

A Simple Solution of Schrödinger's Equation for Atoms

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Descreve-se um método simples para resolver a equação de Schrödinger e calcular a energia eletrônica total de um átomo polieletrônico. Em muitos casos os valores calculados são mais precisos do que os resultados obtidos por um cálculo variacional simples, sem no entanto necessitar de cálculos elaborados.

A simple method to solve Schrödinger's equation and calculate the total energy of a polielectronic atom is described. Despite its simplicity in many cases the calculated values are comparable to a simple variational calculation in spite of the minimum effort required.

Key words: *Schrödinger's equation; electronic energy; atoms.*

Introduction

To solve any Schrödinger's equation for almost any system of a practical interest we normally have to face a quite complicate differential equation. Although this presents a series of difficulties there are today quite a large number of computer algorithms and programs available to solve them. However, even so, in several circumstances would be desirable to access numerical values for the total electronic energy of an atomic system within anything better than an order of magnitude. As we know, the only case quite easy to solve with high accuracy is the Schrödinger's equation for the hydrogen atom. In this case, a non relativistic solution for the total electronic energy of the n states is given by

$$E_n = - \frac{Z^2}{2n^2} e^2/a_0 \quad n = 1, 2, \dots, \infty$$

solutions of

$$\left(- \frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{r} \right) \Psi = E_n \Psi$$

However, as it is known, when we attempt to solve this same equation but for a polieletronic atomic system, $Z \geq 2$, this analytical solution is no longer possible. In this paper we describe a very simple and approximated method to overcome such a difficulty. Although not accurate the method presents a good approach in spite of its simplicity.

Method

Consider the interelectronic repulsion represented by $1/r_{ij}$ such that r_{ij} is the distance between the i and j electrons in an atom. Thus, as usual, we may define r_{ij} as follows

$$r_{ij} = (r_i^2 - 2 r_i r_j \cos \theta_{ij} + r_j^2)^{1/2} \quad (1)$$

Further, we suppose now that electrons being particle with same electric charge have a high probability to stay most of the time as far as possible from each other; consequently, it is reasonable to consider $\theta_{ij} \cong 180^\circ$ and to assume by hypothesis that $r_i = r_j$. Thus, using these values in (1)

$$\begin{aligned} r_{ij} &\cong (r_i^2 + 2r_i r_j + r_j^2)^{1/2} \\ &\cong (r_i^2 + 2r_i + r_i^2)^{1/2} \\ &\cong 2r_i \end{aligned} \quad (2)$$

With this approximation we may now solve Schrödinger's equation quite easily. For He, for instance, we may write

$$\left(- \frac{\hbar^2}{2\mu} \nabla^2 - \frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \right) \Psi = E_n \Psi$$

Making use of (2), we may rewrite (3) as follows

$$\left(-\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{2r_{12}}\right) \Psi = E_n \Psi$$

$$\left(-\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{(Z-1/2)e^2}{r_1} - \frac{Ze^2}{r_2}\right) \Psi = E_n \Psi \quad (4)$$

Finally, considering (4) we may write a solution for the wave function of this system as $\Psi(r_1, r_2) \cong \Psi(r_1) \Psi(r_2)$, and consequently the total electronic energy as $E_n \cong E_1 + E_2$ to get equations (5) and (6)

$$\left(-\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{(Z-1/2)e^2}{r_1}\right) \Psi = E_1 \Psi \quad (5)$$

$$\left(-\frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{Ze^2}{r_2}\right) \Psi = E_2 \Psi \quad (6)$$

Obviously equations (5) and (6) have solutions similar to those for the hydrogen atom; however, for one of them, equation (5), instead of the atomic number Z , we have $Z-1/2$. Therefore, the energy for these equations are given by

$$E_1 = -\frac{(Z-1/2)^2}{2n_1^2} e^2/a_0 \quad n_1 = 1, 2, \dots, \infty$$

$$E_2 = -\frac{Z^2}{2n_2^2} e^2/a_0 \quad n_2 = 1, 2, \dots, \infty$$

$$E_n = E_1 + E_2$$

If we now consider $n_1 = n_2$ for the ground state of He then we are able to write

$$E_1 = -\frac{2Z^2 - Z + 1/4}{2} e^2/a_0$$

For He, taking $Z=2$ we get $E_1 = 12.5/4 e^2/a_0 = 3.125 e^2/a_0$ as compared to 2.75 making use of a first order perturbation, and 2.9037, a much more elaborated calculation done by Scherr and Knight, employing a 100 terms wave function, including correction up to order 10 for the helium atom. In the following table we compare these and the experimental results.

He	
Method	Energy (e^2/a_0) $e^2/a_0 = 13.6 \text{ eV}$
1 st Order Perturbation	-2.75 (>5,3%)
Scherr & Knight (100 terms & order 10) ¹	-2.9037 (>0,01%)
Independent Particle Model	-4.000
This work	-3.125 (<7,6%)
Experimental	-2.904

Although only a quite simple calculation is required, our results do compare with those shown, especially considering a first order perturbation result. For a larger atomic system we offer an improvement. For the ground state of the Li atom we will have three equations

$$\left[-\frac{\hbar^2}{2\mu} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{Ze^2}{r_3} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}}\right] \Psi = E_n \Psi$$

$$\left[-\frac{\hbar^2}{2\mu} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{Ze^2}{r_3} + \frac{e^2}{2r_1} + \frac{e^2}{2r_3} + \frac{e^2}{2r_2}\right] \Psi = E_n \Psi$$

$$\left[-\frac{\hbar^2}{2\mu} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \frac{(Z-1/2)e^2}{r_1} - \frac{(Z-1/2)e^2}{r_2} - \frac{(Z-1/2)e^2}{r_3}\right] \Psi = E_n \Psi$$

and the total energy can be written as follows

$$E_{Li} = -\left[\frac{(Z-1/2)^2}{2n_1^2} + \frac{(Z-1/2)^2}{2n_2^2} + \frac{(Z-1/2)^2}{2n_3^2}\right] e^2/a_0$$

$$= -7.03 e^2/a_0 (\geq 6\%)$$

$$E_{exp} = -7.48 e^2/a_0$$

$$E_{HF} = -7.43 e^2/a_0$$

Li

Method	Energy (e^2/a_0) $e^2/a_0 = 13.6 \text{ eV}$
Hartree-Fock ⁵	-7.432
Config. Interaction (79 terms) ²	-7.4472
Variational (60 terms) ³	-7.4780
This work	7.03 ($\geq 6\%$)
Experimental	-7.48

Our result for the ground state energy of the Li atom is curiously just 6% higher than the experimentally measured value, despite the minimum effort required in the estimation of the energy values. From the first few systems studied it is possible to write a general expression for the energy of an atomic system as

$$E = -\sum_{m=1}^N \frac{\left(Z - \frac{m_i - 1}{2}\right)^2}{2n^2}$$

Thus, making use of this equation the ground state energy for Be will be

$$E = -\frac{Z^2}{2n_1^2} - \frac{(Z-1/2)^2}{2n_1^2} - \frac{(Z-1)^2}{2n_2^2} - \frac{Z-3/2)^2}{2n_2^2} e^2/a_0$$

$$E = -16.03 e^2/a_0$$

Be

Method	Energy
Perturbation Variational ⁴	-13.6555
HF ⁵	-14.277
This work	-16.03

Finally we may say that although this method does not lead us to a precise value for the ground state energy of atomic systems, it offer a possibility to estimate them with an error which in many cases agrees within 10% with results obtained through a quite elaborate and time consuming computation.

References

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