Parameter Perturbation Method for Helium Ground State Energy Calculation

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Abstract. The ground-state energy is one of the most important pieces of information for research in various fields such as spectroscopy. However, the exact calculation of the value turns out to be challenging, and some approximation methods are needed. This paper is mainly focused on one of the approximations, the parameter perturbation method, and tries to investigate how well the method works to the helium ground-state energy calculation by comparing the approximated results with the experimental result and finding the relationship between the accuracy of the approximation and the orders of perturbation. Other commonly used approximation methods such as perturbation theory and variational principle are also introduced for comparisons and discussions. The paper finds that the parameter perturbation method turns out to be a desirable approach to approximate the helium ground-state energy because the approximated result is relatively easy to calculate and will get extremely close to the experimental result only within a few orders of perturbation. Therefore, the parameter perturbation method could become one of the potential candidates that researchers can use to estimate the energy levels for helium.

Keywords: Helium atom; Ground-state energy; Perturbation method; Harmonic oscillator.

1. Introduction

The energy levels for a quantum system are usually those of the essential things that researchers want to know during their investigations among various fields such as spectroscopy, atomic optics, and molecular engineering. In some cases, the wave equation for the quantum system is actually solvable, and thus researchers could get the exact information about the functional expressions of the eigenstates and their associated energies. The one-dimensional harmonic oscillators with potential $V(x) = m\omega^2 x^2$, for example, would have eigenstates $\psi(x)$ (with corresponding energies $E_n = (n + 1/2)\hbar\omega$) expressed as

$$\psi_n(x) = \frac{1}{\sqrt{n!}}(\hat{a}_+)^n \left[\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}\right], \quad (1)$$

Where the creation operator $\hat{a}_+$ is defined as $\hat{a} = (-i\hat{p} + m\omega x)/\sqrt{2\hbar m\omega}$ [1]. Another solvable example is the hydrogen atom with a Coulomb potential $V(r) = -e^2/4\pi\epsilon_0 r$, where r is the distance of the electron from the nucleus. The energy eigenstates the system can then expressed as three quantum numbers n, l, and m as

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n(n+1)!}} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) \cdot \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^{|m|}(\cos\theta), \quad (2)$$

Where L_{n-l-1}^{2l+1} is the associated Laguerre polynomial, and P_l^m is the associated Legendre function [2]. The corresponding energies for the eigenstates are given by $E_n = -m_e e^4/32\pi^2\epsilon_0^2\hbar^2 n^2$.

In most of other cases, however, it is impossible to get the exact energies through an analytical way, and thus scientists have to develop a variety of methods to approximate the energy levels. Some very common ones include the perturbation theory and the variational principle, but they either require much effort of calculations or only give a rough approximation of the real value. For the calculation of the ground state energy of the helium atom, for example, the perturbation theory has

an error of 5.28% compared to the experimental result in the first order of perturbation [3], while the variational principle has an error of 1.92% [4] if one considers the commonly used test wavefunction with the effective charge and screening parameter σ given by

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{(2-\sigma)^3}{\pi a^3} e^{-\frac{(2-\sigma)(r_1+r_2)}{a}}. \quad (3)$$

Although it is possible to get to higher orders of perturbation theory to acquire more precise results, the calculation usually require a large amount of effort.

In order to deal with these existing problems, scientists have come up with various new approaches, and one of them is the so-called parameter perturbation method, which Zhang, Ning, and Lu proposed in their paper an approach called the parameter perturbation method as a combination of perturbation theory and variational principle to calculate the ground state energy of a helium-like atom [5]. Such a method tends to have several advantages: through a reasonable parameter introduced to the system, the parameter perturbation method could make the perturbed term of the Hamiltonian relatively small such that the result would be fairly precise within only a few orders of perturbation, and further precision can be achieved by making use of the fact that the ground state energy is the lowest possible energy for the system [6]. Moreover, since the wavefunctions in different orders of the parameter perturbation method can be easily constructed in a systematic way via considerations of the symmetry and some other properties of the system, it is convenient to attain different levels of precision by adjusting the number of orders involved without too much calculation difficulty [7]. Although this new method is still unknown to many, its desirable advantages have attracted researchers to apply it to various fields such as the calculations of the ground energies of C^{4+}, N^{5+}, O^{6+}, and Be atoms and those of non-linear harmonic oscillators [8,9]. To investigate how well this new method works for the calculation of helium ground state energy, this paper tries to compare the approximated results with the experimental result and find the relationship between the accuracy of the approximation and the orders of perturbation. The usual methods of perturbation theory and variational principle are also introduced for comparisons and contrasts.

2. Method and Procedures

2.1. Construction of Hamiltonians

The total energy of a helium atom is basically composed of three parts: the kinetic energies of the two electrons, the attractive potential energies between the nucleus and the two electrons, and the repulsive potential energy between the two electrons. Therefore, the total Hamiltonian for a helium atom can be expressed as

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}, \quad (4)$$

Where $\vec{r}_1$ and $\vec{r}_2$ are the positions of the two electrons with respect to the nucleus.

In the usual perturbation theory, the last term of the total Hamiltonian would be treated as the perturbed term $\hat{H}'$, with the rest part as the solvable unperturbed term $\hat{H}_0$. However, one problem to this method is that difference between the calculated energy and the experimentally measured value is very large in the first order, and it is difficult to get greater precision because the higher-order corrections to energy usually contains sums over an infinite number of eigenstates or some other complex formulations and thus requires much effort to do the calculation.

Another commonly used method, which is the variational principle, takes into account the fact that the mutual repulsion of the two electrons will reduce the attraction from the nucleus, causing the screening effect. Therefore, it is reasonable to introduce a unitless screening parameter σ, such that the trial wavefunction would be the combination of two $1s$ state wavefunctions for the hydrogen-like atom with nuclear charge $Z = 2 - \sigma$. The upper bound for the ground state energy of a helium

atom can then be found by minimizing the expectation value of the Hamiltonian $\hat{H}$ in eq. (4) over the trial wavefunction. One problem to this method is that the upper bound derived is rough, which is given by $E_0 \leq -77.5$ eV, compared to the experimental value $E_0 = -79.0$ eV [4, 10]. Also, there is no way to get a more precise result unless some other parameters are introduced or the trial wavefunction is reconstructed, as opposed to the perturbation theory, where it is possible to get as precise as possible as along as enough orders are included in the calculation.

This paper tries to examine a new approach, the parameter perturbation method, which combines both the perturbation theory and the variational principle. The first step is to recognize that if the screening parameter σ is introduced to construct a solvable Hamiltonian for an atom with nuclear charge $Z = 2 - \sigma$ and two non-interactive electrons given by

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{(2-\sigma)e^2}{r_1} - \frac{1}{4\pi\epsilon_0}\frac{(2-\sigma)e^2}{r_2}, \tag{5}$$

The difference between this solvable Hamiltonian and the original Hamiltonian for a helium atom, which is given by

$$\hat{H}' = \frac{1}{4\pi\epsilon_0}\frac{\sigma e^2}{r_1} + \frac{1}{4\pi\epsilon_0}\frac{\sigma e^2}{r_2} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}, \tag{6}$$

Could be relatively small if the screening parameter σ is correctly chosen. Therefore, it is possible to treat the solvable Hamiltonian $\hat{H}_0$ in eq. (5) as the unperturbed term of the total Hamiltonian $\hat{H}$ in eq. (4), while the rest part $\hat{H}'$ in eq. (6) can be treated as the perturbed term. The next step would be applying the perturbation theory to the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'$.

2.2. Construction of Wavefunctions

According to the Hamiltonian constructed in section 2.1, the spatial part of the zeroth order ground state wavefunction, which is a solution to the wave equation $\hat{H}_0\psi = E\psi$ ($\hat{H}_0$ defined in eq. (5)), is the same as the formerly introduced trial wavefunction used in the variational principle given by

$$\psi^{(0)} = \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2) = \frac{(2-\sigma)^3}{\pi a^3} e^{-\frac{(2-\sigma)(r_1+r_2)}{a}}, \tag{7}$$

Where ψ_{1s} is the ground state spatial wavefunction of a hydrogen-like atom with nuclear charge $Z = 2 - \sigma$, and a is the Bohr radius for a hydrogen atom. For the wavefunction in the higher nth order, it is assumed that the helium atom is in a certain excited state with non-interacting electrons and nuclear charge $Z = 2 - \sigma$, such that one electron is still in the $1s$ state of a hydrogen-like atom, while the other is in the nth excited s state of a hydrogen-like atom. It is important to note that since the two electrons are in the anti-symmetric spin singlet state $|0\ 0\rangle$, in order to make the total wavefunction to be anti-symmetric (as required for two identical fermions like electrons), the spatial part of the wavefunction has to be in a symmetric form. Therefore, the wavefunctions in the first three orders can be constructed as:

$$\psi^{(1)} = \frac{1}{\sqrt{2}}[\psi_{1s}(\vec{r}_1)\psi_{2s}(\vec{r}_2) + \psi_{2s}(\vec{r}_1)\psi_{1s}(\vec{r}_2)], \tag{8}$$

$$\psi^{(2)} = \frac{1}{\sqrt{2}}[\psi_{1s}(\vec{r}_1)\psi_{3s}(\vec{r}_2) + \psi_{3s}(\vec{r}_1)\psi_{1s}(\vec{r}_2)], \tag{9}$$

$$\psi^{(3)} = \frac{1}{\sqrt{2}}[\psi_{1s}(\vec{r}_1)\psi_{4s}(\vec{r}_2) + \psi_{4s}(\vec{r}_1)\psi_{1s}(\vec{r}_2)], \tag{10}$$

Where $\psi_{ns}(\vec{r})$ is the spatial wavefunction for the ns state of a hydrogen-like atom given by

$$\psi_{ns}(\vec{r}) = \sqrt{\frac{(2-\sigma)^3}{\pi n^5 a^3}} e^{-\frac{(2-\sigma)r}{na}} L_{n-1}^1 \left[\frac{2(2-\sigma)r}{na}\right], \tag{11}$$

Where $L_{n-1}^1(x)$ is the associated Laguerre polynomial given by

$$L_{n-1}^1(x) = -\frac{e^x}{(n-1)!}\left(\frac{d}{dx}\right)^n (e^{-x}x^{n-1}) \tag{12}$$

The next step is to calculate the energy in each order and find an estimated value for the ground state energy of a helium atom.

2.3. Energy Calculation

According to the constructed wavefunctions, the zeroth order energy can be derived from the ground state energy for a hydrogen-like atom as

$$E^{(0)} = 2E_n(Z = 2-\sigma) = -\frac{m_e}{\hbar^2}\left[\frac{(2-\sigma)e^2}{4\pi\epsilon_0}\right]^2 \cong -(2-\sigma)^2 \cdot 27.20 \text{ eV} \tag{13}$$

The energy corrections in higher orders can be calculated as

$$E^{(n)} = \langle\psi_0|\hat{H}'|\psi_{n-1}\rangle \ (n \neq 0) \tag{14}$$

With $\hat{H}'$ defined in eq. (6). After the summation of the energies in all the orders, the total energy would be a function with respect to the screening parameter σ, and the estimated value of the ground state energy for a helium atom is the minimum possible total energy calculated by setting $dE_{total}/d\sigma = 0$. This paper is going to investigate how the number of orders of corrections included in the total energy would affect the precision of the result relative to the experimental value, as well as to compare the results with that got in the usual perturbation theory and the variational principle.

3. Results

Based on the calculation of the inner product $\langle\psi_0|\hat{H}'|\psi_{n-1}\rangle$ $(n \neq 0)$, the energy corrections in the first four orders are given by

$$E^{(1)} = \left(\frac{5}{8} - 2\sigma\right)\frac{2-\sigma}{a}\frac{e^2}{4\pi\epsilon_0} \tag{15}$$

$$E^{(2)} = \left(\frac{8192}{64827} - \frac{8}{27}\sigma\right)\frac{2-\sigma}{a}\frac{e^2}{4\pi\epsilon_0} \tag{16}$$

$$E^{(3)} = \left(\frac{1269\sqrt{6}}{50000} - \frac{\sqrt{6}}{16}\sigma\right)\frac{2-\sigma}{a}\frac{e^2}{4\pi\epsilon_0} \tag{17}$$

$$E^{(4)} = \left(0.039042 - \frac{216\sqrt{2}}{3125}\sigma\right)\frac{2-\sigma}{a}\frac{e^2}{4\pi\epsilon_0} \tag{18}$$

The total energy of various precisions can be obtained by summing the energy corrections up to different orders. The estimated value for the ground state energy of a helium atom is then derived from the equation $dE_{total}/d\sigma = 0$. If the screening parameter σ is set to be 0, the result would be the ground state energy calculated by the usual perturbation theory up to different orders of corrections. All the calculations are summarized by the table below.

Table 1. Ground State Energy Calculated by Three Different Methods (Experimental Value $= -79.00515$ eV) [10]

Orders	Parameter perturbation method			Usual Perturbation Theory $(\sigma = 0)$		Usual Variational Principle
	Total Energy (eV)	σ value	Difference from the Experimental Value	Total Energy (eV)	Difference from the Experimental Value	Total Energy: -77.489 eV [4]
1	-77.489	0.3129	1.92%	-74.831[3]	5.28%	Difference from the Experimental Value: 1.92%
2	-77.409	0.5184	2.02%	-79.121*[11]	-0.15%	
3	-78.313	0.5909	0.88%			
4	-79.093	0.6294	-0.11%			

*The value is calculated by Hylleraas's method using a wavefunction containing 24 terms

As Table 1 shows, the estimated ground state energy derived from the parameter perturbation method is exactly the same in the first order as that derived from the usual variational principle and can achieve a great precision of 0.11% by only four orders calculations. Although roughly the same amount of precision could be obtained from the usual perturbation theory within only two orders using Hylleraas's method, the second order correction to the ground state energy is much more difficult to calculate than four orders of parameter perturbation method because the wavefunction involved is much more complicated. Given all these results, it is clear that the parameter perturbation method is a desirable approximation approach that possesses the strengths of both perturbation theory and variational principle: it could achieve about the same level of precision as that of the perturbation theory and is easy to calculate just like the variational principle. On the other hand, the parameter perturbation method also suggests its potence in terms of the fact that it could generate more precise results than the variational principle and avoid the calculation complexity of the perturbation theory.

Nevertheless, there are also some limitations to the parameter perturbation method. It is important to note that for the parameter perturbation method, higher orders do not necessarily imply greater precision because the result in the second order is obviously less precise than that in the first order. As a result, it is not guaranteed that this method would behave like the usual perturbation theory in terms of the property that an arbitrary amount of precision can be achieved by including sufficient number of orders. Since the result in the fourth order of the parameter perturbation method is lower than the experimental value, this method would not necessarily generate an upper bound for the ground state energy as the variational principle does even though this method includes some ideas variational principle.

4. Conclusion

This paper finds that the parameter perturbation method turns out to be a desirable method to find the ground state energy of a helium atom because the result is relatively easy to calculate and can achieve a precision as great as 0.11% only within four orders of correction. These attractive properties of the parameter perturbation method are generally derived from the fact that this method combines the merits of perturbation theory and variational principle and avoids the defects of the two. Just like the usual perturbation theory, the parameter perturbation method makes it possible to easily adjust the precision of the result by changing the total number of orders calculated, while it is difficult for the variational principle to attain greater precision unless new wavefunctions or new parameters are introduced. On the other hand, the parameter perturbation method resembles the variational principle in terms of the fact that it is relatively easy to construct a set of trial wavefunctions through some simple and reasonable assumptions, and the result are simply obtained by setting the derivative of the total energy with respect to the parameter to zero. Therefore, the parameterized perturbation theory

tends to require less calculation effort than the usual perturbation theory, where infinite sums over eigenstates or some other complex formulations are needed for the second order or higher. Given all these strengths of the parameter perturbation method, this method could become one of the potential methods for researchers to estimate the energy levels for a helium atom.

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