Analysis on Perturbation of Ground State Energy for Anharmonic Oscillator and Helium Atom

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Abstract. This paper discusses some practical problems in quantum mechanics, particularly finding solutions of the Schrödinger equation for some cases, as it is a pivotal part of this area. The article focuses on using perturbation theory to calculate the approximate ground state energy for both helium atom and quartic anharmonic oscillator. For the helium atom, conventional perturbation theory is used to solve for the approximate energy, whilst for the anharmonic oscillator, a slightly different approach, that is perturbation theory incorporating a parameter, is chosen to improve the precision of the approximation. The final relative errors for the ground state energy of helium atom model are, for the first order perturbation, 5.3%, and for the second order, 2.4%, and that for the anharmonic oscillator is 0.2%. The study of perturbation theory gives insights into understandings of how it may be modified further to pursue a better level of precision. This facilitates development of new approximation techniques for solving quantum-mechanical issues.

Keywords: Schrödinger equation; perturbation theory; anharmonic oscillator; helium atom.

1. Introduction

Quantum mechanics is a crucial area of modern physics. It describes the dynamics of microscopic particles. In this area, the solution of Schrödinger equation is a problem being discussed much [1]. The Schrödinger equation for most models has no analytic solutions because of their complexity. For example, when a molecule is being considered, there are many types of coupling terms because of different interactions. Thus, looking for approximate solutions has become one of the primary tasks in quantum mechanics.

There are many methods developed by physicists in the last century. In this article, the author uses perturbation theory to approximate the ground state energy for two models. The research is of great importance because the models both have diverse applications. As an example, the anharmonic oscillator can be used to model anharmonic vibrations in molecular systems, where bond stretching deviates from simple harmonic motion, especially at high energies [2]. As for the helium atom model, the research helps gain insights to understanding its spectral lines. Meanwhile, one can test whether the perturbation theory is a good approximation method or not, by comparing the energy calculated using this method and the experimental facts. Furthermore, the perturbation theory can be extended to more complex models, such as lithium atom and quintic anharmonic oscillator.

The article is divided into four sections. The second section introduces the Schrödinger equations for harmonic oscillator and hydrogen atom and their solutions, and also the perturbation theory and how to use it. The third section elaborates on evaluation of approximate solutions of Schrödinger equations for both models using perturbation theory. The last section is the summary of these works and some further discussions.

2. Methods

2.1. Solutions of Schrödinger Equations

The Schrödinger equation is the core equation in quantum mechanics. It describes the conservation of energy for a system. The 3-D time independent Schrödinger equation (TISE) is given by [3]:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) + V(\boldsymbol{r})\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{1}$$

Where $\hbar$the reduced Planck is constant,r is the position vector, $\mathrm{V}(r)$ is the potential and $\psi(\boldsymbol{r})$ is the wavefunction. Usually, the operator:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}) \tag{2}$$

Is called the Hamiltonian, and so the equation can also be written as:

$$\hat{H}\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{3}$$

The 1-D TISE is:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x) \tag{4}$$

Quantum harmonic oscillator (QHO) and Hydrogen atom are both critical models in quantum mechanics. Their wavefunctions can be obtained by introducing their respective potential function, or Hamiltonian, and substitute them in the TISE, so the equation can be solved. For one dimensional QHO, the potential is given by:

$$V(x) = \frac{1}{2}m\omega^2x^2 \tag{5}$$

In which ω is the angular frequency. The TISE therefore reads:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x) \tag{6}$$

The normalized solutions for this equation are:

$$\psi_n(x) = N_nH_n(\xi)e^{-\xi^2/2} \tag{7}$$

Where N_n are the normalization constants, $H_n(\xi)$ are Hermite polynomials, and

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x \tag{8}$$

The corresponding eigenvalues, which represents discrete energy levels, are:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{9}$$

As for the hydrogen atom in a vacuum, the potential function is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0r} \tag{10}$$

Here, e is unit charge and ϵ_0 is the vacuum permittivity. Hence, the TISE is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) - \frac{e^2}{4\pi\epsilon_0r}\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{11}$$

This equation can be solved by separating variables such that $\psi(r) = R(r)Y(\theta,\phi)$, so two new equations are derived. By solving them respectively, and then combining the solutions, one gets the solutions for (10), which are [4]:

$$\psi_{nlm}(r) = N_{nl}e^{-\frac{r}{na_0}}\left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)Y_l^m(\theta,\phi) \tag{12}$$

Where N_{nl} is the normalization constant, a_0 is the Bohr radius, $L_{n-l-1}^{2l+1}(x)$ are Laguerre polynomials, $Y_l^m(\theta,\phi)$ are spherical harmonics and l, m and n are quantum numbers. The energy levels are [4]:

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} \tag{13}$$

2.2. Introduction to Perturbation Theory

The perturbation theory is a mathematical method used in quantum mechanics. It can help approximate the solutions for a rather complex system by starting from a slightly simpler model with an established exact solution. This method is particularly useful when the Hamiltonian can be written as:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \tag{14}$$

Where $\hat{H}^{(0)}$ is the known non-perturbed term, whilst $\hat{H}'$ is the perturbed counterpart. The perturbed term is intended to serve as a small correction to the non-perturbed term. It helps make the solution more precise for the system.

For non-degenerate case, where every energy level corresponds to a particular eigenstate, the eigenvalues and eigenstates can be treated as functions of a parameter λ that represents a measure of perturbation. Hence, Taylor expansion can be employed to both, giving rise to the following expressions:

$$E_n = \sum_{k=0}^{N} \lambda^k E_n^{(k)}, \qquad \psi_n = \sum_{k=0}^{N} \lambda^k \psi_n^{(k)} \tag{15}$$

The upper bound of the summations N depends on the accuracy one wishes to achieve. Usually, the larger N one chooses, the more accurate the solutions are. The 1-D and 3-D expressions for the first order perturbed energy are:

$$E_n^{(1)} = \int \psi_n^{(0)*}(x)\hat{V}\,\psi_n^{(0)}(x)\,\mathrm{d}x, \quad E_n^{(1)} = \int \psi_n^{(0)*}(r)\hat{V}\,\psi_n^{(0)}(r)\,\mathrm{d}r \tag{16}$$

This method is very developed, and generally applicable to cases where the perturbation is small compared to the non-perturbed term.

3. Examples of Perturbation Theory

3.1. Helium Atom

The Atomic Schrödinger equation (ASE) is given by [5]:

$$\left(-\sum_i \frac{\hbar^2}{2m_e}\nabla_\mathrm{i}^2 + V(r_i)\right)\psi(r) = E\psi(r) \tag{17}$$

Where $\mathrm{V(r_i)}$ is the sum of all Coulomb interactions?

$$V(r_i) = \frac{e^2}{4\pi\epsilon_0}\left(\sum_{i>j}\frac{1}{|r_i - r_j|} - \sum_i \frac{Z}{r_i}\right) \tag{18}$$

For the case of a helium atom, ASE is reduced to:

$$\left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{e^2}{2\pi\epsilon_0 r_1} - \frac{e^2}{2\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|}\right)\psi(r) = E\psi(r) \tag{19}$$

Write the Hamiltonian as a combination of non-perturbed and perturbed term:

$$\widehat{H} = \widehat{H}^{(0)} + \widehat{H}' \tag{20}$$

Where particularly, the perturbed term $\widehat{\mathrm{H}}'$ is the Coulomb repulsion between the two electrons:

$$\widehat{H}' = \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} \tag{21}$$

It can be observed that the non-perturbed term can be considered as a sum of two Hamiltonians $\widehat{H}_1^{(0)}$and $\widehat{H}_2^{(0)}$describing an imaginary atom with an electron but $\mathrm{Z} = 2$. Mathematically, this implies that the eigenfunction of $\widehat{H}^{(0)}$ is the product of the eigenfunctions of $\widehat{H}_1^{(0)}$ and $\widehat{H}_2^{(0)}$, and the eigenvalue of $\widehat{H}^{(0)}$ is the sum of eigenvalues of $\widehat{H}_1^{(0)}$and $\widehat{H}_2^{(0)}$. Thus, the symmetric eigenfunctions with eigenvalues $E = E_m + E_n$ are:

$$\psi_S^{(0)}(r_1, r_2) = \psi_m(r_1)\psi_n(r_2), \quad (m = n) \tag{22}$$

$$\psi_S^{(0)}(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_m(r_1)\psi_n(r_2) + \psi_n(r_1)\psi_m(r_2)], \ (m \neq n) \tag{23}$$

The antisymmetric eigenfunctions are:

$$\psi_A^{(0)}(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_m(r_1)\psi_n(r_2) - \psi_n(r_1)\psi_m(r_2)], \ (m \neq n) \tag{24}$$

According to the eigenstate of the time-independent Schrödinger equation (TISE) for hydrogen atom with $Z = 2$ instead of $Z = 1$, the ground state is:

$$\psi_S^{(0)}(r_1, r_2) = \frac{8}{\pi a_0^3} \exp\left[-\frac{2}{a_0}(r_1 + r_2)\right] \tag{25}$$

The corresponding eigenvalue is:

$$\varepsilon_0^{(0)} = -\frac{mZ^2e^4}{32\pi^2\epsilon^2\hbar^2} = -\frac{me^4}{8\pi^2\epsilon^2\hbar^2} \tag{26}$$

This is half of the non-perturbed approximate ground level energy. The first order perturbation correction can be calculated as follows:

$$E_0^{(1)} = \iint \psi_S^{(0)*}(r_1, r_2) \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} \psi_S^{(0)}(r_1, r_2) \, \mathrm{d}\, r_1 \mathrm{d} r_2 \tag{27}$$

Evaluating this integral, the perturbation is found to be:

$$E_0^{(1)} = \frac{5e^2}{16\pi\epsilon_0 a_0} \tag{28}$$

Overall, the first order perturbation approximation ground state energy is:

$$E_0 = E_0^{(0)} + E_0^{(1)} = -\frac{11me^4}{64\pi^2\epsilon_0^2\hbar^2} = -74.8\, eV \tag{29}$$

In an analogous way, one can compute the second order perturbation for the ground state [6]. The result is $E_0 = -77.1\, eV$. According to experimental data, the relative errors for the first order approximation and the second order one are 5.3% and 2.4% respectively.

3.2. Quartic Anharmonic Oscillator

Consider a first order perturbation [7]:

$$\widehat{H}' = \lambda x^4 \tag{30}$$

So the whole Hamiltonian (one dimensional) for this case is:

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2 + \lambda x^4 \tag{31}$$

Usually, Eq. (30) is directly treated as the perturbation for (31). However, a slightly different approach can be employed [8] because it has been verified that this conventional perturbation gives a rather notable error [9]. Introduce a new parameter ω_0, and rewrite (31) as:

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega_0^2 x^2 + \frac{1}{2}m(\omega^2 - \omega_0^2)x^2 + \lambda x^4 \tag{32}$$

The last two terms are now regarded as the new perturbation term. For ground state, the non-perturbed energy is clear:

$$E_0^{(0)} = \frac{1}{2}\hbar\omega_0 \tag{33}$$

The perturbed term can be evaluated in a similar way to (27):

$$\mathrm{E}_0^{(1)} = \int \psi_0^{(0)*}(x)\left[\frac{1}{2}m(\omega^2 - \omega_0^2)x^2 + \lambda x^4\right]\psi_0^{(0)}(x)\ \mathrm{d}x \tag{34}$$

Plugging in (7), this integral then evaluates to:

$$\mathrm{E}_0^{(1)} = \frac{\hbar}{4}\left(\frac{\omega^2}{\omega_0} - \omega_0\right) + \frac{3\lambda\hbar^2}{4m^2\omega_0^2} \tag{35}$$

Since the ground state energy is not a function of the newly introduced parameter, one can write:

$$\frac{\mathrm{d}E_0}{\mathrm{d}\omega_0} = 0 \tag{36}$$

Where $E_0 = E_0^{(0)} + E_0^{(1)}$. Hence, from (33)(35)(36), one derives an algebraic equation about ω_0:

$$\left(\frac{\omega_0}{\omega}\right)^3 - \frac{\omega_0}{\omega} - \frac{6\lambda\hbar}{m^2\omega^3} = 0 \tag{37}$$

Solving this equation and substitute the value of ω_0 in the expression for E_0, the approximate ground state energy is then found. Since the explicit exact solution of (37) is difficult to find out, the final expression is not given here. Particularly, if $\omega_0 = \omega$, the ground state energy is then actually equivalent to the one found using conventional perturbation theory. For a given λ, one can solve for ω_0 numerically. The author has set $\lambda = \frac{m^2\omega^3}{10\hbar}$, so the solution is $\omega_0 = 1.22\omega$. Hence, for ground state, the relative error for energies in this case can be evaluated. For the energy found using conventional perturbation method, the error is around2.8%, and the one found by the method above has the error around 0.2%. Obviously, the relative error is much smaller when the method of introducing a new parameter is employed. It can also be shown that in virtue of this method, the relative error can be much less significant for other choices of λ.

4. Conclusion

The article covered the solutions of Schrödinger equation for quantum harmonic oscillator and hydrogen atom, and the application of perturbation theory on helium atom and quartic anharmonic oscillator. The approximate ground state energy for both circumstances, together with their relative errors when compared to experimental data, were evaluated. From this paper, one can see perturbation theory is generally a fine approximation method for evaluation of ground state energy, and particularly, if one introduces a suitable parameter for the Hamiltonian, the approximation might be even better. Further to this article, there are many other things that can be discussed in this topic, for instance, the author only considered the ground states, but in fact, this method can be used for higher energy levels. Another example would be higher order of perturbations. In this paper, only first order perturbation was elaborated, also, the second order perturbation was mentioned for the helium atom. The third order could be considered for more refined results. The author will do further research on these in the future. With perturbation theory in hand, one can deal with more complicated models, such as diatomic molecules. Overall, the perturbation method has very wide applications in many systems in quantum mechanics, and it will have even brighter future if some slight modification is done to improve it.

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