Hydrogen Atom - Bound-bound Transitions

ASTR 300B

Let's start by ignoring relativistic effects (including spin) and deal only with the Coulomb interaction between the nucleus and electron. Assume that $V(r)$ is a central force problem that is separable in spherical coordinates:

$$\psi(\vec{r},t) = \psi(\vec{r})\, e^{-iEt/\hbar}$$

$e^{-iEt/\hbar}$ called a Unitary operator $\Rightarrow$ "oscillatory in Hilbert Space"

In General, there are 3 operators that commute in this problem:

$$[H, L^2] = 0 \qquad [H, L_z] = 0 \qquad [L^2, L_z] = 0$$

The eigenvalue/eigenvector equations are:

$$\hat{H}|\psi\rangle = E_n|\psi\rangle$$
$$\hat{L}^2|\psi\rangle = \ell(\ell+1)\hbar^2|\psi\rangle$$
$$\hat{L}_z|\psi\rangle = m_\ell \hbar|\psi\rangle$$

The solution to this problem is the eigenstate denoted by quantum numbers n, ℓ, m_ℓ that satisfies all 3 equations. Lets look at the solutions:

$$H = T + V \quad \text{with} \quad V = \frac{-Ze^2}{r}$$

$$\hat{H}\psi(\vec{r}) = E_n \psi(\vec{r})$$

$$\left(\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}\right)\psi(\vec{r}) = E_n \psi(\vec{r})$$

Note: $\mu = \dfrac{m_{nuc} \cdot m_{e^-}}{m_{nuc} + m_{e^-}}$

In spherical coordinates, the equation is separable and the solutions are:

$$\psi(\vec{r}) = \psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi)$$

$R_{n\ell}$: Proportional to Associated Laguerre Polynomials

$Y_{\ell m_\ell}$: Spherical Harmonics

Let's start with the angular part: (Note: $\hat{L}^2|\psi\rangle = \ell(\ell+1)\hbar^2|\psi\rangle \Rightarrow |\psi\rangle = Y_{\ell m_\ell}(\theta,\phi)$)

Spherical Harmonics

$$Y_{\ell m_\ell}(\theta,\phi) \sim P_{\ell m_\ell}(\cos\theta)\, e^{i m_\ell \phi} \qquad m \geq 0$$

$P_{\ell m_\ell}$: Associated Legendre Polynomials

Allowed values of $m_\ell = -\ell, -\ell+1, \ldots 0, \ldots, +\ell$

When $m_\ell < 0$ $\quad Y^*_{\ell, m_\ell} = Y_{\ell, -m_\ell}$

Now for the radial part: (If we change variable $\rho = \frac{2}{\hbar}\sqrt{-2\mu E_n}\cdot r$)

$$\rho = \frac{2Z}{n a_0} r$$

$$R_{n\ell}(\rho) \sim e^{-\rho/2}\, \rho^{\ell}\, L^{2\ell+1}_{n+\ell}(\rho)$$

$L^{2\ell+1}_{n+\ell}$: Associated Laguerre Polynomials

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \sim \frac{13.6\,\text{eV}}{n^2} \text{ for H atom} \qquad n = 1, 2, \ldots$$

It is from Associated Laguerre Polynomials that we obtain:

$$2\ell + 1 \leq n + \ell$$

$$\Rightarrow \quad \ell \leq n - 1$$

NOTE: normalization for $R_{n\ell}(r)$ and $Y_{\ell m_\ell}(\theta,\phi)$ chosen such that

$$\langle \psi_{n\ell m_\ell} | \psi_{n'\ell'm'_\ell} \rangle = \delta_{nn'}\delta_{\ell\ell'}\delta_{m_\ell m'_\ell} \Rightarrow \text{orthonormal}$$

What about spin? We create a Direct Product Space (a higher dimensional space with both ordinary spatial coordinates and "spin coordinates" represented by spin matrices)

$$\psi_{n\ell m_\ell m_s}(\vec{r}) = \psi_{n\ell m_\ell}(\vec{r})\, \chi_{s m_s}$$

Eigenvalue / eigenvector equations:

$$\hat{S}^2|\chi\rangle = s(s+1)\hbar^2|\chi\rangle$$

$$\hat{S}_z|\chi\rangle = m_s \hbar|\chi\rangle$$

Note for a single e^-, $\chi_{s m_s}$ look like:

$$\chi_{\frac{1}{2},+\frac{1}{2}} = \begin{pmatrix}1\\0\end{pmatrix} \qquad \chi_{\frac{1}{2},-\frac{1}{2}} = \begin{pmatrix}0\\1\end{pmatrix}$$

Denoted: $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$

Putting it all together, bound states of Hydrogen described by 4 quantum numbers:

$n = 1, 2, 3, \ldots$ Principle Quantum Number

$\ell \leq n-1 \quad (\Rightarrow \ell \geq 0)$ Orbital Angular Momentum

$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	$\ell = 5$	etc
s	p	d	f	g	h	
"sharp"	"principle"	"diffuse"	"fundamental"	...		

$m_\ell = -\ell, \ell+1, \ldots, +\ell$ $2\ell+1$ Space Projections of ℓ

$m_s = \pm 1/2$ 2 space Projections of e^- spin

Allowed Transitions: Electric dipole allowed (also called resonant transitions) are found by determining which matrix elements of the electric dipole operator are non-zero:

$$\hat{\mu}_e = -e\vec{r}$$

$$\langle \psi_{n'\ell'm_{\ell'}} | \hat{\mu}_e | \psi_{n\ell m_\ell} \rangle \neq 0$$

$$\int_0^\infty \int_0^{2\pi} \int_0^{\pi} \psi^*_{n'\ell'm_{\ell'}}(\vec{r}) \; (-e\vec{r}) \; \psi_{n\ell m_\ell}(\vec{r}) \sin\theta \, d\theta \, d\phi \, r^2 dr \neq 0$$

Using orthogonality properties of spherical harmonics leads to the following selection rules:

$\Delta\ell = \pm 1$ ← this is in general going to be true for electric dipole transitions — they change by 1 unit of angular momentum.

$\Delta m_\ell = 0, \pm 1$

NOTE change Δn unconstrained

The spontaneous rate (s^{-1}) of a transition is given by the Einstein A of the transition.

$$A \propto |\langle \psi_{n'\ell'm_{\ell'}} | \hat{\mu}_e | \psi_{n\ell m_\ell} \rangle|^2$$