Midterm Review or: Everything you ever wanted to know about the Hydrogen atom (but were afraid of coming to my OHs to ask).

Spectrum: $E_n = -\left[\frac{me^4}{2\hbar^2}\right]\frac{1}{n^2} = -13.6\,\text{eV}\left(\frac{1}{n^2}\right) \quad n = 1,2,3,\ldots$

Ground State, $E_1 = -13.6\,\text{eV}$ (I've written all this in cgs units - you can recover MKS by just making the substitution $e^2 \to \frac{e^2}{4\pi\epsilon_0}$ everywhere). Recall that:

SI Units		Gaussian (cgs)	
1 m	=	100 cm	$\hbar = 1.054\times10^{-34}\,\text{J}\cdot\text{s} = 1.054\times10^{-27}\,\text{erg}\cdot\text{s}$
			$\frac{1}{4\pi\epsilon_0} = 9\times10^9\,\frac{\text{Nm}^2}{\text{C}^2} \qquad \alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}$
1 kg	=	1000 g	$e = 4.803\times10^{-10}$ esu
1 N	=	10^5 dyne	$= 1.602\times10^{-19}$ C
1 J	=	10^7 erg	$1\,\text{eV} = 1.602\times10^{-12}\,\text{erg} = 1.602\times10^{-19}\,\text{J}$
1 Coulomb	=	3×10^9 esu	$a_0 = \frac{\hbar^2}{me^2} = 0.529\,\text{Å} = 5.29\times10^{-9}\,\text{cm}$
1 Ampere	=	3×10^9 esu/sec	$E_1 = -\frac{e^2}{2a_0}$
1 V/m	=	$\frac{1}{3}\times10^{-4}$ statvolt/cm	$m_e = 9.11\times10^{-31}\,\text{kg} = 9.11\times10^{-28}\,\text{g}$
1 Tesla	=	10^4 gauss	$m_p = 1.67\times10^{-27}\,\text{kg} = 1.67\times10^{-24}\,\text{g}$
~~1 eV~~	$\neq$		R = Rydberg Constant $= \frac{me^4}{4\pi c\hbar^3} = 1.097\times10^7\,\text{m}^{-1}$

These energy levels enter most directly into physically observable quantities in experiments observing the emission spectrum of excited Hydrogen. The energies of the emitted photons correspond to the difference in energy between initial & final states:

$$E_\gamma = E_i - E_f = -13.6\,\text{eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad n_i = 2,3,\ldots \quad n_f = 1,2,3,\ldots$$

Now, $E_\gamma = h\nu$ (Planck's Law), $\lambda = c/\nu \Rightarrow \frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$, $R = 1.097\times10^7\,\text{m}^{-1}$

Lyman Series	$n_f = 1$	UV	α-line $n_i = 2 \to n_f = 1$	$n_i \to \infty$ $\lambda \to \frac{1}{R} \simeq 90.9$ nm
Balmer Series	$n_f = 2$	Visible	" $n_i = 3 \to n_f = 2$	
Paschen Series	$n_f = 3$	IR	" $n_i = 4 \to n_f = 3$	

Q: What color is the $n_i = 5 \to n_f = 2$ transition line in the Balmer Series?

A: $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 0.21R \simeq 0.23\times10^7\,\text{m}^{-1} \Rightarrow \lambda = 434$ nm (Blue!)

The visible range is from: 400 nm (violet) – 700 nm (red)

(using $1\,\text{eV} \sim 2.42\times10^{14}$ Hz, $hc = 1.24\times10^3\,\text{eV}\cdot\text{nm}$)

3.1 eV – 1.8 eV

7.64×10^{14} Hz – 4.22×10^{14} Hz

Q: Problem 4.17 in Griffiths: Determine the Bohr energies, $E_n(Z)$, the binding energy $E_1(Z)$, the Bohr radius $a(Z)$ & the Rydberg constant $R(Z)$ for a hydrogenic ion of atomic # Z (ignore relativistic & reduced mass effects!)

A: In this approximation, the only change is that the potential: $V(r) = -\frac{e^2}{r} \to V(r) = -\frac{Ze^2}{r}$. So we get all the corresponding values by making the substitution $e^2 \to Ze^2$ in all formulas!

$E_n(Z)$: $E_n(1) = -\frac{1}{n^2}\frac{me^4}{2\hbar^2} \longrightarrow E_n(Z) = -\frac{1}{n^2}\frac{m(Ze^2)^2}{2\hbar^2} = -\frac{Z^2}{n^2}(13.6\,eV)$

$E_1(Z)$: $E_1(1) = -13.6\,eV \longrightarrow E_1(Z) = -Z^2(13.6\,eV)$

$a(Z)$: $a(1) = a_0 = \frac{\hbar^2}{m_e e^2} \longrightarrow a(Z) = \frac{\hbar^2}{Z m_e e^2} = \frac{a_0}{Z} = 0.529\times 10^{-10}\,m/Z$

$R(Z)$: $R(1) = \frac{me^4}{4\pi c\hbar^3} \longrightarrow R(Z) = Z^2\frac{me^4}{4\pi c\hbar^3} = Z^2(1.097\times 10^{7}\,m^{-1})$

Q: What is the degeneracy of E_5?

A: Given a state with principal quantum number n, the allowed values of ℓ are: $\ell = 0, 1, 2, \cdots, n-1$. Further, for each ℓ, there are $(2\ell+1)$ possible values of m, $m = -\ell, -\ell+1, \cdots, \ell-1, \ell$, so we get:

$$\text{Degeneracy of } n^{th} \text{ state} = \sum_{\ell=0}^{n-1}(2\ell+1) = 2\left(\frac{n(n-1)}{2}\right) + n - 1 = n^2$$

Thus, the degeneracy of E_5 is 25. Note: We have actually neglected several important physical effects in the Hydrogen atom (spin, relativistic corrections, Lamb shift) that break much of this degeneracy (I'll talk a little bit about this in section!)

Other useful facts about Hydrogen Atom:

$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\,Y_\ell^m(\theta,\phi)$ $\qquad R_{n\ell}(r) = \frac{1}{r}\rho^{\ell+1}e^{-\rho}v(\rho)$

where $\rho = \left(\frac{r}{an}\right)$. Note that for large r, $R_{n\ell} \sim e^{-\rho} \sim e^{-r/an}$. Thus, one can qualitatively argue that the "size" of the orbit scales as n, so $\psi_{n\ell m}$ has an "effective" radius of $a(n) \sim a_0 n$. For very small r, one finds $R_{n\ell}(r) \sim r^\ell$, so only for $\ell = 0$ does this stay non-zero near the origin!

$R_{10} = 2a^{-3/2}e^{-r/a}$ $\qquad R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)e^{-r/2a}$

etc... $\qquad R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}e^{-r/2a}$

Angular Momentum: $\vec{L} = \vec{r}\times\vec{p}$ $\qquad [L_x, L_y] = i\hbar L_z$

$[L_z, L_x] = i\hbar L_y$ $\qquad [L_y, L_z] = i\hbar L_x$ $\qquad L^2 = L_x^2 + L_y^2 + L_z^2$

Note: Being observa[bles] $\vec{L}$ are Hermitian: $L_x^\dagger = L_x$, $L_y^\dagger = L_y$, $L_z^\dagger = L_z$

Q: Prove $[L^2, L_x] = 0$

A:
$$[L^2, L_x] = [L_x^2 + L_y^2 + L_z^2, L_x] = \cancel{[L_x^2, L_x]}^{\,0} + [L_y^2, L_x] + [L_z^2, L_x]$$
$$= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z$$
$$= -i\hbar(L_yL_z + L_zL_y) + i\hbar(L_zL_y + L_yL_z) = 0$$

Thus, we in fact have $[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$.

However, as L_x, L_y, L_z do not commute with each other, we can only consider orthonormal bases of simultaneous eigenvectors of L^2 and one of the three - if we choose L_z, we get the $Y_{\ell m}$s! The $Y_{\ell m}(\theta,\phi)$ are a complete set of orthonormal simult. eigenfn's of L^2 + L_z with the properties that:

$$L^2 Y_{\ell m}(\theta,\phi) = \hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\phi) \qquad \ell = 0, 1, 2, \cdots$$
$$L_z Y_{\ell m}(\theta,\phi) = m\hbar\, Y_{\ell m}(\theta,\phi) \qquad m \in -\ell, -\ell+1, \cdots, \ell-1, \ell$$

In the spirit of the SHO problem, I'm going to try to abstractly approach problems involving angular momentum by using operator methods and Dirac bra-ket notation as well as "raising" + "lowering" or ladder operators.

Bra-ket notation: $Y_{\ell m}(\theta,\phi) \longrightarrow |\ell m\rangle$ $\quad \int Y^*_{\ell m}(\theta,\phi)\, d\Omega \longrightarrow \langle \ell m|$

so: $\langle \ell m | \ell' m'\rangle = \delta_{\ell\ell'}\delta_{mm'}$ $\quad L^2|\ell m\rangle = \hbar^2 \ell(\ell+1)|\ell m\rangle$

$L_z|\ell m\rangle = m\hbar |\ell m\rangle$.

Ladder Operators: $L_+ = L_x + iL_y \quad L_- = L_x - iL_y \quad (L_+^\dagger = L_-,\ L_-^\dagger = L_+)$

Properties: ① $[L^2, L_\pm] = [L^2, L_x \pm iL_y] = 0$.

② $L_\pm L_\mp = L^2 - L_z^2 \pm \hbar L_z$ PF: $L_\pm L_\mp = (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \mp i[L_x, L_y]$
$= L_x^2 + L_y^2 \pm \hbar L_z = L^2 - L_z^2 \pm \hbar L_z$

③ $[L_+, L_-] = [L_x + iL_y, L_x - iL_y] = -i[L_x, L_y] + i[L_y, L_x] = 2\hbar L_z$

④ $[L_z, L_\pm] = [L_z, L_x \pm iL_y] = i\hbar L_y \pm i(-i\hbar L_x) = \pm\hbar L_\pm$

⑤ $L_x = \frac{1}{2}(L_+ + L_-)$ ⑥ $L_y = \frac{1}{2i}(L_+ - L_-)$

Q: What are the results of applying ① L^2 + ② L_z to the state $L_\pm|\ell m\rangle$?

A: ① Since $[L^2, L_\pm] = 0 \Rightarrow L^2(L_\pm|\ell m\rangle) = L_\pm(L^2|\ell m\rangle) = L_\pm \hbar^2(\ell(\ell+1))|\ell m\rangle$
$\Longrightarrow L^2(L_\pm|\ell m\rangle) = \hbar^2\ell(\ell+1)(L_\pm|\ell m\rangle)$ Thus, $L_\pm|\ell m\rangle$ has the same value of ℓ as $|\ell m\rangle$ itself.

② $L_z L_\pm |\ell m\rangle = (\text{by prop. ④ above}) = (L_\pm L_z \pm \hbar L_\pm)|\ell m\rangle$
$= (m\hbar L_\pm \pm \hbar L_\pm)|\ell m\rangle = (m\pm 1)\hbar L_\pm|\ell m\rangle$

Thus, $L_\pm$ act like ladder operators increasing or decreasing the value of m by ± 1!

Q: From the result of the above problem, one would guess that $L_\pm|\ell m\rangle = C^\pm_{\ell m}|\ell\, m\pm 1\rangle$. Using the fact that $L_\pm^\dagger = L_\mp$ show that: $L_\pm|\ell m\rangle = \hbar[\ell(\ell+1) - m(m\pm 1)]^{1/2}|\ell m\pm 1\rangle$

PF: All we need to do is find: (as $|\ell m\pm 1\rangle$ is properly normalized!)

$|C^\pm_{\ell m}|^2 = (L_\pm|\ell m\rangle)^\dagger L_\pm|\ell m\rangle = \langle \ell m|(L_\pm)^\dagger L_\pm|\ell m\rangle = \langle \ell m|L_\mp L_\pm|\ell m\rangle$
$= \langle \ell m|(L^2 - L_z^2 \mp \hbar L_z)|\ell m\rangle = \langle \ell m|(\hbar^2\ell(\ell+1) - m^2\hbar^2 \mp \hbar^2 m)|\ell m\rangle$
$= \hbar^2[\ell(\ell+1) - m(m\pm 1)] = |C^\pm_{\ell m}|^2$

$\Rightarrow$ After ~~normalizing, we get~~ taking the square root $\Rightarrow C^\pm_{\ell m} = \hbar[\ell(\ell+1) - m(m\pm 1)]^{1/2}$

Q: In the state $\Psi = \frac{1}{\sqrt{2}}(|\ell m\rangle + |\ell m+1\rangle)$, find $\langle L_x\rangle, \langle L_y\rangle, \langle L_x^2\rangle$ + ~~[illegible]~~

A: $\langle L_x\rangle = \frac{1}{2}(\langle \ell m| + \langle \ell m+1|)(L_x)(|\ell m\rangle + |\ell m+1\rangle)$
$= \frac{1}{2}(\langle \ell m|L_x|\ell m\rangle + \langle \ell m+1|L_x|\ell m\rangle + \langle \ell m|L_x|\ell m+1\rangle + \langle \ell m+1|L_x|\ell m+1\rangle)$

Note, as $L_x = \frac{1}{2}L_+ + L_-$ ~~and~~ as $\langle \ell m|L_\pm|\ell m\rangle = \hbar[\ell(\ell+1) - m(m\pm 1)]^{1/2}\langle \ell m|\ell m\pm 1\rangle$
$= 0 \Rightarrow \langle \ell m|L_x|\ell m\rangle = \langle \ell m+1|L_x|\ell m+1\rangle = 0$!

$\Rightarrow \langle L_x\rangle = \frac{1}{2}(\langle \ell m+1|\frac{1}{2}(L_+ + L_-)|\ell m\rangle + \langle \ell m|L_x|\ell m+1\rangle)$
$= \frac{\hbar}{4}([\ell(\ell+1) - m(m+1)]^{1/2}\langle \ell m+1|\ell m+1\rangle + [\ell(\ell+1) - m(m-1)]^{1/2}\overrightarrow{\langle \ell m+1|\ell m-1\rangle}^{0}$
$+ [\ell(\ell+1) - \underset{(m+2)}{\cancel{m}}(m+1)]^{1/2}\langle \ell m|\ell m+2\rangle + [\ell(\ell+1) - m(m+1)]^{1/2}\langle \ell m|\ell m\rangle]$
$= \frac{\hbar}{2}([\ell(\ell+1) - m(m+1)])^{1/2}$ The rest is part of review problems!