

1. The probability of spontaneous transitions of a charged particle from one initial energy level to another final level is governed by the overlap integral

$$\bar{D}_o = q \int \vec{r} \psi_i^* \psi_f dV,$$

where q is the charge of the particle. If $\bar{D}_o = 0$ between two levels, the transition is forbidden. Searching for such forbidden transitions leads to *selection rules*. Consider the 3D infinite potential well.

- (a) Show that only allowed transitions from ψ_{n_1, n_2, n_3} are to a state where two of the quantum numbers are unchanged and the other quantum number changes by an odd number like 1, 3, 5, etc.
- (b) Show that the emitted photons have energies $E = p(2n - p)E_1$ where the n is the original quantum level and $n - p$ is the final quantum level and E_1 is the ground state energy of the one-dimensional potential well.

The following integral identities are useful:

$$\int_0^L \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx = \frac{L}{2} \delta_{nm} \quad \text{and} \quad \int_0^L x \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx = \begin{cases} \frac{L^2}{4} & n = m \\ \frac{2L^2}{\pi^2} \frac{nm[(-1)^{n-m} - 1]}{(n-m)^2(n+m)^2} & n \neq m \end{cases}$$

The wavefunction for the symmetric 3D potential is given by

$$\psi(x, y, z) = \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right) \sin\left(\frac{o\pi z}{L}\right).$$

Also $\vec{r} = ix + jy + kz$. The overlap integral therefore is

$$\bar{D}_o = e \int_0^L \int_0^L \int_0^L (\mathbf{i}x + \mathbf{j}y + \mathbf{k}z) \sin\left(\frac{n_i\pi x}{L}\right) \sin\left(\frac{m_i\pi y}{L}\right) \sin\left(\frac{o_i\pi z}{L}\right) \sin\left(\frac{n_f\pi x}{L}\right) \sin\left(\frac{m_f\pi y}{L}\right) \sin\left(\frac{o_f\pi z}{L}\right) dx dy dz$$

Considering the x component we find

$$D_{ox} = e \int_0^L x \sin\left(\frac{n_i\pi x}{L}\right) \sin\left(\frac{n_f\pi x}{L}\right) dx \int_0^L \sin\left(\frac{m_i\pi y}{L}\right) \sin\left(\frac{m_f\pi y}{L}\right) dy \int_0^L \sin\left(\frac{o_i\pi z}{L}\right) \sin\left(\frac{o_f\pi z}{L}\right) dz$$

The y and z integral will give zero unless $m_f = m_i$ and $o_f = o_i$. To have a transition we have to go from one state to a different state that is $n_f \neq n_i$. The transition is therefore

$$D_{0x} = e \frac{2L^2}{\pi^2} \frac{n_i n_f [(-1)^{n_i - n_f} - 1]}{(n_i - n_f)^2 (n_i + n_f)^2} \frac{L}{2} \frac{L}{2} \quad \text{where } n_f \neq n_i.$$

Now if $n_i - n_f$ is an even number, $[(-1)^{n_i - n_f} - 1]$ will vanish and D_{0x} will be zero. If $n_i - n_f$ is an odd number, $[(-1)^{n_i - n_f} - 1]$ will equal -2 and thus D_{0x} will be finite.

The y -component of the overlap integral will be

$$D_{0y} = e \int_0^L \sin\left(\frac{n_i \pi x}{L}\right) \sin\left(\frac{n_f \pi x}{L}\right) dx \int_0^L y \sin\left(\frac{m_i \pi y}{L}\right) \sin\left(\frac{m_f \pi y}{L}\right) dy \int_0^L \sin\left(\frac{o_i \pi z}{L}\right) \sin\left(\frac{o_f \pi z}{L}\right) dz$$

But this is identical to the expression for D_{0x} with x and y interchanged. Exactly the same occurs with D_{0z} .

So it is clear that the only transitions that have a non-zero overlap, and hence emit a photon, are those where two quantum numbers remain unchanged and the third changes by an odd number.

The energy levels of the 3D symmetric potential well are given by $E_{nmo} = E_1(n^2 + m^2 + o^2)$, where E_1 is the ground state energy of the 1D infinite square well. If the transition is from n to $n - p$, the difference in energy is

$$\begin{aligned} \Delta E &= E_{nmo} - E_{(n-p)mo} \\ &= E_1(n^2 + m^2 + o^2) - E_1([n - p]^2 + m^2 + o^2) \\ &= E_1(n^2 - [n - p]^2) \\ &= p(2n - p) E_1 \end{aligned}$$

2. For the hydrogen atom prove the selection rules $\Delta m = 0$ or ± 1 and $\Delta l = \pm 1$. Remember, in spherical coordinates, $\vec{r} = ir \sin \theta \sin \phi + jr \sin \theta \cos \phi + kr \cos \theta$. Make use of symmetry where possible. The identities $\int_0^{2\pi} e^{-ib\phi} d\phi = \delta_{b0}$, $\sin \phi = \frac{e^{i\phi} - e^{-i\phi}}{2i}$, and $\cos \phi = \frac{e^{i\phi} + e^{-i\phi}}{2}$ may be of use.

The wavefunctions for the hydrogen atom have the form $\psi_{nlm} = AR_{nl}(r)f_{lm}(\theta)g_m(\phi)$, where A is a normalization constant. The overlap integral indicates possible transitions

$$\bar{D}_o = q \int \vec{r} \psi_i^* \psi_f dV.$$

Let the initial state be denoted by nlm and the final state by qst . Now note that the only imaginary term is $g_m(\phi) = e^{im\phi}$ and its complex conjugate will be $[g_m(\phi)]^* = e^{-im\phi} = g_{-m}(\phi)$.

The overlap integral will be

$$\begin{aligned} \bar{D}_0 &= e \int_0^\infty \int_0^\pi \int_0^{2\pi} \vec{r} R_{nl} f_{lm} g_{-m} R_{qs} f_{st} g_t r^2 \sin \theta dr d\theta d\phi \\ &= \mathbf{i} e \int_0^\infty R_{nl} R_{qs} r^3 dr \int_0^\pi f_{lm} f_{st} \sin^2 \theta d\theta \int_0^{2\pi} g_{-m} g_t \sin \phi d\phi + \\ &\quad \mathbf{j} e \int_0^\infty R_{nl} R_{qs} r^3 dr \int_0^\pi f_{lm} f_{st} \sin^2 \theta d\theta \int_0^{2\pi} g_{-m} g_t \cos \phi d\phi + \\ &\quad \mathbf{k} e \int_0^\infty R_{nl} R_{qs} r^3 dr \int_0^\pi f_{lm} f_{st} \cos \theta \sin \theta d\theta \int_0^{2\pi} g_{-m} g_t d\phi. \end{aligned}$$

Using the given identities, the ϕ integrals become

$$\int_0^{2\pi} g_{-m} g_t \sin \phi d\phi = \int_0^{2\pi} e^{-im\phi} e^{it\phi} \frac{e^{i\phi} - e^{-i\phi}}{2i} d\phi = \frac{-i}{2} \int_0^{2\pi} (e^{-i(m-t-1)} - e^{-i(m-t+1)}) d\phi = \frac{-i}{2} (\delta_{m,t+1} - \delta_{m,t-1})$$

and

$$\int_0^{2\pi} g_{-m} g_t \cos \phi d\phi = \int_0^{2\pi} e^{-im\phi} e^{it\phi} \frac{e^{i\phi} + e^{-i\phi}}{2} d\phi = \frac{1}{2} \int_0^{2\pi} (e^{-i(m-t-1)} + e^{-i(m-t+1)}) d\phi = \frac{1}{2} (\delta_{m,t+1} + \delta_{m,t-1})$$

and

$$\int_0^{2\pi} g_{-m} g_t d\phi = \int_0^{2\pi} e^{-im\phi} e^{it\phi} d\phi = \int_0^{2\pi} e^{-i(m-t)} d\phi = \delta_{m,t}.$$

So we see that to get a non-zero contribution from the ϕ integral we need $t = m$ or $t = m \pm 1$, that is $\Delta m = 0$ or ± 1 .

To determine the selection rule for l , we need to investigate the symmetry of $\sin(\theta)$ and $\cos(\theta)$, and $f_{lm}(\theta)$ over the range $0 \leq \theta \leq \pi$.

First $\sin(\theta)$ is even and $\cos(\theta)$ is odd about the centre value $\pi/2$. Next consider the generating function for $f_{lm}(\theta)$,

$$f_{lm}(\theta) = \frac{\sin^{l+|m|}(\theta)}{2^l l!} \left[\frac{d}{d(\cos(\theta))} \right]^{|m|} (\cos^2(\theta) - 1)^l.$$

The $\sin^{l+|m|}(\theta)$ portion is even. The term $(\cos^2(\theta) - 1)^l$ only has even multiples of $\cos(\theta)$, with leading term $\cos^{2l}(\theta)$, so it is even. Applying the first derivative yields odd multiples of $\cos(\theta)$, with leading term $\cos^{2l-1}(\theta)$, so it is odd. The next derivative returns even multiples again, so overall it is even. The subsequent differentiations change from odd to even, and on and on. Therefore, if $l + |m|$ is even then $f_{lm}(\theta)$ is even, and if $l + |m|$ is odd then $f_{lm}(\theta)$ is odd. Also notice that the leading term after all the differentiations is $\cos^{2l-(l+|m|)}(\theta) = \cos^{l-|m|}(\theta)$. The term after that will be $\cos^{l-|m|-2}(\theta)$ and so on.

Now consider the θ integral of the D_{oz} term where we already know $t = m$,

$$\int_0^\pi f_{lm} f_{sm} \cos \theta \sin \theta d\theta.$$

The symmetry of this integral is determined by the leading term in the integrand,

$$\cos^{l-|m|}(\theta) \cos^{s-|m|}(\theta) \cos(\theta) \sin^{2|m|+1}(\theta) = \cos^{l+s+1-2|m|}(\theta) \sin^{2|m|+1}(\theta).$$

For this term to be even, $l + s + 1 - 2|m|$ must be even. This demands that $l + s$ be an odd number.

Now consider the θ integral of the D_{ox} and D_{oy} terms where we already know $t = m \pm 1$,

$$\int_0^\pi f_{l,m} f_{s,m\pm 1} \sin^2 \theta d\theta.$$

The symmetry of this integral is determined by the leading term in the integrand,

$$\cos^{l-|m|}(\theta) \cos^{s-|m\pm 1|}(\theta) \sin^{2|m|+2}(\theta) = \cos^{l+s-2|m|\pm 1}(\theta) \sin^{2|m|+2}(\theta).$$

For this term to be even, $l + s - 2|m| \pm 1$ must be even. This demands that $l + s$ be an odd number.

So in each case we require $\Delta l = \pm \text{odd}$. We next need to now see why $\Delta l = \pm 1$.

To be continued!

3. Are L_x, L_y, L_z or L^2 eigenfunctions of $\psi(x)$ for the 3D potential well?

The wavefunction for the symmetric 3D potential is given by

$$\psi(x, y, z) = \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right) \sin\left(\frac{o\pi z}{L}\right).$$

These operators are eigenfunctions of $\psi(x, y, z)$ if, when they operate on $\psi(x, y, z)$, they yield a constant, i.e. $O\psi = K\psi$.

The first operator is $L_x = y\left(\frac{\hbar}{i}\frac{\partial}{\partial z}\right) - z\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right)$. Operating on $\psi(x, y, z)$ above yields

$$L_x\psi = \sin\left(\frac{n\pi x}{L}\right) \left[\frac{\hbar}{i} \frac{o\pi y}{L} \sin\left(\frac{m\pi y}{L}\right) \cos\left(\frac{o\pi z}{L}\right) - \frac{\hbar}{i} \frac{m\pi z}{L} \cos\left(\frac{m\pi y}{L}\right) \sin\left(\frac{o\pi z}{L}\right) \right].$$

This isn't an eigenfunction.

The second operator is $L_y = z\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) - x\left(\frac{\hbar}{i}\frac{\partial}{\partial z}\right)$. Operating on $\psi(x, y, z)$ above yields

$$L_y\psi = \sin\left(\frac{m\pi y}{L}\right) \left[\frac{\hbar}{i} \frac{n\pi z}{L} \cos\left(\frac{n\pi x}{L}\right) \sin\left(\frac{o\pi z}{L}\right) - \frac{\hbar}{i} \frac{o\pi x}{L} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{o\pi z}{L}\right) \right].$$

This isn't an eigenfunction.

The third operator is $L_z = x\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right) - y\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)$. Operating on $\psi(x, y, z)$ above yields

$$L_z\psi = \sin\left(\frac{o\pi z}{L}\right) \left[\frac{\hbar}{i} \frac{m\pi x}{L} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi y}{L}\right) - \frac{\hbar}{i} \frac{n\pi y}{L} \cos\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right) \right].$$

This isn't an eigenfunction.

Now $L^2 = L_x^2 + L_y^2 + L_z^2$, so we need to reapply the operators above. We find

$$\begin{aligned}
L_x(L_x\psi) &= \hbar^2 \sin\left(\frac{n\pi x}{L}\right) \left[\left\{ \left(\frac{o\pi y}{L}\right)^2 + \left(\frac{m\pi z}{L}\right)^2 \right\} \sin\left(\frac{m\pi y}{L}\right) \sin\left(\frac{o\pi z}{L}\right) \right. \\
&\quad + 2 \frac{m\pi y}{L} \frac{o\pi z}{L} \cos\left(\frac{m\pi y}{L}\right) \cos\left(\frac{o\pi z}{L}\right) \\
&\quad \left. + \frac{m\pi y}{L} \cos\left(\frac{m\pi y}{L}\right) \sin\left(\frac{o\pi z}{L}\right) + \frac{o\pi z}{L} \sin\left(\frac{m\pi y}{L}\right) \cos\left(\frac{o\pi z}{L}\right) \right]
\end{aligned}$$

Similarly

$$\begin{aligned}
L_y(L_y\psi) &= \hbar^2 \sin\left(\frac{m\pi y}{L}\right) \left[\left\{ \left(\frac{o\pi x}{L}\right)^2 + \left(\frac{n\pi z}{L}\right)^2 \right\} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{o\pi z}{L}\right) \right. \\
&\quad + 2 \frac{n\pi x}{L} \frac{o\pi z}{L} \cos\left(\frac{m\pi y}{L}\right) \cos\left(\frac{o\pi z}{L}\right) \\
&\quad \left. + \frac{m\pi y}{L} \cos\left(\frac{m\pi y}{L}\right) \sin\left(\frac{o\pi z}{L}\right) + \frac{o\pi z}{L} \sin\left(\frac{m\pi y}{L}\right) \cos\left(\frac{o\pi z}{L}\right) \right]
\end{aligned}$$

and

$$\begin{aligned}
L_z(L_z\psi) &= \hbar^2 \sin\left(\frac{o\pi z}{L}\right) \left[\left\{ \left(\frac{m\pi x}{L}\right)^2 + \left(\frac{n\pi y}{L}\right)^2 \right\} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right) \right. \\
&\quad + 2 \frac{n\pi x}{L} \frac{m\pi y}{L} \cos\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi y}{L}\right) \\
&\quad \left. + \frac{n\pi x}{L} \cos\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right) + \frac{m\pi y}{L} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi y}{L}\right) \right]
\end{aligned}$$

Adding the above results, to get $L^2\psi = (L_x^2 + L_y^2 + L_z^2)\psi$ to does not reduce to a constant times ψ so this isn't an eigenfunction either.

4. Determine $\langle r \rangle$, $\langle r^2 \rangle$, and σ_r for ψ_{100} . The integral identity $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$ is helpful.

From the text,

$$\psi_{100} = R_{10}(r)Y_{00}(\theta, \phi) = \frac{2}{\sqrt{4\pi}} \sqrt{\left(\frac{Z}{a_0}\right)^3} e^{-Zr/a_0}.$$

The expectation value of r is given by

$$\begin{aligned} \langle r \rangle &= \int r \psi^* \psi dV \\ &= \frac{4}{4\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^\infty r^3 e^{-2Zr/a_0} dr \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{4}{4\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^\infty r^3 e^{-2Zr/a_0} dr \cdot 2 \cdot 2\pi \\ &= 4 \left(\frac{Z}{a_0}\right)^3 \frac{3!}{(2Z/a_0)^4} \\ &= \frac{3 a_0}{2 Z} \end{aligned}$$

Since $Z = 1$ for hydrogen, $\langle r \rangle = \frac{1}{2}a_0$.

Similarly, the expectation value of r^2 is given by

$$\begin{aligned} \langle r^2 \rangle &= \int r^2 \psi^* \psi dV \\ &= \frac{4}{4\pi} \left(\frac{Z}{a_0}\right)^3 \int_0^\infty r^4 e^{-2Zr/a_0} dr \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{4}{4\pi} \left(\frac{Z}{a_0}\right)^3 \cdot \frac{4!}{(2Z/a_0)^5} \cdot 2 \cdot 2\pi \\ &= 3 \frac{a_0^2}{Z^2} \end{aligned}$$

Since $Z = 1$ for hydrogen, $\langle r^2 \rangle = 3a_0$.

Thus $\sigma_r = \sqrt{r^2 - \bar{r}^2} = \sqrt{\frac{3}{4} \frac{a_0}{Z}}$. Since $Z = 1$ for hydrogen, $\sigma_r = \sqrt{\frac{3}{4}} a_0$.

5. Determine $\langle p_r \rangle$, $\langle p_r^2 \rangle$, and σ_p for ψ_{100} . Note $(p_r)_{op} = -i\hbar \frac{\partial}{\partial r}$ and

$$(p_r^2)_{op} = -\hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) = -\hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right).$$

From the previous question, $\psi_{100} = \frac{2}{\sqrt{4\pi}} \sqrt{\left(\frac{Z}{a_0}\right)^3} e^{-Zr/a_0}$. Thus

$$p_r \psi_{100} = -i\hbar \frac{\partial}{\partial r} \psi_{100} = i\hbar \frac{2}{\sqrt{4\pi}} \sqrt{\left(\frac{Z}{a_0}\right)^3} \frac{Z}{a_0} e^{-Zr/a_0}$$

The expectation value of p_r is given by

$$\begin{aligned} \langle p_r \rangle &= \int \psi^* \left(-i\hbar \frac{\partial}{\partial r} \right) \psi dV \\ &= -i\hbar \frac{4}{4\pi} \left(\frac{Z}{a_0} \right)^4 \int_0^\infty r^2 e^{-2Zr/a_0} dr \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} d\phi \\ &= -i\hbar \frac{4}{4\pi} \left(\frac{Z}{a_0} \right)^4 \int_0^\infty r^2 e^{-2Zr/a_0} dr \cdot 2 \cdot 2\pi \\ &= -i\hbar 4 \left(\frac{Z}{a_0} \right)^4 \frac{2!}{(2Z/a_0)^3} \\ &= -i\hbar \frac{Z}{a_0} \end{aligned}$$

Since $Z = 1$ for hydrogen, $\langle p_r \rangle = -i\hbar/a_0$.

$$\text{Now } (p_r)^2 \psi_{100} = -\hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \psi_{100} = -\hbar^2 \frac{2}{\sqrt{4\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \left[\left(\frac{Z}{a_0} \right)^2 - \frac{2}{r} \frac{Z}{a_0} \right] e^{-Zr/a_0}.$$

The expectation value of p_r^2 is given by

$$\begin{aligned}
\langle p_r^2 \rangle &= \int \psi^* \hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) \psi dV \\
&= -\hbar^2 \frac{4}{4\pi} \left(\frac{Z}{a_0} \right)^3 \int_0^\infty \left[\left(\frac{Z}{a_0} \right)^2 - \frac{2}{r} \frac{Z}{a_0} \right] r^2 e^{-2Zr/a_0} dr \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} d\phi \\
&= -\hbar^2 \frac{4}{4\pi} \left(\frac{Z}{a_0} \right)^3 \left[\left(\frac{Z}{a_0} \right)^2 \frac{2!}{(2Z/a_0)^3} - 2 \frac{Z}{a_0} \frac{1!}{(2Z/a_0)^2} \right] \cdot 2 \cdot 2\pi \\
&= \hbar^2 \left(\frac{Z}{a_0} \right)^2
\end{aligned}$$

$$\text{Thus } \sigma_p = \sqrt{p_r^2 - \bar{p}_r^2} = \hbar \sqrt{\left(\frac{Z}{a_0} \right)^2 - \left(\frac{Z}{a_0} \right)^2} = 0.$$

6. If electrons were spinning balls, they would have moment of inertia $I = \frac{2}{5}MR^2$ and spin angular momentum $S = I\omega$. The maximum speed at which the outside edge of a real ball electron could be spinning is the speed of light. Since we know $|\vec{S}| = \sqrt{s(s+1)}\hbar = \sqrt{\frac{3}{4}}\hbar$, what value of R does this imply? Note that experiment has shown that electrons act like point particles down to distances below 10^{-15} m.

The speed of the outside edge is $v = R\omega$. Thus we have $\frac{2}{5}MR^2 \frac{c}{R} = \sqrt{\frac{3}{4}}\hbar$. Solving for R

$$\text{we find } R = \sqrt{\frac{3}{4} \frac{5}{2} \frac{\hbar c}{Mc^2}} = \sqrt{\frac{3}{4} \frac{5}{2} \frac{197.33 \text{ eV} \cdot \text{nm}}{0.5109989 \times 10^6 \text{ eV}}} = 8.36 \times 10^{-13} \text{ nm}.$$

Note that this implies that the intrinsic quantum mechanical angular momentum called “spin” has no relation to the spin angular momentum of classical mechanics.

7. The deuteron is a hydrogen atom with an extra neutron in the core. The effects the reduced mass μ in our equation for E_n . If $m_p = 1836 m_e$ and $m_n = 1839 m_e$, find the wavelengths of light necessary to ionize a hydrogen atom and a deuteron. What is the difference in these two wavelengths?

The equation for the energy levels of either version of hydrogen is given by

$$E_n = \frac{\mu}{2n^2} \left(\frac{kZe^2}{\hbar} \right)^2 \text{ where } Z=1, \mu = \frac{m_e}{1 + \frac{m_e}{m_N}}, \text{ and } m_N \text{ is the mass of the nucleus. When}$$

we deal just with hydrogen $m_N = m_p$ and $E_n^H = \frac{13.6 \text{ eV}}{n^2}$. For the deuteron, $m_N = m_p + m_n$,

$$E_n^D = \frac{\mu_D}{2n^2} \left(\frac{kZe^2}{\hbar} \right)^2 = \frac{\mu_D}{\mu_H} \frac{\mu_H}{2n^2} \left(\frac{kZe^2}{\hbar} \right)^2 = \frac{1 + \frac{m_e}{m_p + m_n}}{1 + \frac{m_e}{m_p}} \frac{13.6 \text{ eV}}{n^2}.$$

Using the given values for the masses, we find $E_n^D = 0.999728 \frac{13.6 \text{ eV}}{n^2}$. To ionize each atom we need E_1 . The

wavelength in each case is $\lambda_H = \frac{hc}{E_1^H} = \frac{1239.8 \text{ eV} \cdot \text{nm}}{13.6} = 91.162 \text{ eV}$,

$$\lambda_D = \frac{hc}{E_1^D} = \frac{1239.8 \text{ eV} \cdot \text{nm}}{(0.999728)(13.6 \text{ eV})} = 91.187 \text{ eV}, \text{ and the difference is only } 0.025 \text{ nm}.$$

8. We can define the effective charge that an electron sees by the formula

$$E_n = Z_{\text{eff}}^2 \frac{E_0}{n^2} \text{ where } E_0 = 13.6 \text{ eV. The electron configuration of sodium is } 1s^2 2s^2 2p^6 3s. \text{ If}$$

the inner electrons fully shielded the valence electron from the core, what would Z_{eff} be? How much energy would be needed to remove the valence electron from sodium in this case? The actual ionization energy of sodium is 5.1 eV . What is the true Z_{eff} ?

From the electron configuration we see that the sodium valence electron has $n = 3$. If the valence electron was fully shielded then, $E_3 = 1^2 (13.6 \text{ eV})/3^2 = 1.51 \text{ eV}$. This is the amount of energy needed to remove the electron from the $n = 3$ level. Knowing the correct value we see

$$Z_{\text{eff}} = \sqrt{\frac{E_0 n^2}{E_n}} = \sqrt{\frac{5.1}{1.51}} = 1.84.$$

9. Potassium has an electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s$ and an ionization energy of 4.3 eV . What is the true Z_{eff} ? See previous question.

From the electron configuration we see that the potassium valence electron has $n = 4$. If Using the previous formula

$$Z_{\text{eff}} = \sqrt{\frac{E_0 n^2}{E_n}} = \sqrt{\frac{(4.3)(16)}{13.6}} = 2.25.$$

10. Write the electron configurations for the following, use only Fig. 7-19 of the text which shows the relative energies of the atomic shells and subshells.

a) Rubidium, $Z = 37$.

b) Iodine, $Z = 53$.

We have to fill the orbitals shown in Fig. 7-19 starting at the lowest level and stopping when we run out of electrons. The order of filling and number of allowed electrons is $1s$ (2e), $2s$ (2e), $2p$ (6e), $3s$ (2e), $3p$ (6e), $4s$ (2e), $3d$ (10e), $4p$ (6e), $5s$ (2e), $4d$ (10e), $5p$ (6e), $6s$ (2e), $4f$ (e), $5d$ (14e), $6p$ (6e) ...

Hence

a) Rubidium - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$

b) Iodine - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$