} - \frac{1}{n^2} \right) = R_H c \frac{(n+m)(n-m)}{m^2 n^2}$$

当n很大时, 邻能级间跃迁的频率 ($n = m+1 \rightarrow \infty$)

$$v = R_H c \frac{(n+n-1)(n-n+1)}{(n-1)^2 n^2} \approx R_H c \frac{2}{n^3}$$

按照Bohr对应原理,在大量子数极限下,量子计算与经典计算一致

将
$$R_{H} = \frac{m_{e}e^{4}}{(4\pi\varepsilon_{0})^{2}4\pi\hbar^{3}c}$$
 代回 $r_{n} = \frac{1}{4\pi\varepsilon_{0}}\frac{e^{2}}{2R_{H}hc}n^{2}$
得到 $r_{n} = \frac{4\pi\varepsilon_{0}\hbar^{2}}{m_{e}e^{2}}n^{2}$
又 $\frac{1}{2}m_{e}v^{2} = \frac{1}{2}\frac{e^{2}}{4\pi\varepsilon_{0}r}$ $\checkmark v = \sqrt{\frac{e^{2}}{4\pi\varepsilon_{0}}m_{e}r}$
所以, 角动量 $L = m_{e}vr = m_{e}\sqrt{\frac{e^{2}}{4\pi\varepsilon_{0}m_{e}r}} \cdot r = \sqrt{\frac{e^{2}}{4\pi\varepsilon_{0}}m_{e}r} = \sqrt{\frac{e^{2}}{4\pi\varepsilon_{0}}m_{e}}\frac{4\pi\varepsilon_{0}\hbar^{2}}{m_{e}e^{2}}n^{2}}$
 $= n\hbar$
在大量子数极限下, 得到了角动量量子化
 $L = n\hbar$ 其中 $\hbar = \frac{\hbar}{2}$

n =

 2π

假设在小量子数下,即n小的时候也成立。





称为玻尔半径。







H原子的电子运动的速度大小

$$r_n = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}n^2 \quad \text{tt} \lambda \quad v = \sqrt{\frac{e^2}{4\pi\varepsilon_0 m_e r}}$$

得
$$v = v_n = \frac{e^2}{4\pi\varepsilon_0 n\hbar} = \frac{\alpha c}{n}$$

其中
$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137}$$
 称为精细结构常数。

所以,电子的运动速度 v << c,因而不用考虑相对论。



H原子的定态能量

$$r_{n} = \frac{4\pi\varepsilon_{0}\hbar^{2}}{m_{e}e^{2}}n^{2}$$
 代入 $E = -\frac{1}{2}\frac{e^{2}}{4\pi\varepsilon_{0}r}$
得 $E_{n} = -\frac{1}{2}\frac{e^{2}}{4\pi\varepsilon_{0}r_{n}} = -\frac{1}{2}\frac{e^{2}}{4\pi\varepsilon_{0}}\frac{m_{e}e^{2}}{4\pi\varepsilon_{0}\hbar^{2}n^{2}} = -\frac{1}{(4\pi\varepsilon_{0})^{2}}\frac{m_{e}e^{4}}{2\hbar^{2}n^{2}}$
 $= -hcR_{\infty}\frac{1}{n^{2}}$ $n = 1, 2, 3, ...$

里德伯常数的理论公式

$$R_{\infty} = \frac{1}{\left(4\pi\varepsilon_0\right)^2} \frac{m_e e^4}{4\pi\hbar^3 c}$$

$$E_n = -\frac{1}{2}m_e\alpha^2 c^2 \frac{1}{n^2}$$











电子脱离原子核库仑场的束缚, 成为自由电子,称为电离。

自由电子可以具有一定的动能T, 而 $r \rightarrow \infty$ 时,势能V(r) = 0,所 以总能量 E = T > 0,轨道是双 曲线的一支,动能可以为任意 值,不是量子化的。

能级图上是 $n \to \infty$ 时, $E_n \to 0$ 之上连续的正能量区。







大量H原子可以处在n=1, 2, 3, ...等不同的能级,例如 N_1 个H原子处在n=1能级、 N_2 个H原子处在n=2能级、依次类推,服从Boltzmann统计分布。

 $N_i \propto \exp(-E_i / k_B T)$



常温T=300K $\frac{N_2}{N_1} \sim \frac{\exp(-E_2 / k_B T)}{\exp(-E_1 / k_B T)} = e^{-(E_2 - E_1)/k_B T}$ Pfunc -0.9 Boltzmann常数 k = 8.62×10^{-5} eV·K⁻¹ $E_1 = -13.6eV$ $E_2 = \frac{-13.6eV}{2^2} = -3.4eV$ $\frac{N_2}{2} \sim e^{-(-3.4eV + 13.6eV)/(8.62 \times 10^{-5} eV \cdot K^{-1} \cdot 300K)}$ N_1 $=e^{-394.6} \sim 4.2 \times 10^{-172} = 0$ H原子的能级图

常温下,一团冷气体的原子几乎全部处 在基态。白光通过,一些H原子吸收光 子跃迁到激发态。



只有莱曼线系 $hc\tilde{v} = E_n - E_1 = -\frac{1}{2}m_e\alpha^2 c^2 \frac{1}{m^2} + \frac{1}{2}m_e\alpha^2 c^2 \frac{1}{1^2}$







太阳表面 T = 6000K

$$\frac{N_2}{N_1} \sim e^{-(-3.4eV + 13.6eV)/(8.62 \times 10^{-5} eV \cdot K^{-1} \cdot 6000K)}$$
$$= e^{-19.73} \sim 2.7 \times 10^{-9}$$















Level energy / eV 巴尔末线系 (m=2) $\tilde{v} = R_{\infty} \left[\frac{1}{2^2} - \frac{1}{n^2} \right], \qquad n = 3, 4, 5, \cdots$ Pfund series -0.9 Brackett series $R_{m} = 1.097,373,156 \times 10^{7} m^{-1}$ -1.5 Paschen series Balmer series limit 13.6 ev (364.6 kJ) $H_{\delta} H_{\Upsilon} H_{B}$ H_α -3.45 Balmer series continuum 300 500 400 600 700 Wavelength, nm -13.6 $3\rightarrow 2$ $4\rightarrow 2$ $5 \rightarrow 2$ $6 \rightarrow 2$ Name H-α Η-β H-y Η-δ H-E Η-ζ H-ŋ limit Exp. (nm) 656.3 486.1 434.1 410.2 397.0 388.9 383.5 364.6 Theo. (nm) 433.9 656.1 486.0 410.1 364.5









§1.6 氢原子理论的检验

玻尔氢原子理论

- ① 解释了H原子的大小;
- ② 完美地解释了H原子光谱;
- ③理论上精确计算了里德伯常数。









§1.6 氢原子理论的检验-类氢离子光谱



Bohr将其归属于He的一价离子的光谱。 He⁺, Li⁺⁺, Be⁺⁺⁺, 都是类氢离子: +Ze的原子核与核外的一个电子组成。

$$E_{n} = -\frac{1}{2}m_{e}c^{2}\alpha^{2}\frac{Z^{2}}{n^{2}} = Z^{2}E_{H}, \quad n = 1, 2, 3,$$

$$r_{n} = \frac{\hbar cn^{2}}{Zm_{e}c^{2}\alpha} = \frac{r_{H}}{Z}, \quad n = 1, 2, 3, \dots$$

光谱波数
$$\tilde{v} = Z^2 R_{\infty} \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

対于He⁺

$$\tilde{v} = 2^2 R_{\infty} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) = R_{\infty} \left(\frac{1}{(m/2)^2} \right)$$



§1.6 氢原子理论的检验-类氢离子光谱



Pickering series

$$n = 5, \ 6, \ 7, \dots \rightarrow m = 4$$

$$\tilde{v} = 2^2 R_{\infty} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) = R_{\infty} \left(\frac{1}{(m/2)^2} - \frac{1}{(n/2)^2} \right)$$

$$\tilde{v} = R_{\infty} \left(\frac{1}{2^2} - \frac{1}{k^2} \right)$$

$$k = n/2 = 2.5, \ 3, \ 3.5, \ 4, \dots$$

光谱观测

$$\tilde{v} = R' \left(\frac{1}{2^2} - \frac{1}{k^2} \right)$$



 $R' = R_{He^+} = 1.097, 222, 7 \times 10^7 \text{ m}^{-1}$















 $R_{\infty} = 1.097,373,156 \times 10^7 \, m^{-1}$

相应的里德堡常数

$$R_{M} = \frac{1}{(4\pi\varepsilon_{0})^{2}} \frac{\mu e^{4}}{4\pi\hbar^{3}c} = \frac{1}{1 + m_{e}/M} R_{\omega}$$

对于H原子
$$R_{H}^{theo} = \frac{1}{1 + m_{e} / M_{H}} R_{\infty}$$

将 m_e/M_H≈1/1836.15 代入,得

 $R_{H}^{theo} = 1.096,775,832 \times 10^{7} \, m^{-1}$

实验值 $R_{H} = 1.096,775,8 \times 10^{7} \,\mathrm{m}^{-1}$



Franck-Hertz Experiment





James Franck 1882 –1964



¹J. Franck and G. Hertz, Verh. Dtsch. Phys. Ges. 16, 457 (1914). ²J. Franck and G. Hertz, Verh. Dtsch. Phys. Ges. 16, 512 (1914).

> Gustav Ludwig Hertz 1887 –1975



The Nobel Prize in Physics 1925















"Niels Bohr was indeed a keen football player and was the goalkeeper in the Danish team Akademisk Boldklub in the beginning of the 20th century," says Nicolaj Egerod. "But even though AB [as the club is commonly known] were, at the time, one of the best clubs in Denmark, he never made it to the national team. However, his brother Harald - a well-known scientist in his own right - who also played at AB, played for the Danish national team and was part of the team that won silver at the 1908 London Olympics."

Nils Refsdal suggests a possible reason why Niels never made it to the international stage: "According to AB, in a match against the German side Mittweida, one of the Germans launched a long shot and the physicist leaning against the post did not react, missing an easy save. After the game he admitted to his team-mates his thoughts had been on a mathematical problem that was of more interest to him than the game. He only played for the 1905 season."

