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Atomic & Molecular

Physics :

Part-A → Prof. Ashoke Sen

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Book : Brandsen & Joachain (1)
(Physics of Atoms & Molecules)

Convention : $\hbar = c = 1$. (Recover via dimensional analysis)

Gaussian units in Electromagnetism.

$$\begin{aligned}\vec{\nabla} \cdot \vec{E} &= 4\pi\rho & \vec{\nabla} \times \vec{B} &= 4\pi\vec{j} + \frac{\partial \vec{E}}{\partial t} \\ \vec{\nabla} \times \vec{E} &= -\frac{\partial \vec{B}}{\partial t} & \vec{\nabla} \cdot \vec{B} &= 0\end{aligned}$$

Coulomb's Law → $\frac{q_1 q_2}{r^2} \hat{r} = \vec{F}$

Set $\epsilon_0 = \frac{1}{4\pi}$ & $\mu_0 = 4\pi$

↓
vacuum permittivity

↘ vacuum permeability
FOR ANY CONVERSIONS

Plan : (1) Single electron atoms

→ application of techniques learned in QM (1 & 2)
courses
||
+ results

(2) Multi-electron atoms → require new techniques to deal with e-e force.

(3) Molecules

(1) // start . . .

Neutral H-atom (all isotopes)

He⁺

Zeroth-order approximation : Treat the nucleus as a point charge Ze of infinite mass and the electron as a non-relativistic particle. (of charge $-e$.)

$$H = \frac{P^2}{2m} - \frac{Ze^2}{r}$$

$$\hat{H} = -\frac{1}{2m} \nabla^2 - \frac{Ze^2}{r} \quad \text{Find eigenvalues}$$

$\hat{H}\Psi = E_n \Psi$. The eigenfunctions can be labelled by $\{n_r, l, m_l\}$

$$\Psi_{n_r, l, m_l}(r, \theta, \phi) = f_{n_r, l}(r) Y_{l, m_l}(\theta, \phi)$$

n_r takes values $1, 2, 3, \dots$ called n in QM 1, 2

l takes values $0, 1, 2, 3, \dots$ $E_{n_r, l}$

$$E_n = -\frac{m Z^2 e^4}{2n^2} = -\frac{m Z^2 e^4}{\underbrace{(n_r + l)^2}_n}$$

m_l goes from $-l$ to l in integral steps

$\left[\begin{array}{l} n = 1, 2, \dots \\ l = 0, 1, 2, \dots, (n-1) \end{array} \right]$ arbitrary integer

$$f_{n_r, l}(r) \longrightarrow R_{nl}(r)$$

$$-\frac{1}{2mr^2} \frac{d}{dr} \left(r^2 \frac{dR_{nl}}{dr} \right) + \frac{l(l+1)}{2mr^2} R_{nl}$$

$$- Ze^2/r R_{nl} = \mathcal{E} - \frac{m Z^2 e^4}{2n^2} R_{nl}$$

Calculation of total degeneracy for a given n :

$$\sum_{l=0}^{n-1} (2l+1) = 2 \frac{(n-1)n}{2} + n = n^2$$

Introduce spin \vec{S} . \Rightarrow Wavefunction ψ has additional 2-fold degeneracy ($m_s = \pm 1/2$)

\Rightarrow Total degeneracy = $2n^2$.

$|n, l, m_l, s, m_s\rangle \Leftrightarrow R_{nl}(r) Y_{lm}(\theta, \phi) \otimes$

\rightarrow always $1/2$

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

$L^2 |n, l, m_l, s, m_s\rangle = l(l+1) |n, l, m_l, s, m_s\rangle$

$|m_s\rangle$
 \downarrow
 $\pm 1/2$

choice of basis

$S^2 |n, l, m_l, s, m_s\rangle = \frac{3}{4} | \dots \rangle$

$L_z | \dots \rangle = m_l | \dots \rangle$

$S_z | \dots \rangle = m_s | \dots \rangle$

• Choose a different basis

\vec{J}^2, J_z eigenbasis $\Rightarrow |n, l, s, j, m_j\rangle$

$= \sum_{m_l, m_s} C_{m_l m_s}^{j l s} |n, l, m_l, s, m_s\rangle$

\rightarrow Clebsch-Gordan coefficients

$\vec{J}^2 |n, l, j, s, m_j\rangle = j(j+1) | \dots \rangle$

$J_z | \dots \rangle = m_j | \dots \rangle$

(In new basis)

For given n ,

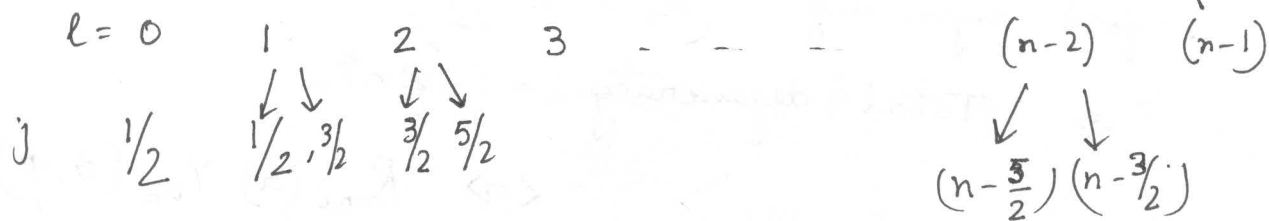
$l = 0, 1, 2, \dots, (n-1)$.

• Verify for degeneracies.

$j = l - \frac{1}{2}$ or $l + \frac{1}{2}$ (for $l = 0$, $j = \frac{1}{2}$)

For given n , l can take values

$(n - \frac{3}{2}), (n - 1)$



$$\text{Total degeneracy} = 2 \sum_{j=\frac{1}{2}, \frac{3}{2}, \dots, (n-\frac{3}{2})} (2j+1) + (2(n-\frac{1}{2})+1)$$

Let $j = (k - \frac{1}{2})$ where $k = 1, 2, \dots, (n-1)$

$$\Rightarrow 2j+1 = 2k$$

$$\text{So, total degeneracy} = 2 \sum_{k=1}^{n-1} 2k + 2n$$

$$= 4 \frac{(n-1)n}{2} + 2n$$

Symbol for l

$$= 2n^2 \text{ (matches!)}$$

$l = 0, 1, 2, 3, 4, 5$

Symbol $s \quad p \quad d \quad f \quad g \quad h \quad \dots$

$$|n \ l \ s \ j \ m_j\rangle \longleftrightarrow n \text{ (symbol of } l) \ j$$

$(2j+1 \text{ fold degenerate})$

$$|n=1, l=0, j=\frac{1}{2}\rangle \Rightarrow 1 \ s \ \frac{1}{2}$$

$$|n=3, l=2, j=\frac{5}{2}\rangle \Rightarrow 3 \ d \ \frac{5}{2}$$

$$\{1 \ s \ \frac{1}{2}\} ; \{2 \ s \ \frac{1}{2}, 2 \ p \ \frac{1}{2}, 2 \ p \ \frac{3}{2}\} ;$$

$$\{3 \ s \ \frac{1}{2}, 3 \ p \ \frac{1}{2}, 3 \ p \ \frac{3}{2}, 3 \ d \ \frac{3}{2}, 3 \ d \ \frac{5}{2}\} ;$$

