STARK EFFECT IN HYDROGEN ATOM

S. Rajasekar
School of Physics
Bharathidasan University
Tiruchirapalli - 620 024
email: rajasekar@cnld.bdu.ac.in
srj.bdu@gmail.com

Stark Effect

The splitting of energy levels of an atom by a uniform external field E is known as *Stark effect*. The effect was discovered by Stark in 1913 during the observation of Balmer series of hydrogen.

Suppose the hydrogen atom is subjected to an electric field along z-direction. The first excited energy level is found to split into three energy levels. This is explained using perturbation theory. The perturbation is $\lambda H^{(1)} = -e\mathcal{E}r\cos\theta$ where $\mathcal{E}$ is the strength of the field. Choosing $\lambda = e\mathcal{E}$ we write $H^{(1)} = -r\cos\theta$. The normalized eigenfunctions of the hydrogen atome are designated as ψ_{nlm}. Here $n = 1, 2, \cdots, m$, $l = 0, 1, \cdots, n-1$ and $m = -l, -(l-1), \cdots, 0, \cdots, l$. Applying the perturbation theory we calculate the change in the energy of the ground state and first excited state due to the applied field.

Ground State $n = 1$

Ground State: $n = 1$

The ground state eigenfunction is $\psi_{100} = \left(1\Big/\sqrt{\pi a_0^3}\right) \mathrm{e}^{-r/a_0}$. According to the first-order perturbation theory for nondegenerate case the change in (ground state)energy E_1 is given by

$$\begin{aligned} E_1^{(1)} &= \lambda \langle H_{100}^{(1)} \rangle \\ &= \lambda \int \psi_{100}^* H_{100}^{(1)} \psi_{100} \, \mathrm{d}\tau \\ &= -\frac{e\mathcal{E}}{\pi a_0^3} \int_0^\infty \int_0^\pi \int_0^{2\pi} r^3 \mathrm{e}^{-2r/a_0} \cos\theta \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi \; . \end{aligned} \tag{1}$$

For the above we find $\int_0^\pi \sin\theta\cos\theta \mathrm{d}\theta = \sin^2\theta/2\Big|_0^\pi = 0$. Therefore, $E_1^{(1)} = 0$. Thus, there is *no change in ground state energy* according to first-order perturbation theory.

Since the first-order correction to E_1 is zero we proceed to calculate the second-order correction. The result is $E_1^{(2)} = -(9/4)\mathcal{E}^2 a_0^3$. Before perturbation, that is, before applying the electric field, the system has one ground state eigenfunction with an eigenvalue $E_1^{(0)}$. Now, the energy is changed to $E_1^{(0)} + E_1^{(1)}$ by the applied field. *There is no Stark effect in the ground state*.

First Excited State: $n = 2$

First Excited State: $n = 2$

Next, work out the effect of the applied field on the first excited state corresponding to $n = 2$. The possible values of (l, m) are $(0, 0)$, $(1, 0)$, $(1, 1)$, $(1, -1)$ (since $l = 0$, 1 and $m = -l$ to l). There are four states given by $\psi_{nlm} \to \psi_{200}, \psi_{210}, \psi_{211}$ and ψ_{21-1}. The first excited state is thus *four-fold degenerate*. In this case the zeroth-order wave function is

$$\psi^{(0)} = c_{00}\psi_{200} + c_{10}\psi_{210} + c_{11}\psi_{211} + c_{1-1}\psi_{21-1} \ . \tag{2}$$

The secular equation is written as

$$\begin{vmatrix} H^{(1)}_{200,200} - E^{(1)}_2 & H^{(1)}_{200,210} & H^{(1)}_{200,211} & H^{(1)}_{200,21-1} \\ H^{(1)}_{210,200} & H^{(1)}_{210,210} - E^{(1)}_2 & H^{(1)}_{210,211} & H^{(1)}_{210,21-1} \\ H^{(1)}_{211,200} & H^{(1)}_{211,210} & H^{(1)}_{211,211} - E^{(1)}_2 & H^{(1)}_{211,21-1} \\ H^{(1)}_{21-1,200} & H^{(1)}_{21-1,210} & H^{(1)}_{21-1,211} & H^{(1)}_{21-1,21-1} - E^{(1)}_2 \end{vmatrix}$$

$$= 0 \ , \tag{3}$$

where

First Excited State: $n = 2$

$$H^{(1)}_{nlm,nl'm'} = \int \psi^*_{nlm} H^{(1)} \psi_{nl'm'} \, \mathrm{d}\tau \; . \tag{4}$$

The eigenfunctions ψ_{200}, ψ_{210}, ψ_{211}, ψ_{21-1} are given by

$$\psi_{200} = N \left(2 - \frac{r}{a_0}\right) \mathrm{e}^{-r/2a_0} \, \mathrm{e}^{im\phi} \; , \quad m = 0 \tag{5a}$$

$$\psi_{210} = N \frac{r}{a_0} \, \mathrm{e}^{-r/2a_0} \cos\theta \, \mathrm{e}^{im\phi} \; , \quad m = 1 \tag{5b}$$

$$\psi_{211} = N \frac{r}{\sqrt{2}\, a_0} \, \mathrm{e}^{-r/2a_0} \sin\theta \, \mathrm{e}^{im\phi} \; , \quad m = 1 \tag{5c}$$

$$\psi_{21-1} = N \frac{r}{\sqrt{2}\, a_0} \, \mathrm{e}^{-r/2a_0} \sin\theta \, \mathrm{e}^{im\phi} \; , \quad m = -1 \tag{5d}$$

where $N = 1/\sqrt{32\pi a_0^3}$. The quantities $H^{(1)}_{2lm,2l'm'}$ are given by

$$\begin{aligned} H^{(1)}_{2lm,2l'm'} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^*_{2lm} H^{(1)} \psi_{2l'm'} r^2 \, \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi \\ &= -\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^*_{2lm} \psi_{2l'm'} r^3 \, \cos\theta \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi. \end{aligned} \tag{6}$$

First Excited State: $n = 2$

First, perform the integration with respect to ϕ. The result is

$$H^{(1)}_{2lm,2l'm'}(\phi) = \int_0^{2\pi} \mathrm{e}^{\mathrm{i}(m'-m)\phi}\,\mathrm{d}\phi = \begin{cases} 2\pi, & \text{if } m' = m \\ 0, & \text{if } m' \neq m. \end{cases} \tag{7}$$

Hence the quantities $H^{(1)}_{2lm,2l'm'}$ with $m' \neq m$ are zero. Now, we need to evaluate the quantities $H^{(1)}_{200,200}$, $H^{(1)}_{200,210}$, $H^{(1)}_{210,200}$, $H^{(1)}_{210,210}$, $H^{(1)}_{211,211}$, $H^{(1)}_{21-1,21-1}$. Integration with respect to θ makes some of these integrals vanish:

$$\begin{aligned}
H^{(1)}_{200,200}(\theta) &= \int_0^{\pi} \sin\theta\cos\theta\,\mathrm{d}\theta = \frac{\sin^2\theta}{2}\Big|_0^{\pi} = 0\,, && \text{(8a)}\\
H^{(1)}_{210,210}(\theta) &= \int_0^{\pi} \cos^3\theta\sin\theta\,\mathrm{d}\theta = -\frac{\cos^4\theta}{4}\Big|_0^{\pi} = 0\,, && \text{(8b)}\\
H^{(1)}_{211,211}(\theta) &= \int_0^{\pi} \sin^3\theta\cos\theta\,\mathrm{d}\theta = \frac{\sin^4\theta}{4}\Big|_0^{\pi} = 0\,, && \text{(8c)}\\
H^{(1)}_{21-1,21-1}(\theta) &= \int_0^{\pi} \sin^3\theta\cos\theta\,\mathrm{d}\theta = \frac{\sin^4\theta}{4}\Big|_0^{\pi} = 0\,. && \text{(8d)}
\end{aligned}$$

Thus, only the integrals $H^{(1)}_{200,210}$ and $H^{(1)}_{210,200}$ have to be evaluated.

First Excited State: $n = 2$

We obtain

$$
\begin{aligned}
H^{(1)}_{200,210} &= \left(H^{(1)}_{210,200}\right)^* \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^*_{210} H^{(1)} \psi_{200} r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi \\
&= -\frac{2\pi N^2}{a_0} \int_0^\infty \int_0^\pi r^4 \left(2 - \frac{r}{a_0}\right) \mathrm{e}^{-r/a_0} \cos^2\theta \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \\
&= \frac{2\pi N^2}{a_0} \int_0^\infty r^4 \left(2 - \frac{r}{a_0}\right) \mathrm{e}^{-r/a_0} \, \mathrm{d}r \, \frac{\cos^3\theta}{3}\bigg|_0^\pi \\
&= -\frac{1}{24a_0^4} \int_0^\infty r^4 \left(2 - \frac{r}{a_0}\right) \mathrm{e}^{-r/a_0} \, \mathrm{d}r \\
&= -\frac{1}{24a_0^4} \left[2\int_0^\infty r^4 \mathrm{e}^{-r/a_0} \, \mathrm{d}r - \frac{1}{a_0} \int_0^\infty r^5 \mathrm{e}^{-r/a_0} \, \mathrm{d}r\right] \\
&= 3a_0 \ ,
\end{aligned} \tag{9}
$$

where we have used the result $\int_0^\infty r^n \mathrm{e}^{-r} \, \mathrm{d}r = n!$.

First Excited State: $n = 2$

Now, the secular equation is written as

$$\begin{vmatrix} -E_2^{(1)} & 3a_0 & 0 & 0 \\ 3a_0 & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = 0 \ . \tag{10}$$

Expanding the determinant we obtain

$$\left(E_2^{(1)}\right)^2 \left[\left(E_2^{(1)}\right)^2 - 9a_0^2\right] = 0 \ . \tag{11}$$

The roots of the above equation are

$$E_2^{(1)} = 0,\ 0,\ 3a_0,\ -3a_0. \tag{12}$$

The energy E_2 to the first-order correction is

$$E_2 = E_2^{(0)} + \lambda E_2^{(1)} = E_2^{(0)},\ E_2^{(0)},\ E_2^{(0)} + 3\lambda a_0,\ E_2^{(0)} - 3\lambda a_0 \ . \tag{13}$$

First Excited State: $n = 2$

The energy of the first excited state level in the presence of the applied field becomes $E_2^{(0)} + 0$, $E_2^{(0)} + 0$, $E_2^{(0)} + 3\lambda a_0$, $E_2^{(0)} - 3\lambda a_0$. That is, the level $n = 2$ is splitted into three levels. The middle level $E_2^{(0)} + 0$ is still doubly degenerate.