Lecture #20: Hydrogen Atom I

Read McQuarrie, Chapter 7

Last time:

Rigid Rotor: Universal θ,ϕ dependence for all central force problems.

$V(\theta,\phi)$ = 0 for rigid rotor $(\vec{J})$

$$\hat{J}^2\psi_{JM} = \hbar^2 J(J+1)\psi_{JM}$$
$$\hat{J}_z\psi_{JM} = \hbar M\psi_{JM}$$
$$\hat{J}_\pm\psi_{JM} = \hbar\left[J(J+1) - M(M\pm1)\right]^{1/2}\psi_{JM\pm1}$$
$$\left[J_i, J_j\right] = i\hbar\sum_k \varepsilon_{ijk}J_k$$

# of Nodes for real part of ψ_{JM} in *x,y* plane ↔ M

# of Nodal surfaces ↔ J

Today: Hydrogen Atom

An exactly soluble quantum mechanical problem. *Every* property is related to *every* other property via the quantum numbers: n, ℓ, m_ℓ. This is what we mean by "structure." It is like saying that a building is more than the bricks it is made up of.

Gives us "cartoons" for understanding more complex systems.

1. H-atom Schrödinger Equation
   separation of variables yields $\psi(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$ expressed as a product

2. Pictures of orbitals
   separate pictures for $R_{n\ell}(r)$ and $Y_\ell^m(\theta,\phi)$

nodes, node spacing, (λ = h/p), envelope for $R_{n\ell}(r)$ (semi-classical)

3. Expectation values of r^k — interpretive picture via $\boxed{n_{\text{effective}}}$: scaling, inter-relationships

4. Evidence for "electron spin"

5. spin-orbit term in $\hat{\mathbf{H}}$.

Lecture #21 will cover

H atom spectra (rigorous selection rule: $\Delta\ell = \pm 1$). Model for Rydberg states of everything
Scaling laws
Rydberg series: "ontogeny recapitulates phylogeny" (Robert Mulliken)
Quantum Defects = Scattering

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l. H-atom Schrödinger equation

attractive

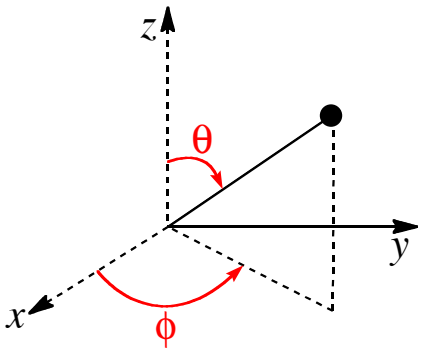
$$\hat{\mathbf{H}} = \hat{T} + \hat{V} \qquad \hat{V} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$$\hat{T} = -\frac{\hbar^2}{2\mu_H}\hat{\nabla}^2$$

($\hat{T}$ contains same terms as a rigid rotor plus r-dependence)

spherical polar coordinates

$$\mu_H = \frac{(m_{e^-})(m_{p^+})}{m_H} \qquad m_H = m_{e^-} + m_{p^+}$$



ϕ starts (ϕ = 0) at +*x* and increases in direction toward *y*. Range of ϕ is $0 \le \phi \le 2\pi$

θ starts (θ = 0) at +*z* and increases in direction toward *xy* plane, $0 \le \theta \le \pi$

volume element for spherical polar coordinates:

$$dx\, dy\, dz = r^2 \sin\theta\, dr\, d\theta d\phi$$

Laplacian:

$$\hat{\nabla}^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.$$

Looks complicated, but there are two parts to $\hat{T}$, radial and angular (and we have solved the universal angular part already).

So we can simplify the Schrödinger Equation (multiplied by $2\mu_H r^2$) to

$$\left\{-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \hat{\mathbf{L}}^2 + 2\mu_H r^2\left[V(r) - E\right]\right\}\psi = 0$$

$\hat{\mathbf{L}}^2$: all θ,ϕ dependence

It is easy to show $\left[\hat{\mathbf{L}}^2, f(r)\right] = 0$ for *any* $f(r)$ because $\hat{\mathbf{L}}^2$ and $f(r)$ involve different coordinates.

Thus, we expect three quantum numbers for ψ: $\psi_{\ell,m_\ell,n}$ ↖ a radial quantum number

Expect to be able to factor $\psi_{n\ell m_\ell} = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$. Basis for separation of variables.

$$\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + 2\mu_H r^2\left[V(r) - E\right]\right]R(r)Y_\ell^m(\theta,\phi) = -\hat{\mathbf{L}}^2 R(r)Y_\ell^m(\theta,\phi)$$

Multiply on left by $\frac{1}{\psi}$, cancel unoperated-on factors, and integrate over θ,ϕ. Rearrange to put r-dependence on LHS and θ,ϕ-dependence on RHS.

$$\frac{1}{R(r)}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + 2\mu_H r^2\left[V(r) - E\right]\right]R(r)$$

$$= -\frac{1}{Y_\ell^m(\theta,\phi)}\hat{\mathbf{L}}^2\underbrace{Y_\ell^m(\theta,\phi)}_{\text{eigenfunction of } \hat{L}^2} = \underbrace{-\hbar^2\ell(\ell+1)}_{\text{known separation constant}}$$

Usual separation argument here. LHS only r, RHS only θ,ϕ. Get a radial Schrödinger equation and an already solved angular Schrödinger equation.

Radial Schrödinger Equation

$$\frac{1}{R(r)}\left[-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+2\mu_H r^2\left[V(r)-E\right]\right]R(r)=-\hbar^2\ell(\ell+1)$$

rearrange, divide by $2\mu_H r^2$ and multiply by $R(r)$ on left:

$$\left[-\frac{\hbar^2}{2\mu_H r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\underbrace{V(r)+\overbrace{\frac{\hbar^2\ell(\ell+1)}{2\mu_H r^2}}^{\text{“centrifugal barrier”}}}_{\text{call this } V_\ell(r) \text{ “effective potential” (actually contains angular kinetic energy)}}-E\right]R(r)=0$$

$$\left(-\frac{\hbar^2}{2\mu_H r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+V_\ell(r)-E\right)R_\ell(r)=0$$

The solutions to this equation will depend on n and ℓ: $R_{n\ell}(r)$.

Can simplify even more using $\chi_\ell(r)$ rather than $R_\ell(r)$:

$\frac{1}{r}\chi_\ell(r)\equiv R_\ell(r)$. After some algebra:

$$\left[-\frac{\hbar^2}{2\mu_H}\frac{\partial^2}{\partial r^2}+V_\ell(r)-E\right]\chi_\ell(r)=0$$

Looks like ordinary 1-D r,p_r Schrödinger Equation!

[But we will mostly not use this super-simplified form of the radial equation in 5.61.] It looks very similar to our other 1-D well Schrödinger Equations, but $V_\ell(r)$ is neither free-particle nor Harmonic Oscillator, and the $r = 0$ boundary condition is subtle.

We know that there can easily be found a complete (infinite) set of $R_{n\ell}(r)$ eigenfunctions.

Note that, although the radial wavefunction does not depend on θ,ϕ, the form of $R_{n\ell}(r)$ does depend on the value of the ℓ quantum number. Recall the Associated Legendre Polynomials. The Θ(θ) part of $Y_\ell^m(\theta,\phi)$ depends on the value of m.

2. Pictures of orbitals

ψ(r,θ,ϕ) specifies a complex # at each point in 3-D space. Difficult to plot on a 2-D page.

Usually plot $\underbrace{R_{n\ell}(r)}_{\substack{\text{specific}\\ \text{system}}}$ separately from $\underbrace{Y_\ell^m(\theta,\phi)}_{\text{universal}}$.

Simple to plot $R_{n\ell}(r)$ vs. r. A lot of insight is encoded in the $R_{n\ell}(r)$ plot.

We have already looked at $Y_\ell^m(\theta,\phi)$ polar plots.

[Clever ways, dot-density and contours, to plot dependence of ψ or ψ*ψ on all 3 variables (see McQuarrie text).]

Dependence of energy levels on reduced mass:

$E_{n\ell m_l} = \dfrac{-\Re hc}{n^2}$ $\Re$ is the "Rydberg constant", consisting entirely of fundamental constants.

$\Re_H = 109737.319\ \text{cm}^{-1}\left(\dfrac{\mu_H}{\mu_\infty}\right) = 109679\ \text{cm}^{-1}$ for H

$\dfrac{m_{e^-}m_\infty}{m_{e^-}+m_\infty} = m_{e^-}$

Ask: what is minimum possible value of μ? positronium (an electron and a positron): $\mu = m_{e^-}/2$.
Maximum value is $\mu_\infty = m_{e^-}$ for nucleus with infinite mass.

Agree perfectly with Bohr atom energy levels but the wavefunctions are certainly not circular orbits (as predicted by the Bohr model)! Also, Bohr ruled out $\ell = 0$.

Form of $R_{n\ell}(r)$

radial nodes is n – 1 – ℓ (no radial nodes for 1s, 2p, 3d, etc.)
(# angular nodes for ψ is ℓ, total # nodes is n – 1, but E *does not* increase in order of *total # of nodes)*. This is not surprising because the θ,ϕ part is independent of the r part.

Now comes some amazing stuff!

1-D *semi-classical* interpretation of node-spacing in $R_{n\ell}(r)$ from $\lambda_r(r) = h/p_r(r)$

$\left[-\dfrac{\hbar^2}{2\mu_H}\dfrac{\partial^2}{\partial r^2} + V_\ell(r) - E_{n\ell}\right]\chi_{n\ell}(r) = 0$ equation.

$p_{r,\text{classical}}(r) = \left[2\mu_H\left(E_{n\ell} - V_\ell(r)\right)\right]^{1/2}$. You know $V_\ell(r)$! Therefore, you know $p_{r,\text{classical}}(r)$.
Now you need to know what to do with this knowledge.

At small r, innermost node spacing is approximately independent of n. This is an important but unexpected simplification.

Non-Lecture: Defer to Lecture #21

3. Expectation values of integer powers of r. a_0 is Bohr radius: $a_0 = 0.0529$ nm

McQuarrie, Page 333

(H-atom and one-electron ions)

k	$\langle r^k \rangle_{n\ell m_\ell}$
2	$\frac{a_0^2 n^4}{Z^2}\left\{1+\frac{3}{2}\left[1-\frac{\ell(\ell+1)-\frac{1}{3}}{n^2}\right]\right\}$
1	$\frac{a_0 n^2}{Z}\left\{1+\frac{1}{2}\left[1-\frac{\ell(\ell+1)}{n^2}\right]\right\}$
–1	$\frac{Z}{a_0 n^2}$
–2	$\frac{Z^2}{a_0^2 n^3(\ell+1/2)}$
–3	$\frac{Z^3}{a_0^3 n^3 \ell(\ell+1/2)(\ell+1)}$.

We use these simple formulas to get (or guess) the n,ℓ-scaling of *all* r-dependent electronic quantities, even for non-Hydrogenic systems.

$\frac{I_n}{hc}$ is energy (in cm^{-1}) required to ionize from the nth energy level

Note that Ionization Energy $= I_n = E_{n=\infty} - E_n > 0$.

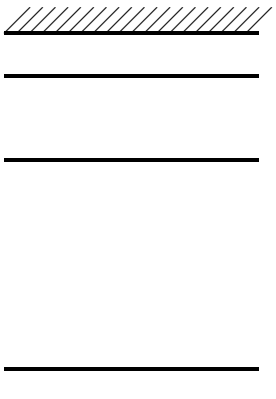
$$I_n = 0 + \frac{Z^2 \Re hc}{n^2}$$

solve for n.

For H, n is integer. For everything else, n is not integer but changes as energy increases in steps of 1.

$$n_{\text{effective}} = \left[\frac{\Re hc}{I_n}\right]^{1/2}$$

I_n is ionization energy from nth energy level



$$\langle r \rangle_{n\ell} = \frac{a_0 n^2}{Z}\left\{\frac{3}{2} - \frac{\ell(\ell+1)}{2n^2}\right\}$$

$$\langle r \rangle_{1s} = \frac{a_0}{Z}\frac{3}{2}$$

replacing $n^2_{\text{effective}}$

$$r_{\text{effective}} = \frac{a_0}{Z}\frac{\Re hc}{I_n}\left\{\frac{3}{2} - \frac{\ell(\ell+1) I_n}{2\Re hc}\right\}$$

Obtained by plugging $n_{\text{effective}}$ into $\langle r \rangle_{n\ell}$.

$$n_{\text{effective}} = \left[\frac{\Re hc}{I_n} \right]^{1/2}$$

$$\langle r \rangle_{n\ell} = \frac{a_0 n^2}{Z} \left\{ \frac{3}{2} - \frac{\ell(\ell+1)}{2n^2} \right\}$$

$$r_{n\ell}^{\text{effective}} = \frac{a_0}{Z} \underbrace{\frac{\Re hc}{I_n}}_{n_{\text{effective}}} \left\{ \frac{3}{2} - \frac{\ell(\ell+1)}{2} \frac{I_n}{\Re hc} \right\}$$

Use $I_{n\ell}$ to estimate $r_{n\ell}^{\text{effective}}$ via $n_{\text{effective}}$. The value of $n_{\text{effective}}$ is the link among all electronic properties of an atom. This is what we mean by "structure".

All properties of highly excited electronic states of atoms and molecules are inter-related or estimated in this way. Intuition is better than memorization (this will be covered more in Lecture #21)!

End of Non-Lecture

4. Need to invoke a new kind of angular momentum: e^- spin

Zeman effect: energy levels are split in a magnetic field due to the magnetic dipole moment associated with circulating charge.

$$\vec{\mathrm{m}} = \frac{-|e|}{2m_e} \vec{\hat{\mathbf{L}}}$$

(We understand **L** in terms of $\vec{r} \times \vec{p}$ and $\vec{m}$ in terms of current in a circular orbit)

This gives a new potential energy term

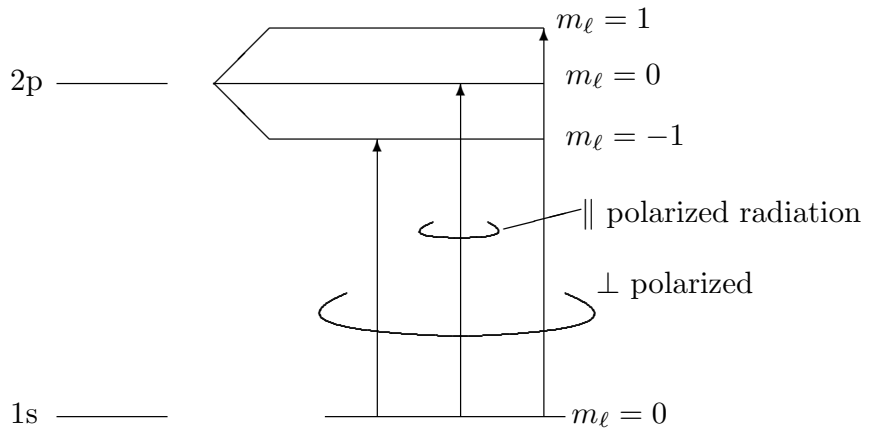
$$V_{\text{mag}} = -\vec{\mathrm{m}} \cdot \vec{\mathbf{B}}$$

$$= \frac{|e| B_z}{2m_e} \underbrace{\hat{\mathbf{L}}_z}_{\hbar m_\ell}$$

Evaluate the effect the magnetic field has on $E_{n\ell \mathrm{m}_\ell}$ using perturbation theory. Since $\hat{\mathbf{L}}_z$ has only $\Delta m_\ell = 0$ matrix elements, we can say that

$$E^{\text{Zeeman}} = E^{(1)}_{m_\ell}.$$

Expect, for B-field along z, z-polarized VUV radiation excites $\Delta m_\ell = 0$ transitions and x,y polarized radiation excites $\Delta m_\ell = \pm 1$ transitions.



In *non-zero* B-field, expect to see the single zero-field 2p ← 1s transition split into 1, 2, or 3 lines depending on light polarization with respect to direction of magnetic field. How many for z-polarized light? How many for x or y polarized light? How many for light linearly polarized somewhere between x and z? What is the ΔM_L selection rule? Where does it come from?

Actually see many more components. Why? For $\ell = 1$, s = 1/2 and $g_\ell = 1$, $g_S = 2$, expect 5 levels: (–1,–1/2), (0, –1/2), [(–1, +1/2), (+1, –1/2)], (0, 1/2), and (1, 1/2). The bracket includes two m_ℓ, m_s components that are unexpectedly degenerate.

Stern-Gerlach Experiment

atomic beam through magnetic field, the strength of which varies linearly in a direction ⊥ to the direction of the atomic beam.
Different deflection of different m-components. Beamlets!

See unexpectedly too many beamlets.

5. Finally, we can understand the very small zero-field splitting in 2p ← 1s transition as arising from "spin-orbit" term in $\widehat{\mathbf{H}}$.

$$\widehat{\mathbf{H}}^{SO} \propto \ell \cdot s$$

$[\vec{\ell}, \vec{s}] = 0$ because ℓ and s operate on different coordinates

$$j \equiv \ell + s$$

$$j^2 = \ell^2 + s^2 + 2\ell \cdot s$$

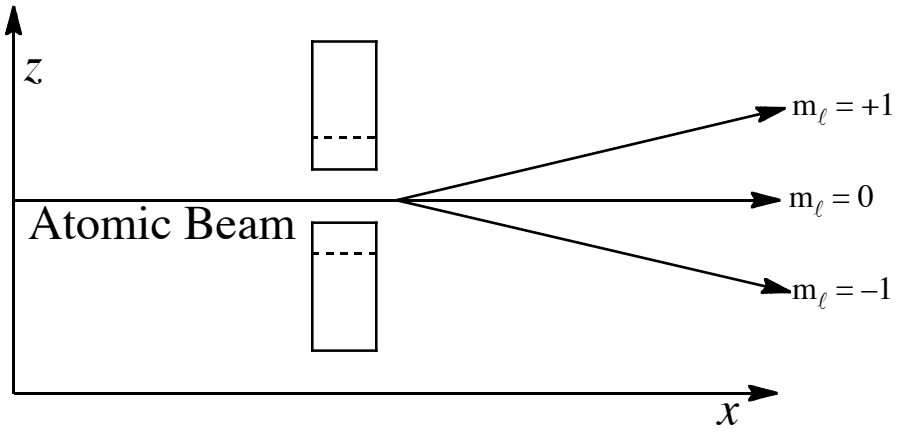
$$\ell \cdot s = \frac{1}{2}\left[j^2 - \ell^2 - s^2 \right] = \ell_z s_z + \frac{1}{2}\underbrace{\left(\ell_+ s_- + \ell_- s_+ \right)}_{\text{spoils } m_\ell, m_s}$$

You show that $\left[\ell \cdot s, j^2 \right] = \left[\ell \cdot s, \ell^2 \right] = \left[\ell \cdot s, s^2 \right] = \left[\ell \cdot s, j_z \right] = 0$

	coupled		uncoupled	
Basis sets	$\underbrace{\left(j\ell sm \right)_j}_{\text{all are good quantum numbers}}$	vs.	$(\ell m_\ell \, s m_s)$ (m_ℓ and m_s are "spoiled" by $\widehat{\mathbf{H}}^{\text{SO}}$).	"coupled" vs. "uncoupled"

$\widehat{\mathbf{H}}^{SO}$ ($j\ell sm$, good) vs. $\widehat{\mathbf{H}}^{\text{Zeeman}}$ ($\ell m_\ell s m_s$ good). $\mathbf{H}_{\text{SO}}$ and $\mathbf{H}_{\text{Zeeman}}$ fight each other.

6. Stern-Gerlach Experiment



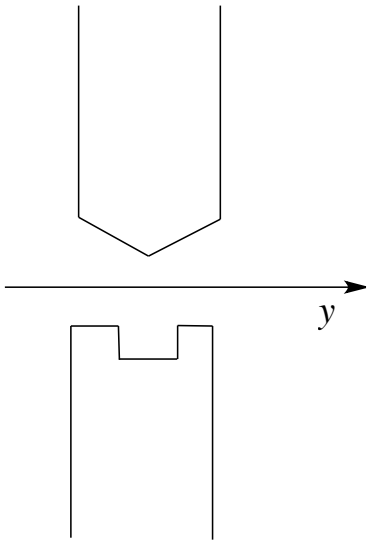
Magnetic field in z-direction
Pole pieces with slanted ends in y direction

$$B_z = \left(B_z^0 - \alpha y \right) \hat{z}$$

$$V(y,z) = -\mu \cdot B = -\mu_z \left(B_z^0 - \alpha y \right)$$

$$\text{Force } (y) = -\frac{dV}{dy} = -\mu_z \alpha = +\frac{|e|}{2m_e} \hat{L}_z \alpha$$

$$\hat{\mu} = -\frac{|e|}{2m_e} \hat{L}$$



(force ⊥ to beam propagation direction)

Atoms follow equi-potential

$m > 0$ high field seeking
$m < 0$ low field seeking

2 Kinds of Experiment

A. Single Stern-Gerlach beam for H in 1s?
Expected no deflection or splitting of beam because $\ell = 0$

Observed two beam-lets, $m_s = +1/2$ and $m_s = -1/2$!

B. Double Stern-Gerlach

Split beam into $m_s = 1/2$ and $m_s = -1/2$ beam-lets

Now put one beam-let through an identical S-G setup, but where the z-axis of the magnets is tilted relative to the original z-axis.

Get two beam-lets, even though input beam to the second S-G apparatus had been pre-selected to be in a single m_s state! What postulate explains this?

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