

## Numerical solution for one-dimensional independent of time Schrödinger Equation

Z. Yousefian<sup>1,2,\*</sup> and N. Shadmani<sup>3</sup>

<sup>1</sup> Ph. D. Student, Department of Chemistry, College of Basic Sciences, Tehran Science and Research Branch, Islamic Azad University, Tehran, Iran

<sup>2</sup> Young Researchers and Elite Club, Shahre -Rey Branch, Islamic Azad University, Tehran, Iran

<sup>3</sup> Young Researchers and Elite Club, Rasht Branch, Islamic Azad University, Rasht, Iran

Received April 2014; Accepted May 2014

### ABSTRACT

In this paper, one of the numerical solution method of one- particle, one dimensional time-independent Schrodinger equation are presented that allows one to obtain accurate bound state eigen values and functions for an arbitrary potential energy function  $V(x)$ .

For each case, we draw eigen functions versus the related reduced variable for the corresponding energies. 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 is represents the top Numerov method for numerical solution Schrodinger equation with different potentials energy.

**Keywords:** Time Independent Schrödinger equation; Numerical solution; Analytical solution; Numero method

### INTRODUCTION

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

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

Wave and energy functions of a molecule are found by solving Schrödinger equation, where  $q_{\alpha}$  and  $q_i$  are electronic and atomic coordinates, respectively.

$$\hat{H}\psi(q_i, q_{\alpha}) = E\psi(q_i, q_{\alpha}) \quad (2)$$

Molecular Hamiltonian (equ.1) is so complicated that one cannot solve it analytically. Fortunately there is a simple estimation with a high degree of accuracy, which is based on the fact that nucleuses are much heavier than electrons:  $m_{\alpha} \gg m_e$ . Therefore, electrons move much faster than nucleuses, and it is possible to consider the nucleuses immobile during electronic moves. Classically, change in nucleus configuration can be ignored during an electronic move cycle. Consequently, we omit nucleus kinetic energy terms from the equation (1) by considering nucleus immobile in order to obtain the Schrödinger equation for

\*Corresponding author: zohreh\_yousefian@yahoo.com

electronic movement:

$$(\hat{H}_{e1} + V_{NN})\psi_{e1} = U\psi_{e1} \quad (3)$$

where:

$$\hat{H}_{e1} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha e^{r_i}}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{e^{r_{ij}}}{r_{ij}} \quad (4)$$

$$V_{NN} = \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta e^{r_{\alpha\beta}}}{r_{\alpha\beta}} \quad (5)$$

It is possible to solve the one-dimensional Schrödinger equation by using different potential energy functions with several methods. Also, it is easily possible to solve the Schrodinger equation for simpler potential energies such as particle in a box, and harmonic oscillator, using analytical method. But analytical method is not able to solve more complicated potential functions. So, there have 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 has been thoroughly described. Using Numero method, it is possible to solve the Schrödinger equation numerically by using different potential functions.

### CALCULATION METHOD

It is worth noting that the Schrödinger equation can be solved by Numero method as follows:

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

where:

$$G = m\hbar^{-2} [2V(x) - 2E], \quad s = x - x_n \quad (7)$$

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:

$$\psi_r = \frac{\psi}{B^{-\frac{1}{2}}}, \quad x_r = \frac{x}{B}, \quad E_r = \frac{E}{A} \quad (8)$$

Then, we guess a certain value for  $E_{guess}$ . For this purpose, we should start with a point that is completely located within the left side classic forbidden region, and plot changes in wave function  $y_r$  versus  $x_r$ , using computer soft wares 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 have 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.

Using the equation (6) and having  $\psi_n$  and  $\psi_{n-1}$  (y values at the two points  $x_n$  and  $x_{n-1}$ ),  $\psi_{n+1}$  (the value of y at the point  $x_{n+1}$ ) can be calculated.

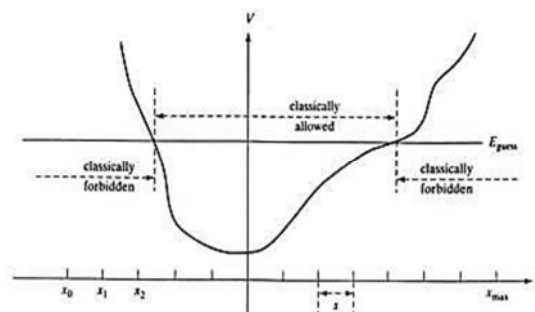


Fig. 1. V versus X for a one-particle and a one-dimensional system.

We start with a point that is located exactly within the left side classic

forbidden region (in the fig. 1). At this point, the value of  $y$  is too small, and we estimate the  $y$  to be zero at this point.  $\psi_0 = \psi(x_0) = 0$ . We also choose the point  $x_{max}$  within the left side classic forbidden region, and make it necessary to meet the equation  $y(x_{max}) = 0$ . We choose a small value for the distance  $s$  between the consecutive points, and choose a small number like 0.0001 for  $y$  at the point  $x_{o+s}$ :  $y, y(x_1), y(x_{o+s}) = 0.0001$ . After determining the values of  $y_1$  and  $y_0$ , values of  $G$  are calculated using  $E_{guess}$ . Then, using the equation (6), value of  $y_2, y_3$  and  $y_4$  are obtained by considering  $n=1, n=2$ , and  $n=3$ , respectively. This procedure continues until we have reached  $x_{max}$ .

If  $y_{guess}$  does not include any nodes between  $x_0$  and  $x_{max}$ ,  $E_{guess}$  is equal to or less than  $E_1$ ; If  $y_{guess}$  includes an internal node,  $y_{guess}$  is between  $E_1$  and  $E_2$  (fig. 2).

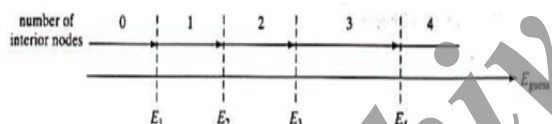


Fig. 2. Number of nodes in Numerov method in the form of a function of Energy  $E_{guess}$

There are several computer soft wares for solving one-dimensional Schrödinger equation by Numerov method. Among them are Q-Basic, Maple5, Matlab, Mathematica, Derive, Mathcad, Theorist and spreadsheet. In this research, the Spreadsheet software has been used. Application procedure of the software Spreadsheet for harmonic oscillator is explained in the book "Levine's Quantum Chemistry".

## RESULTS AND DISCUSSION

### Analytical Solutions to one-dimensional harmonic oscillator function

The independent-of-time Schrödinger equation for one-dimensional harmonic

oscillator is as follows:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2\psi = E\psi \quad (9)$$

Solution of the equation (9) has been described in detail in so many of Quantum Chemistry books and we discuss only results obtained from solutions to the equation. Those solutions to the equation (9) which are squarely integrable exist only for  $E$  values according to the following:

$$E = \left(v + \frac{1}{2}\right) h\nu \quad v = 0, 1, 2, 3, \dots \quad (10)$$

It can be shown that well-behavior solutions for the equation (9) is in form of multiplying  $\exp\left(-\alpha \frac{x^2}{2}\right)$  by a polynomial of  $x$  from the order  $v$ , with  $\alpha = 2\pi\nu \frac{m}{\hbar}$ . Figure. 3 shows explicit forms of some wave function lower than  $y_0, y_1$ , and  $y_3$ . Increase in quantum number causes increase in number of nodes. Harmonic oscillator wave functions consistent with  $x$  reduce to zero exponentially.

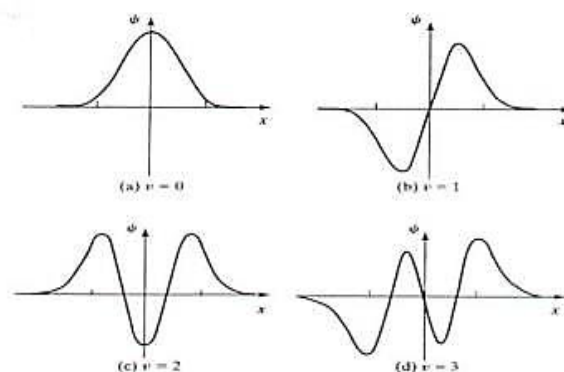


Fig. 3. Wave functions for four states lower than harmonic oscillator,

### Numerical Calculations for simple harmonic oscillator

In order to numerically solve Schrödinger equation for harmonic oscillator using Numerov method and to drawing wave function curve versus  $x$ , we should make the considered equation dimensionless, and

then solve the equation by using Numerov method.

Harmonic oscillator has the term  $v = \frac{1}{2}kx^2$  and Schrödinger equation has three constants including k, m, and h for harmonic oscillator. We name dimensionless reduced energy  $E_r$  and reduced  $x$  parameter " $x_r$ ". These parameters are defined as follows:

$$E_r = \frac{E}{A}, \quad x_r = \frac{x}{B} \quad (11)$$

Energy has dimensions of mass  $\times$  (length)<sup>2</sup>(time)<sup>2</sup> as written in the following:

$$[E] = ML^2T^{-2} \quad (12)$$

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

The equation indicates that k have the dimensions energy  $\times$  length<sup>-2</sup>. From the equation (12), we obtain  $[K] = MT^{-2}$

The constant h has the dimension time  $\times$  energy. So,  $[m] = M$ ,  $[k] = MT^{-2}$ ,  $[\hbar] = MLT^{-1}$  (13)

Dimensions of A and Bin the equation (11) are energy and length, respectively.

$$[A] = ML^2T^{-2}, \quad [B] = L \quad (14)$$

So, solving these equations, we have:

$$A = m^{-\frac{1}{2}} k^{-\frac{1}{2}} \hbar \quad (15)$$

Assume that  $B = M^d K^e \hbar^f$ . So,

$$B = m^{-\frac{1}{4}} k^{-\frac{1}{4}} \hbar^{\frac{1}{2}} \quad (16)$$

$$E_r = \frac{E}{h\nu}, \quad x_r = \alpha^{\frac{1}{2}} x \quad (17)$$

Since  $|\psi(x)|^2$  is a probability parameter and probability parameters are dimensionless, normal  $y_x$  should have the dimensions length<sup>-1/2</sup>. So,

$$\psi_r = \frac{\Psi}{B^{\frac{1}{2}}} \quad (18)$$

$$\psi_r'' = G_r \psi_r, \quad G_r \equiv x_r^2 - 2E_r \quad (19)$$

For harmonic oscillator, using the values  $x_{r,0} = -5$ ,  $x_{r,max} = 5$  and  $s_r = 0.1$ . One can calculate the values of  $\psi_r$  and  $x_r$ . At several  $E_r$  s in an excel sheet, and then draw curves of wave function  $\psi_r$  versus  $x_r$ .

For example, figures 4-a, 4-b, and 4-c show curves of wave function versus  $x_r$  for harmonic oscillator at  $E_r = 0$ , basic state, which does not have any node, and fourth stimulated state of  $E_r = 4.499996$ , which has 4 nodes, respectively.

### Numerical Solution to Schrödinger equation with potential energy function

$$\text{of } V(x) = e^{-ax} \left( \frac{1}{r} - b \right)$$

This equation has three constants including m, h, and n. So, the constants A and B will be as follows:

$$B = \hbar^{\frac{1}{2}} a^{-\frac{1}{2}}, \quad A = \mu^{\frac{1}{2}} \hbar a \quad (20)$$

Also  $a = \left( \frac{\mu T^{-2}}{2} \right)^{\frac{1}{2}}$ , and finally reduced

Schrödinger equation will be equal to:

$$G_r = 2e^{-r_r} \left( \frac{1}{r_r} - b \right) - 2E_r, \quad \psi_r'' = G_r \psi_r \quad (21)$$

Importing the values  $x_{r,max} = 3$ ,  $x_{r,0} = -3$  as well as the relationship (21) and the term of  $\psi$  related to this equation and using the relationship (6), we can draw curves of wave function  $\psi_r$  versus  $x_r$ . For instance, the first stimulated state with  $E_r = 2.21$ ,  $s_r = 0.01$  which has one node (fig. 5-a), the second stimulated state with  $E_r = 5.05$  and  $s_r = 0.01$ , which has two nodes (fig. 5-b).

### Numerical Solution to Schrödinger equation with potential energy function

$$\text{of } V(x) = D_e \left(1 - \frac{r}{r_e} e^{-a(r-r_e)}\right)^2$$

This equation has three constants including m, h, and n. So, the constants A and B will be as follows:

$$B = \mu^{-\frac{1}{4}} \cdot \hbar^{\frac{1}{2}} \cdot k^{-\frac{1}{4}} \quad A = \mu^{\frac{1}{2}} \cdot \hbar \cdot k^{\frac{1}{2}} \quad (22)$$

Also  $a = \left(\frac{k}{\mu}\right)^{\frac{1}{2}}$ , and finally reduced

Schrödinger equation will be equal to:

$$G_r = \left[ 2D_{e,r} \left(1 - e^{-x_r} - \frac{x_r}{r_e} e^{-x_r}\right)^2 - 2E_r \right] \psi_r'' = G_r \psi_r \quad (23)$$

Importing the values  $x_{r, \max} = 1.5$ ,  $x_{r,0} = -1.5$  as well as the relationship (23) and the term of  $\psi$  related to this equation and using the relationship (6), we can draw curves of wave function  $\psi_r$  versus  $x_r$ . For instance, figure 6-a shows the curve of  $\psi_r$  versus  $x_r$  at the second stimulated state with  $E_r = 11.45$ ,  $s_r = 0.01$  which has two nodes, the third stimulated state with  $E_r = 18$  and  $s_r = 0.01$ , which has three nodes (fig. 6-b).

### Numerical Solution to Schrödinger equation with potential energy function

$$\text{of } V(x) = D_e \left(1 - e^{-n \frac{(r-r_e)^2}{2r}}\right)$$

This equation has three constants including m, h, and n. So, the constants A and B will be as follows:

$$B = \mu^{-\frac{1}{4}} \cdot \hbar^{\frac{1}{2}} \cdot k^{-\frac{1}{4}} \quad A = \mu^{\frac{1}{2}} \cdot \hbar \cdot k^{\frac{1}{2}} \quad (24)$$

Also  $n = 2\pi v_e \left(\frac{\mu}{2D_e}\right)^{\frac{1}{2}} = \left(\frac{k}{\mu}\right)^{\frac{1}{2}}$ , and finally

reduced Schrödinger equation will be equal to:

$$G_r = \left[ 2D_{e,r} \left(1 - e^{-\frac{x}{2}}\right) - 2E_r \right] \psi_r'' = G_r \psi_r \quad (25)$$

Importing the values  $x_{r, \max} = 1.5$ ,  $x_{r,0} = -1.5$  as well as the relationship (25) and the term of  $\psi$  related to this equation and using the relationship (6), we can draw curves of wave function  $\psi_r$  versus  $x_r$ . For instance, figure 7-a shows the curve of  $\psi_r$  versus  $x_r$  at the basic state with  $E_r = 21.1194$ ,  $s_r = 0.01$  does not have any nodes, the first stimulated state with  $E_r = 24.2$ ,  $s_r = 0.01$  which has one node (fig. 7-b), the second stimulated state with  $E_r = 26.77$  and  $s_r = 0.01$ , which has two nodes (fig. 7-c).

### Numerical Solution to Schrödinger equation with potential energy function of $V(x) = 1 + x^4 - 2x^2$

Here we have  $x_{r,0} = -2.5$ ,  $x_{r, \max} = 2.5$ ,  $s_r = 0.01$  and  $G_r = (2 + 2x^2 - 4x^2 - 2E_r)$ . Importing the above data into an Excel sheet, we can draw the considered curves; for instance, the first stimulated state with  $E_r = 0.8696$  which has one node (fig. 8).

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

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

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \frac{1}{2} kx^2 = E \psi \quad (26)$$

Analytically solving this equation, allowable energies of the harmonic oscillator will be as follows:

$$E = \left(v + \frac{1}{2}\right) \hbar v \quad v = 0, 1, 2, 3, \dots \quad (27)$$

For instance, value of E will be equal to  $\frac{1}{2}h\nu$ ,  $\frac{3}{2}h\nu$ , and  $\frac{9}{2}h\nu$  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  $X_r = \frac{X}{B}$  are used. The parameters A and B are multiplication of power-having constants  $\hbar \cdot \mu$  and k, and are calculated from the following relationship:

$$A = m^{-\frac{1}{2}} \cdot k^{\frac{1}{2}} \cdot \hbar, \quad B = m^{-\frac{1}{4}} \cdot k^{-\frac{1}{4}} \cdot \hbar^{\frac{1}{2}}$$

Using the above equations, we have

$$\psi_r = \frac{\psi}{B^{\frac{1}{2}}}, \quad E_r = \frac{E}{h\nu}, \quad x_r = \alpha^{\frac{1}{2}} \cdot x$$

and the differential equation of  $\psi_r^N$  will be

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

Now, by specifying classical unallowable regions, we can numerically solve the equation so that the minimum possible value for  $x_r$  will be equal to -5 and the maximum possible value for  $x_r$  will be equal to 5. These values result in different values for  $E_r$  at several states. At the basic state the value of E is 0.499995, at the first

stimulated state we have  $E_r = 1.499996$ , and at the fourth stimulated state, the value of  $E_r$  is equal to 0.499995.

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 are very close to each other.

### CONCLUSION:

We can numerically solve the of one-particle, one-dimensional time-independent Schrödinger equation for simple harmonic oscillator and different functions that allows one to obtain accurate bound state eigen values and eigen functions.

Comparing analytical and numerical solutions to Schrödinger equation for simple harmonic oscillator and different functions, it can be concluded that using Numerov method is 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 is possible to use Numerov method so as to numerically solve Schrödinger equation with several potential functions.

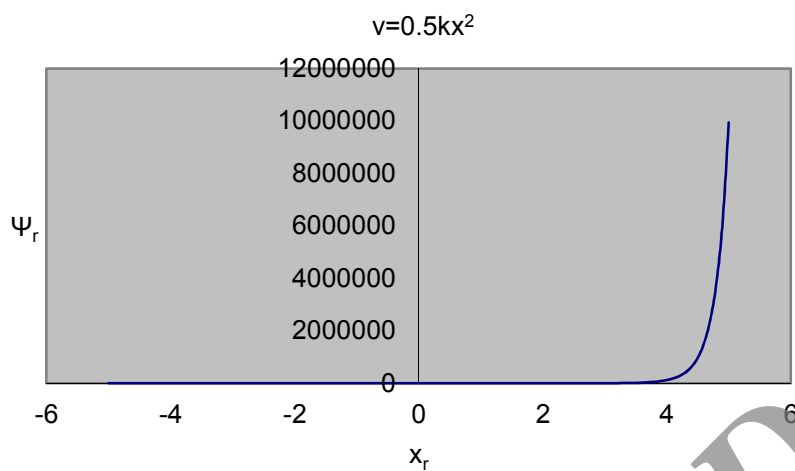


Fig. 4-a. Curve of changes in wave function " $\Psi_r$ " versus  $x_r$  for  $E_r=0$ .

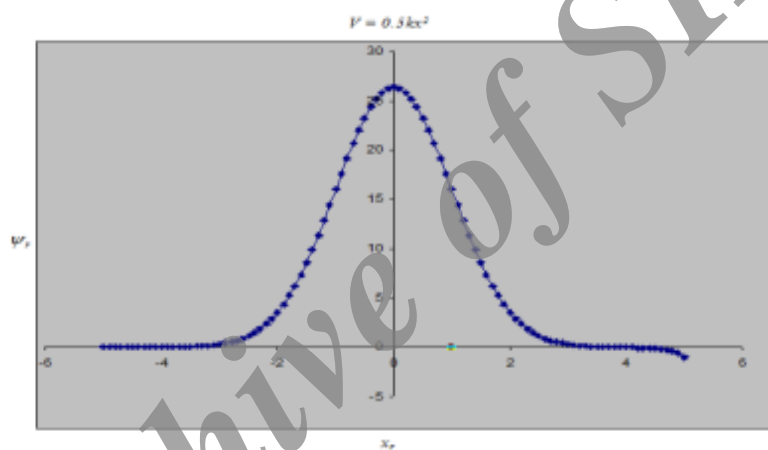


Fig. 4-b. Curve of changes in wave function " $\Psi_r$ " at base state versus  $x_r$ .

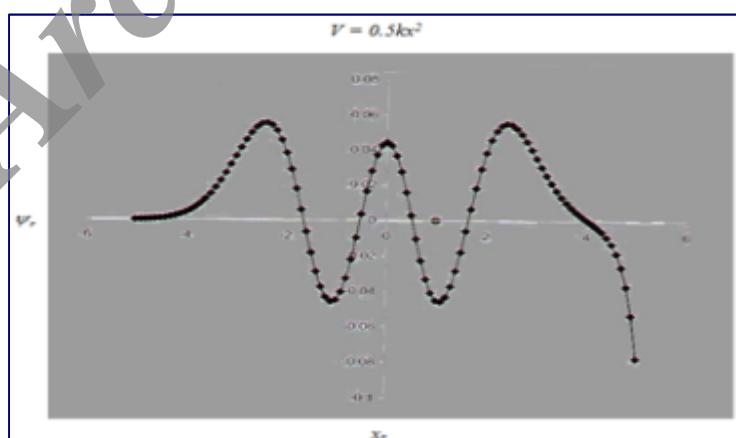


Fig. 4-c. Curve of changes in wave function " $\Psi_r$ " at fourth stimulated state versus  $x_r$ .

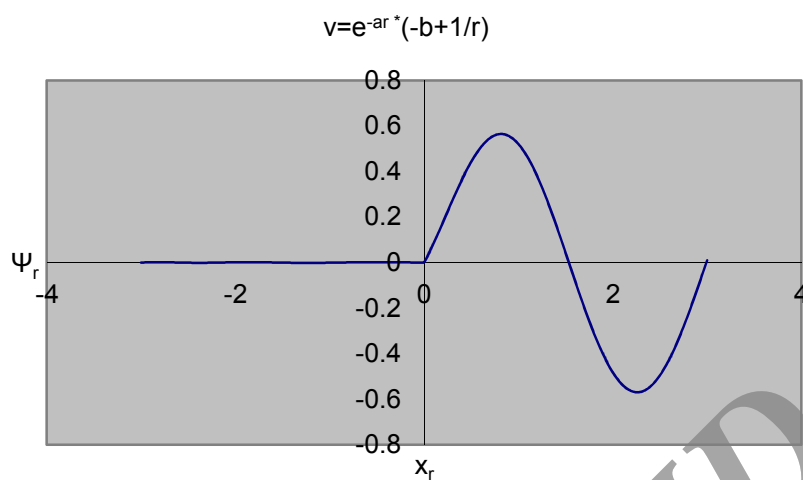


Fig. 5-a. Curve of changes in wave function " $\psi_r$ " at first stimulated state versus  $x_r$ .

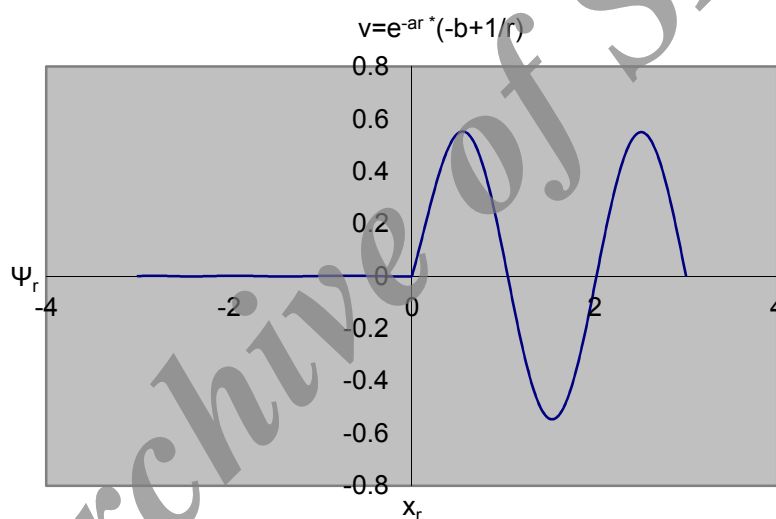


Fig. 5-b. Curve of changes in wave function " $\psi_r$ " at second stimulated state versus  $x_r$ .

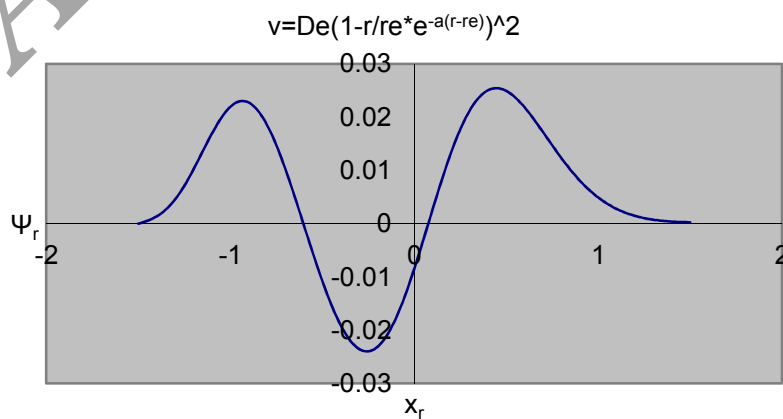


Fig. 6-a. Curve of changes in wave function " $\psi_r$ " at second stimulated state versus  $x_r$ .



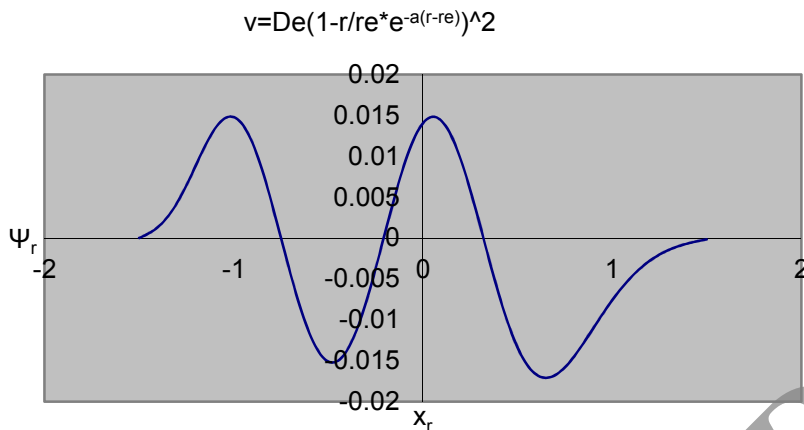


Fig. 6-b. Curve of changes in wave function “ $\psi_r$ ” at third stimulated state versus  $x_r$ .

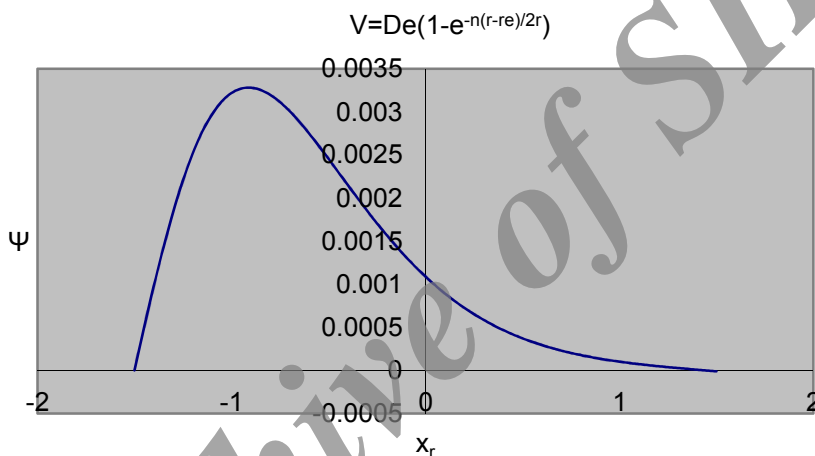


Fig. 7-a. Curve of changes in wave function “ $\psi_r$ ” at base state versus  $x_r$ .

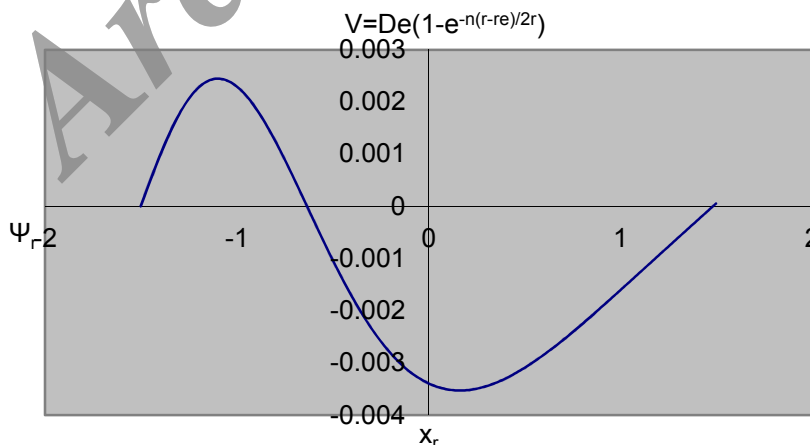


Fig. 7-b. Curve of changes in wave function “ $\psi_r$ ” at fifth stimulated state versus  $x_r$ .

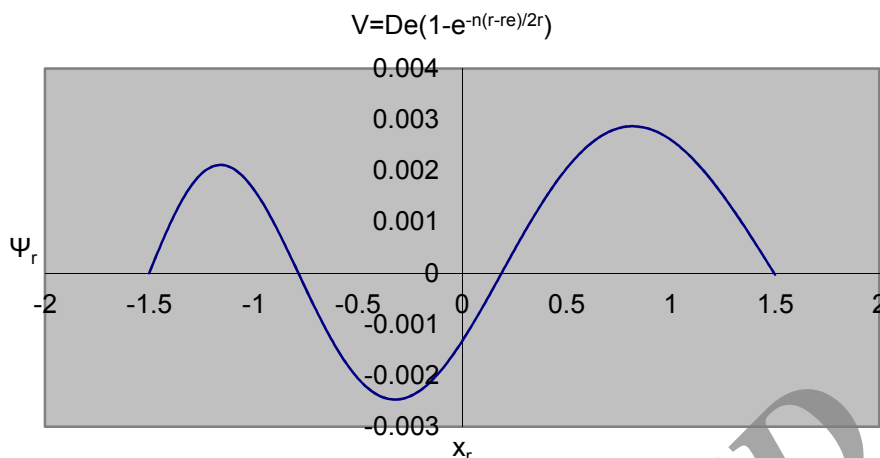


Fig. 7-c. Curve of changes in wave function " $\Psi_r$ " at second stimulated state versus  $x_r$ .

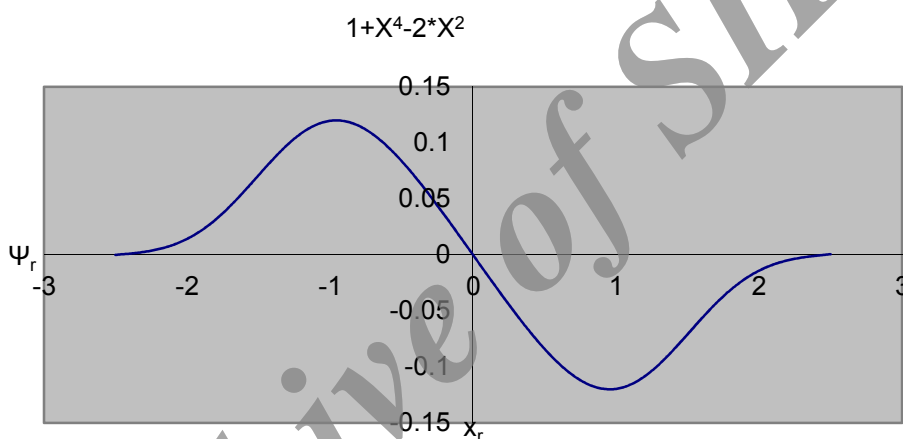


Fig. 8. Curve of changes in wave function " $\Psi_r$ " at first stimulated state versus  $x_r$ .

## 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 – Wesley, 1991.
- [6] J. Tellinghuisen, J. Chem. Educ., 66, 511 (1989).
- [7] J. K. Cashion, J. Chem. Phys., 39, 1872 (1963).
- [8] I. N. Levine, Molecular Spectroscopy, Wiley, 1975.
- [9] P. M. Morse, Phys. Rev., 34, 57 (1929).
- [10] I. 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.