CHEM2024 - Week 26 Lecture 1 - Hydrogen atom, part I

Chapter 3 of "Molecular Quantum Mechanics" by Atkins and Friedman, 5th edition.

1. Problem setup

The hydrogen atom contains an electron and a proton. Both have a mass and a charge. Consider therefore an isolated system with two point charges $q_{1,2}=\pm e$ of masses $m_{1,2}$ with coordinates $\vec{r}_{1,2}$. The total energy of the system is the sum of kinetic and potential energies:

$$E=E_{\text{kin}}+E_{\text{pot}}=\frac{m_1\left|\vec{v}_1\right|^2}{2}+\frac{m_2\left|\vec{v}_2\right|^2}{2}-\frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|} \tag{1}$$

where the last term is Coulomb interaction, and ε_0 is vacuum permittivity (a fundamental constant). Re-writing the kinetic energy using momenta $\vec{p}=m\vec{v}$ instead of velocities, we get:

$$E=\frac{\left|\vec{p}_1\right|^2}{2m_1}+\frac{\left|\vec{p}_2\right|^2}{2m_2}-\frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|} \tag{2}$$

To translate a classical mechanics energy expression into a quantum mechanical Hamiltonian, all coordinates and momenta must be replaced by the corresponding operators:

$$\begin{gathered}\hat{x}=x,\qquad \hat{y}=y,\qquad \hat{z}=z\\ \hat{p}_{\text{X}}=-i\hbar\frac{\partial}{\partial x},\qquad \hat{p}_{\text{Y}}=-i\hbar\frac{\partial}{\partial y},\qquad \hat{p}_{\text{Z}}=-i\hbar\frac{\partial}{\partial z}\end{gathered} \tag{3}$$

With this in place, the Hamiltonian becomes:

$$\hat{H}=-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)-\frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)-\frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|} \tag{4}$$

Where Laplace operators may be abbreviated:

$$\hat{H}=-\frac{\hbar^2}{2m_1}\Delta_{\vec{r}_1}-\frac{\hbar^2}{2m_2}\Delta_{\vec{r}_2}-\frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_2-\vec{r}_1\right|} \tag{5}$$

This equation has six independent variables. It may be simplified if we move into the coordinate system that uses the location of the centre of mass $\vec{R}$ and the inter-particle vector $\vec{r}$:

$$\begin{cases}\vec{r}=\vec{r}_1-\vec{r}_2\\ \vec{R}=\dfrac{m_1\vec{r}_1+m_2\vec{r}_2}{m_1+m_2}\end{cases} \tag{6}$$

A long and tedious derivative transformation yields the following Hamiltonian in the new coordinates:

$$\hat{H}=-\frac{\hbar^2}{2M}\Delta_{\vec{R}}-\frac{\hbar^2}{2\mu}\Delta_{\vec{r}}-\frac{e^2}{4\pi\varepsilon_0\left|\vec{r}\right|} \tag{7}$$

where the total mass M and the reduced mass μ are defined as:

$$M=m_1+m_2,\qquad \mu=\frac{m_1m_2}{m_1+m_2} \tag{8}$$

The first term in Equation (7) corresponds to the kinetic energy of the centre of mass, which is only non-zero if the atom as a whole is moving. If we consider an atom at rest, this term may be dropped:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\Delta_{\vec{r}} - \frac{e^2}{4\pi\varepsilon_0 |\vec{r}|} \tag{9}$$

This Hamiltonian enters the time-dependent Schrödinger equation that we will now solve.

2. Temporal and spatial variable separation

The Hamiltonian in Equation (9) is time-independent. The full Schrödinger equation

$$\frac{\partial}{\partial t}\psi(\vec{r},t) = -i\hat{H}(\vec{r})\psi(\vec{r},t) \tag{10}$$

is therefore separable. We have performed the variable separation procedure in the previous lecture and saw that Equation (10) has the following general solution:

$$\psi(\vec{r},t) = \sum_k a_k \varphi_k(\vec{r}) e^{-iE_k t} \tag{11}$$

where a_k are coefficients determined by the initial condition, $\varphi_k(\vec{r})$ are eigenfunctions (*aka* "orbitals") and E_k are eigenvalues (*aka* "energies") of the Hamiltonian:

$$\hat{H}(\vec{r})\varphi_k(\vec{r}) = E_k \varphi_k(\vec{r}) \tag{12}$$

The problem is therefore reduced to finding the eigensystem of the Hamiltonian. Because the absolute square of the wavefunction is probability density, we will then be able to learn something about what the electron can do inside a hydrogen atom.

3. Radial and angular variable separation

Coulomb interaction is centrally symmetric. This gives the Hamiltonian in Equation (9) spherical symmetry; it therefore makes sense to solve the problem in spherical coordinates. We have already seen the expression for the spherical Laplacian in previous lectures:

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{\partial^2}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\} \tag{13}$$

where $\{r,\theta,\varphi\}$ are spherical coordinates. Our eigenfunction problem becomes:

$$\left[-\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{4\pi\varepsilon_0 r}\right]\varphi(r,\theta,\varphi) = E\varphi(r,\theta,\varphi) \tag{14}$$

The Laplacian in Equation (13) has well separated radial and angular parts, and it makes sense to separate the variables in the solution accordingly:

$$\varphi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) \tag{15}$$

After placing all of this this into Equation (14) we obtain:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\{\ldots\}\right) - \frac{e^2}{4\pi\varepsilon_0 r}\right]R(r)Y(\theta,\varphi) = ER(r)Y(\theta,\varphi) \tag{16}$$

where the curly bracket contains the angular operators from Equation (13). Multiplying both sides by $-2\mu r^2/\hbar^2$ produces a simplification:

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \{\ldots\} + \frac{2\mu r^2}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}\right]R(r)Y(\theta,\varphi) = -\frac{2\mu r^2}{\hbar^2}ER(r)Y(\theta,\varphi) \tag{17}$$

Once the operators are applied to the functions, we obtain:

$$Y(\theta,\varphi)\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R(r)\right)+R(r)\{\ldots\}Y(\theta,\varphi)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R(r)Y(\theta,\varphi)=0 \tag{18}$$

Dividing by $R(r)Y(\theta,\varphi)$ from the left and rearranging separates radial and angular parts:

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R(r)\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=-\frac{1}{Y(\theta,\varphi)}\{\ldots\}Y(\theta,\varphi) \tag{19}$$

The problem splits into a radial and an angular equation:

$$\begin{cases}\dfrac{\partial}{\partial r}\left(r^2\dfrac{\partial}{\partial r}R(r)\right)+\dfrac{2\mu r^2}{\hbar^2}\left(E+\dfrac{e^2}{4\pi\varepsilon_0 r}\right)R(r)=aR(r)\\ \left\{\dfrac{\partial^2}{\partial\theta^2}+\dfrac{\cos\theta}{\sin\theta}\dfrac{\partial}{\partial\theta}+\dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right\}Y(\theta,\varphi)=-aY(\theta,\varphi)\end{cases} \tag{20}$$

where a is the constant that the right and the left hand side of Equation (19) must be equal to.

4. Angular part: φ angle

The eigenfunctions $Y(\theta,\varphi)$ must be periodic in both angles:

$$Y(\theta+2\pi,\varphi)=Y(\theta,\varphi),\qquad Y(\theta,\varphi+2\pi)=Y(\theta,\varphi) \tag{21}$$

Following the variable separation procedure, we will look for solutions of the following form:

$$Y(\theta,\varphi)=T(\theta)F(\varphi) \tag{22}$$

Placing this ansatz into the second Equation (20) yields:

$$\left[\frac{\partial^2}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]T(\theta)F(\varphi)=-aT(\theta)F(\varphi) \tag{23}$$

After opening the square brackets and dividing by $T(\theta)F(\varphi)/\sin^2\theta$, we get:

$$\frac{\sin^2\theta}{T(\theta)}\frac{\partial^2}{\partial\theta^2}T(\theta)+\frac{\sin\theta\cos\theta}{T(\theta)}\frac{\partial}{\partial\theta}T(\theta)+a\sin^2\theta=-\frac{1}{F(\varphi)}\frac{\partial^2}{\partial\varphi^2}F(\varphi) \tag{24}$$

By the same argument that we have previously used in variable separation procedures, the left hand side and the right hand side must be independently equal to a constant. Because we have second derivatives, it is convenient to call that constant m^2:

$$\begin{cases}\dfrac{\sin^2\theta}{T(\theta)}\dfrac{\partial^2}{\partial\theta^2}T(\theta)+\dfrac{\sin\theta\cos\theta}{T(\theta)}\dfrac{\partial}{\partial\theta}T(\theta)+a\sin^2\theta=m^2\\ \dfrac{1}{F(\varphi)}\dfrac{\partial^2}{\partial\varphi^2}F(\varphi)=-m^2\end{cases} \tag{25}$$

We have already seen the solutions to the second equation in the previous lectures – those are complex exponentials. Normalisation in $[0,2\pi]$ interval and the periodicity condition $F(\varphi)=F(\varphi+2\pi)$ yield:

$$F_m(\varphi)=\frac{1}{\sqrt{2\pi}}e^{im\varphi}\qquad m\in\mathbb{Z} \tag{26}$$