Electronic Transition

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UV/vis from an electronic transition

A. Atomic Spectra
   a. Flame emission/discharge tubes
      i. Show line spectra characteristic

1. Hydrogen atom

$$-\frac{\hbar^2}{2\mu}\nabla^2\Phi = -\frac{1}{4\pi\epsilon_o}\frac{Ze^2}{r}\Phi = E\Phi$$

$$\Phi_{n,l,m_l,m_s} = R_{rl}(r)Y_{l,m_l}(\theta,\phi)x\begin{Bmatrix}\alpha\\ \beta\end{Bmatrix}$$

$R_{nl}(r) is\ a\ radial\ wavefunction$

a) Energy spectrum
   a. $E_n = \dfrac{-z^2e^2}{4\pi\epsilon_o 2\alpha_o n^2} = -\dfrac{Z^2}{n^2}(13.6ev)$

      $Here\ \alpha_o\ is\ the\ bohr\ radius\ = 0.529A = \dfrac{4\pi\epsilon_o\hbar^2}{me^2}$

b) Angular wavefunction

   $L^2\left|Y_{l,m_l}\right\rangle = \hbar^2\big(l(l+1)\big)|l,m_l\rangle$

   $L_z|l,m_l\rangle = m_l\hbar|l,m_l\rangle$

c) $S^2|\alpha\rangle = \dfrac{1}{2}\left(\dfrac{1}{2}+1\right)\hbar^2|\alpha\rangle$

   $S^2|\beta\rangle = \dfrac{1}{2}\left(\dfrac{1}{2}+1\right)\hbar^2|\beta\rangle$

   $S_z|\alpha\rangle = \dfrac{1}{2}\hbar|\alpha\rangle, \qquad m_s = \pm\dfrac{1}{2}$

   $S_z|\beta\rangle = \dfrac{1}{2}\hbar|\beta\rangle$

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

e) Selection Rule (El-electric dipole moment)
   a. Electronic electric dipole moment= $\hat{\vec{\mu}} = \mathrm{q}\hat{\vec{\mathrm{r}}} = -\mathrm{er}\,(\sin\theta\cos\phi\,\hat{x} + \sin\theta\sin\phi\,\hat{y} + \cos\theta\,\hat{z})$
   b. $\vec{\mu}_{if} = \langle n,l,m_l,m_s|\vec{\mu}|n',l',m_l',m_s'\rangle = -e\displaystyle\int_0^\infty rR^*R'r^2dr \iint_{(0,0)}^{(\pi,2\pi)} Y^*(\theta,\phi)Y'(\theta,\phi)\begin{Bmatrix}\sin\theta\cos\phi\\ \cos\theta\cos\phi\\ \cos\theta\end{Bmatrix}d\theta d\phi\ \int S^*S'\,ds$
   c. The integrals yields selection rules
      i. $\delta_{m_s,m_s'} \Rightarrow \Delta m_s = 0$
      ii. $\displaystyle\int d\phi\ e^{-im_l\phi}\begin{pmatrix}\cos\phi\\ \sin\phi\\ 1\end{pmatrix}e^{im_l'\phi}$
      iii. $\theta\ int, \qquad \Delta l = \pm 1$

      $any\ \Delta n\ is\ possible$

   f) Transition Frequnecy
   g) $\tilde{v} = R_H\left(\dfrac{1}{n_i^2} - \dfrac{1}{n_f^2}\right)$
   h) $R_H = Rydberg = \dfrac{2\pi^2\mu e^4}{(2\pi\epsilon_o)^2h^3c} = 109{,}737cm^{-1}$

1) Lyman series UV $n_1 = 1$, $n_2 = 2,3,4$
2) Balmber series $n_1 = 2$, $n_2 = 3,4,5$ …. .
3) Pasichinen series , etc

1	Δl	Δm_l	Δm_s	Δn
$E1$	± 1	$0, \pm 1$	0	Any
$M2$	*0*	$0, \pm 1$	0 , $ep12$	0
$E2$	*0,*± 2	$0, \pm 1, \pm 2$	0	any