Perturbation method using chaos structure applied to light atoms

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Various authors developed perturbations methods using mathematical tools to approach energy level of atoms with well known results in quantum mechanics. We shall develop a method with chaos structure to evaluate perturbations for particles system like atoms in order to contribute extending tools for calculating their energy levels. Concept of model with test particle within central potential $V(\vec{r})$ depending upon radial variable r is used. We establish properties of the approach and we make applications to light atoms. Results from applications of the method are discussed. Perturbation techniques using development of wave function ψ in terms of perturbations and variation method are considered for comparison.

1. INTRODUCTION

Rigorous analytical resolution of Schrödinger equation is complicated when dimension of system becomes greater than 3. Approximations techniques are used to contribute alleviate this problem. We develop a method using test electron and chaos structure concept [1] to shape perturbations which affect energy levels of light atoms. For this purpose, we use wave function $\psi_{n,\ell,m}(\vec{r})$ based spherical functions to describe atom states in the calculations of perturbations. Results related to hydrogen like and alkaline atoms for bound state shown in various books [2][3][4][5], as far as determination of energy levels are concerned, are directly used without demonstration.

2. APPROXIMATION CONSIDERATIONS

Let introduce the following considerations:

- we consider a test electron among particles of the atom and we follow its behaviours,

- when perturbations enter into force, behaviours of test electron present certain structure characterized by regular and chaotic aspect,

- when test electron is near the nuclei, it is subject of much more effect of the Coulombian potential of $+Ze$ charges of the nuclei,

- when test electron is far from the nuclei, it sees $+Ze$ charges of nuclei and ï $(Z-\alpha)$e charges within the electronic clouds, α is number of electron in non saturated shell.

3. PERTURBATION APPROACH

Consider atom states described with wave function $\psi_{n,\ell,m}(\vec{r})$ solutions of Schrödinger equation. We start from atom states with $n \neq 0$, $\ell = 0$, $m=0$, which correspond to energy E_{1s}, E_{2s}, E_{3s},... Let be : $b_n = \frac{2Z}{na_o}$, $u = b_n r$.

$$\psi_{n,o,o}(r) = \frac{1}{\sqrt{2\pi}} R_{n,o}(r) L_n^{(1)}{}_1(u),$$

$$\left(-\frac{1}{2}b_n r\right)L_{n\ 1}^{(1)}(u),$$

$$L_{n-1}^{1}(u)=\sum_{k=0}^{\quad}(-1)^{k}\frac{}{k!(n-k-1)!(k+1)!}$$

To simplify notation, let be : $C_{no}=\frac{1}{\sqrt{4\pi}}(b_n)^{\frac{3}{2}}\frac{n!(n-1)!}{\sqrt{2n(n+1)!(n-1)!}}$, and $D(k)=k!(n-k-1)!(k+1)!$

Since continuity conditions for wave function and its first derivatives must be satisfied, let write $\psi_{n,o,o}(\vec{r})$ at points $\vec{r}$ and $\vec{r}'$ such that $r'=r+\varepsilon$, where ε is infinitely small quantity, $\varepsilon << r$, contributing to the extent of chaos structure for one period as effect of perturbations. In other words, $\psi_{n,o,o}(\vec{r}')$ describe then a perturbed state in which r and ε are variables representing respectively regular aspect and chaotic aspect of the electron behaviours. We have :

$$\psi_{n,0,0}(r)=C_{no}\sum_{k=0}^{n-1}(-1)^{k}\frac{b_n^k r^k}{D(k)}exp\left(-\frac{1}{2}b_n r\right), \text{ and } \psi_{n,0,0}(r+\delta r)=C_{no}\sum_{k=0}^{n-1}(-1)^{k}\frac{b_n^k (r+\delta r)^k}{D(k)}exp\left(-\frac{1}{2}b_n (r+\delta r)\right)$$

Since $\varepsilon << r$, in first approximation, we can express $\psi_{n,o,o}(r+\varepsilon)$ in the form:

$$\psi_{n,0,0}(r+\delta r)\approx exp\left(-\frac{1}{2}b_n \delta r\right)\left[1+\delta(n,r,Z)\delta r\right]\psi_{n,0,0}(r), \text{ where } \eta(n,r,Z)=\frac{\sum_{k=0}^{n-1}(-1)^k k b_n^k r^k}{\sum_{k=0}^{n-1}(-1)^k b_n^k r^k}\frac{1}{r}$$

For energy level E_n, we assume $r=n^2 a_o$, with $a_o=\frac{\hbar^2}{m_e Z e^2}$. Then we obtain after calculations of the polynomial division and stopping at the term Z^{n-1}:

$$\delta(n,Z)=\frac{1}{n^2 a_o}\left[1+(-2nZ)^2\sum_{k=0}^{n-3}(-2n)^k Z^k\right]$$

Thus, we write:

$$\begin{pmatrix}\psi_{n,o,o}(\vec{r})\\ \psi'_{n,o,o}(\vec{r})\end{pmatrix}_{per}=\underline{M}\begin{pmatrix}\psi_{n,o,o}(\vec{r})\\ \psi'_{n,o,o}(\vec{r})\end{pmatrix}_{i}$$

where indexes per and i indicate respectively perturbed state and initial non perturbed state, and

$$\underline{M}=exp\left(-\frac{1}{2}b_n \delta r\right)\begin{pmatrix}1+\delta\delta(n,Z) & 0\\ 0 & 1+\delta\delta(n,Z)\end{pmatrix} \qquad (1)$$

At the vicinity of $\varepsilon=0$, $det(\underline{M})\approx 1$. $\underline{M}$ can be expressed in the form of Twist matrix [3][5][6]:

$$\underline{M}=\begin{pmatrix}cos\phi+\alpha\ sin\phi & -\frac{\alpha^2+1}{\beta}sin\phi\\ \beta\ sin\phi & cos\phi-\alpha\ sin\phi\end{pmatrix},$$

where, for $\psi_{n,o,o}(r)$, $\alpha=0$ and β is given by the quantity $B_{n,o}$ such that:

$$B_{no}(Z)=B_{10}\frac{(n-1)!}{n\sqrt{n(n+1)}}\sum_{k=0}^{n-1}\frac{(-2nZ)^k}{k!(n-k-1)!(k+1)!} \text{ with } \qquad B_{10}(Z)=\frac{1}{\sqrt{\ }}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}$$

Then $$\underline{M}=\begin{pmatrix}cos\phi & -\frac{1}{B_{no}}sin\phi\\ B_{no}\ sin\phi & cos\phi\end{pmatrix}$$

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...(n,Z) . It is easy to calculate, by recurrence, matrices in equations (1)

...ulations lead to:

$$\underline{M}^{N} = exp(b_n \hat{U}) \begin{pmatrix} (1+\hat{q})^{N} & 0 \\ 0 & (1+\hat{q})^{N} \end{pmatrix} exp\left(-\frac{1}{2}(N+2)b_n \hat{U}\right)$$

$\underline{M}$ can be written in the form:

$$\underline{M}^{N} = exp(b_n \hat{U}) \underline{A}_N, \qquad \text{where} \quad \underline{A}_N = \begin{pmatrix} \alpha_N & 0 \\ 0 & \alpha_N \end{pmatrix},$$

$$\text{and } \alpha_N = (1+\varepsilon\eta)^N exp(-\frac{1}{2}(N+2)b_n\varepsilon)$$

Since ε is infinitely small quantity, we may write: $\alpha_N \approx (1+N\varepsilon\eta)exp(-\frac{1}{2}(N+2)b_n\varepsilon)$ .At the vicinity of $\varepsilon = 0$, we have , $det(\underline{A}_N) \approx 1$. Then we write $\underline{A}_N$ in the Twist form:

$$\underline{A}_N = \begin{pmatrix} cosN\phi & -\frac{1}{B_{no}} sinN\phi \\ B_{no} sinN\phi & cosN\phi \end{pmatrix}, \text{ with the conditions below:}$$

$$\begin{cases} cosN\phi = (1+N\varepsilon\eta)exp(-\frac{1}{2}(N+2)b_n\hat{U}) \geq 0 \\ sin\, N\phi = 0 \end{cases}$$

We obtain: $\phi = \frac{k\pi}{N}$, and $cos\, N\phi = cos(k\pi) = (-1)^k \geqslant 0$. Therefore, k must be even. Let be $k=2p$, with p natural number. Matrix $\underline{M}^N$ is given by: $\underline{M}^{N} = exp(b_n \hat{U}) \underline{A}_N$

In developing the exponential term within the matrix $\underline{M}^N$ at the vicinity of $\varepsilon = 0$, we have :

$$\underline{M}^{N} = \underline{M}_o + \varepsilon \underline{M}_1 + \varepsilon^2 \underline{M}_2 + ... + \varepsilon^p \underline{M}_p + ...$$

where $\underline{M}_o = \underline{I}$, $\underline{M}_1 = b_n \underline{A}_1$, $\underline{M}_2 = \frac{(b_n)^2}{2!}\underline{A}_2$, é , $\underline{M}_p = \frac{(b_n)^p}{p!}\underline{A}_p$, and

$$\underline{A}_p = \begin{pmatrix} cos\frac{2p\pi}{N} & -\frac{1}{B_{no}} sin\frac{2p\pi}{N} \\ B_{no} sin\frac{2p\pi}{N} & cos\frac{2p\pi}{N} \end{pmatrix}$$

Hence it seems that we are dealing with equation that gives perturbed state from initial one with equation:

$$\begin{pmatrix} \psi(\vec{r}) \\ \psi'(\vec{r}) \end{pmatrix}_{per} = (\underline{M}_o + \hat{U}\underline{M}_1 + \hat{U}^2\underline{M}_2 + ... + \hat{U}^p\underline{M}_p + ...) \begin{pmatrix} \psi(\vec{r}) \\ \psi'(\vec{r}) \end{pmatrix}_i \qquad (2),$$

We can see that when $\varepsilon = 0$, that is there is no perturbation and chaotic aspect vanishes, we have:

$$\begin{pmatrix} \psi(\vec{r}) \\ \psi'(\vec{r}) \end{pmatrix}_{per} = \underline{M}_o \begin{pmatrix} \psi(\vec{r}) \\ \psi'(\vec{r}) \end{pmatrix}_i = \begin{pmatrix} \psi(\vec{r}) \\ \psi'(\vec{r}) \end{pmatrix}_i,$$

since $\underline{M}_o$ become identity matrix.

It is important to note that period is changing due to chaotic aspect. Let write equation (2) with atom states described by ψ_{ns} :

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$$\left|(\psi'_{ns})_{per} = \left(\frac{1}{B_{no}}\sum_{p=1}^{N}\mathring{U}^{p}\sin\frac{2p'}{N}\right)\psi'_{ns}\right.$$
$$\left|(\psi'_{ns})_{per} = \left(B_{no}\sum_{p=1}^{N}\mathring{U}^{p}\sin\frac{2p}{N}\right)\psi_{ns} + \left(1+\sum\mathring{U}^{p}\cos\frac{2p'}{N}\right)\psi'_{ns}\right. \qquad (3)$$

Calculating the derivative of $(\psi_{ns})_{per}$ from the first equation of (3) and identifying it with the second equation, we have the following condition:

$$\left(\sum_{q=1}^{N}\mathring{U}^{q}\sin\frac{2p'}{N}\right)\psi''_{ns} = -(B_{no})^{2}\left(\sum_{p=1}^{N}\mathring{U}^{p}\cos\frac{2p'}{N}\right)\psi_{ns}\ ,$$

which shows that period is changing; one of characteristics of chaotic structure.

Now, consider application to atom state ψ_{1s} for He. From equation (3), we have:

$$(\psi_{1s})_{per} = \psi_{1s} + \varepsilon\left(\psi_{1s}\cos\frac{2'}{N} - \frac{1}{B_{no}}\psi'_{1s}\sin\frac{2'}{N}\right) + \varepsilon^{2}\left(\psi_{1s}\cos\frac{4'}{N} - \frac{1}{B_{no}}\psi'_{1s}\sin\frac{4'}{N}\right) + \ldots$$

Perturbation calculations using usual method through the development of ψ_{1s} in terms of ε gives:

$$(\psi_{1s})_{per} = \psi_{1s}^{(o)} + \varepsilon\psi_{1s}^{(1)} + \varepsilon^{2}\psi_{1s}^{(2)} + \ldots.$$

Comparing two expressions above, we obtain:

$$\psi_{1s} = \psi_{1s}^{(o)},\ (\psi_{1s}^{(1)}) = \left(\psi_{1s}\cos\frac{2'}{N} - \frac{1}{B_{no}}\psi'_{1s}\sin\frac{2'}{N}\right),\ (\psi_{1s}^{(2)}) = \left(\psi_{1s}\cos\frac{4'}{N} - \frac{1}{B_{no}}\psi'_{1s}\sin\frac{4'}{N}\right),\ \text{etc é}$$

Then we can calculate perturbed energy level E_{1s} for He atom. We consider the Hamiltonian of the He of the form [2]:

$H = H^{(o)} + H^{(1)}$, where $H^{(o)} = H_1 + H_2$ is composed of Hamiltonian of hydrogen like atom for which energy levels and associated eigenfunctions are known and $H^{(1)}$ is perturbation of H. Assume each electron lies in fundamental state 1s, we have $\psi^{(o)} = \psi_{1s}(r_1)\psi_{1s}(r_2)$ is eigenfunction of $H^{(o)}$.

$$E_{1s}^{(1)} = \left\langle\psi^{(o)}\middle|H^{(1)}\middle|\psi^{(o)}\right\rangle\ , \qquad \text{with} \qquad H^{(1)} = \frac{e^{2}}{4\pi\varepsilon_{o}r_{12}}$$

$$E_{1s}^{(1)} = \frac{8\pi e^{2}}{\varepsilon_{o}}\int_{0}^{\infty}r_1^{2}(\psi_{1s})^{2}dr_1\int_{r_1}^{\infty}r_2^{2}(\psi_{1s})^{2}dr_2 = \frac{8Z^{2}e^{2}}{4\pi\varepsilon_{o}a_{o}^{6}}\int_{0}^{\infty}r_1^{2}\exp(-b_1r_1)dr_1\int_{r_1}^{\infty}r_2\exp(-b_1r_2)dr_2$$

Finally, $E_{1s}^{(1)} = \frac{5}{4}ZR$ *(4),* where R is the Rydberg constant.

Then, it is easy to show that we have the same perturbation of energy E_{1s} than the usual method applied to He for the first order. For the second order perturbation, we have:

$$E_{1s}^{(2)} = \left\langle\psi^{(o)}\middle|H^{(1)}\middle|\psi^{(1)}\right\rangle, \text{ with } \psi^{(1)} = \psi_{1s}^{(1)}(r_1)\psi_{1s}^{(1)}(r_2)$$

with $(\psi_{1s}^{(1)}) = \left(\psi_{1s}\cos\frac{2'}{N} - \frac{1}{B_{no}}\psi'_{1s}\sin\frac{2'}{N}\right) = \left[\cos\frac{2'}{N} + \left(\frac{'a_o}{Z}\right)^{\frac{1}{2}}\sin\frac{2'}{N}\right]\psi_{1s}$

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$$dr_2 = \left[\cos\frac{2'}{N} + \left(\frac{'a_o}{Z}\right)^{\frac{1}{2}} \sin\frac{2'}{N} \right]^2 \frac{5}{4} ZR \qquad (5)$$

4. DISCUSSIONS

Partial results we get in equations (4) and (5) are similar to that of usual perturbation methods. However, the presence of correction factor between brackets in equation (5) provides more advantage. The correction factor introduced by this method of perturbations gives opportunity to refine calculations and produces results which could be closer to experimental value of energy for the fundamental 1s of He atom, compared to other methods. In fact, correction factor could be appreciated with more precision depending upon the number N of period and hence the magnitude of chaos structure in test electron behaviours. In other words, we can improve calculations to bear better results with the determination of efficient value of N through iterative manner for calculations of the correction factor. The accuracy of results would depend upon the precision we wish to get in values of energy compared to experimental values.

5. CONCLUSION

Application of the method to atom He, in first approximation, gives similar results as well as usual perturbation methods. But the difference lies in the higher order perturbations where the correction factor is playing important role. It can be simulated with numerical calculations to refine value of perturbations and this would enable to go closer to experimental value of energy level for light atoms. The study is not yet completed and in the future, we hope to bring up concrete results from applications of the method to other light atoms like Lithium and so on.

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