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Investigation of analytical and numerical solutions for one-dimensional independent-of-time Schrödinger Equation

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ABSTRACT

In this paper, the numerical solution methods of one- particale, one – dimensional time- independent Schrodinger equation are presented that allows one to obtain accurate bound state eigen values and eigen functions for an arbitrary potential energy function V(x). These methods included the FEM (Finite Element Method), Cooly, Numerov and others. Here we considered the Numerov method in more details. For this purpose, we first reformulated the Shrodinger equation using dimensionless variables, the estimating the initial and final values of the reduced variable *xr* and the value of intervals *sr*, and finally making use of Q-Basic or Spread Sheet computer programs to numerically solved the equation. For each case, we drew the eigen functions versus the related reduced variable for the corresponding energies. The harmonic oscillator, the Morse potential, and the H-atom radial Schrodinger equation, … were the examples considered for the method. The paper ended with a comparison of the result obtained by the numerical solutions with those obtained via the analytical solutions. The agreement between the results obtained by analytical solution method and numerical solution for some Potential functions harmonic oscillator' Morse was represents the top Numerov method for numerical solution Schrodinger equation with different potentials energy.

Keywords: Independent-of-time Schrödinger equation; Numerical solution; Analytical solution; Numero method; Spreadsheet

INTRODUCTION

Assuming nucleuses and electrons as point masses and regardless of relativity interactions, molecular Hamiltonian was as follows:

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla_\alpha^2 - \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_\alpha\sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta e'^2}{r_{\alpha\beta}} - \sum_\alpha\sum_i\frac{Z_\alpha e'^2}{r_{i\alpha}} + \sum_i\sum_{i>j}\frac{e'^2}{r_{ij}} \qquad (1)$$

where α And βrefer to nucleuses, and *i* and *j* were indications of electrons, and the first term in the relationship (1) was kinetic energy operator of nucleuses. The second term was kinetic energy operator of electrons. The third term refer to repulsive potential energy, in which *r*αβ was the distance between the nucleuses α and β with *Z*β , *Z*αas their atomic numbers. The fourth term was gravitational potential energy between electrons and nucleuses, in which *ri*α was the distance between the

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electron "i" and the nucleus α. Finally, the last term refer to repulsive potentials between electrons, where *rij* was the distance between the electrons "*i*" and "*j*". Zero level of potential energy for the equation 1 was according to a configuration in which all electric charges (electrons and nucleuses) are located in an infinite distance from each other.

For instance, consider the molecule H2. Assume α and β as two protons, 1 and 2 as two electrons, and *mp* as mass of the proton. Molecular Hamiltonian of H_2 was as follows:

$$\hat{H} = \frac{-\hbar^2}{2m_p}\nabla_\alpha^2 - \frac{\hbar^2}{2m_p}\nabla_\beta^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + \frac{e'^2}{r_{\alpha\beta}} - \frac{e'^2}{r_{1\alpha}} - \frac{e'^2}{r_{1\beta}} - \frac{e'^2}{r_{2\alpha}} - \frac{e'^2}{r_{2\beta}} + \frac{e'^2}{r_{12}} \quad (2)$$

Wave and energy functions of a molecule are found by solving Schrödinger equation, where *qα* and *qi* are electronic and atomic coordinates, respectively.

$$\hat{H}\psi(q_i, q_\alpha) = E\psi(q_i, q_\alpha) \quad (3)$$

Molecular Hamiltonian (equ.1) was so complicated that one didnot solve it analytically. Fortunately there were a simple estimation with a high degree of accuracy, which was based on the fact that nucleuses were much heavier than electrons: *ma >>me*. Therefore, electrons moved much faster than nucleuses, and it was possible to consider the nucleuses immobile during electronic moves.

Classically, change in nucleus configuration was ignored during an electronic move cycle. Consequently, we omited nucleus kinetic energy terms from the equation (1) by considering nucleus immobile in order to obtain the Schrödinger equation for electronic movement:

$$(\hat{H}_{el} + V_{NN})\psi_{el} = U\psi_{el} \quad (4)$$

where Pure electronic Hamiltonian H_{el} was:

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_\alpha\sum_i \frac{Z_\alpha e'^2}{r_{i\alpha}} + \sum_i\sum_{j>i}\frac{e'^2}{r_{ij}} \quad (5)$$

Electronic Hamiltonian included nucleus repulsion that was equal to *Hel + VNN*. The nucleus repulsion term "*VNN*" was equal to:

$$V_{NN} = \sum_\alpha\sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta e'^2}{r_{\alpha\beta}} \quad (6)$$

The estimation for separating nucleus and electronic movements was called Bowrn-Openhaimer estimation. Based on this estimation, molecular Schrödinger equation was decomposed into two equations: an equation which describes electronics movement, and another equation that describes nucleus movement.

It was possible to solve the one-dimensional Schrödinger equation by using different potential energy functions with several methods. Also, it was easily possible to solve the Shrodinger equation for simpler potential energies such as particle in a box, and harmonic oscillator, using analytical method. But analytical method was not able to solve more complicated potential functions. So, there had been some efforts to solve the Schrödinger equation using other methods. In the recent years, numerical solutions have been used in order to solve the Schrödinger equation in Quantum Mechanics. In general, methods such as Euler, Rung Kutta, Heun and Colli-Numero can be used for solving an equation in a numerical manner. In the present study, Numero method had been thoroughly described. Using Numero method, it was possible to solve the

Schrödinger equation numerically by using different potential functions. It was worth noting that the Schrödinger equation can be solved by Numero method using Taylor series as follows:

$$\psi_{n+1} \approx \frac{2\psi_n - \psi_{n-1} + 5G_n\psi_n \frac{s^2}{6} + G_{n-1}\psi_{n-1}\frac{s^2}{12}}{1+G_{n+1}\frac{s^2}{12}} \quad (7)$$

where:

$$G = m\hbar^{-2}[2V(x) - 2E] \;,\; s = x - x_n \quad (8)$$

In order to numerically solve the Schrödinger equation using the above equations, first, we should write the equation in terms of the following dimensionless variables :

$$\psi_r = \frac{\psi}{B^{-\frac{1}{2}}}\,,\; x_r = \frac{x}{B},\; E_r = \frac{E}{A} \quad (9)$$

Then, we guess a certain value for *Eguess*. For this purpose, we should start with a point that was completely located within the left side classic forbidden region, plot changes in wave function ψ*r* versus *xr*, using computer softwares such as Q-Basic and Spread Sheet, and find eigenvalue of the considered potential function in several electronic conditions, and compare it with the values obtained from analytical solution of Schrödinger equation. In the present research, the authors had tried to present how to use the Numerov method in numerical solution using different potential functions after introducing various methods for numerically solving the Schrödinger equation, and to compare the results obtained from numerical solutions to those of analytical solutions.

CALCULATION METHOD

There were a lot of numerical methods such as Euler, Rung Kutta, Heun's Method, Finite Element Method, Numerov method, and Colli Method to solve an equation. Among them, Colli and Numerov methods were discussed in detail.

Numerov Method

For so many of Potential Energy functions V(*x*), it was not possible to solve the one-dimensional and one-particle Schrödinger equation exactly. In this section, a numerical method was presented in order to solve the one-dimensional and one-particle Schrödinger equation in a computer-based manner. Using this method, it was possible to find eigenvalues and special functions for an arbitrary potential function V(x). The method, named Numerov, was developed by a Russian scientist in the 1920s.

Consider Taylor expansion of the function f(x) around the point x=a.

$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2}f''(a)(x-a)^2 + \ldots \quad (10)$$

Considering the point x=a as xn (i.e. xn = a) and the x-a distance as *s* (i.e. Ș≡x-a = x-xn so that x = xn + s), a new equation was obtained. Replacing s with –s in the last equation and adding the two equations together, we had:

$$f(x_n+s) + f(x_n-s) \approx 2f(x_n) + f''(x_n)s^2 + \frac{1}{12}f^{(iv)}(x_n)s^4 \quad (11)$$

where terms including s^6 and higher powers of s were overlooked. In order to numerically solve the Schrödinger equation, we divided the x coordinate into some small intervals, each equal to s in length (fig. 1). Thus, the points xn – s, xn, and xn + s were the end points of adjacent intervals. Considering the following changes:

$$f_{n-1} \equiv f(x_n - s),\; f_n \equiv f(x_n),\; f_{n+1} \equiv f(x_n+s) \quad (12)$$

The equation (12) was transformed into:

$$f_{n+1} \approx -f_{n-1} + 2f_n + f''_n s^2 + \frac{1}{12} f_n^{(iv)} s^4 \quad (13)$$

Replacing f with the wave function ψ in the equation (13), we had:

$$\psi_{n+1} \approx -\psi_{n-1} + 2\psi_n + \psi''_n s^2 + \frac{1}{12}\psi_n^{(iv)} s^4 \quad (14)$$

Indexes n-1, n, and n+1 did not show several states, but indicated values of a certain wave function ψ and its derivatives in the points located on the coordinate x having the distance s from each other. The n index means functions were evaluated at the point xn [equation (12)].

$$\psi'' = m\hbar^{-2}[2V(x) - 2E]\psi$$
$$\psi'' = G\psi \quad (15)$$

$$G = m\hbar^{-2}[2V(x) - 2E] \quad (16)$$

Value of $\psi_n^{(iv)} s^4$ was obtained by replacing f with ψ″ in the equation (13), multiplying the obtained equation by s^2, and finally ignoring the term s^6.

$$\psi_n^{(iv)} s^4 \approx -\psi''_{n+1} s^2 + \psi''_{n-1} s^2 - 2\psi''_n s^2 \quad (17)$$

Putting the equation (15) in (17), we had:

$$\psi_{n+1} \approx -\psi_{n-1} + 2\psi_n + G_n \psi_n s^2 + \frac{1}{12}[G_{n+1}\psi_{n+1} s^2 + G_{n-1}\psi_{n-1} s^2 - 2G_n \psi_n s^2] \quad (18)$$

Solving this equation for ψ_{n+1}, the final result is:

$$\psi_{n+1} \approx \frac{2\psi_n - \psi_{n-1} + 5G_n \psi_n \frac{s^2}{6} + G_{n-1}\psi_{n-1}\frac{s^2}{12}}{1 - G_{n+1}\frac{s^2}{12}} \quad (19)$$

Using the equation (19) and having ψ_n and ψ_{n-1} (ψvalues at the two points xn and xn-1) ψ_{n+1} (the value of ψat the point xn + s) can be calculated.

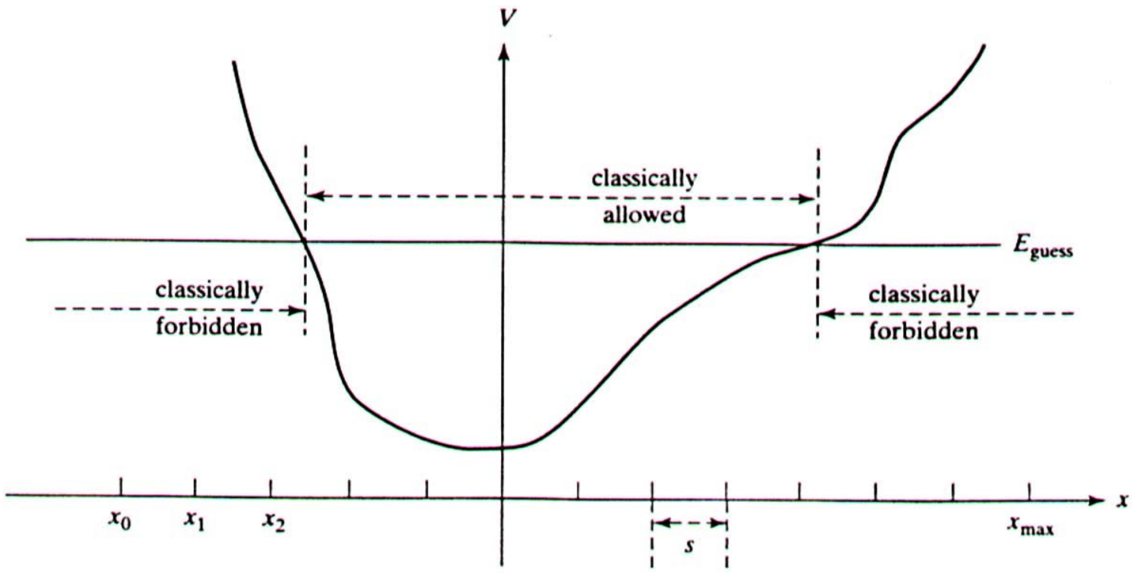

Fig. 1. V versus X for a one-particle and a one-dimensional system.

In order to solve the Schrödinger equation using the equation (13), first, we should guess a value for the energy eigenvalue (*Eguess*). We started with a point that was located exactly within the left side classic forbidden region (in the fig. 1). At this point, the value of ψ was too small, and we estimated the ψ to be zero at this point.

We also choosed the point *xmax* within the left side classic forbidden region, and make it necessary to meet the equation ψ *(xmax)*=0. We choosed a small value for the distance s between the consecutive points, and choosed a small number like 0.0001 for ψ at the point *xo+s*: *ψ1* ≡*ψ(x1)* ≡ ψ(*xo s*) =0.0001. After determining the values of *ψ1* and *ψo*, values of G are calculated using *Eguess*. Then, using the equation (19), value of $\psi_2 \equiv \psi(x_2) \equiv \psi(x_1\ s)$, ψ_3, and ψ_4 were obtained by considering n=1, n=2, and n=3, respectively. This procedure continued until we had reached $x_{\max}$.

If *Eguess* was not equal to or near to an eigenvalue, ψ was not integrable squarely, and $|\psi(x_{max})|$ would been very large. If it was proved that $|\psi(x_{max})|$ was not close to zero, we started with *xo* again, and begin the process guessing a new value for *Eguess*. The process continue as long as we found a value for *Eguess* that make $\psi(x_{max})$ get very close to zero. Then, *Eguess* was necessarily equal to an eigenvalue. Fundamental approach for determining eigenvalues was to count number of nodes at ψ resulted from *Eguess*. Remember that in a one-dimensional problem, number of internal nodes for the first motivated state was equal to 1,… Assume that E1, E2, E3, … refer to basic state energy, firs motivated state, second motivated state, … If ψ_{guess} did not included any nodes between *xo* and *xmax, Eguess* was equal to or less than E1; If ψ_{guess} included an internal node, ψ_{guess} was between E1 and E2 (fig. 2).

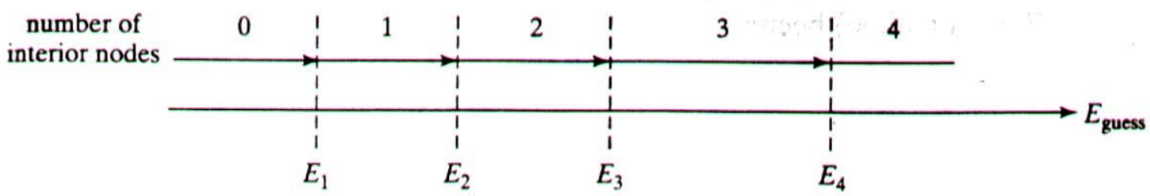

Fig. 2. Number of nodes in Numerov method in the form of a function of Energy Eguess.

One-dimensional Schrödinger equation in terms of dimensionless variables

Numerov method made it necessary to guess some values for E. How much were magnitude order of these guesses: $10^{-15} J$, $10^{-20} J$, In order to answer this question, we firstly wrote the Schrödinger equation in terms of dimensionless variables.

Simple Harmonic Oscillator

Harmonic oscillator had the term V=$\frac{1}{2}kx^2$, and Schrödinger equation had three constants including k, m, and h for harmonic oscillator. We named dimensionless reduced energy "Er, and reduced x parameter "*x*r". These parameters were defined as follows:

$$E_r = \frac{E}{A}, x_r = \frac{x}{B} \tag{20}$$

where A was a constant that was a combination of k, m, and h, hading energy dimensions, and B was a combination of these constants with length dimension. Energy had dimensions of mass × (length)^2 (time)^2 as written in the following:

$$[\,E\,] = ML^2T^{-2} \tag{21}$$

where Bracket was an indication of the dimensions M, L, and T as dimensions of mass, length, and time, respectively.

The equation indicated that k had the dimensions energy × length^{-2}. From the equation (21), we obtain $[k]=MT^{-2}$. The constant h had the dimension time × energy. So,

$$[m]=M \ ,[k]=MT^{-2} \ ,[\hbar]=ML^2T^{-1} \quad (22)$$

Dimensions of A and Bin the equation (20) were energy and length, respectively:

$$[A]=ML^2T^{-2} \quad , \quad [B]=L \quad (23)$$

Assumed that A= $m^a k^b h^c$. We specify the powers a,b , and c so that dimensions of A was equal to ML^2T^{-2}. Now,

$$[A]=[m^a k^b \hbar^c]=M^a(MT^{-2})^b(ML^2T^{-1})^c = M^{a+b+c}L^{2c}T^{-2b-c} \quad (24)$$

So, we had:

$$a+b+c=1 \ ,2c=2 \quad , \ -2b-c=-2$$

Solving these equations, we had:

$$a=-\frac{1}{2}kx^2 \ , \ b=\frac{1}{2} \ , \ c=1$$

So,

$$A=m^{-\frac{1}{2}}k^{\frac{1}{2}}\hbar \quad (25)$$

Assumed that B= $m^d k^e h^f$. Then equations (22) and (23) were obtained:

$$[B]=[m^d k^e \hbar^f]=M^d(MT^{-2})^e(ML^2T^{-1})^f = M^{d+e+f}L^{2f}T^{-2e-f}=L$$

$$d+e+f=0 \ , \ 2f=1 \ , \ -2e-f=0$$

$$f=\frac{1}{2} \ , \ e=-\frac{1}{4} \ , \ d=-\frac{1}{4}$$

$$B=m^{-\frac{1}{4}}k^{-\frac{1}{4}}\hbar^{\frac{1}{2}} \quad (26)$$

Considering equations (20), (25), and (26), we had:

$$E_r=\frac{E}{m^{-\frac{1}{2}}k^{\frac{1}{2}}\hbar} \ , \ x_r=\frac{x}{m^{-\frac{1}{4}}k^{-\frac{1}{4}}\hbar^{\frac{1}{2}}} \quad (27)$$

Using $k^{\frac{1}{2}}=2\pi\nu m^{\frac{1}{2}}$ to omit the constant k from equation (27) and remembering the $a=2\pi\nu\frac{m}{\hbar}$ definition, we obtained other terms for reduced energy and reduced parameter:

$$E_r=\frac{E}{h\nu} \quad , \quad x_r=\alpha^{\frac{1}{2}}x \quad (28)$$

Since $|\psi(x)|^2$ was a probability parameter and probability parameters were dimensionless, normal ψ_x should had the dimensions length$^{-1/2}$. Therefore, we defined reduced wave function ψr. Considering the equation (23), dimension of B was length, so dimension of $B^{-1/2}$ was length$^{-1/2}$. So,

$$\psi_r=\frac{\psi}{B^{-\frac{1}{2}}} \quad (29)$$

Considering the equations (20) and (29), and the equation $\int_{-\infty}^{\infty}|\psi|^2dx=1$ .the function ψr was correctly applied to the equation $\int_{-\infty}^{\infty}\left|\psi_r\right|^2dx=1$. So, we rewrote Schrödinger equation in terms of the reduced variables x_r, ψr, and E_r. So we had

$$\frac{d^2\psi}{dx^2}=\frac{d^2}{dx^2}B^{-\frac{1}{2}}\psi_r=B^{-\frac{1}{2}}\frac{d}{dx}\frac{d\psi_r}{dx}=B^{-\frac{1}{2}}\frac{d}{dx}\frac{d\psi_r}{dx_r}.\frac{dx_r}{dx}$$

$$=B^{-\frac{1}{2}}\frac{d(\frac{d\psi_r}{dx_r})}{dx_r}\frac{dx_r}{dx}.\frac{dx_r}{dx}=B^{-\frac{5}{2}}\frac{d^2\psi_r}{dx_r^2} \quad (30)$$

Because $\frac{dx_r}{dx}=B^{-1}$. Putting the equations (20) and (29) in Schrödinger equation for harmonic oscillator, we obtained:

$$-\frac{\hbar^2}{2m}B^{-\frac{5}{2}}\frac{d^2\psi_r}{dx_r^2}+\frac{1}{2}kx_r^2B^2B^{-\frac{1}{2}}\psi_r=AE_rB^{-\frac{1}{2}}\psi_r \quad (31)$$

Dividing the sides by $B^{-1/2}$ and replacing the equations (25) and (26) for A and B, we had:

$$-\frac{\hbar^2}{2m}m^{\frac{1}{2}}k^{\frac{1}{2}}\hbar^{-1}\frac{d^2\psi_r}{dx_r^2}+\frac{1}{2}kx_r^2\ m^{-\frac{1}{2}}\ \hbar\psi_r = m^{-\frac{1}{2}}k^{\frac{1}{2}}\hbar E_r\psi_r \quad (32)$$

$$\frac{d^2\psi_r}{dx_r^2}=(x_r^2-2E_r)\psi_r \quad (33)$$

$$\psi_r''=G_r\psi_r \quad , \quad G_r\equiv x_r^2-2E_r \quad (34)$$

So, reducing Schrödinger equation for harmonic oscillator in form of the equation (33), which included dimensionless quantities only, we expected the minimum of energy eigenvalue to be of the magnitude order of 1.

Now, we could used the Numerov method for the equation (33). Consequently, $S_r = s/_B$.

Mourse Function

This potential function was in the form of $V=D_{e(1-e^{-ax})}$, and the corresponding Schrödinger equation has the constants a, m, and h. In this case:

$$A=m^{-1}\hbar^2a^2\ ,\ B=a^{-1} \quad (35)$$

and reduced Schrödinger equation would been:

$$\psi_r''=G_r\psi_r \quad , \quad G_r=D_{e,r}(1-e^{-x_r})^2-2E_r \quad (36)$$

Choosing $x_{r,o}$, $x_{r,max}$, and s_r

In order to solve the independent-of-time Schrödinger equation by different potential functions, it was necessary to determine initial and final values of x_r, and the distance s_r between adjacent points. So, we determined these points for harmonic oscillator. Assumed that the goal was to find all eigenvalues and special functions of harmonic oscillator with $E_r \leq 5$. Because of this, we started solving from the right side of unallowable classic region. First, we determined unallowable classic regions for $E_r = 5$. Border between allowable and unallowable regions were positions in which $E_r = E_V$. Using the equation (27), reduced potential energy V_r was obtained as follows:

$$V_r=\frac{V}{m^{-\frac{1}{2}}k^{\frac{1}{2}}\hbar}=\frac{\frac{1}{2}kx^2}{m^{-\frac{1}{2}}k^{\frac{1}{2}}\hbar}=\frac{\frac{1}{2}k^{\frac{1}{2}}x_r^2m^{-\frac{1}{2}}k^{-\frac{1}{2}}\hbar}{m^{-\frac{1}{2}}\hbar}=\frac{1}{2}x_r^2 \quad (37)$$

So the equation $E_r = E_V$ was transformed into $5=\frac{1}{2}X_r^2$, and the allowable classic region for $E_r = 5$ would been $X_r-(10)^{\frac{1}{2}}=-3.16$ to +3.16. For Er < 5, the allowable classic region would been smaller. There for, we would like to find the answered at a point in which wave function ψ was too small, and at another point which was completely located at the left side of the unallowable classic region.

Left unallowable classic region for Er = 5 ends at x_r = -3.16. an acceptable choice was to start calculations from x_r = -5. Since V was symmetric, we should finished the answer at x_r = 5. For more accuracy, it was necessary to choose, at least, 100 points. So, we choosed s_r = 0.1 in order to gain 100 points.

Computer Softwares for solving one-dimensional Schrödinger equation by Numerov method

There were several computer softwares for solving one-dimensional Schrödinger equation by Numero method. Among them were Q-Basic, Maple5, Matlab, Mathematica, Derive, MathCad, Theorist, and spreadsheet. In this research, the Spreadsheet software had been used. Application procedure of the software Spreadsheet for harmonic oscillator was explained in chapter 4 of the book "Luain's Quantum Chemistry".

Colli method

In Numerov method, there was no appropriate method for correcting errors in eigenvalues. On the other hand, sometimes when value of E was exactly equal to a certain eigenvalue, numeric value of ψ enters the non-classical region. Colli method had obviated the two noted problem. Introduced by Colli, the method was integration of Numerov method (N.M.I), along with a formula correcting eigenvalues, which had been developed based on second-order repetition change presented by Lowdin.

Form of this equation was as follows:

$$\frac{d^2\psi}{dr^2} + [E - U(r)]\psi(r) = 0 \qquad (37)$$

where ψ was special radial function multiplied by r, and U(r) was effective potential energy.

$$U(r) = \frac{[J(J+1) - \Lambda^2]}{r^2} + \frac{z_a z_b}{r} + E_{elec}(r) \qquad (38)$$

J and Λ were rotational quantum number and angular momentum, respectively, and $z_a z_b / r$ was repulsive colonic energy between nucleuses, and *Eelec (r)* was electronic energy obtained for each r distance between nucleuses.

For using the equation (37), it was necessary to make energy and length dimensionless. When we measured length at Boor radius, a_0 = *0.529172 A* and unit of energy was equal to $\frac{hN_0}{8\pi^2 C a_0^2 \mu_A}$, where N_0 was Avogadro numbr, and μ_A was reduced mass whose numerical value was equal to $\frac{60.2198}{\mu_A}$.

RESULTS AND DISCUSSION

In this study, first one-dimensional Schrödinger equation for simple harmonic oscillator and Morse functions had been solved by analytical method, and Numerov numerical method, respectively, and then the results were compared to each other. At the next step, numerical solution of other functions were also investigated.

Analytical Solutions to one-dimensional harmonic oscillator function

The independent-of-time Schrödinger equation for one-dimensional harmonic oscillator was as follows:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \qquad (39)$$

where k was force constant and was related to vibrational frequencies according to $V = \frac{1}{2\pi}(\frac{k}{m})^{\frac{1}{2}}$. Solution of the equation (39) had been described in detail in so many of Quantum Chemistry books, and we discussed only results obtained from solutions to the equation. Those solutions to the equation (39) which were squarely integrable exist only for E values according to the following:

$$E = (v + \frac{1}{2})h\nu \qquad v = 0,1,2,3,... \qquad (40)$$

It could been shown that well-behavior solutions for the equation (39) was in form of multiplying $\exp(-\alpha\frac{x^2}{2})$ by a polynomial of x from the order v, with $\alpha \equiv 2\pi v \frac{m}{\hbar}$. Figure. 3. show explicit forms of some wave function lower than ψ_0, ψ_1 and ψ_3. Increase in quantum number causes increased in number of nodes. Harmonic oscillator wave functions consistent with $x \to \pm\infty$ reduced to zero exponentially. However, it should be noted that even for very large value of x that wave function and probability density were not equal to zero; there was a high probability of finding particle at high values of x. For a classic harmonic oscillator with the energy$\left(v+\frac{1}{2}\right)hv$, the equation $E=\frac{1}{2}kA^2$ results in

$\left(v+\frac{1}{2}\right)hv=\frac{1}{2}kA$ and $\left[(2v+1)\frac{hv}{k}\right]^{\frac{1}{2}}$.

A classic oscillator is restricted to move within the range $-A \leq x \leq +A$.

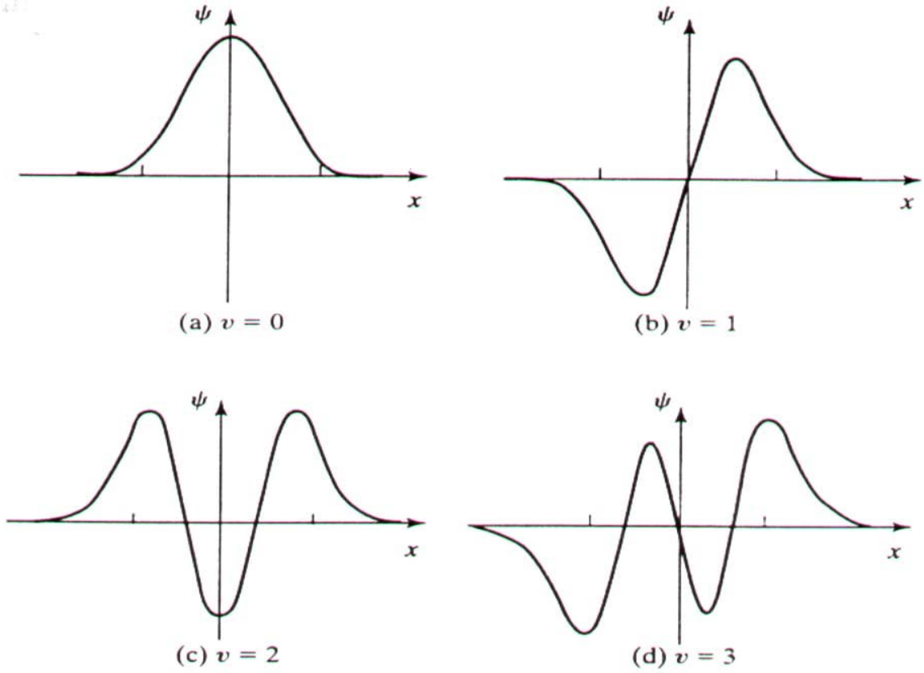

Fig. 3. Wave functions for four states lower than harmonic oscillator.

Analytical Solutions to Morse function

For Morse potential energy at J = 0, we had:

$$-\frac{\hbar^2}{2\mu}\frac{d^2p}{dr^2}+\{D+D[e^{-2a(r-r_e)}-2e^{-a(r-r_e)}]\}P=EP \tag{41}$$

By replacing y with $e^{-a(r-r_e)}$, we had:

$$\frac{dp}{dr}=-a\frac{dp}{dy} \quad , \quad \frac{d^2p}{dr^2}=ay^2\left(\frac{d^2p}{dy^2}+\frac{1}{y}\frac{d^2p}{dy^2}\right) \tag{42}$$

and the equation (41) is transformed into:

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2p}{dy^2}+\frac{1}{y}\frac{dp}{dy}\right)+\frac{1}{a^2}\left(\frac{D-E}{y^2}-\frac{2D}{y}+D\right)p=0 \tag{43}$$

By writing the solutions in form of $P(y)=e^{-\frac{z}{2}}z^{\frac{b}{2}}F(z)$, where and

$b=\frac{2}{a\hbar}\sqrt{2\mu D}\ \frac{y}{a\hbar}$=By

$b=\frac{2}{a\hbar}\sqrt{2\mu(D-E)}$, we had:

$$y^{-1}\frac{dp}{dy}=\beta^2e^{-\frac{z}{2}}z^{\frac{b}{2}}\left[\frac{1}{z}\frac{dF}{dz}+\frac{1}{2}\left(\frac{b}{z^2}-\frac{1}{z}\right)F\right]$$

$$\frac{d^2p}{dy^2}=\beta^2e^{-\frac{z}{2}}z^{\frac{b}{2}}\left\{\frac{d^2F}{dz^2}+\left(\frac{b}{z}-1\right)\frac{dF}{dz}+\left[\frac{b^2}{4z^2}-\frac{b}{2z^2}-\frac{b}{2z}+\frac{1}{4}\right]F\right\} \tag{44}$$

and the equation (39) was transformed into:

$$\frac{d^2F}{dz^2}+\left(\frac{b+1}{z}-1\right)\frac{dF}{dz}+\left[\frac{\beta}{2}-\frac{(b+1)}{2}\right]\frac{F}{z}=0 \tag{45}$$

Using divergent differential equations related Diverging, equation (45) was transformed into:

$$L''+(\frac{2l+1}{z}-1)L'+[\frac{\lambda-l-1}{z}]L=0 \quad (46)$$

when the equation $\tilde{\lambda} l \tilde{\ } 1 = n$ was true, equation (46) had well-behavior solutions, where n was a true and positive number. Equations (45) and (46) would been the same if:

So solutions to the equation (45) did not exist if:

$$b+1=2l+1 \ , \ \lambda=\frac{\beta+1}{2} \quad \text{and}$$

$$\frac{\beta}{2}-\frac{(b+1)}{2}=n \quad or$$

$$\frac{\sqrt{2\mu D}}{a\hbar}-\frac{1}{2}(\frac{2}{a\hbar}\sqrt{2\mu(D-E)}+1)=n$$

where:

$$\frac{E_n}{hc}=(n+\frac{1}{2})\omega_e-(n+\frac{1}{2})^2\omega_e x_e \quad (47)$$

$$\omega_e=\frac{2a\hbar}{hc}\sqrt{\frac{D}{2\mu}} \quad , \quad \omega_e x_e=\frac{1}{hc}(\frac{a^2\hbar^2}{2\mu}) \quad (48)$$

Equation (47) was exact for equation (45) if $0 \le z \le \infty$ and if F(z) reaches z=0 and $z=\infty$. Actually $r \ge 0$, and y and z would never been equal to zero. Equation (47) was a good estimation for molecules.

Numerical Solution of one-dimensional Schrödinger equation using Numerov method and drawing wave function curve versus x_r.

Numerical Calculations for simple harmonic oscillator

In order to numerically solved Schrödinger equation for harmonic oscillator using Numerov method and to drawing wave function curve versus x_r, we should make the considered equation dimensionless, and then solved the equation by using Numerov method. discussed procedure of making the considered equations dimensionless in detail.

For harmonic oscillator, using the values $x_{r,0}=-5$، $x_{r,max}=5$, and $s_r=0.1$ and the relationship (28)$G_r = x_r^2 - 2E_r$, one could calculate the values of ψ_r and x_r At several E_r s in an excel sheet, and then drew curves of wave function ψ_r versus x_r.

For example, fig. 4-a, 4-b, and 4-c showed curves of wave function versus x_r for harmonic oscillator at E_r= 0, basic state, which did not have any node, and fourth stimulated state of E_r= 4.499996, which had 4 nodes, respectively.

Numerical Calculations for fourth-ordered disharmonic oscillator

In order to drew curve of wave function ψ_r versus x_r for fourth-ordered disharmonic oscillator which had the potential energy of $V = ax^4$, we had $G_{r=2x_r^4-2E_2}$, $x_{r,0} = -2.5$, and $x_{r,max} = -2.5$. We also had the terms ψ_r related to fourth-ordered disharmonic oscillator by using the relationship (19).

So, importing the above information into an excel sheet, we could investigate, for instance, the base state E_r= 0.668 with S_r= 0.01, which did not have any nodes (Fig. 5-a), the first stimulated state E_r= 2.3 with S_r= 0.05, which had two nodes (Fig. 5-b), and the fourth stimulated state E_r= 10.244 with S_r= 0. 1, which had four nodes (Fig. 5-c), and drew curves of wave function ψ_r versus x_r for the states remarked.

Numerical Calculations for Morse Oscillator

Morse oscillator had $V = D_e\,(1-e^{-ax})^2$. Consequently, we had $G_r = 2D_{e,r}\,(1-e^{-x_r})^2 - 2E_r$ in which $D_{e,r} = \frac{D_e}{(\frac{h^2}{a^2/m})}$. Also we had the exact term ψ of Morse oscillator by using the relationship (19). It was possible to drew curve of wave function ψ versus x_r in an excel sheet by importing the distance between $x_{r,0} = -1.44$ and $x_{r,max} = -1.5$. Here we had investigated curve of wave function ψ for basic state versus x_r E_r=8.5154 and s_r=0.01, which did not have any nodes (Fig. 6-a), the first stimulated state with E_r=24.80628 and s_r=0.01, which had one node (Fig. 6-b), the second stimulated state with E_r=40.36258 and s_r=0.01, which had two nodes (Fig. 6-c), and the fifth stimulated state with E_r=80.54747 and s_r=0.01, which had five nodes (fig. 6-d).

Numerical Solution to Radial Equation related to movement of particle in central force field

For instance, we consider radial equation of Hydrogen atom with potential function of $V = -\frac{e'^2}{r}$. We had $G_r = \frac{l(l+1)}{r_r^2} - \frac{2}{r_r} - 2E_r$ (relationship (37) and also the exact term of ψ for the system.

Importing the aforementioned data into an Excel sheet, we drew the considered curves; for instance, distance between $r_{r,0} = 0$ to $r_{r,max} = 10$ with E_r=-0.4998 and s_r= 0.025, which did not have any nodes and was related to the orbital 1s (Fig. 7-a), distance between $r_{r,0} = 0$ to $r_{r,max} = 25$ with E_r=-0.1246 and s_r= 0.01, which had one node and was related to the orbital 2S (Fig.7-b), and distance between $r_{r,0} = 0$ to $r_{r,\ max}$=40 with E_r=-0.05526 and s_r= 0.01, which had two nodes and was related to the orbital 3s (Fig. 7-c).

Since in the relationship for G_r value of r_r is put in denominator value, then value of G_r was meaningless. Consequently, value of $r_{r,0}$ was considered as a very small value close to zero like -0.0001.

Numerical Solution to the equation related to angular momentum

First, we drew the wave function of y_r versus θ for the equation with angular momentum at the distance between $r_{r,0} = 0.1$ and $r_{r,max} = 3.03$ with s_r= 0.01. It should been noted that we had $G_r = \left[-l(l+1) - \frac{1}{2} - \frac{1}{4}\cot g^2\theta + \frac{m^2}{sin^2\theta}\right]$, $|m| = 2$, and J=3 (Fig. 8).

Numerical Solution to Schrödinger equation with potential energy function of $V(X) = \frac{-V_a}{1+e^{X/a}}$

This equation had three constants including m, h, and a. So, the constants A and B would been as follows:

$$A = \frac{\hbar^2}{\mu.a^2}\ ,\ B = a \qquad (49)$$

Also $= \frac{L}{Ln(-2)}$, and finally reduced Schrödinger equation was equal to:

$$\psi_2'' = G_r\psi_r\ ,\quad G_r = \left[-2\gamma\left(\frac{v_0}{1+e^{x_r}}\right) - 2E_r\right],$$

$$\gamma = \frac{\mu B^2}{\hbar} \qquad (50)$$

Importing the values $x_{r,max} = 2$, $x_{r,0} = -2$ as well as the relationship (50) and the term of ψ related to this equation and using the relationship (19). For instance, Fig. 9-a. showed the curve of ψ_r versus x_r at the third stimulated state with E_r=1.2 and s_r=0.05, which had three nodes. Also Fig. 9-b. showed the curve of ψ_r versus x_r at the fourth stimulated state with E_r=3.8 and s_r=0.1, which had four nodes.

Numerical Solution to Schrödinger equation with potential energy function of $V(x) = \frac{x^2}{2} - \frac{x^3}{12}$

We had s_r=0.1, $x_{r,max} = 4$, $x_{r,0} = -3.5$ and $G_r = \left[x^2 - \frac{x^3}{6} - 2E_r\right]$. Importing the above data into an Excel sheet, we drew the considered curves; for instance, the basic state with E_r=0.489625did not have any nodes (Fig. 10-a), the first stimulated state with E_r=1.425 had one node (Fig. 10-b), and the second stimulated state with E_r=2.3125 had two nodes (Fig. 10-c).

Numerical Solution to Schrödinger equation with potential energy function of $V(x)=x^2-0.1x^3$

We had s_r=0.1, $x_{r,max} = 3$, $x_{r,0} = -3$ and $G_r = (2x^2 - 0.2x^3 - 2E_r)$. Importing the above data into an Excel sheet, we drew, for instance, curve of the basic state with E_r=0.7035, which did not have any nodes (Fig. 11).

Comparison between numerical and analytical solutions of Schrödinger equation with several potential energies

The independent-of-time Schrödinger equation for one-dimensional harmonic oscillator was as follows:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2 = E\psi \qquad (51)$$

where k was force constant, and was in relation to vibrational frequency according to the relationship $= \frac{1}{2\pi}(\frac{k}{m})^{\frac{1}{2}}$. Analytically solving this equation, allowable energies of the harmonic oscillator was as follows:

$$E = h\nu(v + \frac{1}{2}),\ v= 0,1,2,3,\ldots \qquad (52)$$

For instance, value of E was equal to 0.5 h, 1.5 h, and 4.5 h at the basic state, the first stimulated state, and the fourth stimulated state, respectively.

In the numerical solution to Schrödinger equation for harmonic oscillator by Numerov method, first classical unallowable regions should be determined, then dimensionless reduced variables including $E_r = \frac{E}{A}$ and $x_r = \frac{x}{B}$ were used. The parameters A and B were multiplication of power-having constants $\hbar$, μ and k, and were calculated from the following relationship $A = m^{-\frac{1}{2}}.k^{\frac{1}{2}}.\hbar$, $B = m^{-\frac{1}{4}}.k^{-\frac{1}{4}}.\hbar^{\frac{1}{2}}$.

Using the above equations, we had $\psi_r = \frac{\psi}{B^{\frac{1}{2}}}$, $E_r = \frac{E}{hV}$, $x_{r=a^{\frac{1}{2}}x}$ (relationships (28) and (29), and the differential equation of ψ_r^N was as following:

$$\psi_r'' = (x_r^2 - 2E_r)\psi_r \equiv G_r\psi_r \qquad (53)$$

By specifying classical unallowable regions, we numerically solved the equation so that the minimum possible value for x_r was equal to -5 and the maximum possible value for x_r was equal to 5. These values resulted in different values for E_r at several states. At the basic state the value of E_r was 0.499995, at the first stimulated state we had $E_r = 1.499995$, and at the fourth stimulated state, the value of E_r was equal to 9.499995.

Comparing these values with those obtained from the analytical method indicates that the values calculated from analytical and numerical solutions using Numerov method for Schrödinger equation for simple harmonic oscillator were very close to each other.

So, we compare the analytical solution with numerical one to Schrödinger equation with Morse potential energy:

$$U(r) = U(r_e) + D_e[1 - e^{-a(r-r_e)}]^2 \qquad (54)$$

where:

$$a = 2\pi\nu_e\left(\frac{\mu}{2D_e}\right)^{\frac{1}{2}}, \qquad \frac{D_e}{hc} = 38297cm^{-1},$$

$$\frac{\nu_e}{c} = 4403.2cm^{-1}, r_e = 0.71\overset{o}{A}$$

We used dimensionless reduced variables including $E_r = \frac{E}{A}$ and $x_r = \frac{x}{B}$ in Numerov method. A and B were multiplications of power-having constants $\hbar$, μ and k. In this case, we have $A = \hbar^2 \frac{a^2}{\mu}$ and $B = a^{-1}$.

Putting $x = \frac{x_r}{a}$, $E = \hbar^2 \frac{a^2}{\mu} E_r$, $D_{e,r} = \frac{D_e}{(\hbar^2 \frac{a^2}{\mu})}$ and $S(x) = S_r(x_r) B^{-\frac{1}{2}}$, $S'' = B^{-\frac{1}{2}} a S''_r$.

The differential equation of S(x) was obtained.

$$S''_r(x_r) = [2D_{e,r}(1-e^{-x_r})^2 - 2E_r]S_r(x_r) \equiv G_r S_r(x_r) \quad (55)$$

We choosed the distance between $x_{r,0} = -1.44$ and $x_{r,max} = 1.5$ as classical allowable region. Then we found several values for E_r at lower levels using Spreedsheet computer software.

For instance, values of E_r was equal to 8.5154, 24.86628, 40.36258, and 80.54747 at the basic state, the first stimulated state, the second stimulated state, and the fifth stimulated state, respectively.

Applying $E_r = E/A$, lower levels were equal to $2169.9\ cm^{-1} = \frac{E}{hc}$, $63.2001 cm^{-1}$, $10216.9 cm^{-1}$ and $20388.8\ cm^{-1}$. So, we solved Schrödinger equation for Morse function analytically, eigenvalues for lower levels were equal to:

$20389.02 cm^{-1}$, $10216.9 cm^{-1}$, $6320.03 cm^{-1}$, $2169.9 cm^{-1}$. The consistency between the values obtained from analytical solution for Morse function and those obtained from Numerov method in numerical solution was very good.

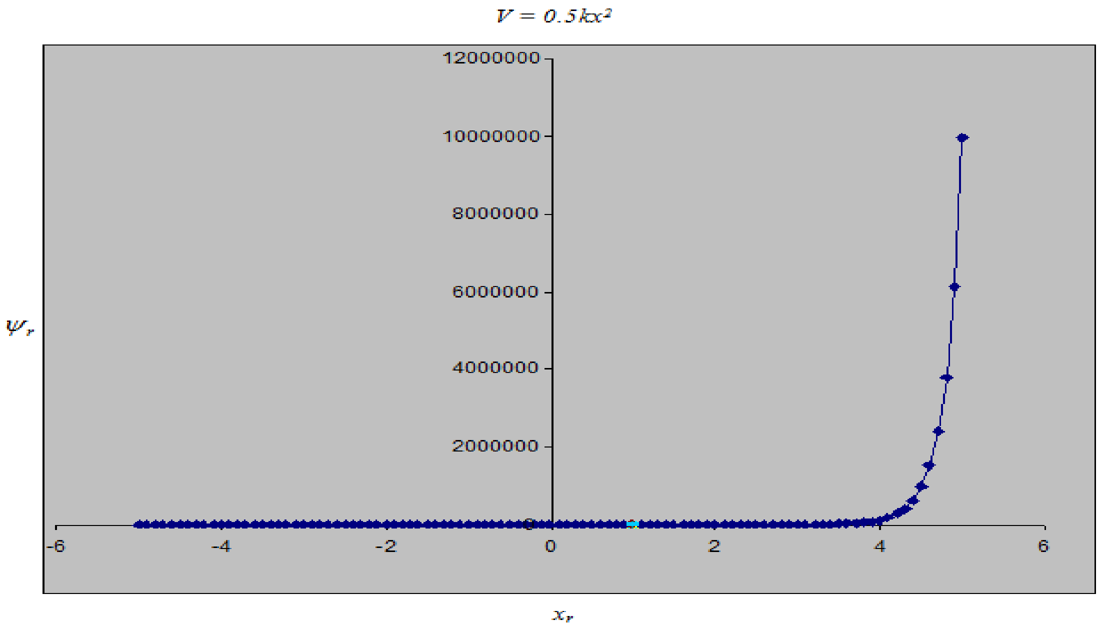

Fig. 4-a. Curve of changes in wave function "ψ_r" versus xr for Er=0.

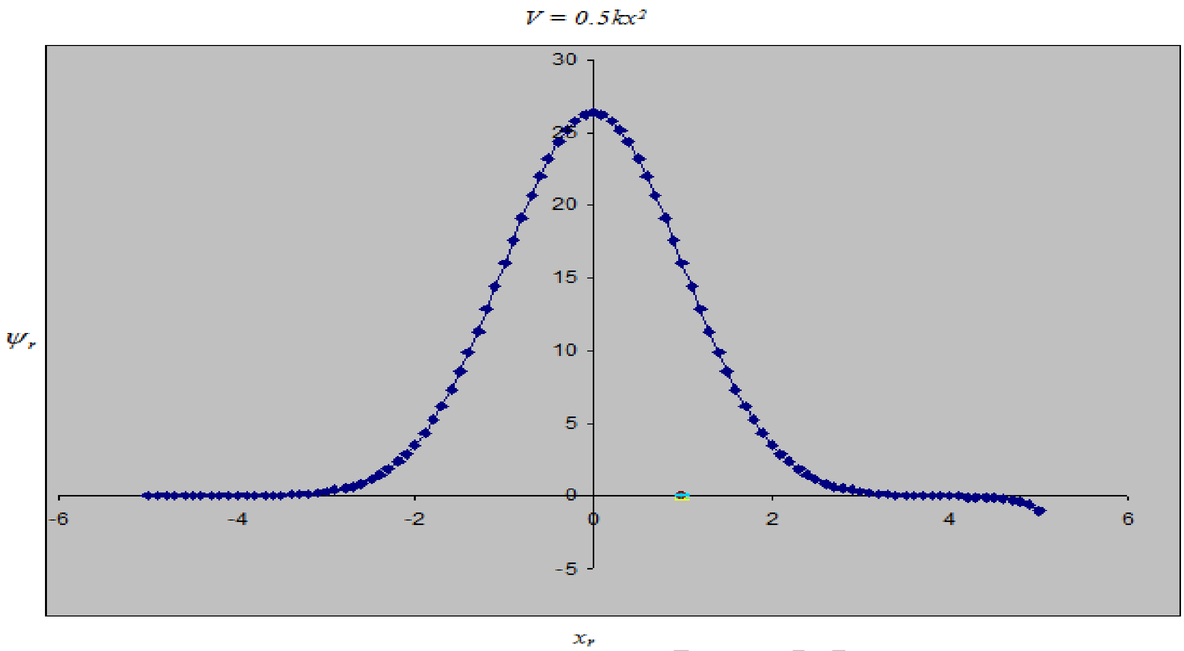

Fig. 4-b. Curve of changes in wave function "ψ_r" at base state versus xr.

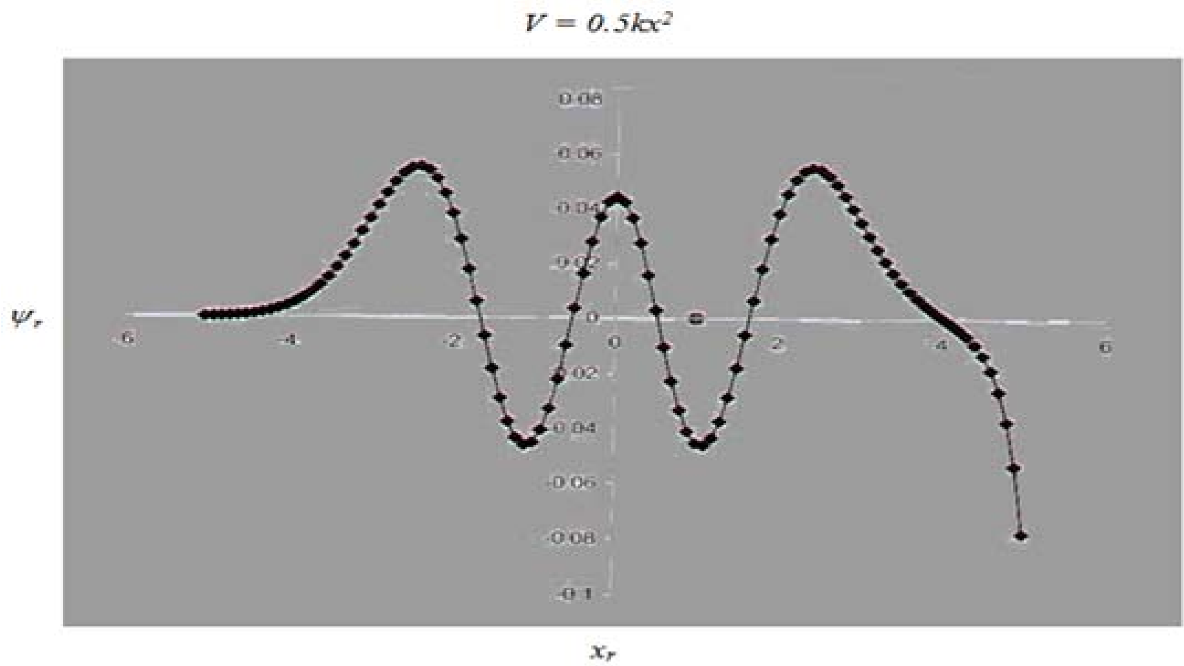

Fig. 4-c. Curve of changes in wave function "ψ_r" at fourth stimulated state versus xr.

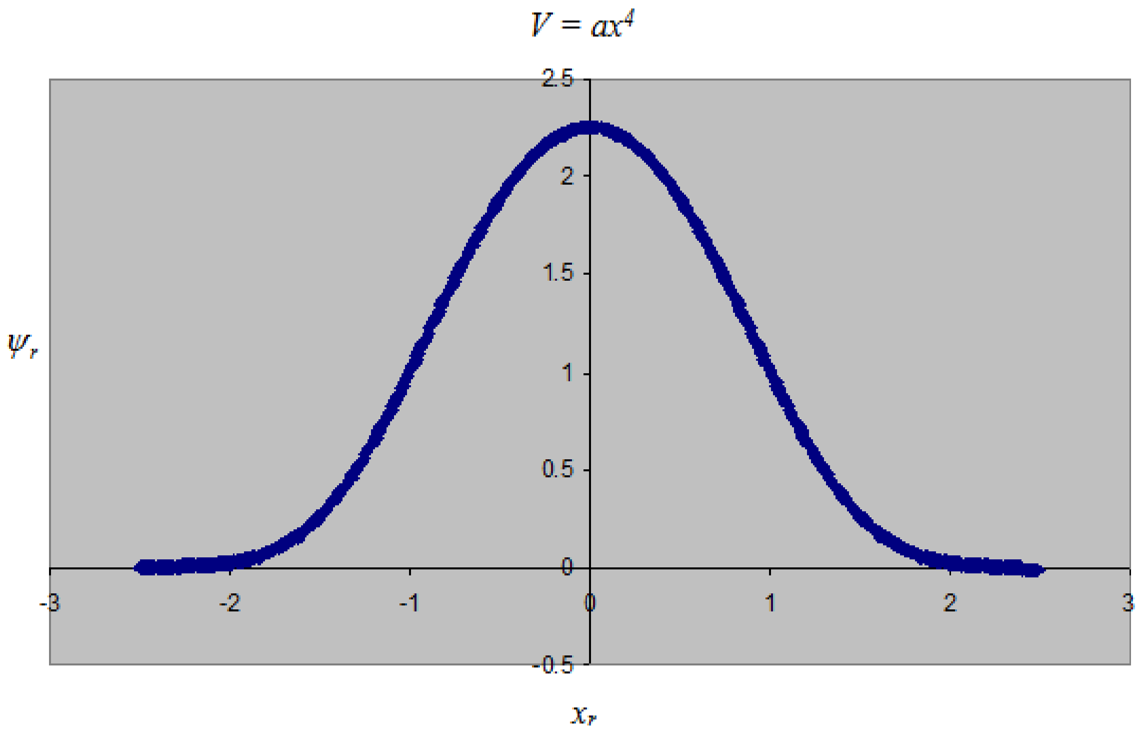

Fig .5-a. Curve of changes in wave function "ψ_r" at base state versus xr.

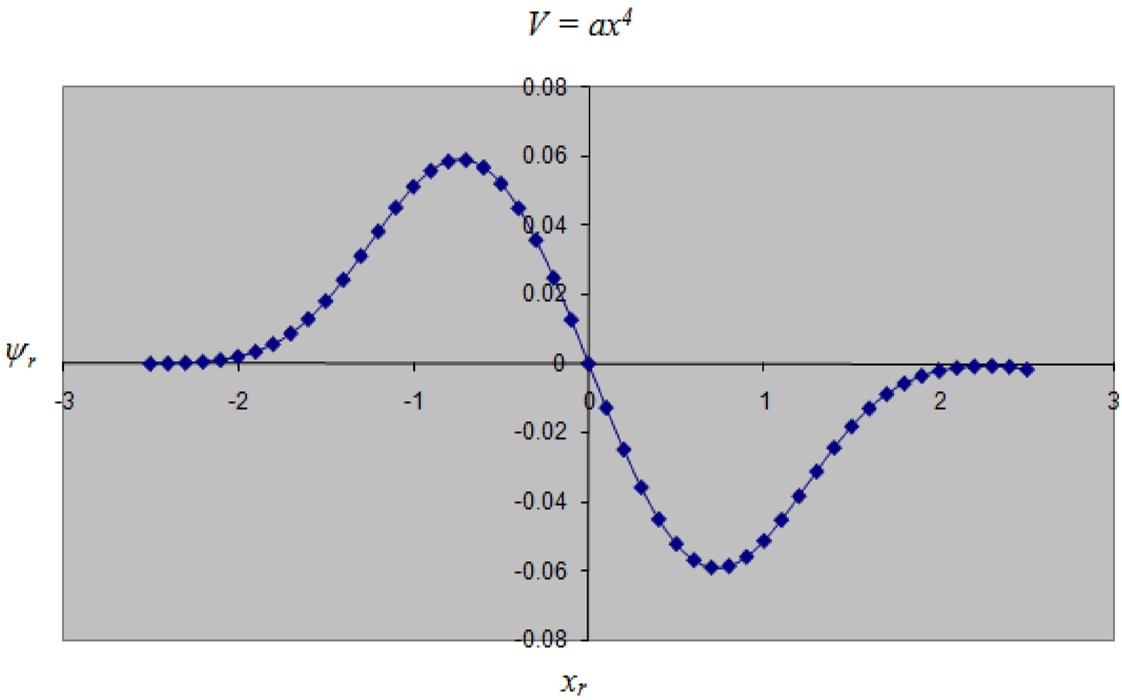

Fig. 5-b. Curve of changes in wave function "ψ_r" at firth stimulated state versus xr.

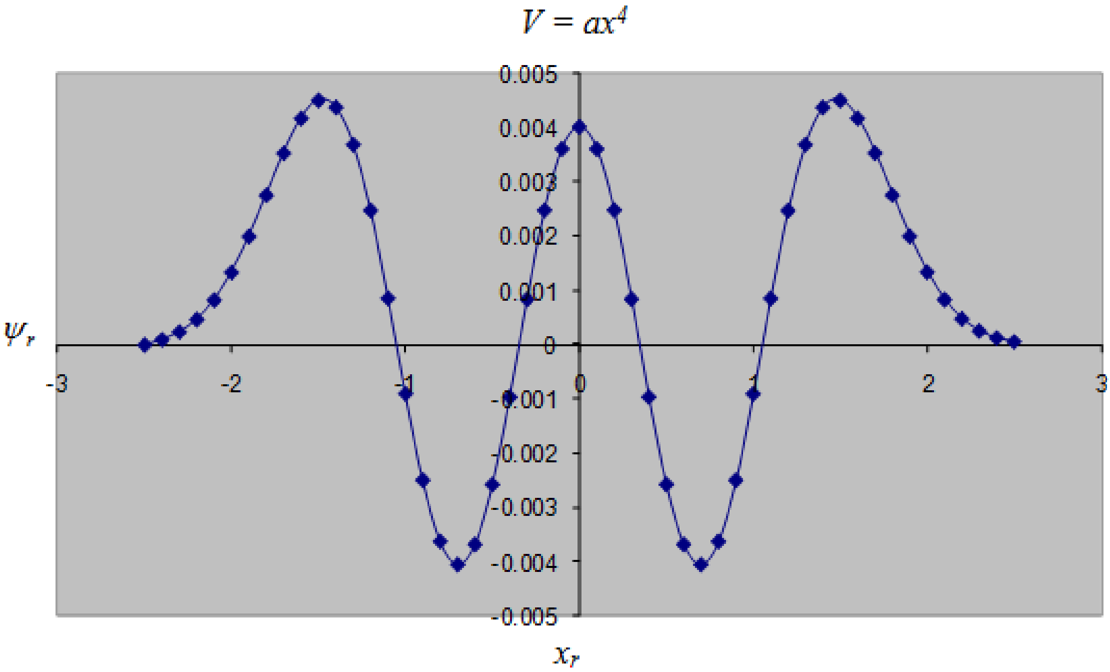

Fig. 5-c. Curve of changes in wave function "ψ_r" at fourth stimulated state versus xr

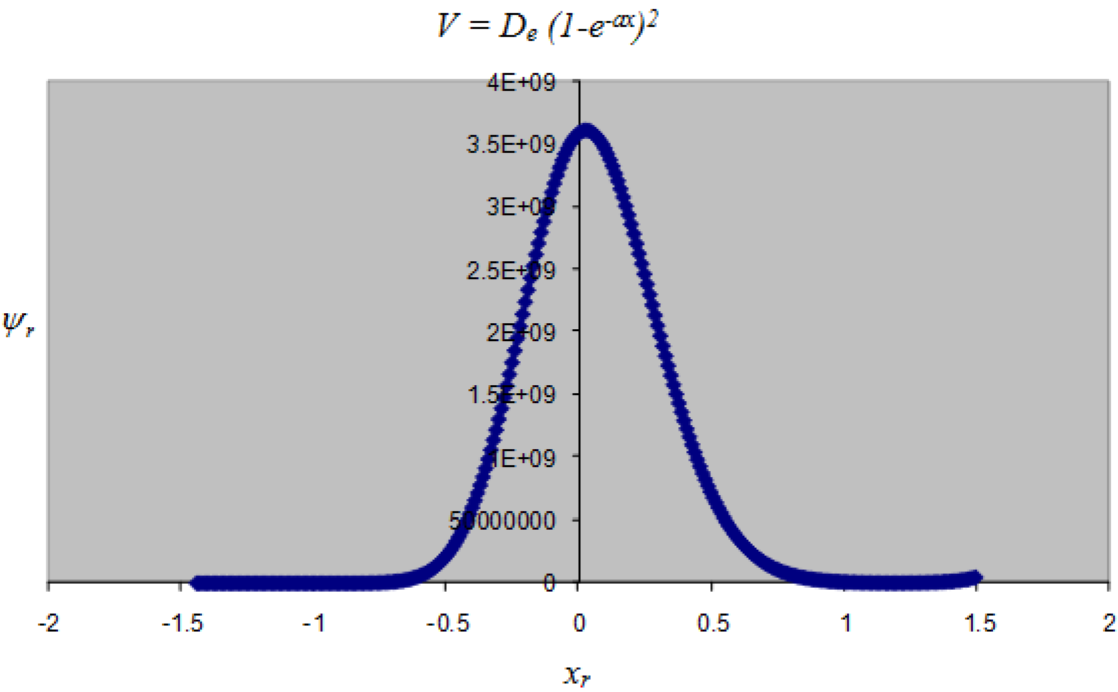

Fig. 6-a. Curve of changes in wave function "ψ_r" at base state versus xr.

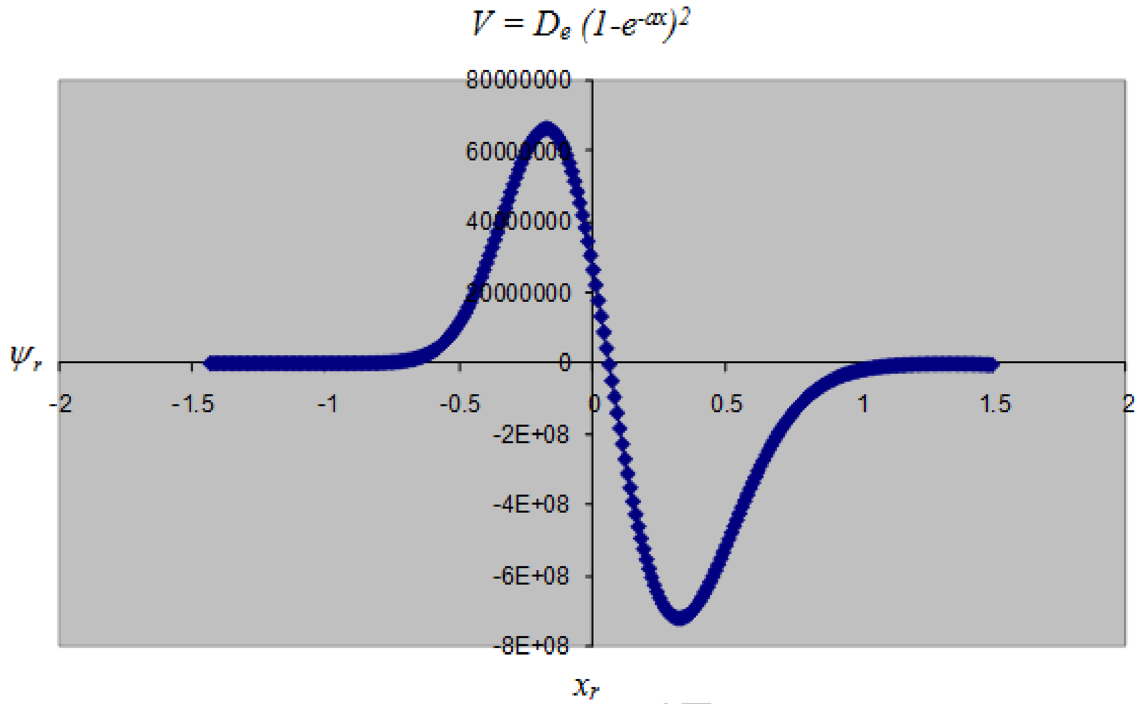

Fig. 6-b. Curve of changes in wave function "ψ_r" at firth stimulated state versus xr.

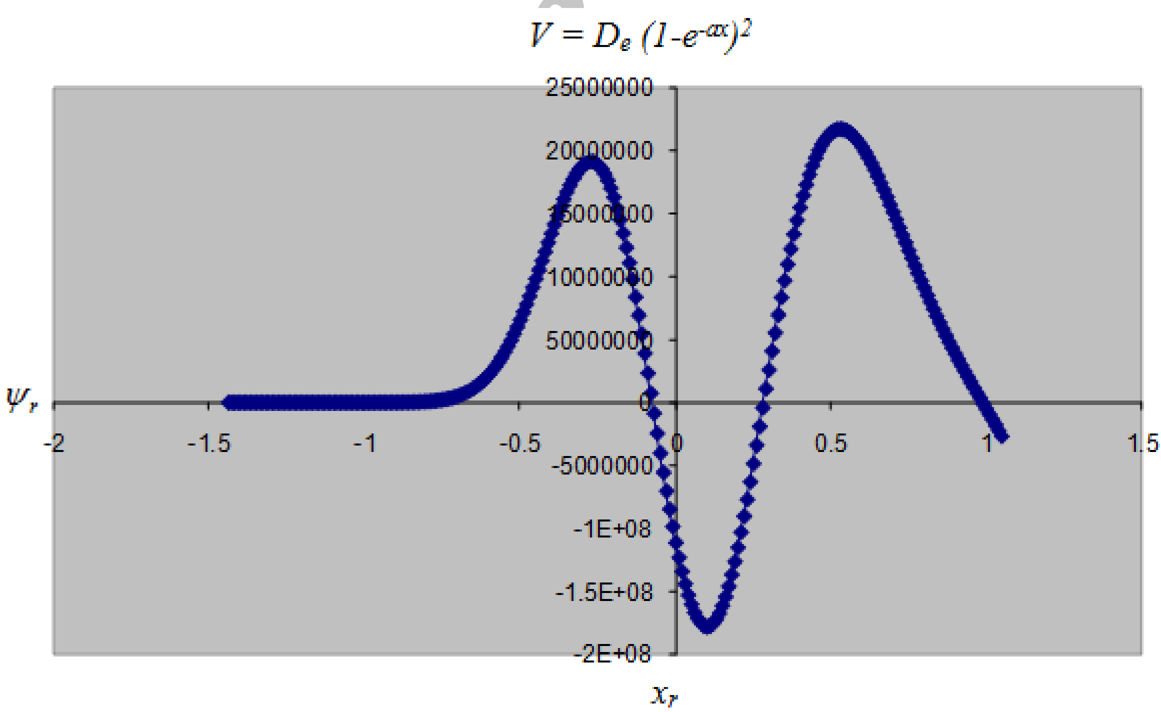

Fig. 6-c. Curve of changes in wave function "ψ_r" at second stimulated state versus xr.

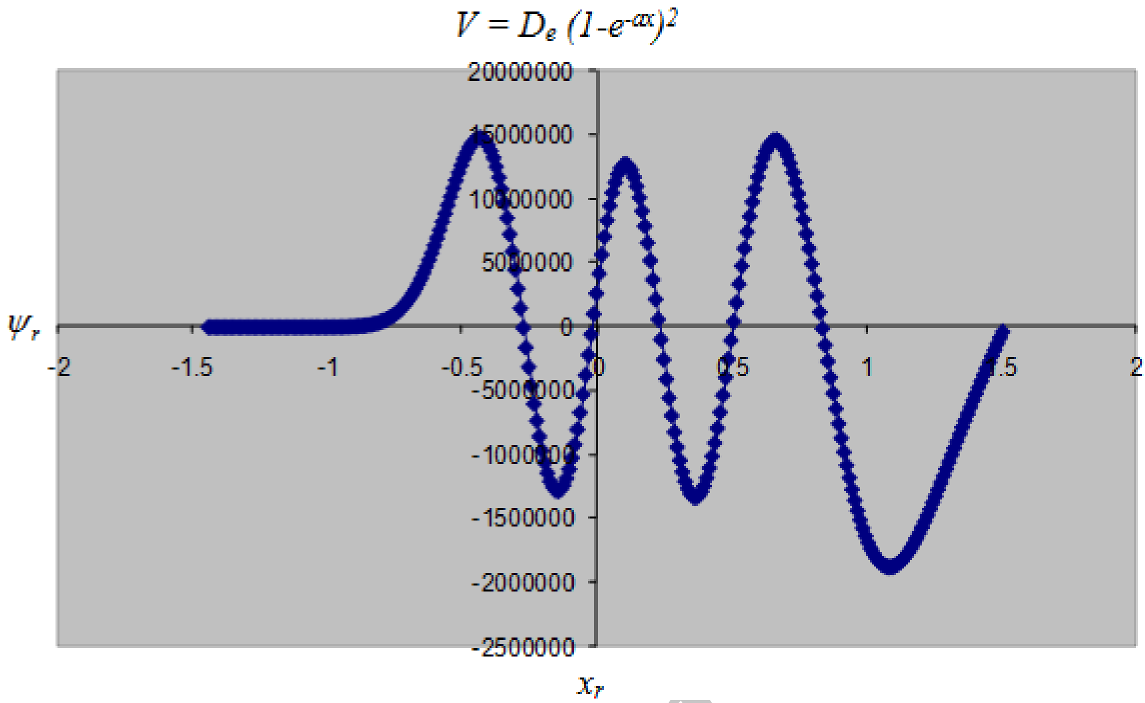

Fig. 6-d. Curve of changes in wave function "ψ_r" at fifth stimulated state versus xr.

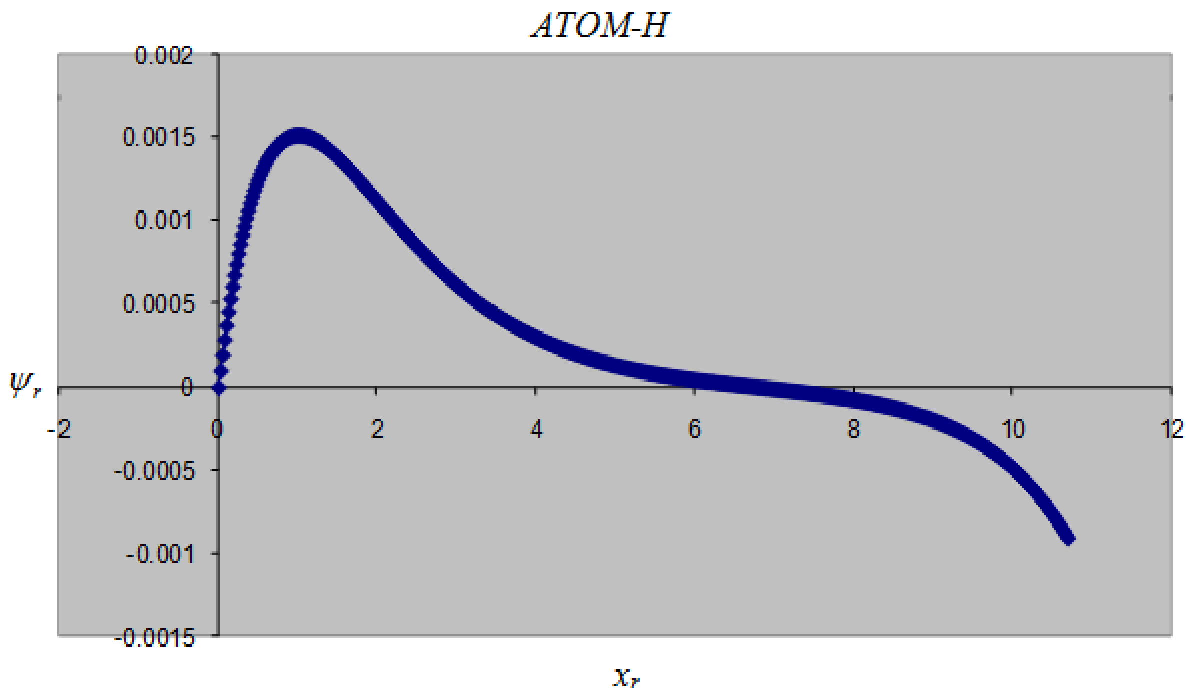

Fig. 7-a. Curve of changes in radial function of the orbital 1s versus xr.

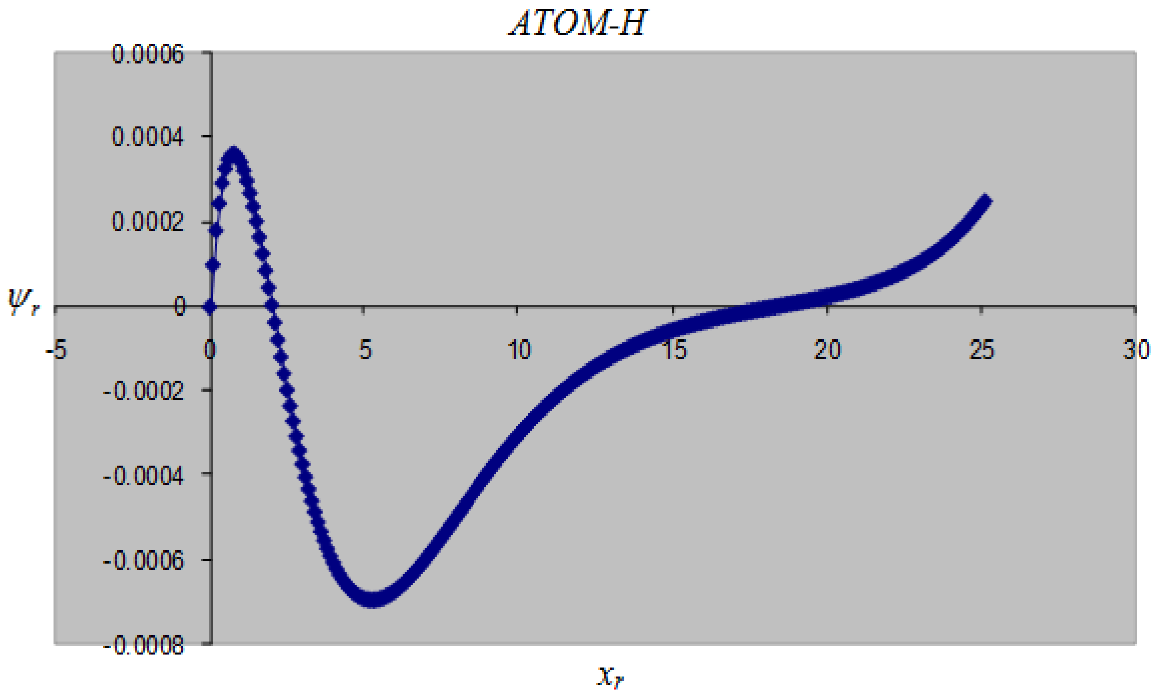

Fig. 7-b. Curve of changes in radial function of the orbital 2s versus xr.

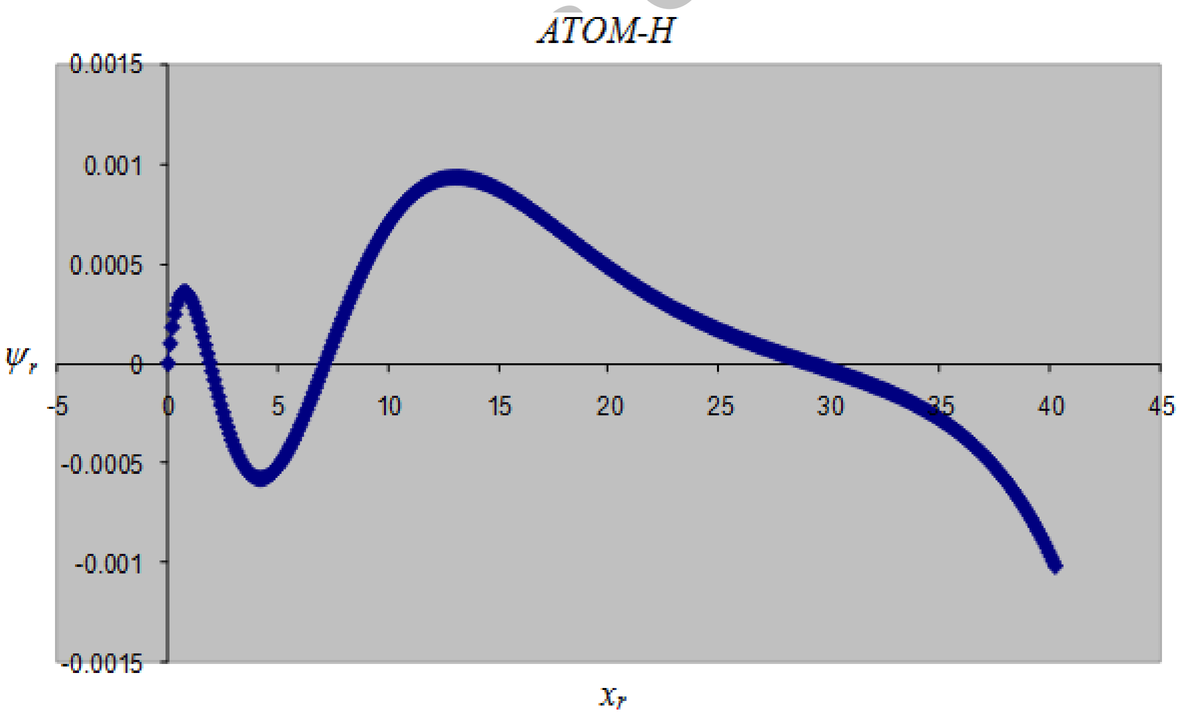

Fig. 7-c. Curve of changes in radial function of the orbital 3s versus xr.

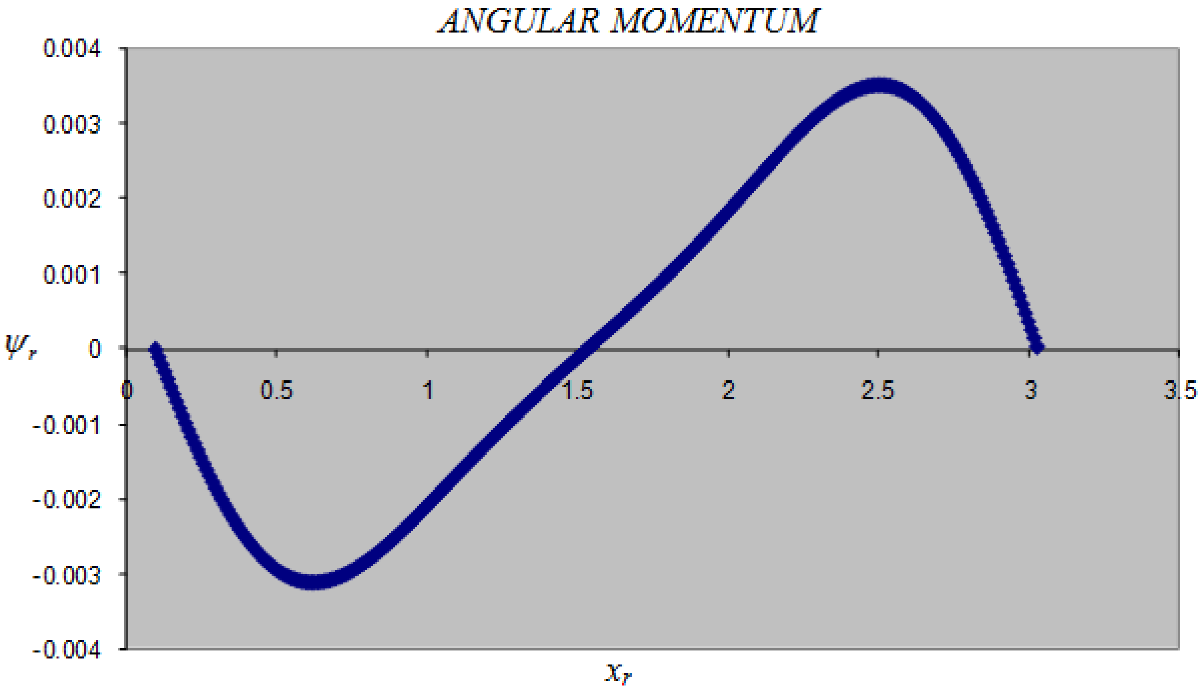

Fig. 8. Curve of changes in wave function yr versus θ.

$$V(x) = \frac{-V_o}{1+e^{x_r}}$$

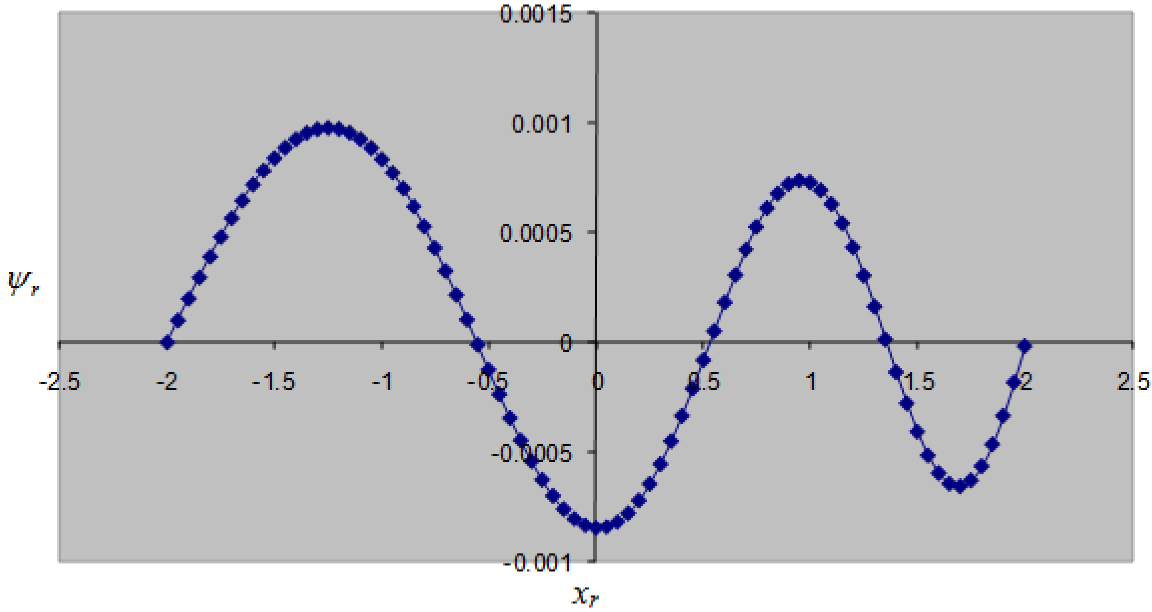

Fig. 9-a. Curve of changes in wave function "ψ_r" at third stimulated state versus xr.

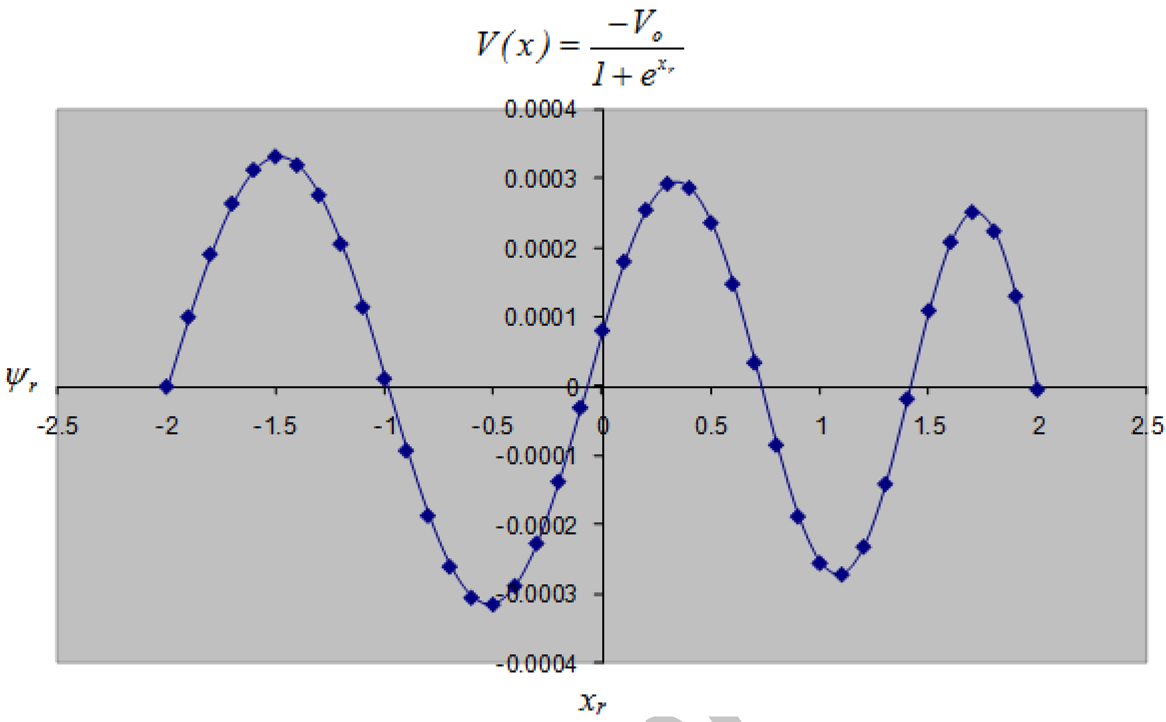

Fig. 9-b. Curve of changes in wave function "ψ_r" at fourth stimulated state versus xr.

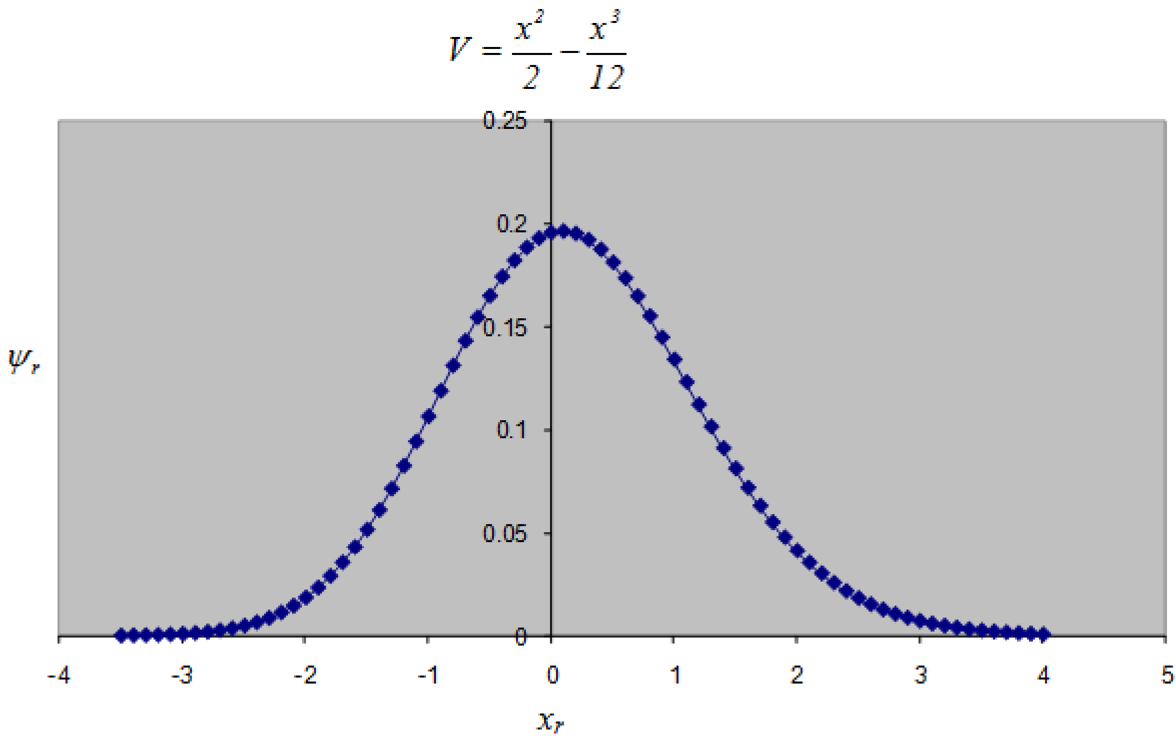

Fig. 10-a. Curve of changes in wave function "ψ_r" at base state versus xr.

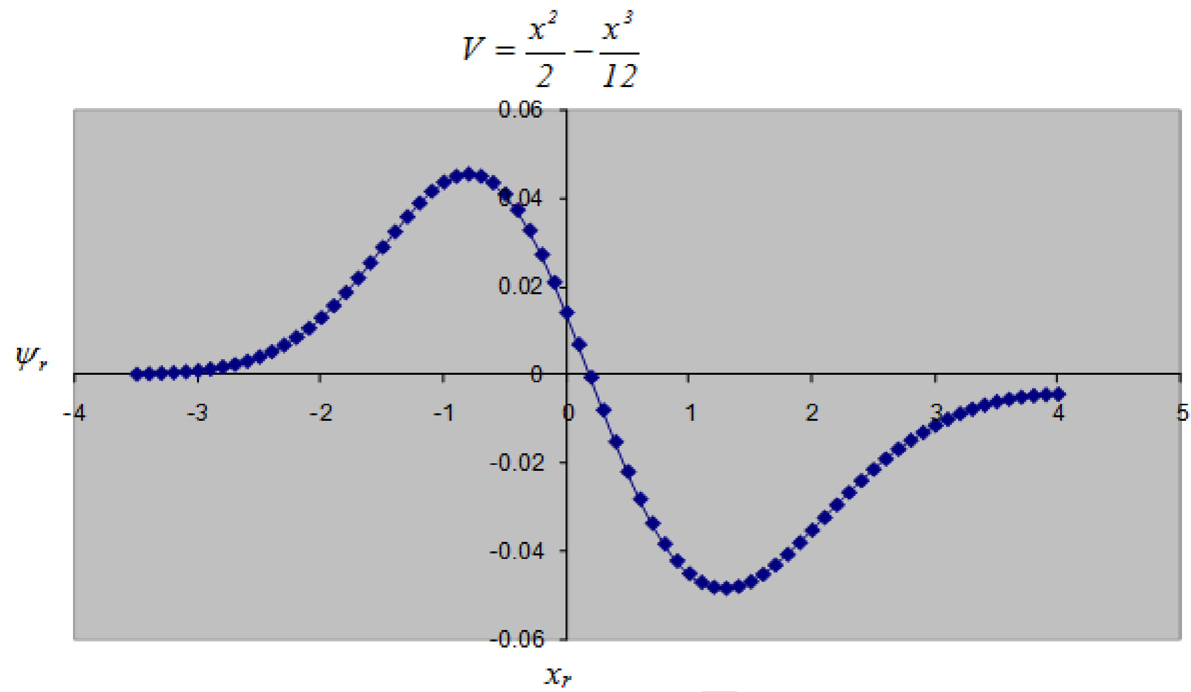

Fig. 10-b. Curve of changes in wave function "ψ_r" at first stimulated state versus xr.

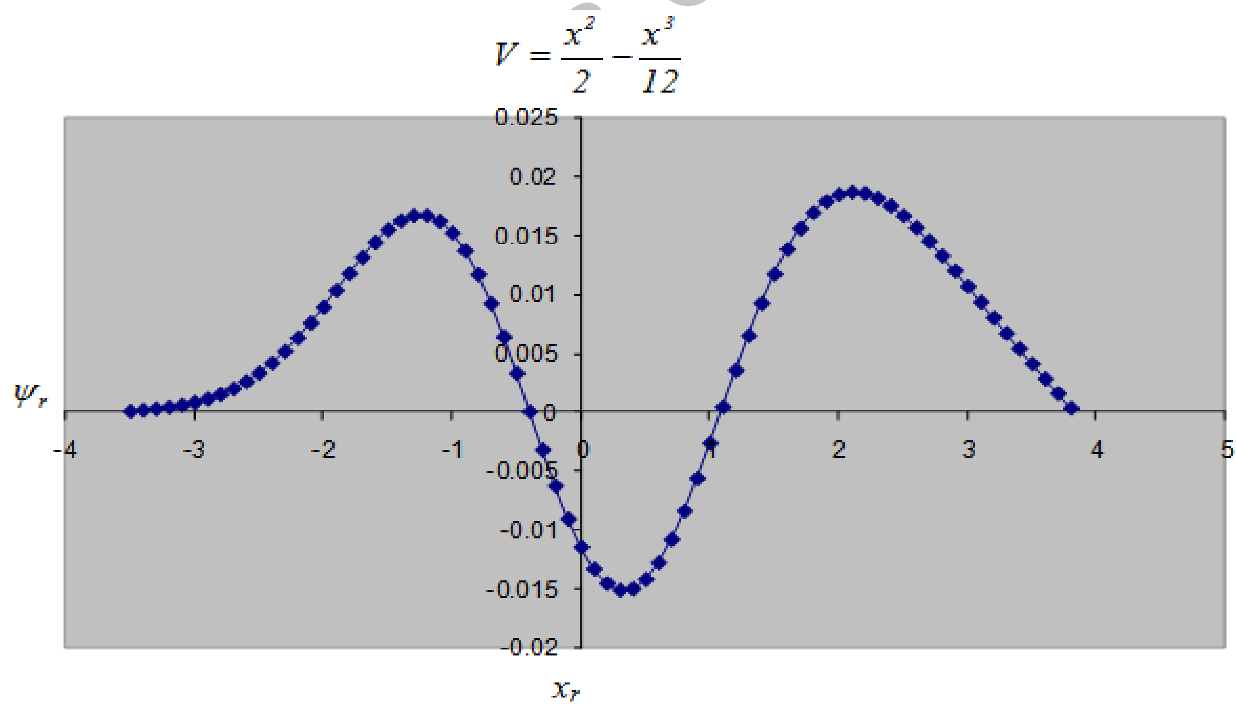

Fig.10-c. Curve of changes in wave function "ψ_r at second stimulated state versus x_r.

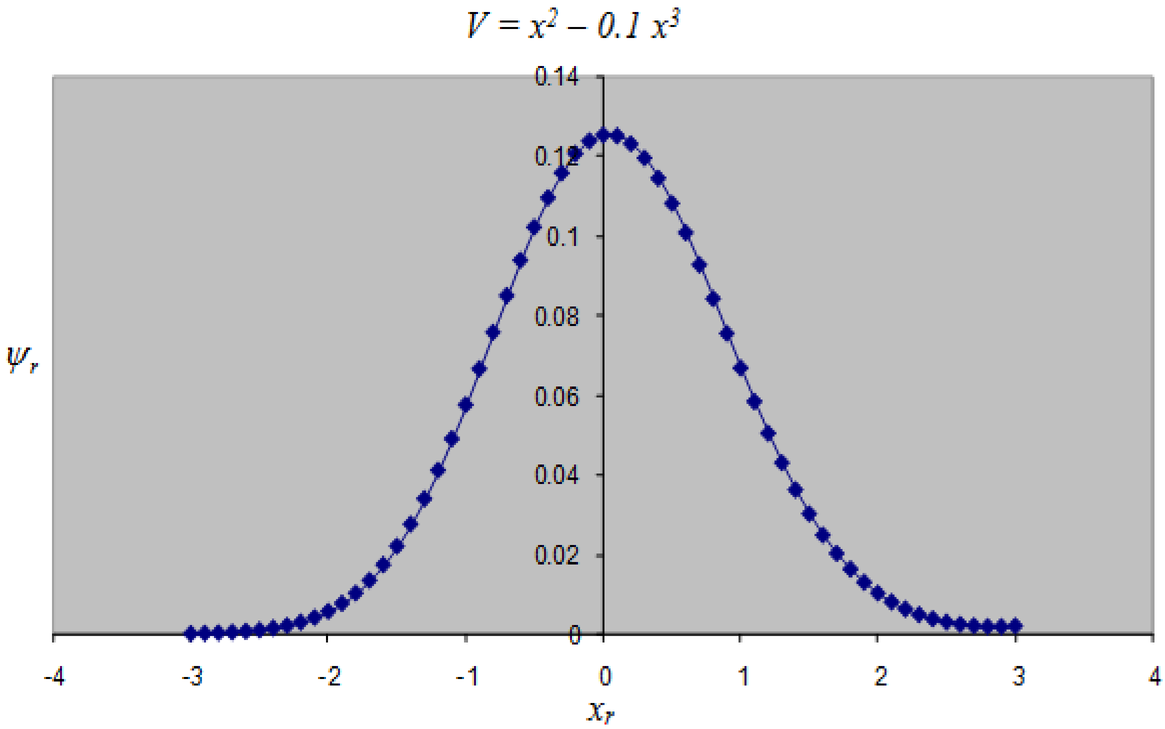

Fig. 11. Curve of changes in wave function "ψ_r" at base state versus xr.

CONCLUSION

Comparing analytical and numerical solutions to Schrödinger equation for simple harmonic oscillator and Morse functions, it was concluded that using Numerov method was an appropriate and acceptable approach to numerically solving Schrödinger equation. Considering the consistency between the results obtained from analytical and numerical solutions for aforementioned potential functions in Schrödinger equation, it was possible to use Numerov method so as to numerically solved Schrödinger equation with several potential functions such as disharmonic oscillator, radial equation related to movement of particle within central force field, equation related to angular momentum, etc.

REFERENCES

[1] J. Goodisman, Diatomic Interaction Potential energy, Academic Press, (1973).

[2] B. T. Sutcliffe, J. Chem. Soc. Faraday Trans., **89**, 2321 (1993).

[3] D. J. Searles and E. I. Von Nagy – Felsobuki, Am. J. Phys., **56**, 444 (1988).

[4] B. R. Johnson, J. Chem. Phys., **67**, 4086 (1977).

[5] F. R. Giordano and M. D.Weir, Differential Equations, Addison – Wesly, (1991).

[6] J. Telling huisen, J.Chem. Educ., **66**, 511 (1989).

[7] [J. K. Cashion, J. Chem. Phys., **39**, 1872 (1963).

[8] N. Levine, Molecular Spectroscopy, Wiley, (1975).

[9] P. M. Morse, Phys. Rev., **34**, 57 (1929).

[10] N. Levine, Quantum Chemistry, Prentice – Hall, Inc. (2000).

[11] F. Prosser and H. Shull, Ann. Rev. Phys. Chem., **17**, 37 (1966).

[12] P. O'D. Offenhartz, Atomic and Molecular Orbital Theory, Mc Graw - Hill Book Co., New york, Ny, (1970).

[13] R. S. Mulliken, Diatomic Molecules, Academic Press, Orlando, FL. (1977).
[14] H. F. Schaefer, The Electronic Structure of Atoms and Molecules, Addison – Wesley, Reading, MA, (1972).