1 Exercise 1 - Bohr Model

a. Radii

Solution: If the electron is moving in circles around a nucleus of charge Ze, with constant tangential velocity v, then in order to stay in any orbit, the centripetal force must be equal to the electric force generated by the electron and the nucleus. Mathematically we can express this as

$$F = \underbrace{\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r^2}}_{\text{Coulomb force}} = \underbrace{\frac{m_e v^2}{r}}_{\text{Centripetal force}} . \tag{1}$$

For this problem I will assume that the angular momentum can take on values $\hbar$, $2\hbar$, ..., but never non-integer values. For circular orbits, the position vector of the electron $\vec{r}$ is always perpendicular to the linear momentum of the particle $\vec{p}$. The angular momentum $\vec{L}$ has magnitude $L = rp = m_e vr$ in this case. As a consequence of this and the previously assumed values of the angular momentum we now know that,

$$m_e vr = n\hbar, \qquad n \in \mathbb{Z}, \tag{2}$$

if we isolate the velocity term from equation 2 then we obtain

$$v = \frac{n\hbar}{m_e r}. \tag{3}$$

Now all we need to do is to insert eq. 3 into eq. 1

$$\frac{m_e v^2}{r} = \frac{m_e}{r}\left(\frac{n\hbar}{m_e r}\right)^2 = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r^2}, \tag{4}$$

and finally we get

$$\frac{\cancel{m_e} n^2\hbar^2}{r^{\cancel{3}} m_e^{\cancel{2}}} = \frac{Ze^2}{4\pi\epsilon_0 \cancel{r^2}},$$

$$\Rightarrow \frac{n^2\hbar^2}{r m_e} = \frac{Ze^2}{4\pi\epsilon_0},$$

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}\frac{n^2}{Z} = \boxed{a_0\frac{n^2}{Z}}, \tag{5}$$

where a_0 is the Bohr radius.

b. Energies

Solution: From eq. 1 we can obtain the kinetic energy K, using r_n

$$\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_n^2} = \frac{m_e v^2}{r_n} \Rightarrow m_e v^2 = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_n},$$

$$\Rightarrow K = \frac{m_e v^2}{2} = \frac{1}{8\pi\epsilon_0}\frac{Ze^2}{r_n}. \tag{6}$$

On the other hand, the potential energy U is easy to calculate, since it only comes from the Coulomb forces. U is then

$$U = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_n}. \tag{7}$$

At this point we use $E = K + U$, therefore

$$E_n = \frac{1}{8\pi\epsilon_0}\frac{Ze^2}{r_n} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_n} = -\frac{1}{8\pi\epsilon_0}\frac{Ze^2}{r_n}. \tag{8}$$

Finally, we use the value for r_n calculated in the previous section and depicted in eq. 5,

$$E_n = -\frac{1}{8\pi\epsilon_0}\frac{Ze^2}{r_n} = -\frac{1}{8\pi\epsilon_0}\frac{Ze^2}{\left(\frac{a_0 n^2}{Z}\right)} = -\frac{1}{8\pi\epsilon_0}\frac{Z^2e^2}{a_0 n^2} = -\frac{Z^2E_1}{n^2}, \tag{9}$$

where $E_1 = e^2/(8\pi\epsilon_0 a_0) = 13.6$ eV.

2 Exercise 2 - Hydrogen Atom

a. Solve Schrödinger Equation

Solution: In this exercise we are going to solve the Schrödinger equation $\hat{H}\psi = E\psi$ for the hydrogen atom. We will consider a hydrogen atom with Z protons, therefore the potential V is described by

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}, \tag{10}$$

We are solving this equation for two bodies, so we need to change the reference system in such a way that our equation accurately represent the system. To solve this predicament we define the reduced mass

$$\mu = \frac{mM}{m+M}, \tag{11}$$

where M is the mass of the nucleus, and m the mass of the electron.

Hence, our Hamiltonian will be

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{12}$$

And at this point we find ourselves in a tight spot, because we usually use cartesian representation of the laplacian operator. We can decide to use the cartesian representation of the potential depicted in eq. 10, or use the spherical representation of the laplacian. The latter is usually taken, because it offers certain advantages. For example, spherical coordinates accurately represent one of the symmetries of our problem, and therefore the solutions obtained in spherical coordinates are easier to understand an analyze in comparison with solutions viewed in cartesian coordinates. If we take then the spherical representation of the laplacian, Schrödinger equation for the hydrogen atom becomes

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi.$$

Both sides have ψ, so we can simplify the equation further

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi = 0. \tag{13}$$

As we know the wavefunction ψ might depend on 3 variables namely r, θ, ϕ. So we can propose a solution which is product of radial, and angular functions.

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi).$$

As a result of this assumption we now know that the radial derivatives don't affect the radial part, and the angular derivatives don't affect the angular part, hence eq. 13 changes once again to

$$\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r}\right)RY = 0.$$

Multiplying by r^2 and dividing by RY, we attain this equation

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + \frac{2\mu r^2}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r}\right) = 0. \tag{14}$$

Now we note that we have in fact two idependent equations inside eq. 14, one part depending only on the angular variables, and the other one exclusively depending on r. For this equation to be true both parts must balance each other throughout the space, this happens only when the radial and angular terms are the same constant (we'll call it A) but with oposite sing. Therefore we can separate into a radial equation

$$\begin{aligned}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r}\right) &= A,\\ \frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r}\right)R - AR &= 0,\end{aligned} \tag{15}$$

and an angular equation

$$\begin{aligned}\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} &= -A,\\ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + AY &= 0.\end{aligned} \tag{16}$$

At this point is important to look at eq. 16. If we define

$$\nabla^2_{\theta,\phi} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2},$$

we can also write eq. 16

$$\begin{aligned}\nabla^2_{\theta,\phi}Y + AY &= 0,\\ \nabla^2_{\theta,\phi}Y &= -AY.\end{aligned} \tag{17}$$

Now remebering the definition of the angular momentum operator $\hat{L}$

$$\hat{L}^2 = -\hbar^2\nabla^2_{\theta,\phi},$$

and its eigenvalues ($\hbar^2 l(l+1)$) and eigenfunctions ($Y_{l,m}(\theta,\phi)$) we can compare the eigenequation for the angular momentum (eq. 18) and eq. 17

$$\hat{L}^2 Y_{l,m}(\theta,\phi) = -\hbar^2\nabla^2_{\theta,\phi}Y_{l,m}(\theta,\phi) = -\hbar^2 l(l+1)Y_{l,m}(\theta,\phi). \tag{18}$$

From both equations we can deduce that $A = l(l+1)$, and $Y = Y_{l,m}(\theta,\phi)$, where $Y_{l,m}(\theta,\phi)$ are of course the spherical harmonics.

Now, we just need to solve the radial equation (eq. 15), we can begin by inserting the now known value of A, expanding the derivative and dividing by r^2.

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu r^2}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2}\right)R = 0. \tag{19}$$

The highlighted terms in eq. 19 go to zero as r goes to infinity, if that's the case the equation to solve is easier

$$\frac{d^2R_\infty}{dr^2} + \frac{2\mu E}{\hbar^2}R_\infty = 0, \tag{20}$$

whose solution is

$$R_\infty(r) = c_1 \exp\left(i\sqrt{\frac{2\mu E}{\hbar^2}}r\right) + c_2 \exp\left(-i\sqrt{\frac{2\mu E}{\hbar^2}}r\right).$$

We look for solutions where E becomes negative as the electron approaches the nucleus, and $E \to 0$ as the electron goes away from it. If we choose $c_2 = 0$ and the fact that $E < 0$ the asymptotic solution looks like

$$R_\infty(r) = c_1 \exp\left(\sqrt{-\frac{2\mu E}{\hbar^2}}r\right). \tag{21}$$

Closer to the nucleus we can propose a expansion in series, so the radial part looks like

$$R(r) = R_\infty(r)\sum_{i=0}^{\infty} b_i r^i. \tag{22}$$

Plugin this into eq. 19 we find a recurrence relation for the coefficients of the series (b_i). And finally we come to the radial solution

$$R_{n,l}(r) = R_\infty(r) b_0 \exp\left(\frac{\mu Z e^2 r}{2\pi\epsilon_0\hbar^2 n}\right), \tag{23}$$

the l dependence is hidden in b_0.

While finding the coefficients b_i we notice that they generate a series leading to an exponential term, so, we are required to truncate the series for some value. This truncation leads to the eigenenergies, and when solved, such energies are found to be

$$E_n = -\frac{\mu Z^2 e^4}{8\epsilon_0^2\pi^2\hbar^2 n} \tag{24}$$

b. Quantum numbers

Solution: In our solution just 3 quantum numbers are required (n, l, m), but eventually spin effects need to be considered, then the set of quantum numbers necessary to specify one electronic state extends to 4, (n, l, m, s).

The quantum numbers can be linked to physical properties according to this:

1. n: The principal quantum number designates the principal electron shell.
2. l: The orbital angular momentum quantum number determines the shape of an orbital, and as a consequence the angular distribution.

3. m: The magnetic quantum number determines the number of orbitals and their orientation within a subshell.
4. s: The electron spin quantum number designates the direction of the electron spin.

Whithout external fields the energy state depends only on n.

c. Degeneracies

Solution:

All values sharing the same n have the same energy, so let's count how many states are for a given n.

If n is the principal quantum number then $l = 0, 1, \ldots, n-1$, and $m = -l, \ldots, l$. So given n and l there is $(2l+1)$ states, then the total number (without considering spin) is

$$\sum_{l=0}^{n-1}(2l+1) = n^2. \tag{25}$$

Considering spin, the number of states is doubled.

To split some degeneracies the following effects are used:

1. Zeeman effect - Split with magnetic field
2. Stark effect - Split with electric field
3. Jahn-Teller effect - Split of electronic levels in a molecule
4. Spin-Orbit effect - This split appears as a consequence of the interaction of the orbital and magnetic moments.
5. Paschen-Back effect - same principles as Zeeman.

3 Exercise 3 - Real Spherical Harmonics

a. Sketchs

Solution:

By definition, the qubic harmonics for d states are the following.

$$d_{3z^2-1} = Y_{2,0} = \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right) \tag{26}$$

$$d_{zx} = \sqrt{\frac{1}{2}}\left(Y_{2,-1} - Y_{2,1}\right) = \sqrt{\frac{5}{16\pi}}\sin 2\theta\cos\phi \tag{27}$$

$$d_{yz} = \sqrt{\frac{1}{2}}i\left(Y_{2,-1} + Y_{2,1}\right) = \sqrt{\frac{5}{16\pi}}\sin 2\theta\sin\phi \tag{28}$$

$$d_{x^2-y^2} = \sqrt{\frac{1}{2}}\left(Y_{2,-2} + Y_{2,2}\right) = \sqrt{\frac{5}{16\pi}}\sin^2\theta\cos 2\phi \tag{29}$$

$$d_{xy} = \sqrt{\frac{1}{2}}i\left(Y_{2,-2} - Y_{2,2}\right) = \sqrt{\frac{5}{16\pi}}\sin^2\theta\sin 2\phi \tag{30}$$

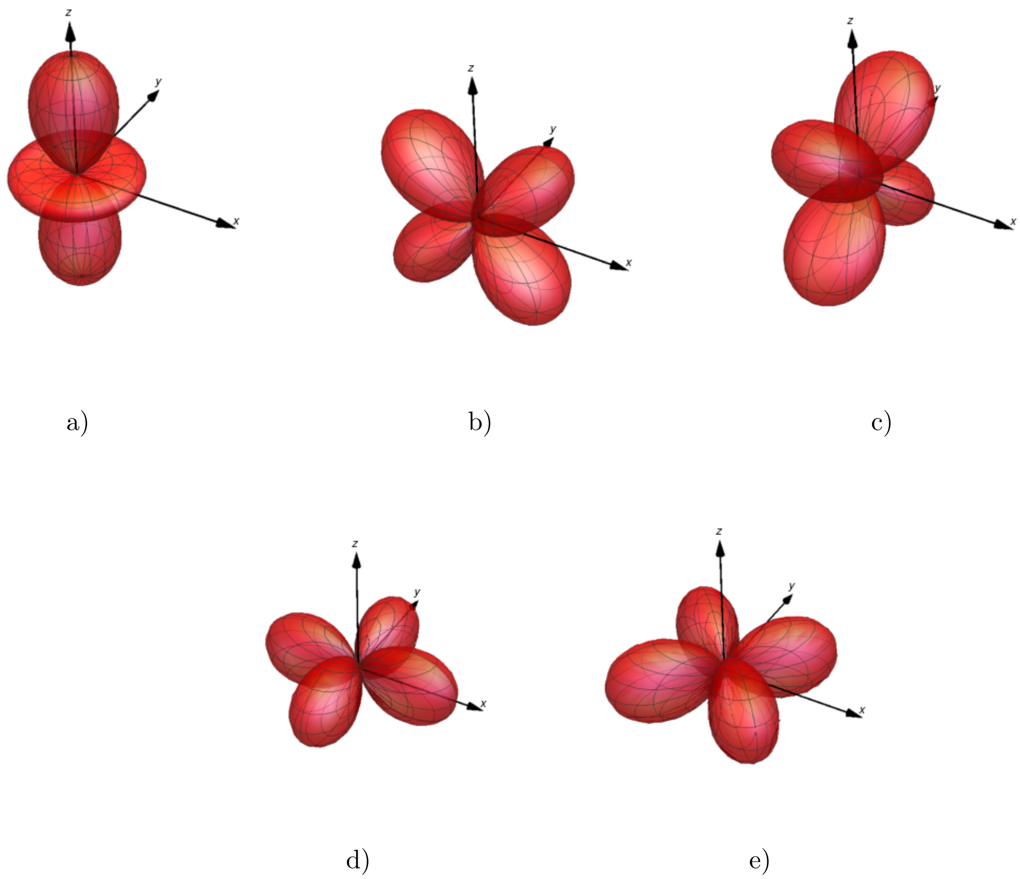

Figure 1: Qubic harmonics, ploted as defined in eqs. 26-30, and organized as follows a) d_{3z^2-1}, b) d_{xz}, c) d_{yz}, d) $d_{x^2-y^2}$, e) d_{xy}

4 Exercise 4 - Crystal Field Splitting

a. Atom in Octahedron

Solution: As we can see in the previous plots shown in Fig. 1 the five d orbitals have different orientations. So what we expect is:

- The orbitals d_{xz}, d_{yz}, and d_{xy} will have the same energy.
- The orbitals d_{3z^2-1} and $d_{x^2-y^2}$ will have a higher energy than the previously mentioned orbitals.

Naturally the energy of all of them will rise, because it will be now harder to put an electron on the d-shells, and because of the overlap of the electronic clouds.

Following the very same idea of the overlaping clouds we can see that if we place all the ions at the same distance then the final arrangement of the d orbitals and the ions will be the same except for a rotation, but we know this does not affect the energy. Therefore we can conclude that the orbitals d_{xz}, d_{yz}, and d_{xy} will have the same energy. On the other hand, we can also see that the overlap of the electronic clouds of the ions and the d_{3z^2-1} and $d_{x^2-y^2}$ orbitals is greater than for the remaining 3 orbitals, thus supporting our initial guess that the orbitals d_{3z^2-1} and $d_{x^2-y^2}$ will have a higher energy than the d_{xz}, d_{yz}, and d_{xy} orbitals.

Now it is a matter of calculation whether the d_{3z^2-1} and $d_{x^2-y^2}$ orbitals have the same energy. It turns out they do. So at the end, we have a splitting from the degeneracy of the d states due to the field generated by a crystal field.