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Calculations of Energies of Atoms (H, He) by Variational Method in Linear and Nonlinear Approximations

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Abstract:

The exact solution the wave function of several particles is not possible so in this research the Variational method has been used in linear and non linear approximation. The linear Hamiltonian operator was obtained from the Schrodinger equation whereas the non linear Hamiltonian operator was obtained from Gross-Pitaevskii equation. These linear and non linear Hamiltonian operators were used in the Varational method to calculate the ground state energy of the wave function of atoms (H, He). From linear and non linear *approximation result, the new difference in the ground state energy of atoms was obtained. This gave us the new difference between the energies of different wave functions. From our theoretical result, the changes in energies were due to nonlinear behavior of particles and particularly in bosons particles.*

Key words: state energy, celestial body, wave function, Hamiltonian, nonlinearity

1. Introduction

The Variation method is one of the most useful approximation method in estimating the energy eigen values of the ground state and the first few excited states of a system which we only have a qualitative idea about the wave function. When the system contains a single particle the exact solution of Schrodinger wave equation is possible, as in the case of hydrogen like atom. However, if several particles are involved, the exact solution is not possible and approximation methods are used. The variation method is most useful in the treatment of chemical bonding. The Variation method is one of the most useful approximation method in estimating the energy eigen values of the ground state and the first few excited states of a system which we only have a qualitative idea about the wave function.

From Schrodinger equation we have

$$E = \frac{\int \Psi^* H \Psi \mathrm{dV}}{\int \Psi^* \Psi \mathrm{dV}} \qquad (1)$$

We can find the energy of any known wave function by using the above equation. According to the variation principle it can be shown that if Ψ_0 is the correct wave function for a system whose correct energy is E_0, then any other acceptable wave function Ψ_i will give energy greater than E_0. Therefore any energy E_i, obtained from a wave function Ψ_i, will be greater than E_0; although it is not a correct wave function, it will at least, tell us which of the several trial wave functions is close to the true wave function in the series of giving the best energy.

Schrodinger [1] first formulated the new mechanics as a variational principle and for many purposes, particularly where approximate solutions are being sought, this is the most convenient form of the theory to use.

The Schrodinger differential equation describes the motion of the wave packet $\Psi(r,t)$. The wave associated with a free moving non relativistic particle of well defined momentum "P" and energy "E" is represented by

$$\Psi(r,t) = Ae^{\frac{i(r.P-Et)}{\hbar}} \qquad (2)$$

Where $P = \hbar K$ and $E = \hbar\omega$, K is propagation vector and ω is angular velocity.

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(r,t) \qquad (3)$$

Equation (3) is the discrete Schrodinger wave equation for free particle in the non-relativistic approximation. Where ∇^2 is the Laplacian operator.

In the case of external forces that may be acting on the particle, we assume that these forces such that they are derivable from a real P.E function $V(r)$. i.e $F = -\nabla V$

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right\}\Psi(r,t) = i\hbar\frac{\partial\Psi(r,t)}{\partial t} \qquad (4)$$

The above equation describes the motion of the particle of mass "m" in a force field ($F = -\nabla V$) and it can also be written as

$\hat{H}\Psi = \hat{E}\Psi$.

Where $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$, $\hat{E} = i\hbar\frac{\partial}{\partial t}$ and $\hat{H}$ is called linear Hamiltonian operator which gives the total energy of the particle when operates on Ψ.

Within the dilute limit, the assumption that only two particles participate in any single scattering event is consistent with the assumption that the characteristic length scales of the system are much larger than the range of the particle scattering potential. Thus we have calculated the matrix elements using any alternate theory which accurately reproduces the effects of the particle interactions at the macroscopic scale.

Our interest lies not with the microscopic details of the scattering, but instead with the macroscopic effects of the scattering on the mode amplitudes. Thus rather than considering matrix elements in terms of the scattering potential, we can treat the scattering in terms of the two-body matrix, which gives the probability amplitude that a scattering event between two particles will lead to transitions into a particular set of modes. The non linear Hamiltonian is obtained by treating the scattering in terms of a two-body matrix, rather than via the bare interaction potential. Thus the contact potential is introduced not as a direct approximation to the interaction potential but rather as a form of two-body operator.

The nonlinear Schrodinger equation is derived independently by Gross [2] and Pitaevskii [3,4]. The Gross-Pitaevskii equation (GPE) has proven extremely successful in reproducing many experimentally observed Bose-Einstein condensate behaviors, yet it fails to account for the quantum-statistical effects required for treating spontaneously initiated processes[5,6].

In addition, Hamiltonian operator of the time-independent GPE is used to calculate the ground state of different wave functions. It is therefore both useful and instructive to devote some space to this very successful equation.

The Gross-Pitaevskii equation is the same as Schrodinger equation but with addition of an interacting term and G.P.E. is nonlinear equation. The coupling constant V_0 which is proportional to the scattering length of two bosons a_s .

$$V_0 = \frac{4\pi\hbar^2 a_s}{m} \qquad (5)$$

Where $\hbar$ Plank's constant and m is the mass of the boson.
The time dependent G.P.E is

$$i\hbar\frac{\partial\Psi(r)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(r) + V(r)\Psi(r) + V_0|\Psi(r)|^2\Psi(r) \qquad (6)$$

In the case of G.P.E the Hamiltonian operator becomes nonlinear

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) + V_0|\Psi(r)|^2 \qquad (7)$$

2. Case of Linear Hamiltonian

Linear method is one of the familiar methods to find the solution of any mathematical equation or physical system. This method gives us an exact solution. The ground state energy of the atoms can be calculated with the help of linear Schrodinger equation.

Here the linear Hamiltonian operator is used. i.e. $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$,

2.1 Hydrogen Atom

In this case the wave function is of the general form

$$\Psi(r) = e^{-ar} \qquad (8)$$

For the ground state of hydrogen atom, the potential energy will be $-\frac{e^2}{r}$ and hence the value of Hamiltonian operator will be

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \qquad (9)$$

According to the variation method (2.1) the energy of hydrogen atom can be calculated as

$$E = \frac{\int e^{-ar}(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r})e^{-ar}dV}{\int e^{-ar}e^{-ar}dV}$$

Where $dV = 4\pi r^2 dr$ is the volume of spherical shell at distance r and $r + dr$ from the nucleus. The limit of integration varies from 0 to ∞ as r goes from zero to infinity. As the energy occurs in the radial equation, we need only to consider the radial part of the Laplacian operator ∇^2.

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

And also the volume element in the radial case will be $4\pi r^2 dr$. So the energy equation for hydrogen will be

$$E = \frac{\hbar^2 a^2}{2m} - e^2 a \qquad (10)$$

Now we choose $"a"$ in such a manner as to give a minimum energy. Thus equation

(10) implies that

$$\frac{\partial E}{\partial a} = \frac{\hbar^2 a}{m} - e^2 = 0$$

$\Rightarrow \quad a = \frac{me^2}{\hbar^2}$, Substituting the value of $"a"$ in equation(10), we get

$$E = -\frac{me^4}{2\hbar^2} \qquad (11)$$

This is the ground state energy of hydrogen atom.

2.2 Helium Atom

The Schrodinger equation of hydrogen atom can be solved exactly, but the Schrodinger equation of helium atom cannot because it is a three body problem but the Variational method can be used to obtain the ground-state energy of helium atom in the normal state. The helium atom consist of a nucleus of charge +Ze (Z=2) and two electrons each of charge –e as shown in figure 1.

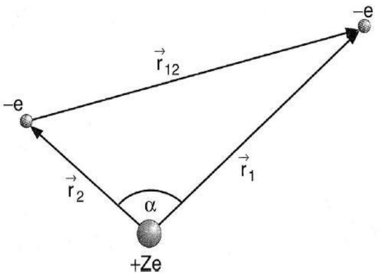

Fig: 1

In this case the trial wave function is of the general form

$$\Psi(r_1, r_2) = \Psi_1(r_1)\Psi_2(r_2)$$

Where $\Psi_j(r_j) = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{Z r_j}{a_0}}$ *j=1, 2……*

and the total wave function is $\Psi(r_1, r_2) = \frac{Z^3}{\pi a_0^3} e^{-\frac{Z(r_1+r_2)}{a_0}}$ where $a_0 = \frac{\hbar^2}{me^2}$

The potential energy of the system is given by

$$V(r) = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \qquad (12)$$

In which r_1 and r_2 are the distances of electrons from the nucleus and r_{12} is the separation of two electrons. The Hamiltonian operator is given by

$$H = -\frac{\hbar^2}{2m}(\nabla^2{}_1 + \nabla^2{}_2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

First we calculate $H\Psi$ and consider the first two terms.

$$\left[-\frac{\hbar^2}{2m}\nabla^2{}_1 - \frac{Ze^2}{r_1}\right]\Psi = \left[-\frac{\hbar^2}{2m}\nabla^2{}_1 - \frac{Ze^2}{r_1}\right]\frac{Z^3}{\pi a_0^3} e^{-\frac{Z(r_1+r_2)}{a_0}}$$

$$= \left[-\frac{\hbar^2}{2m}\left\{\frac{1}{r_1^2}\frac{\partial}{\partial r_1} r_1{}^2 \frac{\partial}{\partial r_1}\right\} - \frac{Ze^2}{r_1}\right]\frac{Z^3}{\pi a_0^3} e^{-\frac{Z(r_1+r_2)}{a_0}}$$

$$= -\frac{Z^2\hbar^2}{2m{a_0}^2}\left[\frac{Z^3}{\pi {a_0}^3} e^{-\frac{Z(r_1+r_2)}{a_0}}\right]$$

Similarly we can calculate

$$\left[-\frac{\hbar^2}{2m}\nabla^2{}_2 - \frac{Ze^2}{r_2}\right]\Psi = \left[-\frac{\hbar^2}{2m}\nabla^2{}_2 - \frac{Ze^2}{r_2}\right]\frac{Z^3}{\pi {a_0}^3} e^{-\frac{Z(r_1+r_2)}{a_0}}$$

$$= -\frac{Z^2\hbar^2}{2m{a_0}^2}\left[\frac{Z^3}{\pi {a_0}^3} e^{-\frac{Z(r_1+r_2)}{a_0}}\right]$$

So we get

$$H\Psi = \left[2\left(-\frac{Z^2\hbar^2}{2m{a_0}^2}\right) + \frac{(Z-2)e^2}{r_1} + \frac{(Z-2)e^2}{r_2} + \frac{e^2}{r_{12}}\right]\frac{Z^3}{\pi {a_0}^3} e^{-\frac{Z(r_1+r_2)}{a_0}}$$

Although it is not easy to estimate the inaccuracy in the function so obtained, something can be said about the energy values [7, 8].

It can be shown that the characteristic solutions of given wave function for energy is

$$E = \int \Psi^* H\Psi \mathrm{dV}$$

$$E = \int \Psi^*\left(-\frac{Z^2\hbar^2}{m{a_0}^2}\right)\Psi dV + \int \Psi^*(Z-2)e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\Psi dV + \int \Psi^*\frac{e^2}{r_{12}}\Psi dV$$

$$E = \left(Z^2 - \frac{27}{8}Z\right)\frac{me^4}{\hbar^2}$$

For minimum values $\frac{\partial E}{\partial Z} = 0$ which implies that $Z = \frac{27}{16} < 2$

So

$$E = -2.8477\frac{me^4}{\hbar^2} \qquad (13)$$

3. Case of Non Linear Hamiltonian

In this case of the G.P.E has been used to derive the Hamiltonian operator which becomes non linear.

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) + V_0|\Psi(r)|^2$$

3.1 Hydrogen Atom

We consider the hydrogen atom as system of two interaction point particles (nucleus and electron). The interaction arises due to Coulomb attraction of electric charges. Let the charge on nucleus be Ze, and the charge on electron is $-e$. The non linear Hamiltonian for hydrogen atom is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} + V_0|e^{-ar}|^2 \qquad (14)$$

From the variation method the energy can be calculated as

$$E = \frac{\int e^{-ar}(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} + V_0|e^{-ar}|^2)e^{-ar}dV}{\int e^{-ar}e^{-ar}dV}$$

Applying the relation $\int_0^\infty x^n e^{-ax}dx = \frac{\Gamma(n+1)}{a^{(n+1)}}$

Where $\Gamma(n) = (n-1)!\Gamma(n) = (n-1)!$

$$E = \frac{\hbar^2 a^2}{2m} - e^2 a + \frac{V_0}{8} \qquad (15)$$

As $= \frac{me^2}{\hbar^2}$, Substituting the value of "a" in equation(13), we get

$$E = -\frac{me^4}{2\hbar^2} + \frac{V_0}{8}$$

Where $V_0 = V_{0(H)} = \frac{4\pi\hbar^2 a_{+-}}{m_H}$ and a_{+-} is the scattering length for hydrogen atom.

So the ground state energy for hydrogen atom in the case of non linear Hamiltonian is

$$E = -\frac{me^4}{2\hbar^2} + \frac{\pi\hbar^2 a_{+-}}{2m_H} \qquad (16)$$

3.2 Helium Atom

The helium atom is a system of three interaction point particles - nucleus and two electrons. The interaction arises due to

Coulomb attraction of electric charges. Let the charge on nucleus be Ze, and the charge on each electron is $-e$ s shown in figure. The potential energy of the system in the absence of external field is $-\frac{2e^2}{r_1}-\frac{2e^2}{r_2}+\frac{e^2}{r_{12}}$, in which r_1 and r_2 are the distances of electrons from the nucleus and r_{12} is the separation of two electrons. The non linear Hamiltonian for helium atom is

$$H=-\frac{\hbar^2}{2m}(\nabla^2{}_1+\nabla^2{}_2)-\frac{2e^2}{r_1}-\frac{2e^2}{r_2}+\frac{e^2}{r_{12}}+V_0|\Psi(r_1,r_2)|^2$$

All calculations are same except non linear term.

$$\int \Psi^* g|\Psi(r_1,r_2)|^2\Psi dV=\int_0^\infty g\left(\frac{Z^3}{\pi a_0{}^3}\right)^4 e^{-4Z\frac{(r_1+r_2)}{a_0}}4\pi r_1{}^2dr_1\times 4\pi r_2{}^2dr_2$$

$$=\left(\frac{Z^3}{\pi a_0{}^3}\right)^4\times g(4\pi)^2\int_0^\infty e^{-4Z\frac{r_1}{a_0}}r_1{}^2dr_1\times\int_0^\infty e^{-4Z\frac{r_2}{a_0}}r_2{}^2dr_2$$

Applying the relation $\int_0^\infty x^n e^{-ax}dx=\frac{\Gamma(n+1)}{a^{(n+1)}}$

Where $\Gamma(n)=(n-1)!$

$$=V_0\frac{Z^6}{64\pi^2a_0{}^6}=V_0\frac{Z^6\mathrm{m}^6\mathrm{e}^{12}}{64\pi^2\hbar^6}$$

Where $a_0=\frac{\hbar^2}{me^2}$ So the by summarizing we get net result

$$E=\left(Z^2-\frac{27}{8}Z\right)\frac{me^4}{\hbar^2}+V_0\frac{Z^6\mathrm{m}^6\mathrm{e}^{12}}{64\pi^2\hbar^6}$$

As $Z=\frac{27}{16}$ So we get

$$E=-2.8477\frac{me^4}{\hbar^2}+V_0\left(\frac{27}{16}\right)^6\frac{\mathrm{m}^6\mathrm{e}^{12}}{64\pi^2\hbar^6}$$

Where $V_0=V_{0(He)}=\frac{4\pi\hbar^2(2a_{+-}+a_{--})}{m_{He}}$

Where a_{+-} is the scattering length for electron and proton pair, and a_{--} is the scattering length for electron electron pair in helium atom.

$$E = -2.8477\frac{me^4}{\hbar^2} + \left(\frac{27}{16}\right)^6 \frac{(2a_{+-} + a_{--})}{m_{He}}\left(\frac{m^6e^{12}}{16\pi\hbar^4}\right) \qquad (17)$$

4. Results

The differences between the linear and non linear methods for the ground state energies calculation of hydrogen and helium atom are found.

For hydrogen atom

$$\Delta E_H = \frac{\pi\hbar^2 a_{+-}}{2m_H}$$

and for helium atom

$$\Delta E_{He} = \left(\frac{27}{16}\right)^6 \frac{(2a_{+-} + a_{--})}{m_{He}}\left(\frac{m^6e^{12}}{16\pi\hbar^4}\right)$$

We have seen the difference between these energies calculated by Schrodinger equation and by the Gross-Pitaevskii equation as given. This gives us the new difference between the energies of different wave functions. These new differences of the ground state energy may tell us which method is good to find the accurate energies of different wave functions.

The linear Schrodinger equation and non linear Gross-Pitaevskii equation have been used to find the ground state energy of various wave functions as discussed. By using non linear Hamiltonian, it is clear that there is one additional term in each case, this term may give the precise value of energy which may be close to the experimental value.

In the recent research in physics and mathematics, the researchers have keen interest to find the exact solution of non linear equation and they can not find the exact solutions of non linear equations. The researchers have used some physical conditions to find the approximate solutions of non linear equations. So here we conclude that our research gives some important calculation by using non linear equations and these

important calculations have been calculated first time.
This change in energy is due to nonlinear behavior of particles which is found at a very low temperature, i.e.$T = 2mK$ in Bose Einstein condensation.

As the slowing of atoms by the use of cooling produces a singular quantum state, this is known as a Bose condensate or Bose–Einstein condensate. The result of the struggle of Bose and Einstein is based on the concept of a Bose gas which is governed by the Bose Einstein statistics and that describes the statistical distribution of indistinguishable particles with integer spin and well known as bosons. The boson particles consist of the photons as well as atoms such as helium-4 and they are allowed to share quantum states with each other. Einstein speculated that the bosonic atoms cooling to a very low temperature would cause them to fall (condense) into the very low quantum state and in resulting this, the concept of a new form of matter would appear.

In Bose Einstein condensation at very low temperature all atoms go to single state and become one atom which is called super atom. There is too much interaction between the particles at this single state due to which the above change in energy may occur.

Our research is theoretical and in future these results may be verified experimentally. Methods used for the ground state energy calculation of Helium atom can extend to solving many-electron atoms.

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