Quantum Defects in Hooke's Atom

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1 Introduction

In quantum mechanics there are few systems in which the allowable energies can be calculated exactly. An example of such a system is the hydrogen atom. Most sytems are far more complex involving many interacting particles. Calculating the exact allowable energies for an electron in a complex system consisting of many interacting particles is often impossible and can become quite complex even when using various approximation methods . A solution to this problem is to view the complex system as a more simple system. A theory know as Quantum Defect Theory has been formulated to do just this. In Quantum Defect Theory, the highly-excited states for a single electron in an atom have been related to the electron energies of a hydrogen atom via a parameter which is known as the "quantum defect" [1, 2].

Though currently there is a good basic understanding of the quantum defect, quantum defects have only been calculated for atoms. Thus, there is a need to calculate and understand the "quantum defects" of different systems. In particular, one system of interest is Hooke's atom [3]. Hooke's atom is essentially a three-dimensional harmonic oscillator. It is a relatively simple simple system consisting of two interacting electrons in a potential well. The energies of a simple harmonic oscillator can easily be calculated. However,this is not true of the more complex Hooke's atom. But for very highly excited states of one electron, the system can be viewed as a system of two non-interacting electrons. Hence, quantum defect theory for the Hooke's atom system can be formulated where the energies of the excited electron can be written in the same form as the harmonic oscillator energies, but with a quantum defect parameter. Furthermore, studying the Hooke's atom system will help to provide a clearer picture of how complex quantum systems act.

2 Quantum Defect Theory

In Quantum Defect Theory the true energies of a singly excited many electron system are comparable to the energies of an appropriate one-electron system. Traditionally, Quantum Defect Theory was formulated for the Rydberg atoms [4, 5]. Rydberg atoms are atoms in which there is one electron in a highly excited state. When the electron is in this state, the electron's orbit or energy level will be very far away from the rest of the atom , and the systems acts as a hydrogenic atom. Thus, the energy states of the electron will deviate from the energies of a hydrogenic atom via the quantum defect parameter,

$$E_n = -\frac{1}{(n-\mu_{n,l})^2}, \tag{1}$$

where $\mu_{n,l}$ is the quantum defect. Here the quantum defect depends on the n and l quantum numbers, and decreases with increasing the quantum numbers. In fact, for Rydberg atoms, the quantum defect will converge to a finite number [1, 6, 7].

In general, the quantum defect for a system can be found for a single excited electron in a complex system, when the potential of the complex system differs from the potential of a simple one-electron system only at short distances. The eigenvalues of the more complex system can be written in the same form as the simple system, but including the quantum defect, this can be thought of as replacing the n quantum number with an effective quantum number.

An expression for the quantum defect may be derived semiclassically from the action and the Bohr-Sommerfield quantization condition [1, 8]. The action of a system is defined to be

$$S(E) = 2\int_a^b \sqrt{2m(E - V(r))}dr, \tag{2}$$

and the Bohr-Sommerfield quantization condition is

$$S(E) = 2\pi\hbar(n + \alpha). \tag{3}$$

The parameter α in the quantization conditions comes from the number of classical turning points in the potential. For the hydrogen atom, $\alpha = 0$ and for the harmonic oscillator, $\alpha = \frac{1}{2}$. The quantum defect is calculated by looking at the difference in the action in the true potential and the one-electron potential.

3 Hooke's Atom

Hooke's atom is a two particle system; it consists of two interacting electrons in a harmonic potential. Though Hooke's atom does not exist in nature, it can be used as a model for "quantum dots" in semiconductors.

The Hamiltonian for the system in spherical coordinates is

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}kr_1^2 + \frac{1}{2}kr_2^2 + \frac{1}{|r_1 - r_2|}, \tag{4}$$

where r_1 and r_2 are the distances from the center of the two electrons. Using the Schrödinger equation,

$$\hat{H}\Psi(r_1, r_2) = E\Psi(r_1, r_2), \tag{5}$$

the energy eigenvalues E can be found and $\Psi(r_1, r_2)$ is the wavefuntion. However, equation (6) is not seperable in this form, which makes the calculation rather difficult. Therefore, it is convenient to make a change variables to $R = \frac{r_1+r_2}{2}$ and $u = r_2 - r_1$, which are the center of mass and relative coordinates respectively. With this change of variables the equation (6) becomes

$$\hat{H}\Psi(R, u) = E\Psi(R, u) \tag{6}$$

and now the equation is separable, i.e. $\Psi(r_1, r_2) = \Psi(R, u) = \Phi(R)\varphi(u)$. The focus will be on examining the states where the angular momentum $l = 0$. After some straighforward algebra, the Schrödinger equation is separated into the following two differential equations ,

$$\left[-\frac{1}{4}\nabla_R^2 + kR^2]\Phi(R) = E_R\Phi(R)\right] \tag{7}$$

and

$$\left[-\nabla_u^2 + \frac{1}{4}ku^2 + \frac{1}{u}\right]\varphi(u) = E_u\varphi(u). \tag{8}$$

The eigenvalues E_R are known for the first equation; they are the eigenvalues for the three-dimensional harmonic oscillator. However, the eigenvalues for the second equation need to be calculated.

3.1 Methods of Calculation

The calculation of the eigenvalues for the relative coordinate part of Hooke's atom will be done for the case of angular momentum $l = 0$. Though there are analytic solutions for certain values of k, the majority of the calculations are done by using numerical methods to solve the differential equation. This way the energy eigenvalues can be calculated for any value of k.

In order to carry the numerical calculations, it is convenient to make another change of variables, $x = \frac{u}{u_0}$ where $u_0 = \sqrt{\frac{2}{\omega}}$. Then the equation (8) becomes

$$\left(-\frac{d^2}{dx^2} - \frac{2}{x}\frac{d}{dx} + x^2 + \sqrt{\frac{2}{\omega}}\frac{1}{x}\right)\varphi(x) = \varepsilon\varphi(x), \tag{9}$$

where the energy eigenvalues have been scaled, $\varepsilon = \frac{2E}{\omega}$. The numerical method that was used to calculate the energy levels was the fourth order Runge-Kutta method [9]. Given a first order differential equation y' with an initial condition,

$$k_1 = hf(x_n, y_n), \tag{10}$$

$$k_2 = hf(x_n + \frac{h}{2}, y_n + \frac{k_1}{2}), \tag{11}$$

$$k_3 = hf(x_n + \frac{h}{2}, y_n + \frac{k_2}{2}), \tag{12}$$

$$k_4 = hf(x_n + h, y_n + k3), \tag{13}$$

where h is the step size and $f(x, y)$ is the derivative (y'). Given the initial condition y_n, y can be calculated approcimately at the next point,

$$y_{n+1} = y_n + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} + O(h^5). \tag{14}$$

Hooke's atom is described by a second order differential equation, so it will be necessary to write equation (8) as a set of coupled first-order differential equations in order to use the Runge-Kutta method. The initial conditions for the system are $\varphi(0) = 1$, and $\varphi'(0) = \frac{1}{2}\sqrt{\frac{2}{\omega}}$. These initial conditions are determined by looking at the power series expansion solution for $\varphi(x)$.

By looking at equation (8), one can see that when solving it, there will be a dependence on ε. Therefore, in order to determine which ε's are eigenvalues, another condition is necessary. This condition is that it is desireable that the wavefunction φ tend to zero as x tends to infinity. Hence, one will need to scan through energy values in order to find the eigenvalue. One will find that wavefunction will diverge quite quickly to eitherpositive or negative infinity when ε is not an eigenvalue, and the true eigenvalue will lie between a positive and negative divergence. Thus, it is possible to “zoom in” on the correct eigenvalue, this method is known as the Shooting Method [9]. Varying degrees of accuracy can obtained for the eigenvalues depending on the step size that is chosen and how quickly φ is expected to approach zero. To better illustrate how the shooting method works refer to fig.3.1, which shows how when ε is greater than and less than the correct eigenvalue, the wavefunction diverges quickly, and when ε is equal to the eigenvalue, the wavefuntion goes to zero for large x values.

4 Quantum Defect in Hooke's Atom

To determine the quantum defect of Hooke's atom, the three-dimensional harmonicoscillator is chosen as the one-electron system with comparable energy levels [10]. The Hamiltionian for the 3-D harmonic oscillator in spherical coordinates is

$$\hat{H} = -\frac{1}{2}\nabla_r^2 + \frac{1}{2}kr^2, \tag{15}$$

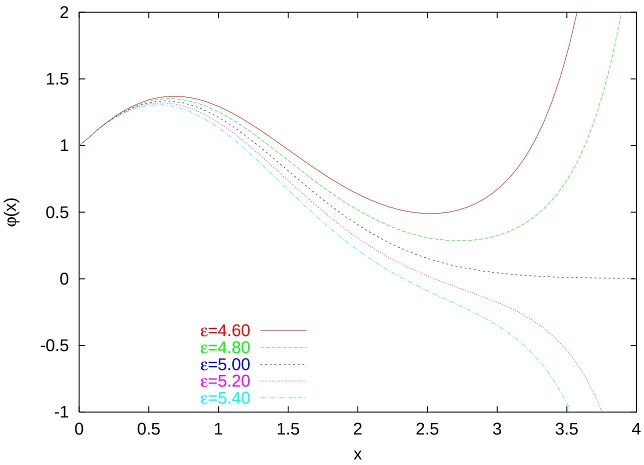

Figure 1: Illustration of the shooting method: $\varepsilon = 5$ is the true energy eigenvalue, and for values greater than or less than this φ diverges.

and the energies can be calculated exactly,

$$E_{n,l} = (2n + l + \frac{3}{2})\omega. \tag{16}$$

From looking at the form of the energies of the 3-D harmonic oscillator, one may write the energies of Hooke's atom in a similar form including the quantum defct μ,

$$E_{n,l} = \left(2(n - \mu) + l + \frac{3}{2}\right)\omega. \tag{17}$$

Again the focus will be on the $l = 0$ states.

The quantum defect can be calculated semiclassically by looking at the difference in action, for $l = 0$,

$$\mu = \frac{2}{2\pi}\left(\int_{TP_1}^{TP_2}\sqrt{2m\left(E - \frac{1}{2}ku^2 - \frac{1}{u}\right)}du - \int_{TP_1}^{TP_2}\sqrt{2m\left(E - \frac{1}{2}ku^2\right)}du\right). \tag{18}$$

The calculation of thess intergral is actually non-trivial and they are difficult to compute analytically. Thus, only the large energy behavior of the quantum defect has been determined analytically,

$$\mu \sim -\frac{3}{4\pi\sqrt{E}}\log E - \frac{1}{2\pi\sqrt{E}}\left(\log\left(\frac{16}{\omega}\right) + 1 + \frac{\omega^2}{48}\right) \tag{19}$$

In this case, the behavior of quantum defect μ is a different from the Rydberg quantum defect, as $\mu \to \infty$ when $E \to \infty$.

The quantum defect is extracted from the numerically calculated energy eigenvalues for Hooke's atom by looking at the deviation of the energy levels from the coressponding harmonic oscillators.

5 The Kohn-Sham Potential

Another important system to consider when calculating the energy levels of Hooke's atom, is the Kohn-Sham system. The Kohn-Sham system relies on the Kohn-Sham (KS) potential, which is a purely mathematical construct and does not have any physical meaning. The KS potential is defined as the one body potential acting on N non-interacting electrons such that the non-interacting system will have the same ground state density as the interacting system [11, 12]. The KS equation is

$$\left[-\frac{1}{2}\nabla^2 + v_{KS}\right]\phi_i(r) = \epsilon_i\phi_i(r), \tag{20}$$

where v_{KS} is the KS potential. And the density is

$$n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2. \tag{21}$$

The actual value of the eigenvalues of equation (20) have no real meaning, but rather it is the separation between the eigenvalues that correspond quite accurately to the energy level separations in the real system.

To find the Kohn-Sham potential for two electrons, one can invert equation (20) and express the potential in terms of the ground state density. For Hooke's atom, when $k = \frac{1}{4}$, the KS potential has an analytic form [13],

$$\begin{aligned} v_{KS}(r) = & [32r^2(-1-8r^2+r^4) + 8e^{\frac{r^2}{2}}\sqrt{2\pi}r(r^3(-45-2r^2 \\ & +r^4) + 4(1-5r^2-7r^4+r^6)erf(\frac{r}{\sqrt{2}})) \\ & +e^{r^2}\pi(r^4(-210-55r^2+4r^4+r^6) + 8erf(\frac{r}{\sqrt{2}}) \\ & (r^3(-13-43r^2-r^4+r^6) + 2(-1+2r^2-8r^4 \\ & -6r^6+r^8)erf(\frac{r}{\sqrt{2}})))]/[8\pi r^2(4\sqrt{\frac{2}{\pi}}r + e^{\frac{r^2}{2}}(r(7+r^2) \\ & +4(1+r^2)erf(\frac{r}{\sqrt{2}})))^2]. \end{aligned} \tag{22}$$

A plot of v_{KS} is shown in fig. 5 along with the analogus harmonic potential, and one can see that though equation (22) may appear quite complex, it basically has a parabolic form like the oscillator potential.

The same numerical methods that were used to find the exact eigenvalues for Hooke's atom are used to find the eigenvalues of the Kohn-Sham equation.

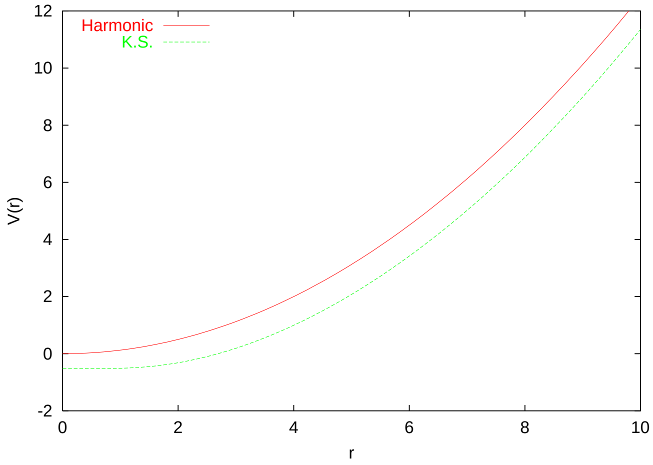

Figure 2: The Kohn-Sham potential for Hooke's atom and harmonic potential, both for $k = \frac{1}{4}$.

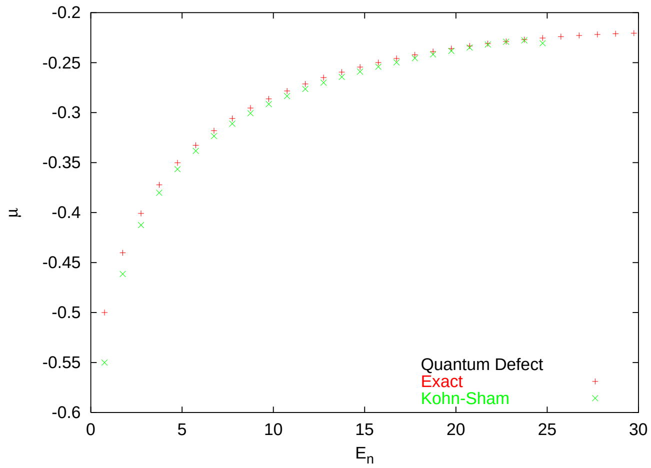

Figure 3: The quantum defect for the exact Hooke's atom and the Kohn-Sham system, where $k = \frac{1}{4}$.

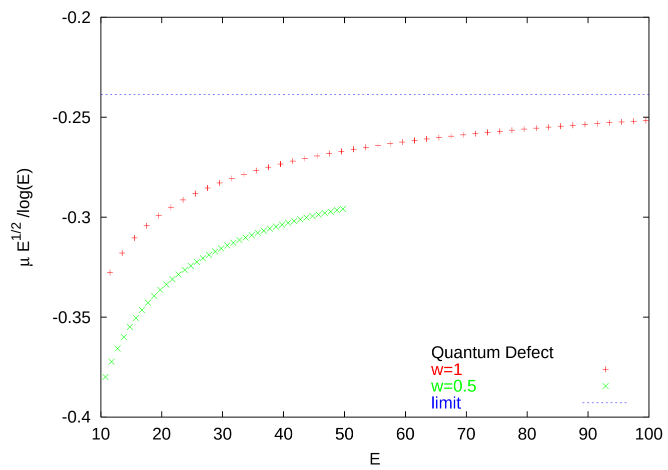

Figure 4: Theoretical limit for the quantum defect at large energies.

6 Results

7 Conclusion

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