Non-Hermitian Hamiltonian Treatment of Stark Effect in Quantum Mechanics

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Abstract

The Non-Hermitian aspect of Quantum Mechanics has been of great interest recently. There have been numerous studies on non-Hermitian Hamiltonians written for natural processes. Some studies have even expressed the hydrogen atom in a non-Hermitian basis. In this paper the principles of non-Hermitian quantum mechanics is applied to both the time independent perturbation theory and to the time dependant theory to calculate the Stark effect. The principles of spherical harmonics has also been used to describe the development in the non-Hermitian case. Finally, the non-Hermitian aspect has been introduced to the well known Stark effect in quantum mechanics to find a condition in which the Stark effect will still be true even if a non-Hermitian Hamiltonian is used. This study completes the understanding at a fundamental level to understand the well known Stark effect.

1- Introduction

In physics, the most successful theory which we have till now id quantum mechanics. The predictions made by quantum mechnics has been corroborated by the various experiments ranging from low energy experiments to high energy experiments. Quantum mechanics has been one of the theories in physics which has found numerous applications in interdisciplinary fields such as chemistry and biology, and fields as diverse as finance. Despite of it being a major success, it has been widely accepted that quantum mechanics has not been completely understood. Time and again it surprises and baffles researchers with its results.

The main requirement of quantum mechanics is that it lives in a Hermitian space. This means that the quantum mechanical operators which expresses the behavior of a quantum system are Hermitian. This requirement points towards the well known principle that the energy spectrum should be real because all measurements of the energy of a system should give real results [1-3]. The aspect of an operator being Hermitian is pure mathematical in nature. The condition of an operator H being Hermitian is given by,

$$H = H^{\dagger} \tag{1}$$

Where the symbol † represents the combined operations of matrix transposition and complex conjugation [1, 2]. The operator H is referred to as a Hamiltonian and the eigenvalues of H are real.

It has been seen [1] that H does not necessarily have to be Hermitian to necessarily obtain a real energy eigenvalue spectra. This gives us the opportunity to study and understand the aspects of quantum mechanics related with non-Hermitian operators as well, which is also known as $\mathcal{PT}$-symmetry theory [1]. There have been some studies which

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deal with non-Hermitian operators, and one such study deals with a complex-valued potential function whose spectra results are real [4-6]. Similarly, another study uses the same formulation to understand the Pais-Uhlenbeck oscillator model [5-7]. There have been continuous efforts in applying this formulation to understand quantum mechanical phenomena of known processes [6, 8, 9].

This paper studies the non-Hermitian Hamiltonian as described in Bender (2005), Hamazaki et al. (2020), Ernzerhof et al. (2020), Romero et al. (2013) and Bagarello and Gargano (2020) [1, 3, 5, 10, 11] and studies the spherical harmonics and hydrogen atom through the $\mathcal{PT}$-symmetry theory. Then this is applied to the well known result of time-independent perturbation theory in quantum mechanics and the very well known Stark effect.

2- Methodology

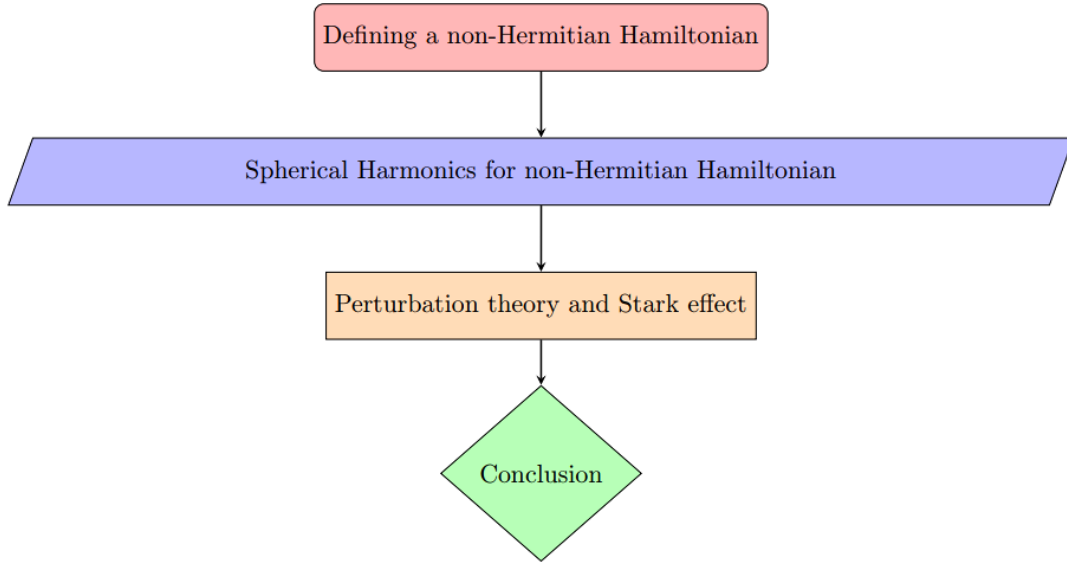Figure 1 shows the flowchart of the research methodology.

Figure 1. Flowchart of the research methodology.

3- Spherical Harmonics & Angular Momentum

3-1- Spherical Harmonics

Spherical harmonics play an important part in the description of the H-atom because they represent the solutions to the angular part of the wave function. The wave-function of the H-atom is given as [11-13].

$$\Psi_{nlm}(r,\theta,\phi) = R_{n,l}(r)Y_{lm}(\theta,\phi) \tag{2}$$

Where the $Y_{lm}(\theta,\phi)$ are known as spherical harmonic functions given by:

$$Y_{lm}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{lm}(\cos\theta)e^{(im\phi)} \tag{3}$$

for $m \geq 0$, and

$$Y_{l,-m}(\theta,\phi) = Y_{lm}^*(\theta,\phi) \tag{4}$$

for $m < 0$.

$P_{lm}(\cos\theta)$ are the associated Legendre polynomials given by:

$$P_{lm}(x) = (-1)^m \sqrt{(1-x^2)^m} \frac{d^m}{dx^m} P_l(x) \tag{5}$$

Where $P_l(x)$ are Legendre polynomials. These polynomials can be generated using:

$$P_l(x) = \frac{(-1)^l}{2^l l!} \frac{d^l}{dx^l}(1-x^2)^l \tag{6}$$

Where $R_{n,l}(r)$ is the Radial part of the H-atom wave-function and is given by:

$$R_{n,l}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \, e^{-r/3a_0} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \tag{7}$$

Where $L_{n-l-1}^{2l+1}(\frac{2r}{na_0})$ and is known as the associated Laguerre polynomials given by:

$$L_{n-l-1}^{2l+1}(s) = \sum_{q=0}^{n-l-1} (-1)^q \frac{(n+l)!}{(n-l-q-1)!(q+2l+1)!} s^q \tag{8}$$

or, more generally as

$$L_p^j(s) = \sum_{q=0}^{p} (-1)^q \frac{(p+j)!}{(p-q)!(j+q)!q!} s^q \tag{9}$$

The spherical harmonics in Equation 3 satisfy the orthonormality relations

$$\langle Y_{l',m'}(\theta,\phi)|Y_{lm}(\theta,\phi)\rangle = \int d\Omega\, Y_{l',m'}(\theta,\phi)Y_{lm}(\theta,\phi) = \delta_{m,m'}\,\delta_{l,l'} \tag{10}$$

Where δ_{ab} is the Kronecker delta function.

The spherical harmonic functions form an orthonormal basis and hence, any function $f(\theta,\phi)$ can be written as:

$$f(\theta,\phi) = \sum_{l\geq 0} \sum_{m=-l}^{l} C_{lm}Y_{lm}(\theta,\phi) \tag{11}$$

Where the coefficients C_{lm} are:

$$C_{lm} = \int d\Omega\, Y_{lm}^*(\theta,\phi)f(\theta,\phi) \tag{12}$$

Substituting C_{lm} in Equation 11 and changing variables $u' = cos\theta'$ and $u = cos\theta$ results in:

$$f(\theta,\phi) = \int_0^{2\pi} d\phi \int_{-1}^{1} du' f(u',\theta')(\sum_{l\geq 0} \sum_{m=-l}^{l} Y_{lm}^*(u',\phi')Y_{lm}(u,\phi)) \tag{13}$$

Where the completeness relation for the spherical harmonics is given as:

$$\sum_{l\geq 0} \sum_{m=-l}^{l} Y_{lm}^*(\theta',\phi')Y_{lm}(\theta,\phi) = \delta(\theta-\theta')\,\delta(cos\theta - cos\theta') \tag{14}$$

3-2- Angular Momentum

The angular momentum operators in the Hermitian space are given by $L_x = -i(y\partial_z - z\partial_y)$, $L_y = -i(z\partial_x - x\partial_z)$, $L_z = -i(x\partial_y - y\partial_x)$ and the angular momentum algebra is $[L_x, L_y] = iL_z$, $[L_z, L_x] = iL_y$, $[L_y, L_z] = iL_x$ and $L_x^2 + L_y^2 + L_z^2 = L^2$ also, $[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$.

The eigenvalue equation is given by

$$L^2 Y_{lm}(\theta,\phi) = l(l+1)Y_{lm}(\theta,\phi) \tag{15}$$

Where $l = 0,1,2....$

4- $\mathcal{PT}$ Symmetric Spherical Harmonics & Angular Momentum

This section is a brief review of $\mathcal{PT}$ symmetry and the application to spherical harmonics and angular momentum [10, 13].

4-1- $\mathcal{PT}$ Symmetry Basics

In $\mathcal{PT}$ symmetry, $\mathcal{P}$ stands for the parity operator and $\mathcal{T}$ stands for the time reversal operator. When the parity operator is applied to a function it results in $\mathcal{P}f(x,y,z) = f(-x,-y,-z)$ and the time reversal operator is defined when $t \to -t$ or $i \to -i$. So when the operator is applied $\mathcal{PT}$ the result is $\mathcal{PT}[f(\tilde{x})] = f^*(-\tilde{x})$.

In spherical harmonics the parity operator transforms as $(r,\theta,\phi) \to (r,\pi-\theta,\phi+\pi)$, so $\mathcal{PT}[f(r,\theta,\phi)] = f^*(r,\pi-\theta,\phi+\pi)$ and with two functions $f\&g$:

$$\langle f|g\rangle = \int d\tilde{x}[\mathcal{PT}f(x)]g(x) \tag{16}$$

4-2- $\mathcal{PT}$ Symmetric Spherical Harmonics

Under the parity operator the spherical harmonics transform as:

$$\mathcal{P}[Y_{lm}(\theta,\phi)] = Y_{lm}(\pi-\theta,\phi+\pi) = (-1)^l Y_{lm}(\theta,\phi) \tag{17}$$

and operated on by the $\mathcal{PT}$ operator:

$$\mathcal{PT}[Y_{lm}(\theta,\phi)] = Y_{lm}^*(\pi-\theta,\phi+\pi) = (-1)^l Y_{lm}^*(\theta,\phi) \tag{18}$$

defining the $\mathcal{PT}$ symmetric spherical harmonics as:

$$Y_{lm}^g(\theta,\phi) = e^g\, Y_{lm}(\theta,\phi) \tag{19}$$

Where $g \equiv g(r,\theta,\phi)$ is any function and the inner product is given as:

$$\langle Y_{l',m'}^{g}(\theta,\phi)|Y_{lm}^{g}(\theta,\phi)\rangle = \int d\Omega \, \mathcal{PT}[Y_{l',m'}^{g}(\theta,\phi)]Y_{lm}^{g}(\theta,\phi) \tag{20}$$

And also;

$$\mathcal{PT}[Y_{l',m'}^{g}(\theta,\phi)] = e^{g(r,\pi-\theta,\phi+\pi)}(-1)^{l}Y_{lm}^{*}(\theta,\phi) \tag{21}$$

Hence,

$$\langle Y_{l',m'}^{g}(\theta,\phi)|Y_{lm}^{g}(\theta,\phi)\rangle = (-1)^{l}\int d\Omega \, e^{[g^{*}(r,\pi-\theta,\phi+\pi)+g(r,\theta,\phi)]}Y_{l',m'}^{*}(\theta,\phi)Y_{lm}(\theta,\phi) \tag{22}$$

If the following condition [3, 10] is fulfilled,

$$e^{[g^{*}(r,\pi-\theta,\phi+\pi)+g(r,\theta,\phi)]} = \alpha \tag{23}$$

Then;

$$\langle Y_{l',m'}^{g}(\theta,\phi)|Y_{lm}^{g}(\theta,\phi)\rangle = (-1)^{l}\alpha \, \delta_{m,m'} \, \delta_{l,l'} \tag{24}$$

So it is observed that the spherical harmonics are orthogonal under $\mathcal{PT}$ transformation if Equation 23 is satisfied. Applying the $\mathcal{PT}$ transformation,

$$f(\theta,\phi) = \sum_{l\geq 0}\sum_{m=-l}^{l}C_{lm}Y_{lm}^{g}(\theta,\phi) \tag{25}$$

And applying the orthonormality conditions results in:

$$C_{lm} = \frac{(-1)^{l}}{\lambda}\langle Y_{lm}^{g}(\theta,\phi)|f(\theta,\phi)\rangle = \frac{(-1)^{l}}{\lambda}\int d\Omega \mathcal{PT}[Y_{lm}^{g}(\theta,\phi)f(\theta,\phi) \tag{26}$$

So the $\mathcal{PT}$ symmetric hydrogen atom wave function can be defined as

$$\Psi_{nlm}^{g} = e^{g(r,\theta,\phi)}\Psi_{nlm} \tag{27}$$

Where Ψ_{nlm} is defined in Equation 2. For simplicity we will write this as:

$$|nlm\rangle^{g} = e^{g}|nlm\rangle \tag{28}$$

and the complex conjugate as,

$$\langle nlm|^{g} = e^{g^{*}}\langle nlm| \tag{29}$$

4-3- $\mathcal{PT}$ Symmetric Angular Momentum

As defined, $g \equiv g(r,\theta,\phi)$, the angular momentum operator is [10]:

$$L_{i}^{g} = e^{g}L_{i}e^{-g} \tag{30}$$

In general L_{i}^{g} is non-Hermitian, and their algebra is given as:

$$[L_{x}^{g},L_{y}^{g}] = iL_{z}^{g}, [L_{z}^{g},L_{x}^{g}] = iL_{y}^{g}, [L_{y}^{g},L_{z}^{g}] = iL_{x}^{g} \tag{31}$$

Also,

$$(L^{g})^{2} = (L_{x}^{g})^{2} + (L_{y}^{g})^{2} + (L_{z}^{g})^{2}, [(L^{g})^{2},L_{i}^{g}] = 0 \tag{32}$$

Similar to Equation 15:

$$(L^{g})^{2}Y_{lm}^{g}(\theta,\phi) = l(l+1)Y_{lm}^{g}(\theta,\phi), Y_{lm}^{g}(\theta,\phi) = e^{g}Y_{lm}(\theta,\phi) \tag{33}$$

and similar to Equation 10.

5- Transformations

If A, B and C are operators that satisfy commutation relations such as:

$$[A,B] = C \tag{34}$$

These operators transform as;

$$A^{g} = e^{g}Ae^{-g}, \quad B^{g} = e^{g}Be^{-g}, \quad C^{g} = e^{g}Ce^{-g} \tag{35}$$

now the commutation rules are,

$$[A^{g},B^{g}] = C^{g} \tag{36}$$

Taking the transformation of the position and the momentum operator as:

$$x_i^g = e^g x_i e^{-g}, p_i^g = e^g p_i e^{-g} \tag{37}$$

The following commutation rules using this transformation are given as,

$$[L_i^g, x_j] = i\epsilon_{ijk} x_k \tag{38}$$

$$[L_i^g, p_j] \neq i\epsilon_{ijk} p_k \tag{39}$$

And,

$$[L_i^g, p_j^g] = i\epsilon_{ijk} p_k^g \tag{40}$$

Defining the Hamiltonian in the $\mathcal{PT}$ symmetric case as:

$$H^g = e^g H e^{-g} \tag{41}$$

then the commutation relations with the Hamiltonian are given as,

$$[L_i, H^g] \neq 0 \tag{42}$$

and

$$[L_i^g, H^g] = 0 \tag{43}$$

So we see that L_i is a conserved quantity but L_i^g is not.

6- Time Independent Perturbation Theory & Stark Effect

The methodology of a perturbation theory is to apply a slight deformation or deviation in the system and observe as to how the system is behaving. The complete Hamiltonian is the unperturbed Hamiltonian plus the perturbation term [14, 15]. The Stark effect is the phenomena of altering atomic energy levels by an external electric field. The external electric field can be applied to an atom or molecule and acts as a perturbation. This effect, though small compared to the spacings between the unperturbed atomic levels, is quite significant. The Stark effect can be readily observed as shifting and splitting of spectral lines in atoms and molecules. Here we have calculated the Stark effect in a Hydrogen atom, and in the following sections applied this to the non-Hermitian case.

6-1- Basics of Perturbation Theory (Time-independent)

Considering the time-independent case, let us write the total Hamiltonian as [14],

$$H = H_0 + aH' \tag{44}$$

Where H_0 is the unperturbed Hamiltonian and H' is the interaction term with "a" as a small quantity. We consider that H_0 is solved and has well-known eigenfunctions and eigenvalues, $i.e.$

$$H_0|m^{(0)}\rangle = E_m^{(0)}|m^{(0)}\rangle \tag{45}$$

Where the eigenfunctions are normalized, $i.e.$

$$\langle m^0|n^0\rangle = \delta_{mn} \tag{46}$$

So now we can write the total Hamiltonian and calculate the energy eigenvalues E_m and eigenfunctions $|m\rangle$ of the total Hamiltonian,

$$H|m\rangle = E_m|m\rangle \tag{47}$$

The idea of perturbation theory is to find the change in energy and the wavefunctions which arises because of the perturbation. To get that we will expand the eigenvalues and eigenfunctions in a power series. Let the power series of the eigenvalues and eigenfunctions be written as,

$$E_m = E_m^{(0)} + aE_m^{(1)} + a^2 E_m^{(2)} + ----- \tag{48}$$

and

$$|m\rangle = |m^{(0)}\rangle + a|m^{(1)}\rangle + a^2|m^{(2)}\rangle + ---- \tag{49}$$

Using Equations 48 and 49 we get Equation 44 as,

$$(H_0 + aH')(|m^{(0)}\rangle + a|m^{(1)}\rangle + a^2|m^{(2)}\rangle + ...) = \\ (E_m^{(0)} + aE_m^{(1)} + a^2 E_m^{(2)} + ...) \\ (|m^{(0)}\rangle + a|m^{(1)}\rangle + a^2|m^{(2)}\rangle + ...) \tag{50}$$

Now, equating coefficients of a^0, a^1 and a^2 we get,

$$H_0|m^{(0)}\rangle = E_m^{(0)}|m^{(0)}\rangle \tag{51}$$

$$H_0|m^{(1)}\rangle + H'|m^{(0)}\rangle = E_m^{(0)}|m^{(1)}\rangle + E_m^{(1)}|m^{(0)}\rangle \tag{52}$$

And,

$$H_0|m^{(2)}\rangle + H'|m^{(1)}\rangle = E_m^{(0)}|m^{(2)}\rangle + E_m^{(1)}|m^{(1)}\rangle + E_m^{(2)}|m^{(0)}\rangle \tag{53}$$

Respectively. We have neglected the terms with higher powers of a because we are taking into account the dominant terms only.

First and Second Order Corrections: Using Equation 52 we get the energy corrections for the first order as,

$$E_m^{(1)} = \langle m^{(0)}|H'|m^{(0)}\rangle \tag{54}$$

The first order corrections to the eigenstate is given by,

$$|m^{(1)}\rangle = \sum_{n \neq m} |n^{(0)}\rangle\langle n^{(0)}|m^{(1)}\rangle \tag{55}$$

Using Equation 52 it is trivial to show that:

$$\langle n^{(0)}|m^{(1)}\rangle = \frac{\langle n^{(0)}|H'|m^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}} \tag{56}$$

So the first order corrections to the eigenstate is given by substituting Equation 56 in Equation 55 which is,

$$|m^{(1)}\rangle = \sum_{n \neq m} \frac{\langle n^{(0)}|H'|m^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}} |n^{(0)}\rangle \tag{57}$$

Similarly, we can calculate the second order corrections to the energy and we get,

$$E_m^{(2)} = \sum_{n \neq m} \frac{|\langle n^{(0)}|H'|m^{(0)}\rangle|^2}{E_m^{(0)} - E_n^{(0)}} \tag{58}$$

Here we have not calculated the higher orders because they will be negligible.

6-2- Stark Effect

The Stark effect occurs when a Hydrogen atom is subjected to an electric field. This results in splitting of the energy levels because of the externally applied electric field. The term which includes the electric field acts as the perturbation term, which results in the splitting of the energy levels. This splitting of energy levels is due to the corrections in the energy of the unperturbed Hamiltonian. There have been various studies on the Stark effect with different conditions as mentioned in [16-19]. The unperturbed Hamiltonian for the Hydrogen atom is,

$$H_0 = \frac{p^2}{2m} - \frac{ke^2}{r^2} \tag{59}$$

all the quantities in Equation 59 are defined for the electron. The perturbation term is given by,

$$H' = e\mathcal{E}z \tag{60}$$

Where $\mathcal{E}$ denotes the magnitude of the electric field and the direction of electric field is along the z-axis.

The energy eigenstate of the unperturbed Hamiltonian is characterized in terms of quantum numbers, namely n, l and m. So we can define the eigenstate of the H-atom as $|nlm\rangle$ and the energy eigenvalues as E_{nlm}. Using Equation 54 and 58 the first and second order energy corrections can be written as,

$$\Delta E_{nlm} = e\mathcal{E}\langle nlm|z|nlm\rangle + \sum_{n'l'm' \neq nlm} \frac{e^2\mathcal{E}^2|\langle nlm|z|n'l'm'\rangle|^2}{(E_{n'l'm'} - E_{nlm})} \tag{61}$$

This shift in the energy from the unperturbed energy is called the Stark effect. Here again we have neglected higer order energy corrections becauase we are interested only in the dominant terms. The selection rules for the quantum numbers l and m are,

$$l' = l \pm 1 \tag{62}$$

$$m' = m \tag{63}$$

This results in Equation 61 giving the first term as zero and so we get the energy correction which is only the second order corresction as,

$$\Delta E_{nlm}^{(2)} = \sum_{n'l' \neq nl} \frac{e^2\mathcal{E}^2|\langle nlm|z|n'l'm\rangle|^2}{(E_{nlm} - E_{n'l'm})} \tag{64}$$

➤ $\underline{n = 1, l = 0, m = 0}$

$$\Delta E_{100}^{(2)} = \sum_{n' > 1} \frac{e^2 \mathcal{E}^2 |\langle 100|z|n'10 \rangle|^2}{(E_{n'10} - E_{100})} \tag{65}$$
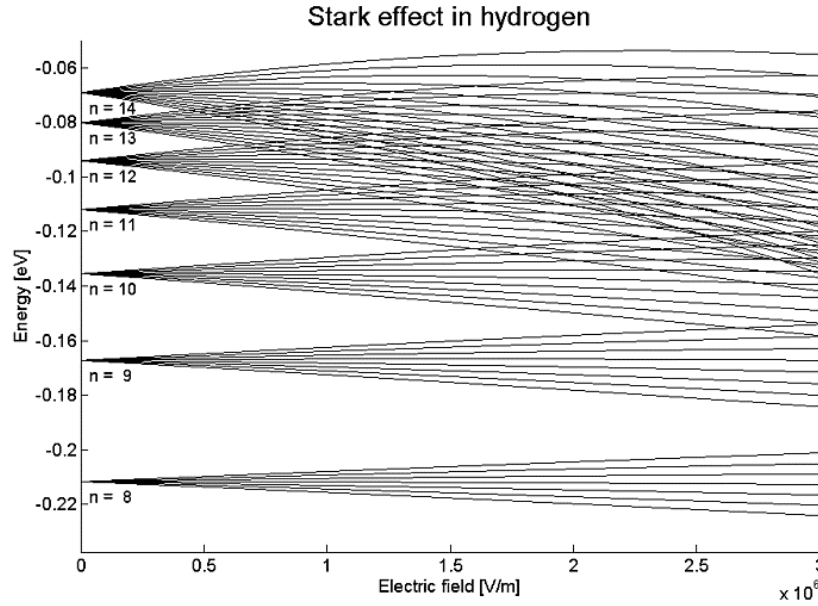

Figure 2. The Stark effect shows the splitting of lines in Hydrogen atom. source(starkeffects.com).

For $n' = 2$ and using the inequality [14];

$$E_{n'00} - E_{100} \geq E_{200} - E_{100} \tag{66}$$

And defining α' as the polarizability [14] where:

$$\alpha' = 2e^2 \sum_{n' > 1} \frac{|\langle 100|z|n'10 \rangle|^2}{(E_{n'10} - E_{100})} \tag{67}$$

We get;

$$\alpha' < \frac{16}{3} a_0^3 \tag{68}$$

Where we know that the expectation value $\langle z^2 \rangle = a_0^3$ with a_0 being the Bohr radius. The experimental value for the polarizability [14] is,

$$\alpha' = \frac{9}{2} a_0^3 \tag{69}$$

6-3- $\mathcal{PT}$ Symmetric Perturbation Theory & Stark Effect

In this section we have calculated the energy corrections for the hydrogen atom using the $\mathcal{PT}$ symmetric wavefunction which is given in Equation 27. We know that the Stark effect is described as given in Equation 50. The total Hamiltonian in the non-Hermitian case can be expressed using as,

$$H^g = e^g H e^{-g} \tag{70}$$

$$H^g = e^g (H_0 + H') e^{-g} \tag{71}$$

Where H_0 is the unperturbed Hamiltonian and $H' = e\mathcal{E}z$ is the perturbation as shown in Equation 60. So we get Equation 71 as,

$$H^g = e^g (H_0 + e\mathcal{E}z) e^{-g} \tag{72}$$

Which simplifies to,

$$H^g = e^g H_0 e^{-g} + e\mathcal{E}z \tag{73}$$

Using Equations 27 to 29, we see that Equation 68 can be written as a result from Equation 67 as,

$$\alpha' < |e^{(g+g^*)}|^2 \frac{16}{3} a_0^3 \tag{74}$$

Comparing with Equation 69 it follows that:

$$e^{g(r,\theta,\phi)+g^*(r,\theta,\phi)} = \pm 1 \tag{75}$$

So, if the $\mathcal{PT}$ symmetric wavefunction for the hydrogen atom is defined as in Equation 27, the condition which has to be satisfied is that given in Equation 71. We see that even though we express the Hamiltonian as a non-Hermitian one, we can still express the result from Stark effect if the condition given by Equation 75 is satisfied.

7- Conclusion

There have been numerous studies which describe the application of non-Hermitian quantum mechanics to calculate matrices and eigen values which is an important way to understand the mathematical aspects of quantum mechanics [3, 6, 13].

Our approach to understanding the non-Hermitian quantum mechanics is to understand the well known experimental results in quantum mechanics through the non-Hermitian way which were initially explained using Hemitian properties. In this paper we have shown how to express a $\mathcal{PT}$ symmetric wave function for the hydrgen atom using the radial function and spherical harmonics [10]. Using this wave function we calculated the wavefunction of the hydrogen atom in the $\mathcal{PT}$ symmetric case and we have shown that the multiplicative factor should equal one if the results of the $\mathcal{PT}$ symmetric case should match with the experimental results of Stark effect. Thus, we have shown the conditions under which the $\mathcal{PT}$ symmetric Stark effect can be calculated and compared with experimental result.

8- Acknowledgements

9- Conflict of Interest

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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