Optical Interactions in Hydrogen

Project 2b

1 The Schrödinger Equation: A Brief Overview

In quantum mechanics, the nature of an electron's existence (or its "state") is described by a wave function that varies with space and time, which we will call $\Psi(\vec{r},t)$. This wave function is complex (it has real and imaginary parts), and its time evolution is described by the Schrödinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi(\vec{r},t) \tag{1}$$

Here, $\hbar = h/(2\pi)$ where h is Plank's constant, and $\hat{H}$ is the Hamiltonian operator, with the hat symbol indicating that this quantity is an operator (like a derivative) and not simply a variable or function. Classically, the Hamiltonian is equal to a particle's kinetic energy plus its potential energy. But in the quantum world these energies are also operators. When written in the so-called "position-basis", position variables like r, x, y, and z appear as normal, but corresponding "conjugate" variables like velocity (or more generally, momentum) appear as position derivatives. Specifically, the momentum operator is given by $\hat{\vec{p}} = -i\hbar\vec{\nabla}$. The kinetic energy operator must then be :

$$\hat{K} = \frac{1}{2}m\hat{\vec{v}}^2 = \frac{(m\hat{\vec{v}})^2}{2m} = \frac{\hat{\vec{p}}^2}{2m} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 \tag{2}$$

The potential energy could depend on space and/or time, but it typically does not depend on velocity or momentum. In the case of a hydrogen atom, the electron is attracted to the nucleus, experiencing a point charge potential of

$$\hat{U}_{\text{hydrogen}} = -\frac{1}{4\pi\epsilon_0}\frac{e_0^2}{r}, \tag{3}$$

where e_0 is the charge on the proton which is located at the origin. In the case of an electron in a laser field, the electron also experiences the time dependent potential of a dipole $(\hat{\vec{d}} = -e_0\vec{r}\,)$ in the electric field of the laser $\vec{E}(t)$:

$$\hat{U}_{\text{dipole}} = -\hat{\vec{d}}\cdot\vec{E}_L(t) = e_0\,\vec{r}\cdot\vec{E}_L(t) \tag{4}$$

In this assignment we will solve the Schrödinger equation for laser interactions with a hydrogen atom. First, the bad news... Technically this means we'll be solving the partial differential equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi(\vec{r},t) - \frac{1}{4\pi\epsilon_0}\frac{e_0^2}{r}\Psi(\vec{r},t) + e_0\,\vec{r}\cdot\vec{E}_L(t)\Psi(\vec{r},t) \tag{5}$$

But here's the good news... In practice, we'll assume separation of variables and turn this PDE into this into two separate equations: a purely spatial PDE (the so-called time-independent Schrödinger equation,

or TISE) and a purely time-dependent ODE. We don't have to solve the TISE because it's already done for us in every intro to quantum physics textbook in the world (not to mention every physical chemistry textbook also). But, using the known solutions to the TISE, we will solve the remaining time-dependent equation for the optical excitations using Runge-Kutta methods.

2   Solutions to the spatial TISE

In the absence of the laser field, $\vec{E}_L(t) = 0$ and we just have the equation for the hydrogen atom:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi(\vec{r}, t) - \frac{1}{4\pi\epsilon_0} \frac{e_0^2}{r} \Psi(\vec{r}, t) \tag{6}$$

We can assume separation of variables such that

$$\Psi(\vec{r}, t) = \psi(\vec{r})\, \Upsilon(t)$$

Dividing both sides by $\Psi(\vec{r}, t)$ then leaves the LHS as a time equation and the RHS as a spatial equation:

$$i\hbar \frac{\partial \Upsilon}{\partial t} \frac{1}{\Upsilon(t)} = -\frac{\hbar^2}{2m} \frac{\vec{\nabla}^2 \psi(\vec{r})}{\psi(\vec{r})} - \frac{1}{4\pi\epsilon_0} \frac{e_0^2}{r}$$

Since the LHS and RHS are completely independent, the only way that this equation is true for all space and time is if both sides are equal to the same constant; we'll call that constant ε, which turns out to be the electron's energy. From the LHS we get the ODE for $\Upsilon(t)$ and its solution

$$i\hbar \frac{\partial \Upsilon}{\partial t} = \varepsilon\, \Upsilon(t) \implies \Upsilon(t) = \exp\left(-i\varepsilon\, t/\hbar\right)$$

Likewise, we can create a spatial PDE known as the time independent Schrödinger equation (TISE)

$$\varepsilon\, \psi(\vec{r}) = -\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi(\vec{r}) - \frac{1}{4\pi\epsilon_0} \frac{e_0^2}{r} \psi(\vec{r}). \tag{7}$$

Because the math is extensive, I'll point you to any credible quantum textbook for the details of solving the TISE. But in summary, you assume separation of variables such that

$$\psi(\vec{r}) = R(r)\, \Phi(\phi)\, \Theta(\theta). \tag{8}$$

Putting these into the TISE and solving the resulting three equations shows that there is an infinite number of solutions for $\psi(\vec{r})$, known as "Eigen functions". However, all of these solutions are of the same form, and involve the quantum number integers $n \geq 1, l = \{0...n-1\}$, and $m = \{-l ... +l\}$. These Eigen functions are notated as $\psi_{n,l,m}(\vec{r})$. If you are curious what they actually look like, you can find the first several at hyperphysics, although the general solution for the hydrogen Eigen function is:

$$\psi_{n,l,m}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}}\; e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) Y_l^m(\theta, \phi) \tag{9}$$

Here, $L_b^a(x)$ are the associated Laguerre polynomials and $Y_l^m(\theta, \phi)$ are the Spherical Harmonic functions. The Eigen functions $\psi_{n,l,m}(\vec{r})$ obey the important principle of orthogonality for the quantum state specified by n, l, and m such that:

$$\int_{-\infty}^{\infty} \psi_{n',l',m'}^*(\vec{r})\, \psi_{n,l,m}(\vec{r})\, d^3r = \delta_{n',n}\, \delta_{l',l}\, \delta_{m',m} \tag{10}$$

For these solutions to be valid, the aforementioned electron energy must also depend on n and is given by

$$\varepsilon_n = -\left(\frac{e_0^2}{8\pi\epsilon_0 a_0}\right)\frac{1}{n^2} \simeq \frac{-13.6\,\text{eV}}{n^2}, \tag{11}$$

where a_0 is the Bohr radius. With these constraints, the general solution to Eq. 6 can be written as:

$$\Psi(\vec{r}, t) = \sum_{n,l,m} c_{n,l,m}\,\psi_{n,l,m}(\vec{r})\,\exp\left[-i\varepsilon_n t/\hbar\right] \tag{12}$$

Here, the "probability amplitude" $c_{n,l,m}$ is a complex number where $|c_{n,l,m}|^2$ gives the probability that the electron will be in the $\{n, l, m\}$ quantum state (or orbital). Furthermore, since the electron must exist in some state somewhere, we can say that

$$\sum_{n,l,m} |c_{n,l,m}|^2 = 1 \tag{13}$$

3   Deriving the Time-Dependent ODE for Laser Excitations

Now that we are armed with solutions to the TISE (the hydrogen Eigen functions), we put the laser-dipole potential back into the Schrödinger equation. Then we must allow the probability amplitude $c_{n,l,m}$ to change with time as the electric field excites electrons to different quantum states of the hydrogen atom. So now we have

$$\Psi(\vec{r}, t) = \sum_{n,l,m} c_{n,l,m}(t)\,\psi_{n,l,m}(\vec{r})\,\exp\left[-i\varepsilon_n t/\hbar\right] \tag{14}$$

Our ultimate goal is to solve for each $c_{n,l,m}$ as a function of time. From this calculation we can easily calculate the probability of finding the electron in a certain quantum state at a certain time, as well as the atom's optical response (its polarization). We start by putting Eq. 14 into Eq. 5. The LHS gives:

$$i\hbar\frac{\partial\Psi}{\partial t} = \sum_{n,l,m}\left[i\hbar\frac{dc_{n,l,m}}{dt}\,e^{-i\frac{\varepsilon_n t}{\hbar}}\,\psi_{n,l,m}(\vec{r}) + \varepsilon_n c_{n,l,m}\,e^{-i\frac{\varepsilon_n t}{\hbar}}\,\psi_{n,l,m}(\vec{r})\right] \tag{15}$$

Next, we look at the first two terms (the hydrogen terms) on the RHS:

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{1}{4\pi\epsilon_0}\frac{e_0}{r}\right]\Psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{1}{4\pi\epsilon_0}\frac{e_0^2}{r}\right]\sum_{n,l,m} c_{n,l,m}(t)\,e^{-i\frac{\varepsilon_n t}{\hbar}}\,\psi_{n,l,m}(\vec{r}) \tag{16}$$

$$= \sum_{n,l,m}\varepsilon_n c_{n,l,m}(t)\,e^{-i\frac{\varepsilon_n t}{\hbar}}\,\psi_{n,l,m}(\vec{r}). \tag{17}$$

This RHS term simply cancels with the last term on the LHS (see Eq. 15). Finally, we look at the third RHS term involving the laser field:

$$+e_0\,\vec{r}\cdot\vec{E}_L(t)\Psi(\vec{r}, t) = e_0\,\vec{r}\cdot\vec{E}_L(t)\sum_{n,l,m} c_{n,l,m}(t)\,e^{-i\frac{\varepsilon_n t}{\hbar}}\,\psi_{n,l,m}(\vec{r}) \tag{18}$$

$$= e_0\vec{E}_L(t)\,\cdot\sum_{n,l,m} c_{n,l,m}(t)\,e^{-i\frac{\varepsilon_n t}{\hbar}}\,\vec{r}\,\psi_{n,l,m}(\vec{r}) \tag{19}$$

Now we must get rid of the spatial dependence in the Schrödinger equation and pick a specific state to solve for. We can do that by exploiting orthogonality of the TISE solutions (see Eq. 10). Multiply both sides of the Schrödinger equation by the Eigen function $\psi_{n',l',m'}(\vec{r}, t)$ and then integrate over all space. This

introduces a $\delta_{n',n}\delta_{l',l}\delta_{m',m}$ in every term (except the last RHS term) and those collapse the summation, picking out a single $\{n', l', m'\}$ term from the summation. The resulting equation for $c_{n,l,m}(t)$ is:

$$\frac{d\,c_{n,l,m}}{dt} = -\frac{i}{\hbar}e_0\vec{E}_L(t) \cdot \sum_{n',l',m'} c_{n',l',m'}(t)\,e^{-i\frac{(\varepsilon_{n'}-\varepsilon_n)t}{\hbar}}\,\vec{r}^{\,n,l,m}_{n',l',m'} \tag{20}$$

We will be solving this equation computationally for the effective probability amplitude $c_{n,l,m}(t)$ for each n, l, m state under consideration. Note that the position matrix element in the last term is defined as

$$\vec{r}^{\,n,l,m}_{n',l',m'} = \int_{-\infty}^{\infty} \psi^*_{n',l',m'}(\vec{r})\,\vec{r}\,\psi_{n,l,m}(\vec{r})\,d^3r \tag{21}$$

4   Instructions and Simplifications

Equation 20 is quite general. Let's get specific with the following assumptions and instructions for your assignment:

- The quantum integer n goes from 1 to infinity, but we have to cut off our calculations somewhere. So we'll only allow excitations up through the $n \leq 3$ states.

- We assume that the laser electric field is polarized in the $\hat{z}$ direction: $\vec{E}_L(t) = E_L(t)\hat{z}$. This means that we only need to evaluate the z-position matrix element:

$$z^{n,l,m}_{n',l',m'} = \int_{-\infty}^{\infty} \psi^*_{n',l',m'}(\vec{r})\,z\,\psi_{n,l,m}(\vec{r})\,d^3r$$
$$= \int_{-\infty}^{\infty} \psi^*_{n',l',m'}(r,\theta,\phi)\,r\,\cos(\theta)\,\psi_{n,l,m}(r,\theta,\phi)\,d^3r$$

For this project, we'll assume that

$$z^{n,l,m}_{n',l',m'} = a_0\delta_{m,m'}\left(\delta_{\ell,\ell+1} + \delta_{\ell,\ell-1}\right)(1 - \delta_{n,n'})$$

- The position matrix element above will be zero unless $m = m'$.

- The position matrix element above will also be zero unless $l = l' \pm 1$.

- $E_L(t) = E_i\cos(\omega_i t)\exp[-(t/\tau)^2]$. Assume the same electric field as in project 1, where the maximum electric field $E_i = \{10^0, 10^8, 10^{10}\}$ and the frequency $\omega_i = (\varepsilon_2 - \varepsilon_1)\,hbar$, which corresponds to hitting the atom at resonance between the first excited state.

- For the first simulation, assume that the electron begins in the ground state:
  $C_{n=1,\ell=0,m=0}(t = -\infty) = 1$ and $C_{n\neq1,\ell\neq0,m\neq0}(t = -\infty) = 0$.
  Plot $|C_{n=1,\ell=0,m=0}(t)|^2$ and $|C_{n=2,\ell=1,m=0}(t)|^2$, and make sure all other populations are zero.

- For the second simulation, assume that the electron begins half in the ground state and half in a $n = 2$ state:
  $C_{n=1,\ell=0,m=0}(t = -\infty) = 1/\sqrt{2}$, $C_{n=2,\ell=1,m=1}(t = -\infty) = 1/\sqrt{2}$, zero otherwise.
  Plot all $|C_{n,\ell,m}(t)|^2$ populations that are not zero.