Stark Effect

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1 Introduction

The Stark effect is a phenomenon in quantum mechanics that describes the splitting and shifting of spectral lines of an atom's electronic energy levels when it is placed in an strong external electric field. It is like the electric analogue of the Zeeman effect, i.e. a particle carrying an electric dipole moment, like the H-atom, will get a splitting of its energy levels when subjected to an exterior electric field. Earlier experiments had failed to maintain a strong electric field because of high electrical conductivity of luminous gasses and vapors used in conventional spectroscopic techniques used then.

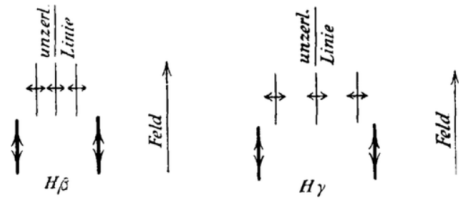

fig 1: The Splitting of two spectral lines as shown in Stark's first paper

Stark observed the hydrogen spectrum emitted just behind the perforated cathode in a positive-ray tube. With a second charged electrode parallel and close to this cathode, he was able to produce a strong electric field in a space of a few millimeters. At electric field intensities of 100,000 volts per centimeter, Stark observed with a spectroscope that the characteristic spectral lines, called Balmer lines, of hydrogen were split into a number of symmetrically spaced components, some of which were linearly polarized (vibrating in one plane) with the electric vector parallel to the lines of force, the remainder being polarized perpendicular to the direction of the field except when viewed along the field.

2 Perturbation in Stark Effect

The unperturbed Hamiltonian is simply due to the Coulombic nature of charges but when an external electric field is applied a perturbation in the Hamiltonian must be added, this additional term, also called the **Stark term** H_{Stark}.

$$H_{Stark} = -\overrightarrow{\varepsilon}\,\overrightarrow{\mu}_{el} \tag{1}$$

$$H_{Stark} = -q\overrightarrow{\varepsilon}\,\overrightarrow{z} = |e|\,\varepsilon r cos\theta \tag{2}$$

where $\overrightarrow{\varepsilon}$ denotes the external electric field which, we take along *z-direction*, and $\overrightarrow{\mu}_{el}$ is the electric dipole moment. We can of course consider the dipole to be placed along the *x-direction* where the proton in placed at *(x,y)=(0,0)* and we can simply write the dipole moment as $\overrightarrow{\mu}_{el} = -|e|\,\overrightarrow{x}$.

The unperturbed Hamiltonian for Hydrogen atom can be written as,

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_o}\frac{e^2}{r} \tag{3}$$

2.1 Perturbation in Energy

We will be calculating the corrections for n=1 and n=2 here in the energy eigenvalue due to the **Stark effect** in the hydrogen atom. Say the states are of the form $\langle n, l, m_l|$.The selection rule is as follows.

$$\langle n', l', m_l'|\overrightarrow{x}|n, l, m_l\rangle \neq 0,\ l' = l \pm 1 \tag{4}$$

and for electric field that we have along the z-direction as,

$$\langle n', l', m_l'|\overrightarrow{x}|n, l, m_l\rangle \neq 0,\ l' = l \pm 1,\ m' = m \tag{5}$$

Let us calculate for only n=1, n=2, we already have the radial wave function for n=1 and n=2. For n=1 only one state exists i.e.

$$\Psi_{100} = \frac{1}{\sqrt{\pi a^3}}\exp\frac{-r}{a} \tag{6}$$

The first order perturbation in energy for n=1 can be written as,

$$E_1^1 = \langle\Psi_{100}|H_{Stark}|\Psi_{100}\rangle = |e|\,\varepsilon\frac{1}{\pi a^3}\iiint exp\frac{-2r}{a}(rcos\theta)r^2 sin\theta dr d\theta d\phi \tag{7}$$

$$E_1^1 = |e|\,\varepsilon\frac{1}{\pi a^3}\int r^3 exp\frac{-2r}{a}dr\int_0^{\pi} cos\theta\ sin\theta d\theta\int_0^{2\pi} d\phi \tag{8}$$

The integral $\int_0^{2\pi} cos\theta\ sin\theta d\theta$ is equal to 0. So $E_1^1 = 0$. So, there is no first order Stark effect that we can observe.

Let us now calculate for n=2 which will result in 4 states having different sets of $\langle n, l, m_l|$ values. These states are four-fold degenerate and are :

$$\Psi_{200} = |1\rangle = \frac{1}{\sqrt{2\pi a}}\frac{1}{2a}\left(1 - \frac{r}{2a}\right)\exp\frac{-r}{2a} \tag{9}$$

$$\Psi_{211} = |2\rangle = -\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2} r e^{(\frac{-r}{2a})} sin\theta e^{\iota\phi} \tag{10}$$

$$\Psi_{210} = |3\rangle = \frac{1}{\sqrt{2\pi a}}\frac{1}{4a^2} r e^{(\frac{-r}{2a})} cos\theta \tag{11}$$

$$\Psi_{21-1} = |4\rangle = \frac{1}{\sqrt{\pi a}}\frac{1}{8a^2} r e^{(\frac{-r}{2a})} sin\theta e^{-\iota\phi} \tag{12}$$

The possible combination of states that occur are 16 in total including the complex conjugates of each other ($say \langle 1\,|H'_s|\,2\rangle$ and $\langle 2\,|H'_s|\,1\rangle$) give the same energy eigen value. It can be calculated and shown that all such combinations give the energy eigenvalue as 0 only the states $\langle 1\,|H'_s|\,3\rangle$ and $\langle 3\,|H'_s|\,1\rangle$ survive which are complex conjugates of each other so one needs to calculate only one of these states, say the state $\langle 1\,|H'_s|\,3\rangle$.

$$\begin{aligned}
\langle 1\,|H'_s|\,3\rangle = {} & |e|\,\varepsilon \frac{1}{\sqrt{2\pi a}}\frac{1}{2a}\frac{1}{\sqrt{2\pi a}}\frac{1}{4a^2} \iiint \left(1 - \frac{r}{2a}\right) e^{-r/2a} r\, e^{\frac{-r}{2a}}\, cos\theta(rcost\theta) \\
& r^2\, sin\theta\, dr d\theta d\phi \\
= {} & \frac{|e|\,\varepsilon}{2\pi a 8a^3}(2\pi)\left[\int_0^{\pi} cos^2\theta\, sin\theta\, d\theta\right]\int_0^{\infty}\left(1 - \frac{r}{2a}\right) e^{\frac{-r}{a}} r^4 dr \\
= {} & \frac{|e|\,\varepsilon}{12a^4}\left\{\int_0^{\infty} r^4 e^{\frac{-r}{a}} dr - \frac{1}{2a}\int_0^{\infty} r^5 e^{\frac{-r}{a}}\right\} \\
= {} & \frac{|e|\,\varepsilon}{12a^4}\left(4! a^5 - \frac{1}{2a} 5! a^6\right) \\
= {} & -3a\,|e|\,\varepsilon
\end{aligned} \tag{13}$$

In matrix form to represent all the possible states one can write,

$$W = -3a\,|e|\,\varepsilon \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{14}$$

So it's clear that only the 3^{rd} column of the 1^{st} row and 1^{st} column of the 3^{rd} row exist and the rest of the energy eigenvalues are zero. We can now easily calculate the eigenvalues. The characteristic equation is:

$$\begin{aligned}
& \begin{vmatrix} -\lambda & 0 & 1 & 0 \\ 0 & -\lambda & 0 & 0 \\ 1 & 0 & -\lambda & 0 \\ 0 & 0 & 0 & -\lambda \end{vmatrix} = -\lambda \begin{vmatrix} -\lambda & 0 & 0 \\ 0 & -\lambda & 0 \\ 0 & 0 & -\lambda \end{vmatrix} + \begin{vmatrix} 0 & -\lambda & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -\lambda \end{vmatrix} = 0 \\
& \Rightarrow -\lambda(-\lambda)^3 + (-\lambda^2) = 0 \\
& \Rightarrow \lambda^2(\lambda^2 - 1) = 0
\end{aligned} \tag{15}$$

$\therefore$ the eigenvalues are 0, 0, 1, -1, so the perturbed energies are:

$$\boxed{E2,\ E2,\ E2+3a\left|e\right|\varepsilon,\ E2-3a\left|e\right|\varepsilon}$$

2.2 Perturbation in Wave Function

After calculating the energy eigenvalues we now move on to the perturbation in the wave function i.e. to calculate the good eigen function corresponding to the eigenvalues that we got.

Let us calculate for $\lambda = 0$ The eigenvalue equation as : $[W - \lambda I]\, X = 0$ which gives us two states as:

$$|2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} and\ |4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{16}$$

The eigen function having eigenvalue $\lambda = \pm 1$ are:

$$|\pm\rangle \equiv \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ \pm 1 \\ 0 \end{pmatrix} \tag{17}$$

$\therefore$ the good states are $\boxed{\Psi_{211},\ \Psi_{21-1},\ \frac{1}{\sqrt{2}}(\Psi_{200}+\Psi_{210}),\ \frac{1}{\sqrt{2}}(\Psi_{200}-\Psi_{210})}$

Fig 2: The states 2 0 0 and 2 1 0 and their superposition

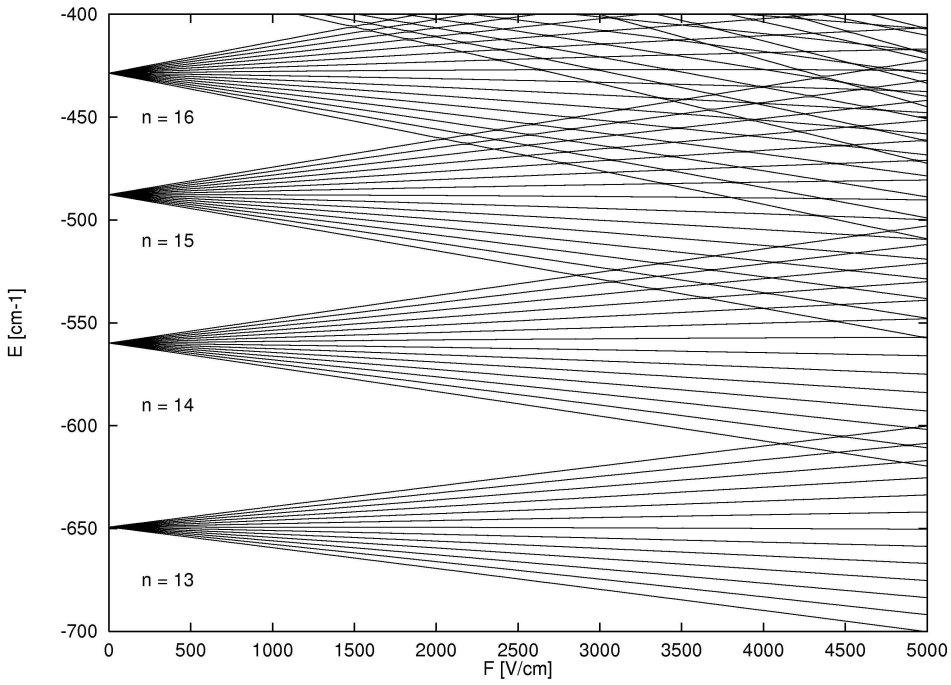

fig 2: Computed energy level spectrum of hydrogen as a function of electric field near n=15 for magnetic quantum number m=0. Each n level consists of n-1 degenerate sub levels, application of electric field breaks the degeneracy.

3 Conclusion

In conclusion, the Stark effect in the hydrogen atom is a fundamental phenomenon in atomic physics that arises due to the interaction between the electric field and the charged electron in the atom. It was first discovered by Johannes Stark in 1913 and represents one of the earliest pieces of evidence for the quantization of energy levels in atoms.

The Stark effect has provided valuable insights into the behavior of electrons in atoms subjected to external electric fields. It has shown that the energy levels of hydrogen atoms can be shifted and split in the presence of an electric field, leading to the observation of spectral lines with different energies in the hydrogen spectrum. This effect has played a crucial role in confirming the principles of quantum mechanics and has been instrumental in the development of atomic and molecular spectroscopy.

Furthermore, the Stark effect has practical applications in fields such as astrophysics and plasma physics, where it is used to analyze the spectra of atoms

and ions in strong electric fields, providing information about the conditions and composition of distant stars and astrophysical plasmas.

In summary, the Stark effect in the hydrogen atom has not only deepened our understanding of the quantum nature of matter but has also had a lasting impact on the way we study and interpret the behavior of atoms and ions in diverse physical and astronomical environments. Its historical significance and continued relevance make it a crucial topic in the study of atomic physics.

References

i) Compendium of Quantum Physics by Klaus Hentschel ch-10 Springer Publication
ii)Introduction to Quantum Mechanics by David J. Griffith
iii)A chapter about Perturbation Theory, Zeeman Effect and Stark effect by Reinhold Bertlmann
iv) Images were taken from the original paper by Stark and from Wikipedia, Britannica and chem.libretext.org.