Lecture 21. Introduction to the Hydrogen Atom

Simple estimate of the eigenvalues:

a = radius of the electron's orbit

Condition for standing waves: $n\lambda = 2\pi a$

De Broglie condition: $p = \frac{h}{\lambda} = \frac{hn}{2\pi a} = \frac{n\hbar}{a}$

Centrifugal force = - electrostatic force (using rationalized MKS units):

$$\frac{\mu v^2}{a} = \frac{Ze^2}{4\pi\varepsilon_0 a^2}$$

$$\frac{p^2}{\mu a} = \frac{Ze^2}{4\pi\varepsilon_0 a^2}$$

Eliminating p gives

$$\frac{n^2\hbar^2}{\mu a^3} = \frac{Ze^2}{4\pi\varepsilon_0 a^2}$$

Solving for a,

$$a = \frac{4\pi\varepsilon_0 n^2\hbar^2}{\mu Z e^2}$$

Now let's solve for the energy eigenvalues:

$$T = \frac{p^2}{2\mu} = \frac{p^2}{\mu a}\frac{a}{2} = \frac{Ze^2}{8\pi\varepsilon_0 a} = \frac{Ze^2}{8\pi\varepsilon_0}\left(\frac{\mu Z e^2}{8\pi\varepsilon_0 n^2\hbar^2}\right)$$

Using the virial theorem,

$$\langle E\rangle = -\langle T\rangle = -\frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2}$$

Define the Bohr radius,

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = \frac{1.11265x10^{-19}\left(1.055x10^{-34}\right)^2}{9.109x10^{-31}(1.602x10^{-19})^2} = 5.29x10^{-11}m = 1 \text{ a.u.}$$

We get for the energy eigenvalue

$$E_n = -\frac{Z^2 e^2}{8\pi\varepsilon_0 \; a_0 n^2}$$

$$\langle V \rangle = -2\langle T \rangle = 2\langle E \rangle = -\frac{Z^2 e^2}{4\pi\varepsilon_0 \; a_0 n^2}$$

For Z=1, $E_1 = \frac{\left(1.602x10^{-19}\right)^2}{2x1.11265x10^{-10}(5.29x10^{-11})} = 13.607eV$ = 0.5 a.u.

Now let's get the exact solution. The Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

The first tem is the radial kinetic energy. The second is the centrifugal energy, which creates a barrier. The last is the potential energy.

Invoke separability:

$$\psi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi)$$

$$\hat{H}\psi = -\frac{\hbar^2}{2\mu}\left(R'' + \frac{2}{r}R'\right)Y_{lm} + \frac{l(l+1)\hbar^2}{2\mu r^2}RY_{lm} - \frac{Ze^2}{4\pi\varepsilon_0 r}RY_{lm} = ERY_{lm}$$

$$-\frac{\hbar^2}{2\mu}\left(R'' + \frac{2}{r}R'\right) + \frac{l(l+1)\hbar^2}{2\mu r^2}R - \frac{Ze^2}{4\pi\varepsilon_0 r}R = ER$$

$$R'' + \frac{2}{r}R' + \frac{l(l+1)\hbar^2}{r^2}R + \frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0 r}R + \frac{2\mu}{\hbar^2}ER = 0$$

Making the substitution,

$$\frac{\mu}{\hbar^2} = \frac{4\pi\varepsilon_0}{a_0 e^2}$$

we get

$$R'' + \frac{2}{r}R' + \left[\frac{8\pi\varepsilon_0}{a_0 e^2}E + \frac{2Z}{a_0 r} - \frac{l(l+1)}{r^2}\right]R = 0$$

Before solving this equation, let's look at its asymptotic behavior:

$$R'' + \frac{8\pi\varepsilon_0 E}{a_0 e^2} R = 0 .$$

This equation has the form

$$R'' = c^2 R$$
$$c = \sqrt{\frac{-8\pi\varepsilon_0 E}{a_0 e^2}} = \sqrt{-2\mu E} / \hbar$$

The asymptotic solution is

$$R(r) \sim Ae^{\pm cr}$$

where c looks like the reciprocal of the deBroglie wavelength.

For a free particle, E > 0, and

$$R(r) = Ae^{\pm i(2\mu E)^{1/2} r/\hbar}$$

For a bound particle, E < 0, and only the negative sign is meaningful:

$$R(r) = Ae^{-(2\mu|E|)^{1/2} r/\hbar}$$

To get the complete solution, let's first convert to dimensionless variables. We are given E (which we will assume to be negative), and we already defined a_0. Let's define a parameter n (not yet an integer), by the expression

$$E = -\frac{Z^2 e^2}{8\pi\varepsilon_0 n^2 a_0}$$

We define the dimensionless variable

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

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

$$\frac{d}{dr} = \frac{2Z}{a_0 n}\frac{d}{dx}$$

$$\frac{d^2}{dr^2} = \left(\frac{2Z}{a_0 n}\right)^2 \frac{d^2}{dx^2}$$

$R(r)$ transforms into $G(x)$, which satisfies

$$G'' + \frac{2}{x}G' + \left[-\frac{1}{4} + \frac{n}{x} - \frac{l(l+1)}{x^2}\right]G = 0$$

The asymptotic behavior is

$$G'' - \frac{1}{4}G = 0$$

$$G(x) \sim e^{-x/2}$$

Let's look for solutions of the form

$$G(x) = u(x) x^l e^{-x/2}$$

After a lot of algebra,

$$xu'' + (2l + 2 - x)u' + (n - l - 1)u = 0$$

Compare this with the associated Laguerre Equation:

$$xu'' + (\beta + 1 - x)u' + (\alpha - \beta)u = 0\,,$$

were α and β are integers.

We make the identification

$$\beta + 1 = 2l + 2$$
$$\alpha - \beta = n - l - 1$$

or

$$\beta = 2l + 1$$
$$\alpha = n + l$$

The solution is

$$u(x) = L_{\alpha}^{\beta}(x) = L_{n+l}^{2l+1}(x)$$
$$R_{n,l}(r) = c_{n,l}\left(\frac{2Z}{a_0 n} r\right)^{l} L_{n+l}^{2l+1}\left(\frac{2Z}{a_0 n} r\right) e^{-rZ/a_0 n}$$
$$c_{n,l} = \left[\left(\frac{2Z}{a_0 n}\right)^{3} \frac{(n-l-1)!}{2^n [(n+l)!]^3}\right]^{1/2}$$

n is a positive integer, and l ranges from 0 to n-1.

Properties of Laguerre polynomials:

$$L_{\alpha}(x) = e^{x} \frac{d^{\alpha}}{dx^{\alpha}}\left(x^{\alpha} e^{-x}\right)$$
$$L_{\alpha}^{\beta}(x) = \frac{d^{\beta}}{dx^{\beta}} L_{\alpha}(x)$$

Normalization and orthogonality:

$$\int_{0}^{\infty} R_{nl}(r) R_{n'l}(r) r^2 dr = \delta_{nn'}$$

No statement is made about orthogonality of radial wave functions with different l quantum numbers, but the orthogonality of the spherical harmonics takes care of that.

The eigenvalues are

$$E_n = -\frac{Z^2 e^2}{2n^2 a_0}$$

Recall that previously we defines a parameter n so that the above relation is correct. At that point n was simply a scale parameter. Later the Strum-Liouville condition informed us that n is an integer, thereby quantizing the energy.

Noting that E_n does not depend on *l* or *m*, we conclude that the degeneracy is

$$g_n = 1 + 3 + 5 + ... + 2n - 1 = n^2$$

This does not include spin.

The differences between the eigenvalues give the transition energies.

$$E_{n_2} - E_{n_1} = h\nu$$
$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} = \frac{E_{n_2} - E_{n_1}}{hc} = Z^2 R_H \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$
$$R_H = \frac{e^2}{2a_0 hc} = 109{,}677.6 cm^{-1}$$

R_H is the Rydberg constant for the H atom. It equals its ionization potential (0.5 a.u.) expressed in cm^{-1}.

Various series of transitions result by fixing n_1 and looking at a progression of n_2 values.

Let n_1 = n and n_2 = n +s.

$$\tilde{\nu} = R_H \left(\frac{1}{n^2} - \frac{1}{(n+s)^2} \right) = R_H \frac{s(2n+s)}{n^2 (n+s)^2}$$

For n >> s, $\tilde{\nu} \sim n^{-3}$

$n_1 = 1$ Lyman series
$n_1 = 2$ Balmer series
$n_1 = 3$ Paschen series

The lowest ground state transition of the H atom produces the Lyman α line:

$$\frac{1}{\lambda} = R_H \left(1 - \frac{1}{4} \right), \qquad \lambda = 121.6 nm$$

Lecture 22. Properties of the Radial Wave Functions

Where is the probability density greatest? At the maximum of $\left|R_{nl}\right|^{2.}$

Example: 1s: $\left|R_{10}\right|^{2.} \sim e^{-2Zr/a_0}$ has a maximum at r = 0.

2s: $\left|R_{20}\right|^{2.} \sim \left(1-\frac{Zr}{2a_0}\right)e^{-2Zr/a_0}$ has a maximum at $r=\frac{2a_0}{Z}$.

This is not the same thing as asking what is the most probable value of r. That quantity is found by solving the equation

$$\frac{d}{dr}\left\{\left|R_{nl}\right|^{2.} r^2\right\}=0$$

Here is a simple shortcut: The maximum occur at the same values of r that rR_{nl} reaches a maximum.

Example: 1s:

$$\frac{d}{dr}\left\{re^{-zr/a_0}\right\}=0$$

$$1-r\left(\frac{Z}{a_0}\right)=0$$

$$r=\frac{a_0}{Z}$$

A cleaner way of solving this problem is to define the reduced variable

$$\rho=\frac{Zr}{na_0}$$

For the 1s problem,

$$\frac{d}{d\rho}\left(\rho e^{-\rho}\right)=0$$

$$\rho_{mp}=1$$

Another example: 3d

$$\rho = \frac{Zr}{3a_0}$$
$$\frac{d}{d\rho}\left\{\rho^3 e^{-\rho}\right\}$$
$$3\rho^2 - \rho^3 = 0$$
$$\rho = 3$$
$$r = \frac{9a_0}{Z}$$

What is the expectation value of r?

$$\langle r \rangle = \int_0^\infty \left| R_{nl}(r) \right| r^3 dr$$

Example: 1s state.

$$\psi_{1s}(r) = \frac{1}{\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} = \frac{1}{\sqrt{4\pi}} 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-ZR/a_0}$$

Verify the normalization.

Set Z = 1, $\rho = r/a_0$

$$R_{1s} = 2a_0^{-3/2} e^{-\rho}$$
$$\langle r \rangle = \frac{4}{a_0^3}\int_0^\infty e^{-2\rho} r^3 dr = 4a_0 \int_0^\infty e^{-2\rho} \rho^3 d\rho$$
$$\int_0^\infty e^{-qx} x^n dx = \frac{n!}{q^{n+1}}$$
$$\langle r \rangle = 4a_0 \frac{3!}{2^4} = \frac{3}{2} a_0$$

What is the transition probability? It is proportional to the square of the integral $\langle n_1 l_1 m_1 |\vec{\mu} \cdot \vec{E}| n_2 l_2 m_2 \rangle$. Here we will consider only the radial contribution, with the radial part of the dipole operator proportional to r. Then transition matrix element for the 1s-2p transition is

$$\frac{2}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^4 \int_0^\infty e^{-Zr/a_0} r e^{-Zr/2a_0} r \cdot r^2 dr$$

For Z=1,

$$\frac{1}{\sqrt{6}} a_0 \int_0^\infty e^{-3x/2} x^4 dx = \frac{1}{\sqrt{6}} \frac{4!}{\left(\frac{3}{2}\right)^5} a_0 = 1.2903 a_0$$

This method is very useful for calculating selection rules and relative transition strengths.

Spatial properties of the Wave Functions

What effect does *l* have on the motion of the electron? The classical (Kepler) orbit of a particle subject to an inverse square force,

$$F = -\frac{k}{r^2}$$
$$V = -\frac{k}{r}$$

is an ellipse with semi-major axis a and semi-minor axis b.

For energy E, we find that

$$a = -\frac{k}{2E}$$
$$b = \sqrt{\frac{al^2}{\mu k}}$$

Verify that this value of *a* is consistent with the equation for E_n derived previously.

The maximum value of L occurs when $\frac{\mu v^2}{a} = -\frac{k}{a^2}$ or $\frac{L^2}{\mu k} = a$. In this case, $b = a$, and the orbit is a circle. As L gets smaller, the orbit becomes an ellipse, with greater and greater eccentricity. The nucleus lies at one focus of this ellipse. For L = *0* (impossible classically), the electron passes through the nucleus, and for small values of L it passes very close to the nucleus. Such a close encounter is essential for absorption of a photon.

Lecture 23. Hydrogen Atom Transitions

Angular contribution to the transition probability:

The transition dipole operator is given by

$$\vec{\mu}\cdot\vec{E} = e(r\sin\theta\cos\phi E_x + r\sin\theta\sin\phi E_y + r\cos\theta E_z).$$

We wish to calculate the matrix element $\langle l_1 m_1 | \vec{\mu}\cdot\vec{E} | l_2 m_2 \rangle$ term by term.

Recall that $Y_{lm} \propto P_l^{|m|}(\cos\theta)e^{im\phi}$

Lets look at the ϕ part first. For the E_z term, the relevant integral is

$$\int_0^{2\pi} e^{i(m_2-m_1)\phi}d\phi.$$

This integral vanishes unless $m_1 = m_2$.

Now look at the E_x term. Recall that

$$\cos\phi = \frac{1}{2}\left(e^{i\phi} + e^{-i\phi}\right)$$

The first exponential leads to the integral

$$\int_0^{2\pi} e^{i(m_2-m_1+1)\phi}d\phi \Rightarrow m_2 = m_1 - 1$$

The second exponential leads to the integral

$$\int_0^{2\pi} e^{i(m_2-m_1-1)\phi}d\phi \Rightarrow m_2 = m_1 + 1$$

The E_y term gives the same result.

Now look at the θ part. Recall the recursion relations

$$xP_l^{|m|}(x) = \cos\theta P_l^{|m|}(\cos\theta) = \frac{1}{2l+1}\left\{(l-|m|+1)P_{l+1}^{|m|} + (l+|m|)P_{l-1}^{|m|}\right\}$$

$$\sqrt{1-x^2}P_l^{|m|}(x) = \sin\theta P_l^{|m|}(\cos\theta)$$

$$= \frac{1}{2l+1}\left\{P_{l+1}^{|m|+1} - P_{l-1}^{|m|+1}\right\} = \frac{1}{2l+1}\left\{(l+|m|)(l+|m|-1)P_{l-1}^{|m|-1} - (l-|m|)(l-|m|+2)P_{l+1}^{|m|-1}\right\}$$

Look at the E_z term. The integral of interest is

$$\int_0^\pi P_{l_1}^{m_1}(\cos\theta)\cos\theta P_{l_2}^{m_2}(\cos\theta)\sin\theta d\theta = \int_0^\pi P_{l_1}^{m_1}(x) x P_{l_2}^{m_2}(x)dx$$

The first recursion relation tells us immediately that $l_2 = l_1 \pm 1$.

The E_x and E_y terms don't give any more information, but it is hard to use the $\sin\theta$ recursion relation.

Now let's ask what physical situations the various selection rules pertain to. This is related to how we define the z-axis.

Plane polarized light: The radiation travels in the x-direction and the electric vector points along the z-axis. In this case the selection rule is $\Delta m = 0, \Delta l = \pm 1$

Suppose the light is circularly polarized. In this case, the light travels in the z-direction and the electric vector rotates in the x-y plane.

$$E_x = E_0 e^{i\omega t}$$
$$E_y = E_0 e^{i(\omega t \pm \pi/2)} = \pm i E_x$$
$$E_z = 0$$

For right circularly polarized light, $E = E_0 r \sin\theta(\cos\phi + i\sin\phi) = E_0 r\sin\theta e^{i\phi}$

The relevant integral is $\int_0^{2\pi} e^{i(m_2 - m_1 + 1)\phi} d\phi \Rightarrow m_2 = m_1 - 1$

Now we can use the $\sin\theta$ recursion relation to derive $\Delta l = \pm 1$.

For left circularly polarized light, $E = E_0 r \sin\theta(\cos\phi - i\sin\phi) = E_0 r\sin\theta e^{-i\phi}$ and we deduce $\Delta m = 1, \Delta l = \pm 1$

The underlying physical basis for this is that the photon carries an angular momentum equal to one unit of $\hbar$.

Magnetic Effects

Magnetic moment of an electron current in an atom: $\vec{\mu} = IA\hat{n}$

Energy resulting from that moment interacting with a magnetic field: $E_B = -\vec{\mu} \cdot \vec{B}$

What is the current for a charge Q? $I = \frac{Q}{t} = \frac{Q}{2\pi r / v} = \frac{Qv}{2\pi r}$

The area is $A = \pi r^2$ giving $IA = \frac{Qvr}{2} = \frac{Qrp}{2m}$

The magnetic moment for orbital motion is

$$\vec{\mu}_l = \frac{Q\vec{r}x\vec{p}}{2m} = \frac{Q}{2m}\vec{L} = -\frac{e}{2\mu_e}\vec{L}$$

$$\mu_l = -\frac{e\hbar\sqrt{l(l+1)}}{2\mu_e}$$

$$\mu_{l_z} = -\frac{e\hbar m_l}{2\mu_e}$$

Bohr magneton: $\mu_B = \frac{e\hbar}{2\mu_e}$ J/Tesla

It follows that $\mu_l = \mu_B\sqrt{l(l+1)}$ and $\mu_{l_z} = \mu_B m_l$

The magnetic moment for spin is $\vec{\mu}_s = -g_s \frac{e}{2\mu_e}\vec{S}$

The Lande g-factor: $g_S \approx 2$

The Hamiltonian for an H atom in a magnetic field:

$$H = H_0 - (\vec{\mu}_l + \vec{\mu}_S)\cdot\vec{B} = H_0 - (\mu_B / \hbar)B_z\left(\hat{L}_z + g_s\hat{S}_z\right)$$

What are the eigenvalues of this Hamiltonian?

$$E = E_0 - \mu_B B_z\left(m_l + g_s m_s\right)$$

The magnetic field lifts the m degeneracy. This is called the Zeeman effect.

Electric field effects:

$$E_e = -e\vec{r} \cdot \vec{E} = -ezE_z = -eE_z r\cos\theta$$

In this case we cannot simply say what the eigenvalues are without first solving the Schrodinger equation. One approach is to use perturbation theory. The lifting of |m| degeneracy by an elcctric field is called the Stark effect.