APPLICATION OF PERTURBATION THEORY FOR THE DETERMINATION OF THE GROUND STATE ENERGY SHIFT OF THE NEUTRAL HYDROGEN ATOM IN THE PRESENCE OF AN EXTERNAL ELECTRIC FIELD.

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Abstract

The behaviour of the electrically neutral hydrogen atom in the presence of an external electric field has been studied. The hydrogen atom sees the application of the external electric field as a perturbation. The perturbation induces an electric dipole moment and lowers the ground state energy. The shift in the energy is the well-known stack effect phenomenon. The aim of the paper is to use an analytical method such as the techniques of differential equations and necessary mathematical assumption to obtain the solutions for the perturbed wave function and the second order energy correction, instead of applying the time independent perturbation approximation method which is beset by mathematical complexities. It is worthwhile to mention that the analytical techniques presented in this paper provide the simplest way of deriving the result. Our approach corresponds with other methods discussed in literatures.

Keywords: Perturbation theory, Stack effect, hydrogen atom polarization, differential equation

1.0   Introduction

If an external electric field is applied to the neutral hydrogen atom in its ground state, the atom sees it as a perturbation. The neutral atom will experience a net zero force and the energy levels are shifted. This shift is known as the stack effect. The disturbance occasioned by the applied electric field would cause the electron and the proton to be displaced in different direction in such a way that the field induces an electric dipole moment $\bar{P}$ given as

$$\bar{P} = \alpha E_{ext} \tag{1}$$

Where E_{ext} is the external electricfield in $Volts/meter$ and α is the atomic polarizability of a system given as

$$\alpha = 4\pi\varepsilon_0 a_0{}^3 \tag{2}$$

Where a_0 is the Bohr radius given by

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$$

The resulting energy shift is given as

$$\Delta E = -\frac{1}{2}(\bar{P}.E_{ext}) = -\frac{1}{2}\alpha E^2{}_{ext} \tag{3}$$

Equation (3) is the classical result and the direct proportionality of the energy shift to the square of the applied electric field is also reproduced when the perturbation theory is applied to the neutral hydrogen atom [1].The authors [1-3] state that the energy shift can be determined by solving the Schrodinger Wave Equation for the perturbed system. These statements follow from the fact that the perturbation approximation method for higher order corrections is beset with some mathematical difficulties. However, Merzbacher [4] notes that the perturbation approximation method can be used to evaluate the second order energy correction by using the technique originated by Dalgarno and Lewis [5]. This paper presents a more tractable and detailed approach for evaluating the second order energy correction by first evaluating the perturbed wave function using the techniques of convergence series to solve the second-order inhomogeneous differential equation arising from the application of the external electric field to the neutral hydrogen atom. It is also noteworthy to mention that mathematical assumptions were used to arrive at the result with precision.

2.0 Theoretical Background.

The perturbation approximation method can be used to predict the eigenstate of a system. According to Davies and Betts[1], the use of approximation and numerical methods in both classical and quantum mechanics is crucial because of limited

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number of exact soluble systems. Starting from the Schrodinger Wave Equation, the energy and wave function corrections can be estimated.

Suppose H, Ψ_n and E_n represent the Hamiltonian, Eigen-function and Eigen-value for the system, then we can write the Schrodinger equation as

$$H\Psi_n = E_n \Psi_n \qquad (4)$$

If the system experiences a perturbation H', then the Hamiltonian for the perturbed system becomes

$$H = H_0 + \beta H' \qquad (5)$$

Where β is a constant and has value between 0 to 1. The series expansions for the eigenvalues and Eigen-functions respectively, are given by

$$E_n = \sum_{k=0}^{\infty} \beta^k E_n^{(k)} \qquad (6)$$

$$\Psi_n = \sum_{k=0}^{\infty} \beta^k \Psi_n^{(k)} \qquad (7)$$

Substituting equations (5), (6) and (7) into (4) for lower values of k say $k = 0, 1, 2$ and equating the resulting corresponding coefficients of β powers, we obtain the equations for the first and second order energy corrections respectively as

$$E_n^{(1)}\Psi_n^{(0)} = H'\Psi_n^{(0)} + (H_0 - E_n^{(0)})\Psi_n^{(1)} \qquad (8)$$

$$E_n^{(2)}\Psi_n^{(0)} = (H' - E_n^{(1)})\Psi_n^{(1)} + (H_0 - E_n^{(0)})\Psi_n^{(2)} \qquad (9)$$

A further simplification of (8) shown in [1] gives the equations for the first order energy and wave-function corrections as

$$E_n^{(1)} = \langle \Psi_n^{(0)*}|H'|\Psi_n^{(0)}\rangle = H'_{nn} = \int \left(\Psi_n^{(0)*}|H'|\Psi_n^{(0)}\right)dV \qquad (10)$$

$$\Psi_n = \Psi_n^{(0)} + \beta \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \Psi_m^{(0)} \qquad (11)$$

Where H'_{mn} is the matrix element and $\Psi_n^{(0)*}$ is the complex conjugate of the wave-function.

Also it can be easily shown (see [3]) that a further simplification of equation (9) gives the second order energy correction as

$$E_n^{(2)} = \langle \Psi_n^{(0)*}|H'|\Psi_n^{(1)}\rangle \qquad (12)$$

The correction Eigen-function in terms of orthonormal set is given as

$$\Psi_n^{(1)} = \sum_m a_{nm} \Psi_m^{(0)} \qquad (13)$$

Where a_{nm} are the coefficients of the series expansion which can be evaluated (see [1] and [3]) from (8) as

$$a_{nm} = \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \qquad (14)$$

By substituting (13) with a_{nm} into (12) we can re-write the second order energy correction as

$$E_n^{(2)} = \sum_{m \neq n} \left(\frac{(H'_{mn})^2}{E_n^{(0)} - E_m^{(0)}}\right) \qquad (15)$$

3.0   Methodology

The perturbation theory was first applied to calculate the shift in energy arising from the application of external electric field to the neutral hydrogen atom. The perturbing Hamiltonian $H' = -eEz$ along the z-axis is considered. The first order energy correction vanishes, indicating that the ground state energy is not affected by the presence of an external field. Further to this, equation (8) was transformed into a second order inhomogeneous equation using spherical polar coordinates. To obtain the solution, we assume that the complementary function of the inhomogeneous differential equation must completely vanish at the boundary $\rho_c(r) = \frac{d\rho_c(r)}{dr} = 0$ at $r = 0$.

4.0   Results and Discussions

The first order energy correction is given in equation (10) as

$$E_n^{(1)} = \langle \Psi_n^{(0)*}|H'|\Psi_n^{(0)}\rangle = H'_{nn} = \int \left(\Psi_n^{(0)*}|H'|\Psi_n^{(0)}\right)dV$$

With volume element $\int dV = \iiint r^2 \sin\theta \, dr d\theta d\phi$, $H' = -eE_{ext} z$ ($z = r\cos\theta$), and ground state wave function $\Psi_0^{(0)} = \frac{\exp(-r/a_0)}{\sqrt{\pi(a_0)^3}}$, the integration would vanish for $0 < r < \infty$, $0 < \theta < \pi$ and $0 < \phi < 2\pi$. This indicates that the first order energy correction to the ground state yields a null value. That is

$$E_0^{(1)} = 0 \qquad (16)$$

The physical significance of (16), implies that there is no induced dipole for linear stack effect and the perturbation does not affect the ground state energy of the neutral hydrogen atom. If the approximation computations for the first order energy correction is inadequate, we can proceed to the second order energy correction by using (12). To evaluate (12), we need to determine the first order wave function by using (8) instead of evaluating the summation in (13) which is not so easy to do.

The ground state energy, $E_0^{(0)}$, the unperturbed Hamiltonian H_0 in spherical polar coordinates, the perturbingHamiltonian H', the ground state wave function $\Psi_0^{(0)}(r, \theta)$ and the potential $V(r)$ are given as

$$\begin{cases} E_0^{(0)} = \frac{-me^4}{32\pi^2(\varepsilon_0)^2\hbar^2} & H_0 = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{L^2}{2mr^2} + V(r) \\ H' = -eE_{ext}r\cos\theta \ , \quad V(r) = -\frac{e^2}{4\pi\varepsilon_0 r^2}, \quad \Psi_0^{(0)}(r,\theta) = \frac{\exp(-r/a_0)}{\sqrt{\pi(a_0)^3}} \end{cases} \quad (17)$$

Where L^2 is the angular momentum operator and does not depend on the radius r of the sphere. Also the energy level does not depend on the spin because the $z-axis$ orientation can be neglected in a spherically symmetric system [1]. The Eigen-value equation for the angular momentum operator is given as

$$L^2\Psi(r,\theta) = l(l+1)\hbar^2\Psi(r,\theta) \qquad (18)$$

By substituting (16), (17), (18) into (8) with $l=1$ and $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$ we obtain

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - 2 + \frac{2r}{a_0} - \frac{r^2}{(a_0)^2}\right]\Psi_0^{(1)}(r,\theta) = -\frac{2(4\pi\varepsilon_0)E_{ext}\,r^3\cos\theta}{a_0 e\sqrt{\pi(a_0)^3}}\exp\left(-r/a_0\right) (19)$$

Equation (19) is a second order inhomogeneous ordinary differential equation separable in r and θ. We set the solution to (19) as

$$\Psi_0^{(1)}(r,\theta) = f(r)\cos\theta \qquad (20)$$

Substituting $\Psi_0^{(1)}(r,\theta)$ in (20) into (19), we obtain

$$\frac{d}{dr}\left(r^2\frac{df}{dr}\right) + \left(-2 + \frac{2r}{a_0} - \frac{r^2}{(a_0)^2}\right)f(r) = -K\,r^3\exp\left(-r/a_0\right) \ (21)$$

To further simplify (21) we set

$$f(r) = \rho(r)\exp\left(-\frac{r}{a_0}\right) \qquad (22)$$

$$r^2\frac{d^2\rho}{dr^2} + \left(2r - \frac{2r^2}{a_0}\right)\frac{d\rho}{dr} - 2\rho(r) = -Kr^3 \qquad (23)$$

For simplicity sake, we have set $K = \frac{2(4\pi\varepsilon_0)E_{ext}}{a_0 e\sqrt{\pi(a_0)^3}}$ (24)

The general solution to (23) is given as

$$\rho(r) = \rho_c(r) + G(r) \qquad (25)$$

Where $\rho_c(r)$ is the complementary function for the homogeneous equation and $G(r)$ is the particular integral function. To evaluate the complementary solution of (23), we set the right hand side to zero.

$$r^2\frac{d^2\rho_c}{dr^2} + \left(2r - \frac{2r^2}{a_0}\right)\frac{d\rho_c}{dr} - 2\rho_c(r) = 0 \qquad (26)$$

As r becomes infinite, the wave-function blows up and the solution is not acceptable, so we assume the value of r that will make the wave-function finite by setting $r = 0$. We now apply the method of convergent series, in particular we use the Frobenius method because the point $r = 0$ is a regular singular point. This method enable us to write the solution as

$$\rho_c(r) = \sum_{n=0}^{\infty} c_n r^{n+\sigma} \qquad (27)$$

The parameter σ is an integer that determines the approach for obtaining two linearly independent solution of (26). If we substitute (27) into (26) we obtain

$$\sum_{n=0}^{\infty}[(n+\sigma)(n+\sigma-1) + 2(n+\sigma) - 2]c_n r^{n+\sigma} - \frac{2}{a_0}\sum_{n=0}^{\infty}c_n r^{n+\sigma+1} = 0 \ (28)$$

We set $r = 0, n = 0$ and demand that the terms in the summation independently vanish so as to obtain the indicial equation

$$\sigma^2 + \sigma - 2 = 0$$

The roots of the indicial equation are $\sigma = 1$ or $\sigma = -2$

Clearly, the roots differ by an integer and we may not be able to find two linearly independent solutions that satisfy (26) but we can obtain a solution corresponding to the larger root [6].

On substituting the larger indicial root ($\sigma = 1$) into (28) and shifting the index of the second summation, we obtain the recursion relation as

$$c_n = \frac{2}{(n+3)a_0}c_{n-1} \ n \geq 1 \qquad (29)$$

Calculating the coefficients c_n in (29) and substituting into (27) we obtain the solution of (26) as

$$\rho_c(r) = \left\{r + \frac{1}{2a_0}r^2 + \frac{1}{15(a_0)^3}r^3 + \dots\dots\dots\right\}c_0 \qquad (30)$$

To obtain the general solution of (23), we use the assumption stated in section 3.0. This requires that the complimentary function(30) must vanish completely. To achieve this purpose, we use the one point boundary condition $\rho_c(r) = \frac{d\rho_c(r)}{dr} = 0$ at $r = 0$. We found $c_0 = 0$. Thus (30) yields a null value.

$$\rho_c(r) = 0 \qquad (31)$$

Now we guess the solution for the particular integral function of (23) by letting

$$G(r) = Ar^3 + Br^2 + Cr + D (32)$$

Where $A, B\ C$ and D are arbitrary constants. When we substitute (32) into (23), we found

$\left\{A = D = 0, B = \frac{a_0 K}{4}, \ and\ C = \frac{(a_0)^2 K}{2}\right.$ (33)

Putting (33) into (32) yields the particular integral solution as

$G(r) = \frac{(a_0)^2 K}{2} r + \frac{a_0 K}{4} r^2$ (34)

The general solution to (23) then becomes

$\rho(r) = \rho_c(r) + G(r) = \frac{(a_0)^2 K}{2} r + \frac{a_0 K}{4} r^2$ (35)

The first order wave function correction to the ground state now yields

$\Psi_0^{(1)}(r, \theta) = f(r)cos\theta = \rho(r)exp⁡(-\frac{r}{a_0})cos\theta = \left(\frac{(a_0)^2 K}{2} r + \frac{a_0 K}{4} r^2\right) exp⁡(-\frac{r}{a_0})cos\theta$

Finally, by substituting K term in (24) we obtain

$\Psi_0^{(1)}(r, \theta) = \frac{(4\pi\varepsilon_0)E_{ext}}{e\sqrt{\pi(a_0)^3}} \left(a_0 r + \frac{1}{2} r^2\right) exp⁡(-\frac{r}{a_0})cos\theta$ (36)

Now we can evaluate the second-order energy correction to the ground state by putting (36) into (12). With $H' = -eE_{ext} z = -eE_{ext} rcos\theta$, $\Psi_0^{(0)} = \frac{exp⁡(-r/a_0)}{\sqrt{\pi(a_0)^3}}$ we have that

$E_n^{(2)} = \langle\Psi_n^{(0)*}|H'|\Psi_n^{(1)}\rangle = \int\langle\Psi_n^{(0)*}|H'|\Psi_n^{(1)}\rangle dV$ (37)

Therefore we write the volume element as

$\int dV = \iiint r^2 sin\theta dr d\theta d\phi$ For $0 < r < \infty,\ \ 0 < \theta < \pi\ and\ 0 < \phi < 2\pi$ so that

$E_0^{(2)} = -\frac{(4\pi\varepsilon_0)(E_{ext})^2}{\pi(a_0)^3} \int_0^\infty \left(a_0 r^4 + \frac{1}{2} r^5\right) exp\left(-\frac{2r}{a_0}\right) dr \int_0^\pi cos^2\theta sin\theta d\theta \int_0^{2\pi} d\phi$ (38)

By using special function (gamma function) and substitution integration technique in (38), we obtain

$E_0^{(2)} = -\ 4\pi\varepsilon_0 (a_0)^3 \frac{9}{4} (E_{ext})^2$ (39)

If we substitute (2) into (39) we have

$E_0^{(2)} = -\ \frac{9}{4} \alpha(E_{ext})^2$ (40)

5.0 Conclusion

The perturbation approximation method has been applied to evaluate the energy shift of the neutral hydrogen atom in the presence of an external electric field. A series of mathematical techniques were used to calculate the first order wave function correction (36) and the second order energy correction to the ground state (40). Equation (40) gives a good estimation of the energy shift when compared to the classical result (3). It is worthwhile to note that the analytical approach presented in this paper allows us to evaluate (36) and (40) with ease and precision. Thus this approach helps in avoiding needless computations in using the perturbation theory in equations (13) and (15). The results in literatures [1-4] thus validate the mathematical procedure applied.

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