อนุภาคในสถานะที่ถูกกักภายใต้ศักย์แบบเลนนาร์ด-โจนส์โดยอาศัยระเบียบวิธีเชิงตัวเลขแบบผลต่างจำกัด

Particles in Bound State System under the Lennard-Jones Potential by Using Finite Difference Methods

มฤเคนทร์ จอมเพชร[1], อาณาจักร พลจันทึก[2], ภ.พึ่งบุญ ปานศิลา[3], ณรงค์ฤทธิ์ มณีจิระปราการ[4], เสกสรร สุขะเสนา[4*]

Maruekhen Chomphet[1], Anajak Phonchantuek[2], P. Pungboon Pansila[3], Narongrit Maneejiraprakarn[4], Seckson Sukhasena[4*]

Received: 19 December 2018; Revised: 11 April 2019; Accepted: 1 May 2019

บทคัดย่อ

บทความฉบับนี้มีจุดประสงค์เพื่อนำเสนอการคำนวณระดับพลังงานของระบบอนุภาคคู่ในศักย์เชิงควอนตัมแบบ (12-6) เลนนาร์ด-โจนส์ โดยใช้ระเบียบวิธีคำนวณเชิงตัวเลขแบบผลต่างจำกัด ในแบบจำลองทางคณิตศาสตร์ได้ใช้การประมาณค่าความผิดพลาดอันดับสอง เพื่อสร้างเมตริกซ์ของสัมประสิทธิ์ตัวดำเนินการแฮมิลโตเนียน แล้วคำนวณหาค่าเจาะจงหรือพลังงานสถานะและฟังก์ชันคลื่นของแต่ละสถานะ ของศักย์แบบเลนนาร์ด-โจนส์ ซึ่งเป็นอันตรกิริยาของการผลักและการดูดกันของระบบสองอนุภาค การคำนวณหาระดับพลังงานที่ได้นี้คือพลังงานของอนุภาคที่อยู่ในสถานะกักกัน จากการคำนวณระดับพลังงานด้วยวิธีเชิงตัวเลขนี้ ทำให้ได้พารามิเตอร์ของพลังงานที่สถานะต่าง ๆ และได้แสดงกราฟของการกระจายของความน่าจะเป็นในแนวรัศมีมาด้วย

คำสำคัญ: ศักย์แบบเลนนาร์ด-โจนส์ ระเบียบวิธีเชิงตัวเลขแบบผลต่างจำกัด กลสาสตร์ควอนตัมเชิงแมทริกซ์ ระดับพลังงานในสถานะถูกกักกัน

Abstract

This paper aims to present a calculation of energy levels of (12-6) Lennard-Jones potential of the quantum mechanical system of the bound state problem by using finite difference methods (FDMs) with a truncation error $o(h^2)$ for constructing a proper Hamiltonian matrix and calculating the eigenvalues (λ) and eigenvectors (Ψ) from this matrix. The interaction potential between two-particle system in the atom is in the kind of attraction and repulsion. As a result, we represent the energy in each level through a unitless energy parameter (ε) and the radial probability distribution of energy levels is also presented. Moreover, we also illustrate graphs of radial probability distribution with respect to the distance in each energy level.

Keywords: Lennard-Jones Potential, Finite Difference Method, Matrix Quantum Mechanics, Energy Levels in Bound State

---

[1] นิสิตระดับปริญญาโท, [2]นิสิตระดับปริญญาเอก, [4]ผู้ช่วยศาสตราจารย์, วิทยาลัยเพื่อการค้นคว้าระดับรากฐาน "สถาบันสำนักเรียนท่าโพธิ์" มหาวิทยาลัยนเรศวร อำเภอเมือง จังหวัดพิษณุโลก 65000 ประเทศไทย

[3] อาจารย์, ภาควิชาวิทยาศาสตร์พื้นฐานและพลศึกษา คณะวิทยาศาสตร์ ศรีราชา วิทยาเขตศรีราชา, มหาวิทยาลัยเกษตรศาสตร์, อำเภอศรีราชา จังหวัดชลบุรี

[1] Master degree student, [2]Ph.D. degree student, [4]Assistant Professor. The Institute for Fundamental Study "The Tah Poe Academia Institute" Naresuan University, Mueang District, Phitsanulok 65000, Thailand.

[3] Lecturer, Department of Science and Physical Education, Faculty of Science at Siracha, Kasetsart University, Chon Buri 20230, Thailand

** Corresponding author. Seckson Sukhasena. The Institute for Fundamental Study "The Tah Poe Academia Institute" Naresuan University, Mueang District, Phitsanulok 65000, Thailand. E-mail: secksons@nu.ac.th*

Introduction

The interaction at quantum scale between two atoms is often described by the Lennard-Jones potential[1-3]:

$$\mathrm{v(r)} = u\left[\left(r_e / r\right)^{2k} - \left(r_e / r\right)^{k}\right], \qquad (1)$$

where $u = \hbar^2\sigma / 2\mathrm{m}r_e^2$, $\hbar$ is the Plank's constant divided by 2π, m stands for the reduced mass of two atoms and r_e is the equilibrium distance or the classical turning point of atoms which is the minima of interaction potential. The σ is the intensity parameter of this potential, as in the bound state energies are defined the intensity range of $\sigma \geq 0$. The term that stands for the attractive part is r^{-k} and the repulsive term is represented by r^{-2k}. The exponents of $2k$ and k represent the short and long range parts of the potential.

These are divided into three different values, i.e., with $k = 4$ for the case of interaction between atom and ion collision[5-6], and $k = 6$ for the two neutral atoms (the usual Lennard-Jones potential) or a familiar van der Waals potential[7], and $k = 7$ for two retarded atoms potential as known as the Casimir-Polder potential between two neutral polarizable atoms[8].

To explain the interaction between two-atom problems in the quantum point of view, for the simple case, we deal with the Schrödinger equation which is the equation of motion for the quantum system. It is difficult to solve the exact solution from the equation of motion which is always expressed by a second-order differential equation. Many problems reduce to the coefficients of a polynomial or to the Frobenius method[9-11]. We can evaluate an analytical solution as well as the numerical method to solve the problem [12-13]. In this paper, we show how to solve the Schrödinger equation numerically by using a finite difference method with a specific interaction, namely the Lennard-Jones potential. The latter potential is expected to be an interaction potential in the reversed process of making a bound state for the atomic layer deposition thin film technique for our future work. So our present study will be beneficial for that future project.

The formalism and method

In order to analyze a spherically symmetric system we write the general form of Hamiltonian as

$$\hat{H}\psi = E\psi, \qquad (2)$$

and for

$$\hat{H} = \frac{\hat{p}^2}{2\mathrm{m}} + \frac{\hat{L}^2}{2\mathrm{m}r^2} + \hat{V}, \qquad (3)$$

where $\hat{p}$ stands for the linear momentum operator, $\hat{L}$ is the angular momentum operator and $\hat{V}$ is for the interaction potential. The (12-6) Lennard-Jones potential can be expressed in term of the radius as (numbers in round bracket are the exponent of two terms in square bracket respectively)

$$V_{LJ}(\mathrm{r}) = \frac{\hbar^2\sigma}{2\mathrm{m}r_e^2}\left[\left(\frac{r_e}{r}\right)^{12} - \left(\frac{r_e}{r}\right)^{6}\right], \qquad (4)$$

where m is the reduced mass of two particles, r represents the relative distance between the particles, r_e is the equilibrium distance or the classical turning point and σ stands for the intensity parameter of the potential. The bound state energies, which are defined by the angular momentum quantum number ℓ, are shown in figure 1 for various values of its angular momentum. The relation of potential $(V(r))$ and the relative distance (r) following from eq. (4) is shown in Figure 2.

Substituting eq. (4) into the Hamiltonian eq. (3) leads to the Schrödinger equation; then, we use the separation of variables method to define the wave functions in term of radius, azimuthal and horizontal angles as

$$\Psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi). \qquad (5)$$

This method is very useful in the spherical symmetry. Following this assumption, we obtain the partial differential equations including of radial and spherical harmonic wave functions. The equation of

motion that is obtained in the radial wave function with the spherical symmetry is shown as follows.

$$-\frac{\hbar^2}{2\mathrm{m}}\frac{1}{\mathrm{r}^2}\frac{\mathrm{d}}{\mathrm{dr}}\left(\mathrm{r}^2\frac{\mathrm{d}}{\mathrm{dr}}\right)R(\mathrm{r})+\frac{\hbar^2\ell(\ell+1)}{2\mathrm{mr}^2}R(\mathrm{r})$$
$$+V_{LJ}(\mathrm{r})R(\mathrm{r})=\mathrm{E}R(\mathrm{r}). \quad (6)$$

For the expression of the radial wave equation in terms of unitless radial variable, we let $z=r/r_e$, and the unitless energy parameter we also let $\varepsilon=2mr_e^2\,\mathrm{E}/\hbar^2$. So the new radial wave function is as follows.

$$w(z)=R(r). \quad (7)$$

Then the equation of motion in eq. (6) and (7) can be rewritten as

$$-\left(\frac{2}{z}\frac{\mathrm{d}}{\mathrm{d}z}+\frac{\mathrm{d}^2}{\mathrm{d}z^2}\right)w(z)+\frac{\ell(\ell+1)}{z^2}w(z)$$
$$+\sigma\left(\frac{1}{z^{12}}-\frac{1}{z^6}\right)w(z)=\varepsilon w(z). \quad (8)$$

The atomic unit is usually used in the SI unit for the solutions. However, for convenience we choose the unit of physical quantities as followed in Table 1.

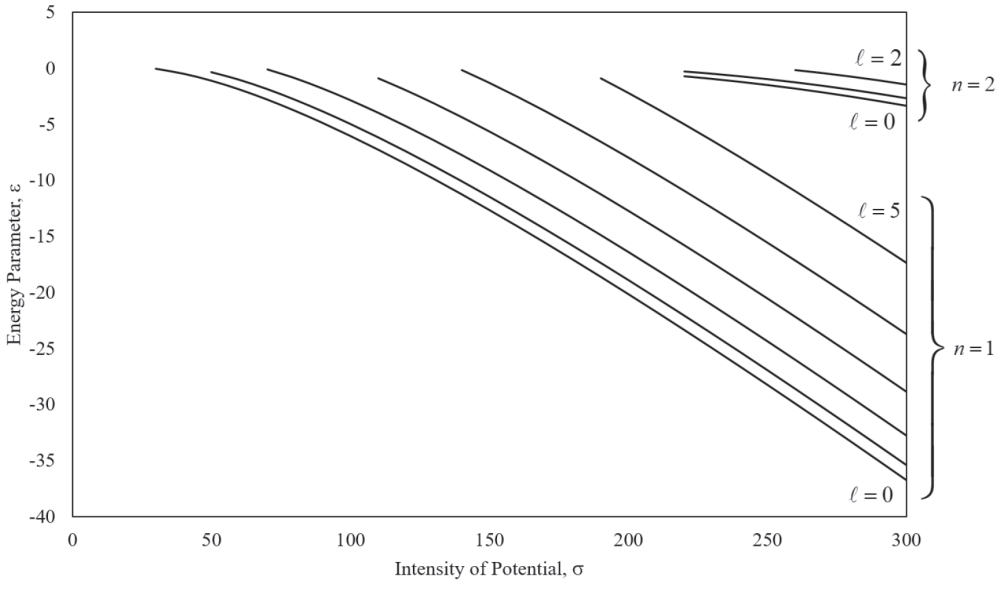

Figure 1 The bounded energy parameter versus the intensity of Lennard-Jones potential by varying the intensity of range of $0\le\sigma\le300$. This relation shows the ground state of the angular momentum quantum number $\ell=0,1,2,3,4,5$ and the first excited state $\ell=0,1,2$.

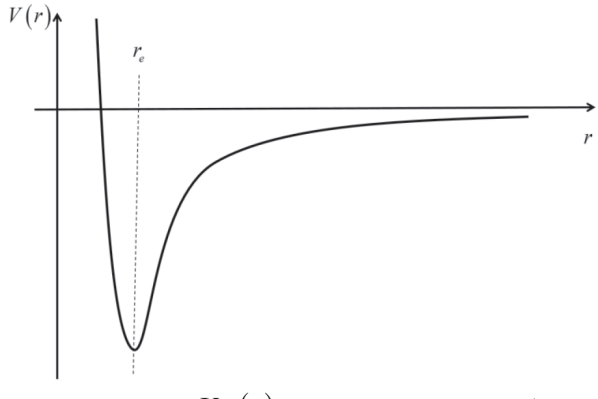

Figure 2 Generalized Lennard-Jones potential $V_{LJ}(r)$, r is the radius and r_e is the equilibrium distance (the classical turning point of the minima of potential).

Table 1 Relationship of quantity between SI and atomic units

Quantity	SI unit	Atomic Unit	Comparison
Energy	J, eV	Hatree	1 Hatree = 27.2 eV
Mass	kg, eV/c^2	m_e	1 m_e = 9.1x10^{-31} kg
Length	m, Å	Bohr's radius	1 Bohr's radius = 0.529 Å

For simplicity, we set $\hbar=1$, $m_e=1$, $\frac{1}{4\pi\varepsilon_0}=1$.

1. Procedures of numerical methods

According to the partial differential equations in eqs. (6)-(8), it is difficult to solve for the exact solution. To solve the approximate solution for sake of brevity, we introduce the numerical method for this problem. In this article, we prefer to present the method that is used to solve for the eigenvalues, λ and eigenvectors, Ψ (or eigenenergies and eigenstates respectively), by using the finite difference method on the real space.

The finite difference method[16-19] is the development to estimate the solution of a differential equation. Some coefficients come from the Taylor series. The small step size is defined as h and the coefficient is brought to multiply with parameters. We show how this method works as following:

$$f(x+h)=f(x)+hf'(x)+\frac{h^2}{2!}f''(x)+\frac{h^3}{3!}f'''(x)+o\left(h^4\right), \quad (9)$$

and

$$f(x-h)=f(x)-hf'(x)+\frac{h^2}{2!}f''(x)-\frac{h^3}{3!}f'''(x)+o\left(h^4\right), \quad (10)$$

where

$$f'(x)=\frac{d}{dx}f(x), \qquad f''(x)=\frac{d^2}{dx^2}f(x),$$
$$f'''(x)=\frac{d^3}{dx^3}f(x), \quad (11)$$

$o(h^n)$ is called the n^{th} truncations error. The combination between eqs. (9) and (10), leads to

$$f(x+h)+f(x-h), =2f(x)+h^2f''(x)+o\left(h^4\right) \quad (12)$$

As for the centered two points stencil for the first and the centered three points stencil for the second order derivative approximation, are shown as in eqs. (13) and (14) respectively,

$$f'(x)=\frac{f(x+h)-f(x-h)}{2h}+o\left(h^2\right), \quad (13)$$

and

$$f''(x)=\frac{f(x+h)-2f(x)+f(x-h)}{h^2}+o\left(h^2\right). \quad (14)$$

Changing the indices of implementation into i, we have the first and second derivatives in terms of i respectively as

$$f_i'=\frac{f_{i+1}-f_{i-1}}{2h}+o\left(h^2\right), \quad (15)$$

$$f_i''=\frac{f_{i+1}-2f_i+f_{i-1}}{h^2}+o\left(h^2\right). \quad (16)$$

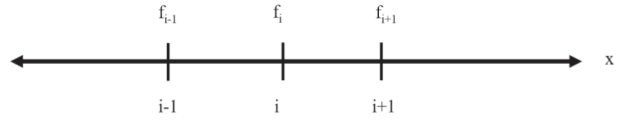

Figure 3 Define the position in finite difference method

2. The Eigenvalue equation and estimated values by using finite difference method

According to the quantum matrix mechanism as

$$\tilde{H}\bar{\chi}=\lambda\bar{\chi}, \quad (17)$$

where $\tilde{H}$ is the square Hamiltonian matrix, in which every diagonal elements does not vanish. The specific vector $\vec{\chi}$ is called the eigenvector which can span in term of matrix $\tilde{H}$ and multiply by the constant λ, is the so-called eigenvalue. Then, we introduce the determinant equation, to find the eigenvalue as

$$det\left|\tilde{\mathrm{H}}-\mathrm{I}_n\lambda\right|=0, \tag{18}$$

where I_n is an identity matrix $n\times n$. Consider the energy level from the wave function only the radial wave function in eq. (6) by using the finite difference method, the equation of motion in the radial part yields as eq. (19). By using the atomic unit, we can create the update equation

which is the matrix formalism in eqs. (20) and (21)

$$-\left[\frac{2}{z_i}\frac{w_{i+1}-w_{i-1}}{2\Delta z}+\frac{w_{i+1}-2w_i+w_{i-1}}{(\Delta z)^2}\right]+\frac{\ell(\ell+1)}{(z_i)^2}w_i+\sigma\left[\left(\frac{1}{z_i}\right)^{12}-\left(\frac{1}{z_i}\right)^{6}\right]w_i=\varepsilon w_i\ , \tag{19}$$

$$w_{i-1}\left[-\frac{1}{(\Delta z)^2}+\frac{1}{z_i}\right]+w_i\left[\frac{2}{(\Delta z)^2}+\frac{\ell(\ell+1)}{(z_i)^2}+\sigma\left(\frac{1}{(z_i)^{12}}-\frac{1}{(z_i)^{6}}\right)\right]+w_{i+1}\left[-\frac{1}{(\Delta z)^2}-\frac{1}{z_i}\right]=\varepsilon w_i \tag{20}$$

multiplying by $(\Delta z)^2$ on both sides of eq. (20) to obtain

$$w_{i-1}\left[A_{i,i-1}\right]+w_i\left[B_{i,i}\right]+w_{i+1}\left[C_{i,i+1}\right]=(\Delta z)^2\varepsilon w_i=\lambda w_i. \tag{21}$$

In this paper, we consider only the radial part wave function, R, because only this part yields the eigenvalue in each states. The coefficients in eq. (21) are used to create the Hamiltonian matrix $\tilde{\mathrm{H}}$, which is the $N\times N$ square matrix. As in the calculation for the eigenvalues and eigenvectors, we have to use this Hamiltonian matrix where the parameter of eigenvalue is λ. The eigenenergy is in the form of $\varepsilon=\lambda/(\Delta z)^2$, inally, we calculate the wave function $\vec{\chi}$ from this method. The solution of λ or ε is the diagonal matrix but $\vec{\chi}$ is in the column matrix. The treatment of the Hamiltonian matrix is to concern in the indices i from 1 to N. We obtain the eigenvalue equation as follow in the eqs.(22) and (23):

$$\varepsilon\begin{pmatrix}1 & & & 0\\ & 1 & & \\ & & \ddots & \\ 0 & & & 1\end{pmatrix}\begin{pmatrix}w_1\\ w_2\\ \vdots\\ w_{N-1}\\ w_N\end{pmatrix}=\tilde{H}\begin{pmatrix}w_1\\ w_2\\ \vdots\\ w_{N-1}\\ w_N\end{pmatrix} \tag{22}$$

$$\tilde{H}=\begin{bmatrix}B_{1,1} & C_{1,2} & 0 & 0 & 0 & 0\\ A_{2,1} & B_{2,2} & C_{2,3} & 0 & 0 & 0\\ 0 & A_{3,2} & B_{3,3} & C_{3,4} & 0 & 0\\ 0 & 0 & \ddots & \ddots & \ddots & 0\\ 0 & 0 & 0 & A_{N,N-1} & B_{N,N} & C_{N,N+1}\end{bmatrix} \tag{23}$$

The computational solution using the finite difference method, in the implementation, we define the radius between two particles (L) equals 5 Bohr radius by spanning the small pieces of area of 2000 slots (N is a number of Max Step). Each slot is called a step size ($\Delta z\equiv$ Step Size $=L/N$). We let the intensity of potential $\sigma=260$ by using the relationship between the unitless of energy and intensity potential parameters[5] in figure 1. The ground state and the excited states are defined by the principal quantum number n, and the angular quantum number, ℓ.

The results of numerical method

According to the ground state energy of $n=1$ and $\ell=1$ where these quantum number refer to the S-orbital and the excited energies of $n>1$ refer to the higher orbitals. The radial probability distribution $P_n=z^2\,|\,w_n\,|^2$ versus the unitless ratio of radius $z=r/r_e$ is shown in figures 4(a)-4(e) with the increasing of the energy parameters of bound state ε for the first-five states i.e. n = 1 to 5 equal to -28.5887, -1.2399, 1.4189, 4.6293 and 9.3165 respectively.

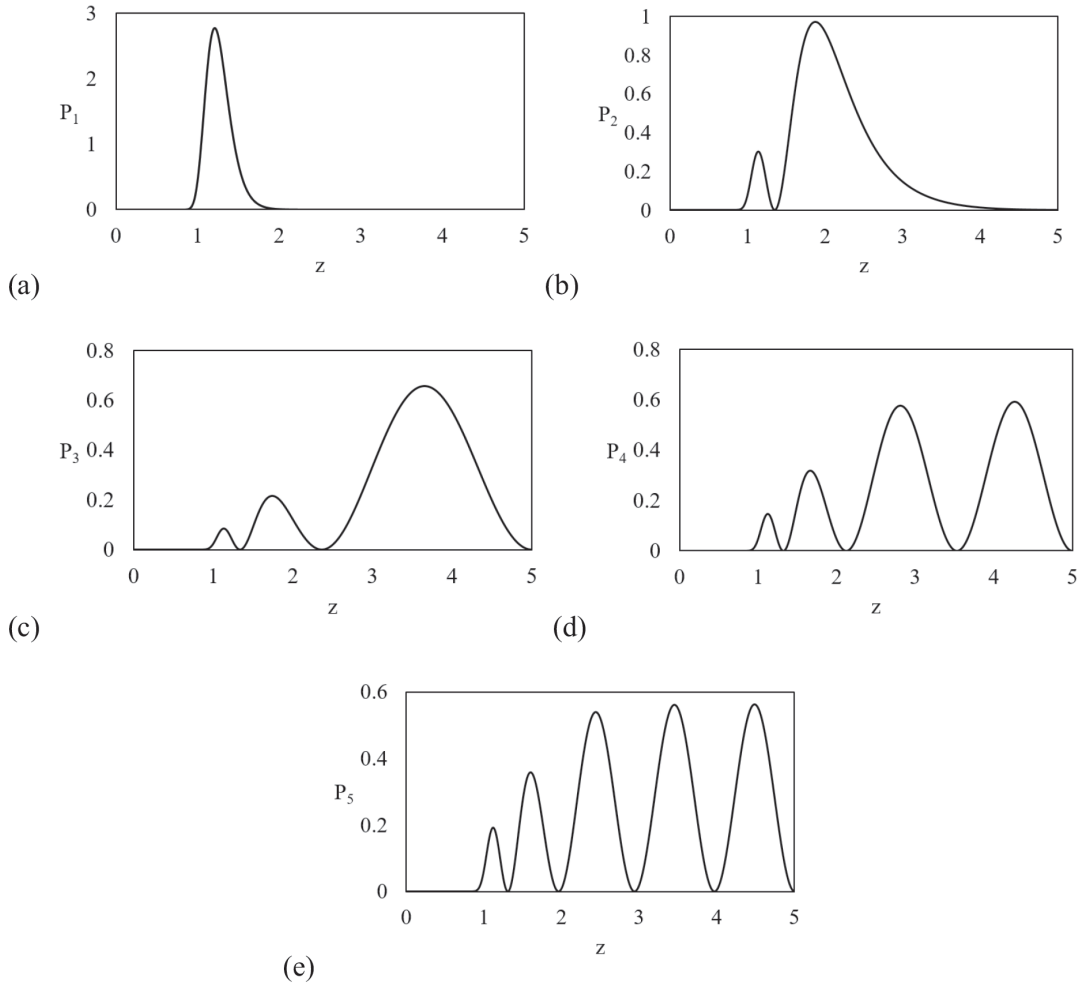

Figure 4 Plot of the radial probability distribution as a function of z where (a) The ground state $n=1, \ell=1$, and $\varepsilon=-28.5887$. (b) The 1st excited state, $n=2, \ell=1$, and $\varepsilon=-1.2399$. (c) The 2nd excited state, $n=3, \ell=1$, and $\varepsilon=1.4189$. (d) The 3rd excited state, $n=4, \ell=1$, and $\varepsilon=4.6293$. (e) The 4th excited state, $n=5, \ell=1$,, and $\varepsilon=9.3165$

Discussion and conclusion

The bound state energies of two-particle system in the Lennard-Jones potential are studied in several states and correspond to the spanned wave function in each quantum state. We have considered the numerical solution by using a finite difference method and showed the graphical solution by the radial probability distribution of the first-five states, n = 1 to 5. The negative energy levels refer to the bound state because of the influence of the potential energy is greater than the kinetic energy. In the other way, the positive energy levels refer to the excited (unbound) state of particles, which means when we increase n (principle quantum number) then the energy level of two-particle system is also increased. So they are in excited state or unbounded state. The numerical results show that it is easy to excite the two-particle system. The number of peaks in Figure 4 refers to the principal quantum number n [18-19].

The accuracy of the calculation depends on numbers of step size (Δz) or the width of potential well (L). In this implementation, we choose the width of the potential well of 5 Bohr radius then the numerical unitless max step and step size are 2000 and 0.0025, respectively. The results are represented for the energy levels of the first-five states which are illustrated in F igure 4.

As the results, the finite difference method is used to implement calculation of the energy levels and the radial probability distribution of the one dimensional

Schrödinger equation with the Lennard-Jones potential. This proposed method is highly useful, efficient and easy to implement.

The finite difference scheme is wildly used in several research problems even referred to the differential equation with the truncation error of $O\left(h^2\right)$ for a centered three points stencil for a second derivative.

Acknowledgements

The authors would like to thank their colleague, B. Gumgudpai, and P. Vanichchapongjaroen at *The Institute for Fundamental Study* for their help to improve this manuscript. Finally, the authors would greatly thanks to E.B. Manoukian for a final check and remarkable comment for this manuscript.

References

1. Jones, J E. On the determination of molecular fields.—II. From the equation of state of a gas. Proc. R. Soc. Lond. A 1924; 106(738): 463-477.
2. Zhen, S, & Davies, G J. Calculation of the Lennard‐Jones n–m potential energy parameters for metals. Physica Status Solidi (a) 1983; 78(2): 595-605.
3. Ishimori, Y. Solitons in a one-dimensional Lennard-Jones lattice. Progress of Theoretical Physics 1982; 68(2): 402-410.
4. Cashion, J K. Simple Formulas for the Vibrational and Rotational Eigenvalues of the Lennard‐Jones 12‐6 Potential. The Journal of Chemical Physics 1968; 48(1):94–103.
5. Idziaszek, Z, Calarco, T, & Zoller, P. Controlled collisions of a single atom and an ion guided by movable trapping potentials. Physical Review A 2007; 76(3), 033409.
6. Pade, J. Exact scattering length for a potential of Lennard-Jones type. The European Physical Journal D 2007; 44(2): 345-350.
7. Sesma, J. Exact solution of the Schrödinger equation with a Lennard–Jones potential. Journal of Mathematical Chemistry 2013; 51(7): 1881-1896.
8. Casimir, H B G, Polder, D. The influence of retardation on the London-van der Waals forces. Physical Review 1948; 73(4), 360.
9. Gómez, F J, Sesma, J. Scattering length for Lennard-Jones potentials. The European Physical Journal D 2012; 66(1), 6.
10. Lim, T C. Approximate relationships between the Generalized Morse and the Extended-Rydberg potential energy functions. Acta Chim. Slov 2005; 52: 149-152.
11. Lim, T C. Connection among classical interatomic potential functions. Journal of mathematical chemistry 2004; 36(3): 261-269.
12. Chachiyo, T. Lecture Note on Numerical Method for Physics and Engineers[Internet], Khon Kaen: Khon Kaen University 2011. [Cited 2018 Oct 20]. Available from: https://sites.google.com/site/siamphysics/numerical-methods
13. Garcia, A L. Numerical methods for physics. Englewood Cliffs, NJ: Prentice Hall; 2000. p. 15-16.
14. King, J, Dhakal, P. Finite Difference Schemes and the Schrodinger Equation. [Internet] 2014 Jun 2 [cited 2018 Oct 20]. Available from: http://www.dartmouth.edu/~pawan/final%20project.pdf
15. Hao, R, Simos, T E. New Runge–Kutta type symmetric two step finite difference pair with improved properties for second order initial and/or boundary value problems. Journal of Mathematical Chemistry 2018; 56(10): 3014-3044.
16. Clougherty, D. P, Kohn, W. Quantum theory of sticking. Physical Review B 1992; 46(8), 4921.
17. Kohn, W. Quantum Mechanics of Sticking. Surface Review and Letters 1994; 1(01): 129-132.
18. Simos, T E, & Williams, P S. A finite-difference method for the numerical solution of the Schrödinger equation. Journal of Computational and Applied Mathematics 1997; 79(2): 189–205.
19. Simos, T E, & Williams, P S. On finite difference methods for the solution of the Schrödinger equation. Computers & Chemistry 1999; 23(6): 513–554.