Polarization of the Hydrogen Atom

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🦣 The Problem 📎

All models are wrong, but some are useful.

George E. P. Box

When a neutral atom like Hydrogen is exposed to an electric field, the atom becomes polarized and develops a dipole moment in the direction of electric field. Experimentally, it has been observed that in the presence of an constant electric field E, the dipole moment p follows the equation:

$$p = \alpha E$$

Where α is known as the atomic polarizability and can be experimentally determined.

But what is the theoretical basis for this? Like all phenomena at this scale, this is a quantum mechanical problem. However, can we attempt to analyze this problem from a classical and electrostatic perspective?

The problem will be analyzed using model building of the atom and the physical concept that any system eventually attains the configuration of minimum of potential energy.

1 Electrostatic Model of the Atom

To solve the problem, we first need an electrostatic model for the atom, atleast for single electron systems like Hydrogen atom in ground state.

The Hydrogen atom is approximated with a point charge (proton) surrounded by a uniform thin shell of total charge the same as the electron and radius r (electron cloud). If we consider only electrostatic interactions, the atom is unstable. This can be seen if we write the potential energy of the configuration

$$
\begin{aligned}
U &= U_{sphere} - \frac{ke^2}{r} && (1)\\
&= \frac{1}{2}\frac{ke^2}{r} - \frac{ke^2}{r} && (2)\\
&= -\frac{1}{2}\frac{ke^2}{r} && (3)
\end{aligned}
$$

The self energy of a sphere is derived in the appendix. This potential energy is strictly decreasing with decrease in r, therefore the electron cloud will collapse.

To prevent this collapse, we introduce a 'magic' potential U_{magic}, a potential that has no physical basis and is just there to prevent the collapse of our atom. At this point, we can also take motivation from Bohr's model of the atom and construct the magic potential such that, in equilibrium, the electron cloud is at a distance same as the Bohr radius.

Remark: The magic potential is non-unique, however, it must be logically chosen to satisfy some qualitative theory or experimental data like Bohr's radii.

The potential energy can be written as:

$$U = U_{magic} - \frac{1}{2}\frac{ke^2}{r} \tag{4}$$

The system will attain the configuration of minimum potential energy, in other words $\frac{\mathrm{d}U}{\mathrm{d}r} = 0$.

$$\left.\frac{\mathrm{d}U}{\mathrm{d}r}\right|_{r=r_0} = \frac{\mathrm{d}U_{magic}}{\mathrm{d}r} + \frac{1}{2}\frac{ke^2}{r^2} = 0 \tag{5}$$

Where $r_0 = \frac{\hbar^2}{kme^2}$ is the Bohr radius. For the purposes of this problem, we do not need to explicitly find a suitable magic potential, but a couple of sample potentials are given in the appendix.

2 Energies of Atom in Uniform Electric Field

When the Hydrogen atom is placed in a uniform electric field $-E\hat{z}$, the electron cloud changes in both shape and charge distribution, while the nucleus shifts in position along z axis. We make the approximation that the electron cloud remains spherical with same radius. We also make the assumption that the charge density varies as $\sigma(\theta) = \sigma_0 + \delta\cos\theta$ where $\sigma_0 = \frac{-e}{4\pi r^2}$.

The nucleus is initially taken at $\vec{r} = \vec{0}$, the potential due to the electric field can be written as $V = Ez = Er\cos\theta$.

2.1 Energy due to Potential of External Field

The energy of the nucleus is given by $eV = eEz$, while the energy of the cloud is:

$$\begin{aligned}
U_{E,cloud} &= \int V dq = \int V\sigma\, dA && (6)\\
&= \int_0^\pi V\sigma 2\pi r^2 \sin\theta\, d\theta && (7)\\
&= \int_0^\pi Er\cos\theta(\sigma_0 + \delta\cos\theta)2\pi r^2 \sin\theta\, d\theta && (8)\\
&= 2\pi Er^3 \int_0^\pi \cos\theta(\sigma_0 + \delta\cos theta)\sin\theta\, d\theta && (9)\\
&= 2\pi Er^3 \int_0^\pi \delta\cos^2\theta\sin\theta\, d\theta && (10)\\
&= \frac{4\pi Er^3}{3}\delta && (11)
\end{aligned}$$

The total energy due to the field is then:

$$U_E = eEz + \frac{4\pi Er^3}{3}\delta \tag{12}$$

2.2 Energy of Interaction of Nucleus and Electron Cloud

The energy is given by:

$$
\begin{aligned}
U_{p,e} &= \int \frac{ke\,dq}{|\vec{r} - z\hat{z}|} && (13)\\
&= \int_0^\pi \frac{ke\sigma 2\pi r^2 \sin\theta\, d\theta}{\sqrt{|\vec{r} - z\hat{z}|^2}} && (14)\\
&= 2\pi k e r^2 \int_0^\pi \frac{(\sigma_0 + \delta\cos\theta)\sin\theta\, d\theta}{\sqrt{r^2 + z^2 - 2rz\cos\theta}} && (15)\\
&= 2\pi k e r^2 \frac{\sqrt{r^2 + z^2 - 2rz\cos\theta}(\delta(r^2 + z^2 + rz\cos\theta) + 3rz\sigma_0)}{3r^2 z^2}\Big|_0^\pi && (16)\\
&= -\frac{ke^2}{r} + \frac{2\pi k e\delta}{3z^2}\sqrt{r^2 + z^2 - 2rz\cos\theta}(r^2 + z^2 + rz\cos\theta)\Big|_0^\pi && (17)\\
&= -\frac{ke^2}{r} + \frac{2\pi k e\delta}{3z^2} 2z^3 && (18)\\
&= -\frac{ke^2}{r} + \frac{4\pi k e}{3}\delta z && (19)
\end{aligned}
$$

2.3 Self Energy of Electron Cloud

The self energy formula for non uniform spherical surface is derived in the Appendix. However, it requires calculating the potential due to the cloud close to it. This is potentially problematic as the potential calculation involves complicated integrals. Therefore, we first approximate the potential function.

Because of the symmetry of the distribution, the potential at $\theta = \frac{\pi}{2}$ is $-\frac{ke}{r}$. If we calculate the potential at $\theta = 0, \pi$, we might be able to interpolate and get the potential function $V(\theta)$.

The potential at $\theta = 0$ is given by:

$$
\begin{aligned}
V(\theta = 0) &= \int \frac{k\,dq}{|\vec{r} - r\hat{z}|} && (20)\\
&= \int_0^\pi \frac{k\sigma 2\pi r^2 \sin\theta\, d\theta}{\sqrt{2r^2(1-\cos\theta)}} && (21)\\
&= \int_0^\pi \frac{k(\sigma_0 + \delta\cos\theta)2\pi r^2 \sin\theta\, d\theta}{\sqrt{4r^2\sin^2\frac{\theta}{2}}} && (22)\\
&= k\pi r \int_0^\pi \frac{(\sigma_0 + \delta\cos\theta)\sin\theta\, d\theta}{\sin\frac{\theta}{2}} && (23)\\
&= 2k\pi r \int_0^\pi (\sigma_0 + \delta\cos\theta)\cos\frac{\theta}{2}\, d\theta && (24)\\
&= -\frac{ke}{r} + 2k\pi r\delta \int_0^\pi \cos\theta\cos\frac{\theta}{2}\, d\theta && (25)\\
&= -\frac{ke}{r} + \frac{4k\pi r}{3}\delta && (26)
\end{aligned}
$$

By the symmetry of the distribution, it is easy to see that $V(\theta = \pi) = -\frac{ke}{r} - \frac{4k\pi r}{3}\delta$. A good interpolating function is

$$
V(\theta) = -\frac{ke}{r} + \frac{4k\pi r}{3}\delta\cos\theta \qquad (27)
$$

Now, the self energy of the cloud is given by

$$
\begin{aligned}
U_{cloud} &= \frac{r^2}{2}\int_0^\pi \int_0^{2\pi} V\sigma \sin\theta\, d\phi\, d\theta && (28)\\
&= \pi r^2 \int_0^\pi V\sigma\sin\theta\, d\theta && (29)\\
&= \pi r^2 \int_0^\pi \left(-\frac{ke}{r} + \frac{4k\pi r}{3}\delta\cos\theta\right)(\sigma_0 + \delta\cos\theta)\sin\theta\, d\theta && (30)\\
&= \frac{1}{2}\frac{ke^2}{r} + \pi r^2 \int_0^\pi \frac{4k\pi r}{3}\delta^2\cos^2\theta\sin\theta\, d\theta && (31)\\
&= \frac{1}{2}\frac{ke^2}{r} + \frac{8k\pi^2 r^3}{9}\delta^2 && (32)
\end{aligned}
$$

2.4 Energy due to Magic Potential

In general, the magic potential will vary with charge distribution and position of the nucleus. However, for cases like the 'pressure' model of the magic potential lead to energies independent of charge distribution and position of nucleus. We consider that the magic potential is independent of z and δ.

3 Polarization of Atom in Electric Field

The total energy of the system is given by

$$U = U_E + U_{p,e} + U_{cloud} + U_{magic} \tag{33}$$

$$U(z, \delta) = eEz + \frac{4\pi E r^3}{3}\delta + \frac{8k\pi^2 r^3}{9}\delta^2 + \frac{4\pi ke}{3}\delta z + \dots \tag{34}$$

Where terms independent of z, δ have been omitted. The system will have z, δ such that

$$\frac{\partial U}{\partial z} = eE + \frac{4\pi ke}{3}\delta = 0 \tag{35}$$

$$\frac{\partial U}{\partial \delta} = \frac{4\pi E r^3}{3} + \frac{16k\pi^2 r^3}{9}\delta + \frac{4\pi ke}{3}z = 0 \tag{36}$$

Solving the system of equations gives $\delta = -\frac{3E}{4\pi k} = -3\epsilon_0 E$ and $z = 0$. We can now calculate the dipole moment of the cloud

$$p = \int_0^\pi z\sigma 2\pi r^2 \sin\theta \, d\theta \tag{37}$$

$$= \int_0^\pi (\sigma_0 + \delta\cos\theta) 2\pi r^3 \cos\theta \sin\theta \, d\theta \tag{38}$$

$$= 2\pi r^3 \int_0^\pi \delta \cos^2\theta \sin\theta \, d\theta \tag{39}$$

$$= \frac{4\pi r^3}{3}\delta \tag{40}$$

$$= -4\pi\epsilon_0 r^3 E \tag{41}$$

This points along the electric field as expected and is proportional to the magnitude of the field.

The atomic polarizability is given by $4\pi\epsilon_0 r^3$.

4 Comparision with Experimental Data

The experimental value of $\frac{\alpha}{4\pi\epsilon_0}$ is $0.667 \cdot 10^{-30} m^3$, while the theoretical model gives $0.148 \cdot 10^{-30} m^3$. This is good agreement considering the approximations made.

Remark: Quantum mechanics predicts the phenomena of tunnel ionization, where strong electric fields can cause the atom to be ionized. For Hydrogen atom, this is of the order $10^{11} V/m$.

With the current calculations, given sufficient electric field, the electron cloud will contain regions of positive charge density for $\delta > \sigma_0$. This is not physical and corresponds to the ionization electric field. A simple calculation gives that $E > \frac{ke}{3r^2}$ would yield this situation.

The numerical value of minimum E is $1.715 \cdot 10^{11} V/m$, the same order as experimental data.

🦣 Appendix

🦣.1 Self Energy of Sphere

The problem is to find the potential energy of a spherical shell of radius r and charge Q distributed uniformly. To construct this system, take an uncharged sphere and slowly add small charges to it, bringing the charges from infinity. If at any point the system has charge q and a charge dq is brought from infinity, the increase in potential energy is:

$$dU = \frac{kq}{r} dq \tag{42}$$

$$U = \int_0^Q \frac{\mathrm{d}U}{\mathrm{d}q} dq \tag{43}$$

$$= \frac{1}{2}\frac{kQ^2}{r} \tag{44}$$

🦣.2 Self Energy of non-uniform Sphere

Consider a charge sphere with surface charge distribution $\sigma(r, \theta, \phi)$. We construct such a sphere by bringing shells of charge $d\lambda\sigma$ from infinity to the radius of the sphere.

Let the potential due to the distribution be $V(r, \theta, \phi)$. When the sphere has distribution $\lambda\sigma$, $0 < \lambda < 1$, the potential due to it will be λV. The increase in potential energy by bringing a charge $d\lambda\sigma dA$ at (r, θ, ϕ) is given by

$$dU = \lambda V \sigma r^2 \sin\theta \, d\theta \, d\phi \, d\lambda \tag{45}$$

Integrating λ from 0 to 1 and the rest as usual, we get:

$$U = \frac{r^2}{2} \int_0^{\pi} \int_0^{2\pi} V\sigma \sin\theta \, d\phi \, d\theta \tag{46}$$

🦣.3 Magic Potential (Pressure)

Here we construct a magic potential whose source is physical and is attributed to 'pressure' due to charge density which prevents further collapse of the electron cloud.

Consider a simple magic potential which follows a power law $\frac{\lambda}{r^\alpha}$, then the total energy is:

$$U = \frac{\lambda}{r^\alpha} - \frac{1}{2}\frac{ke^2}{r} \tag{47}$$

Differentiating, equating to 0 and using Bohr's radius $r = \frac{\hbar^2}{mke^2}$, we get the value of λ as:

$$\lambda = \frac{1}{2\alpha}\frac{k^{2-\alpha}}{m^{\alpha-1}}e^{2(2-\alpha)}\hbar^{2(\alpha-1)} \tag{48}$$

It is intuitive enough that this magic potential must be increasing with charge of cloud, hence the power of e must be positive and $\alpha < 2$. Note that $\alpha = \frac{3}{2}$ gives particularly 'nice' results:

$$\lambda = \frac{\hbar}{3}\sqrt{\frac{k}{m}}e \tag{49}$$

This is even 'nicer' because it depends only on the total charge of the cloud, not the distribution of the charge. We can write the energy in differential form like:

$$dU_{magic} = \frac{\hbar}{3}\sqrt{\frac{k}{m}}\frac{\sigma\, dA}{r^{\frac{3}{2}}} \tag{50}$$

Integrating $\sigma\, dA$ just gives e and we need not worry about the distribution, this will be especially useful when considering a polarized atom.

> **Remark:** Note that this magic potential will not yield the radii from Bohr's model for a nucleus with charge Ze.

🦣.4 Magic Potential (Bohr's Model)

Here we construct a magic potential that leads to radii that conform to Bohr's atomic model.

Following notation from Bohr's model, suppose the nucleus has charge Ze, and let U_{magic} be the potential energy due to one unit charge on nucleus. The energy of the system is then:

$$U = ZU_{magic} - \left(Z - \frac{1}{2}\right)\frac{ke^2}{r} \tag{51}$$

Differentiating and using the fact that radius of atom is $\frac{r_0}{Z}$,

$$\left.\frac{\mathrm{d}U_{magic}}{\mathrm{d}r}\right|_{r=\frac{r_0}{Z}} = -\left(Z - \frac{1}{2}\right)\frac{ke^2}{Z\left(\frac{r_0}{Z}\right)^2} \tag{52}$$

$$= -\left(\frac{1}{\left(\frac{r_0}{Z}\right)^2} - \frac{1}{2r_0\frac{r_0}{Z}}\right)ke^2 \tag{53}$$

$$= -\left(\frac{1}{r^2} - \frac{1}{2r_0 r}\right)ke^2 \tag{54}$$

For simplicity, assume that this is valid for all r, we can then get U_{magic} by integrating:

$$U_{magic} = \left(\frac{\ln r}{2r_0} + \frac{1}{r}\right)ke^2 \tag{55}$$