

IQM Bonus Project

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Animation Link

Improved Animation Link (Post Submission)

1 Derivation of the First order correction

In order to plot the wave function a function for the first order wavefunction with first-order corrections must be derived. The Hamiltonian can be expressed as:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad (1)$$

Where \hat{H}_0 is the unperturbed Hamiltonian, and \hat{H}_1 is the perturbing Hamiltonian. This is transformed into:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1 \quad (2)$$

Where λ is used to adjust the strength of the perturbation term. The respective eigenstates and eigenvalues of this Hamiltonian are:

$$|\psi_n\rangle = |\varphi_n^{(0)}\rangle + \lambda |\varphi_n^{(1)}\rangle \quad (3)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} \quad (4)$$

Inserting this in to the equation $\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle$, we recieve:

$$(\hat{H}_0 + \lambda \hat{H}_1)(|\varphi_n^{(0)}\rangle + \lambda |\varphi_n^{(1)}\rangle + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \dots)(|\varphi_n^{(0)}\rangle + \lambda |\varphi_n^{(1)}\rangle + \dots) \quad (5)$$

With the zero-th and first order of this respectively being:

$$\hat{H}_0 |\varphi_n^{(0)}\rangle = E_n^{(0)} |\varphi_n^{(0)}\rangle \quad (6)$$

$$\hat{H}_0 |\varphi_n^{(1)}\rangle + \hat{H}_1 |\varphi_n^{(0)}\rangle = E_n^{(0)} |\varphi_n^{(1)}\rangle + E_n^{(1)} |\varphi_n^{(0)}\rangle \quad (7)$$

In order to find the first order correction for the eigenstate, we take the inner product of the first order equation with $\langle \varphi_k^{(0)} |$ with $k \neq n$:

$$\langle \varphi_k^{(0)} | \hat{H}_0 | \varphi_n^{(1)} \rangle + \langle \varphi_k^{(0)} | \hat{H}_1 | \varphi_n^{(0)} \rangle = E_n^{(0)} \langle \varphi_k^{(0)} | \varphi_n^{(1)} \rangle + E_n^{(1)} \langle \varphi_k^{(0)} | \varphi_n^{(0)} \rangle \quad (8)$$

Where the second term on the RHS goes to zero, we get:

$$\langle \varphi_k^{(0)} | \varphi_n^{(1)} \rangle = \frac{\langle \varphi_k^{(0)} | \hat{H} | \varphi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}, \mathbf{k} \neq \mathbf{n} \quad (9)$$

By using the identity operator on the first order eigenstate $|\varphi_n^{(1)}\rangle$ we get:

$$|\varphi_n^{(1)}\rangle = \sum_k |\varphi_k^{(0)}\rangle \langle \varphi_k^{(0)} | \varphi_n^{(1)} \rangle \quad (10)$$

And substituting that into the eigenstate of the Hamiltonian we get the first order eigenstate:

$$|\psi_n\rangle = |\varphi_n^{(0)}\rangle + \lambda \sum_{k \neq n} |\varphi_k^{(0)}\rangle \frac{\langle \varphi_k^{(0)} | \hat{H}_1 | \varphi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \quad (11)$$

2 Analytical Simplifications and Solutions to the Spherical Schrodinger Equation

With a three-dimensional wavefunction described by the eigenket $|\psi\rangle$ that is dependent on a spatial coordinate \mathbf{r} , the wave function can be written as:

$$\langle \mathbf{r} | \psi \rangle = \langle \mathbf{r} | n, l, m \rangle = R(r)\Theta(\theta)\Phi(\phi) \quad (12)$$

In spherical coordinates, this wave function can be rewritten:

$$\langle \mathbf{r}, \theta, \phi | \psi \rangle = \langle \mathbf{r}, \theta, \phi | n, l, m \rangle = R(r)Y_{l,m}(\theta, \phi) \quad (13)$$

The wave function can be solved with the spherical Schrodinger Equation:

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \psi}{\partial r}) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} (\sin(\theta) \frac{\partial \psi}{\partial \theta}) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \psi = E\psi \quad (14)$$

The following separated differential equations were used to solve for the radial wave function, azimuthal wave equation, and polar wave function respectively:

$$\frac{d}{dr} (r^2 \frac{dR}{dr}) + \frac{2\mu r^2}{\hbar^2} (E + \frac{e^2}{4\pi\epsilon_0 r}) R - AR = 0 \quad (15)$$

$$\frac{\sin(\theta)}{\Theta} \frac{d}{d\theta} (\sin(\theta) \frac{d\Theta}{d\theta}) + A \sin^2(\theta) - B = 0 \quad (16)$$

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + B = 0 \quad (17)$$

$Y_{l,m}(\theta, \phi)$ is expressed as:

$$Y_{l,m}(\theta, \phi) = \frac{-1^l}{2^l l!} \sqrt{\frac{(2l+1)(l+m)!}{4\pi(l-m)!}} e^{im\phi} \frac{1}{\sin^m(\theta)} \frac{d^{l-m}}{d(\cos^m(\theta))} \sin^{2l}(\theta) \quad (18)$$

The radial equation $R(r)$ has solutions given by the **Laguerre polynomials**. The azimuthal component (provided by the **Legendre polynomials**) and polar components can be combined to form the **Spherical Harmonics**. In order to calculate the first order energy shift caused by a time-independent perturbative Hamiltonian, we will make use of the unique properties of these equations. To properly determine the wave function of a perturbed Hydrogen atom in the ground state, an inner product will have to be computed with all of the possible quantum states an electron can be found in (described by n , l , and m). In order to simplify the wave function analytically, we can first look to one particular component within $Y_{l,m}(\theta, \phi)$: $(-1)^l$. This phase factor introduces a unique effect on a given complex conjugate of $Y_{l,m}(\theta, \phi)$, where the inner product of two states with the same l state will vanish. This can be shown by applying the parity operator to the azimuthal-polar wave function:

$$\hat{\Pi}(Y_{l,m}(\theta, \phi)) = (-1)^l Y_{l,m}(\theta, \phi) \quad (19)$$

With this state of **definite parity**, the integration of an inner product between two states with the same quantum number l will result in zero because the inner product would be an odd function. Therefore, our first simplification can be made with the following condition:

$$l \neq l' \quad (20)$$

Additionally, another simplification can be made due to the relationship between the perturbative Hamiltonian \hat{H}_1 and the orbital angular momentum operator about the z-axis \hat{L}_z . Because the perturbative Hamiltonian acts along the z-axis, it does not commute with this angular momentum operator because \hat{L}_z only acts along the XY-plane:

$$[\hat{H}_1, \hat{L}_z] = 0 \quad (21)$$

As a result, the eigenvalue associated with \hat{L}_z must be the same for two different wave functions in order for the Stark Effect to have a non-vanishing effect on the wave function with a given quantum number m . Thus the second simplification can be made with the condition:

$$m = m' \quad (22)$$

Since we have that $m = 0$ for non-vanishing states, we find that only states $|k \neq 1, 1, 0\rangle$ have a non-vanishing value for $\langle k, l, m | \hat{H}_1 | 1, 0, 0 \rangle$, by the following property (note: $P_{l,0} = P_l$, i.e. the l -th $m = 0$ associated Legendre Polynomial is just the l -th Legendre Polynomial: We can make the substitution $x = \cos(\theta)$ and we find the left hand side becomes:

$$\int_0^\pi P_L(\cos(\theta)) \cos(\theta) P_N(\cos(\theta)) \sin(\theta) d\theta$$

which matches the form of the integral taken to find $\langle k, l, m | \hat{H}_1 | 1, 0, 0 \rangle$ for the polar term involving Legendre Polynomials, and thus this term vanishes for $l \neq 1$. Thus we have further restricted the non-vanishing terms and we have that the non-vanishing terms will be:

$$|k \neq 1, 1, 0\rangle.$$

$$\int_{-1}^1 x P_L(x) P_N(x) dx = \begin{cases} \frac{2(L+1)}{(2L+1)(2L+3)} & \text{for } N = L+1 \\ \frac{2L}{(2L-1)(2L+1)} & \text{for } N = L-1 \end{cases}$$

Figure 1: Legendre Polynomial Identity (<https://mathworld.wolfram.com/LegendrePolynomial.html>)

To calculate the perturbative effect on the ground state wavefunction, we used the equation for first-order corrections:

$$|\psi_n\rangle = |\varphi_n^{(0)}\rangle + \lambda \sum_{k \neq n} |\varphi_k^{(0)}\rangle \frac{\langle \varphi_k^{(0)} | H_1 | \varphi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

The ground state $|\phi_n^{(0)}\rangle$ is given by $|1, 0, 0\rangle$. In addition, the first-order Hamiltonian is defined as $e|E|\hat{z}$. So, the ground state correction is

$$e|E| \sum_{k \neq 1} \sum_{l, m} |k, l, m\rangle \frac{\langle k, l, m | \hat{z} | 1, 0, 0 \rangle}{E_1^{(0)} - E_k^{(0)}}$$

Based on the simplifications from earlier, we know that $l = 1$ and $m = 0$ for the terms that don't disappear.

Next, we project both sides onto the position bra, using P to denote only the perturbative term:

$$P \langle r, \theta, \phi | \psi_n \rangle = e|E| \sum_{k \neq 1} \langle r, \theta, \phi | k, 1, 0 \rangle \frac{\langle k, 1, 0 | \hat{z} | 1, 0, 0 \rangle}{E_1^{(0)} - E_k^{(0)}}$$

Since the spherical harmonics depend only on l and m , all the perturbative wavefunctions must have the same spherical harmonics. So, we can integrate the spherical harmonics and place those outside the sum as prefactors.

Polar part ($\Theta_{00} = \frac{1}{\sqrt{2}}$, $\Theta_{10} = \frac{\sqrt{6}}{2} \cos \theta$):

$$\int_0^\pi \Theta_{10}(\theta) \cos(\theta) \Theta_{00}(\theta) \sin(\theta) d\theta = \frac{\sqrt{3}}{2} \int_0^\pi \cos^2(\theta) \sin(\theta) d\theta = \frac{1}{\sqrt{3}}$$

Azimuthal part ($\Phi_0 = \frac{1}{\sqrt{2\pi}}$):

$$\int_0^{2\pi} \left(\frac{1}{\sqrt{2\pi}}\right)^2 d\phi = 1$$

So, with our spherical harmonic prefactor of $\frac{1}{\sqrt{3}}$, we can express the term in a radial integral:

$$\langle k, 1, 0 | \hat{z} | 1, 0, 0 \rangle = \langle k, 1, 0 | r \cos(\theta) | 1, 0, 0 \rangle = \frac{1}{\sqrt{3}} \int_0^\infty R_{k,1}(r) R_{1,0}(r) r^3 dr$$

3 Plotting the Perturbation Effect

We plotted the perturbed wavefunctions with respect to a changing electric field. To find the maximum value of the electric field that should be used to fully capture the effects, we set the potential energies of the non-perturbed and of the first order effects equal to each other at twice the Bohr radius:

$$\frac{e^2}{4\pi\epsilon_0(2a_0)} = e|\mathbf{E}|(2a_0)$$

We say that r_c is the distance from the $x - y$ plane where the Hamiltonians are similar:

$$\frac{H_1(r_c)}{H_0(r_c)} \sim 1$$

since $H_1 = e|E|r$ with $|E| \propto 1/r_c^2$ and $H_0 \propto 1/r$, then

$$\frac{H_1(r)}{H_0(r)} \sim \frac{r^2}{r_c^2}$$

Thus, the first order Stark Effect will be about $1/4$ the magnitude of the unperturbed Hamiltonian at the Bohr Radius. This makes sense, and is the reason the radius was set to $2a_0$. We expect the electron to move opposite the direction of the electric field which is what our model predicts.

The final animation of the first-order correction to the Hydrogen atom is linked [here](#).

EDIT: An improved animation created after the original submission can be found [here](#).

Our code used for the animation is linked <https://github.com/schwas3/iqm-bonus-problem>.

4 References

Solution to the Hydrogen Atom
Hyperphysics Hydrogen Atom
Wolfram - Laguerre Polynomials
Wolfram - Legendre Polynomials