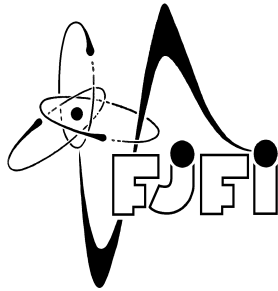


CZECH TECHNICAL UNIVERSITY IN PRAGUE
FACULTY OF NUCLEAR SCIENCES AND PHYSICAL ENGINEERING



BACHELOR 'S THESIS

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Název práce:

Neanalytické metody řešení jednodimenzionální časově nezávislé Schrödingery rovnice

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Abstrakt: V práci vyšetřujeme dvoukrokové schéma adaptované na specifickou formu lineární diferenciální rovnice druhého řádu. Detailně se zabýváme metodami Numerova, Raptise a Allisona a metodou Ixaru a Rizea. Výhody uvažovaného přístupu demonstrujeme na numerických příkladech s potenciálem Lennarda-Jonese pro výpočet problému vázaných stavů, Morseho potenciálu k výpočtu rozptylového problému a reálného interakčního potenciálu pro výpočet rozptylové délky.

Klíčová slova: Radiální Schrödingerova rovnice, metoda sítí, problém vázaných stavů, stavy kontinua, fázový posun, rozptylová délka

Title:

Non-analytical methods for the time-independent one-dimensional Schrödinger equation

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Abstract: We construct and investigate a two-step numerical scheme adapted for a particular form of linear second-order differential equations. We derive the exponentially fitted method, we look on the method of Raptis and Allison and the method of Ixaru and Rizea in details. The benefit of using this approach is demonstrated by considering some numerical examples based on the Lennard-Jones potential to solve the bound-state problem, the Morse potential to compute scattering problem and a real interaction interatomic potential to calculate the scattering length.

Key words: Radial Schrödinger equation, finite difference methods, phase shift, bound-states problem, scattering problem, scattering length

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Introduction

One-dimensional radial Schrödinger equation occurs very frequently in many scientific areas, such as theoretical physics, chemistry quantum physics and physical chemistry. Numerical methods for its solution have been the subject of great interest in recent years, the aim being to achieve a fast and reliable method that generates an approximate numerical solution.

The most widely used technique for numerical integration of the Schrödinger equation is Numerov's method [1] using a polynomial approximation. A fruitful way for developing efficient methods for the solution of the Schrödinger equation is to use exponential fitting. Raptis and Allison [2] derived the first type of Numerov exponentially fitted method, exploiting the oscillatory behaviour of the solution. The computational results obtained in their paper indicate that these fitted methods are more accurate than Numerov's method. Since then, exponential fitting has been the subject of great activity. In this thesis we present and compare the results based on Numerov and exponentially fitted method of Raptis and Allison gained by a computer program. The fitting version of certain products of algebraic and trigonometric or transcendental function, i.e. $x^l \exp(kx)$, is examined by Ixaru and Rizea [3].

Let us do the brief overview of the contents of this thesis. In Chapter 1 we start with two-step numerical scheme adapted for a particular form of linear second-order differential equations. In Chapter 2 we derive the exponentially fitted method for general problems and look at the method of Raptis and Allison and the method of Ixaru and Rizea also in detail. The chapter 3 presents the computer-based implementation of selected methods for the computation of bound states and phase shifts. The calculation of the scattering length in atomic collision is also included in this chapter. The subroutines are created in the programming language FORTRAN 95 and are enclosed in Appendix.

Chapter 1

Fundamental numerical integration methods of second-order ODE

In this section we give basic formulas concerning Numerov numerical procedure for solution of the well-known potential-based equation describing certain physical system. The aim is to obtain an approximate the solution of the second order differential equation

$$y''(x) = (V(x) - E)y(x), \quad x \in \langle a, b \rangle. \quad (1.1)$$

1.1 The finite difference method for boundary value problem

To obtain a difference equation whose solutions approximate the solutions of (1.1) we put

$$\begin{aligned} x_k &:= a + kh, & k = 0, 1, \dots, N, \\ x_N &= a + Nh = b, \end{aligned}$$

with a step interval h . In the whole paragraph we use the following notation:

$$y(x_k) \equiv y_k,$$

$$V(x_k) \equiv V_k,$$

$$\frac{d^n y}{dx^n} \equiv y^{(n)}.$$

Applying the Taylor series both for $y(x_k + h)$ and $y(x_k - h)$ we come to

$$y_{k+1} + y_{k-1} = \sum_{j=0}^{\infty} \frac{2h^{2j}}{(2j)!} y_k^{(2j)} \quad (1.2)$$

and

$$y_{k+1}^{(2)} + y_{k-1}^{(2)} = \sum_{j=0}^{\infty} \frac{2h^{2j}}{(2j)!} y_k^{(2j+2)}. \quad (1.3)$$

By dropping the sixth and higher order terms in (1.2) one obtains (in Bachmann-Landau notation)

$$y_{k-1} - 2y_k + y_{k+1} = h^2 y_k^{(2)} + \frac{h^4}{12} y_k^{(4)} + O(h^6). \quad (1.4)$$

Likewise, neglecting the sixth and higher order terms in h in (1.3) one obtains

$$y_{k-1}^{(2)} - 2y_k^{(2)} + y_{k+1}^{(2)} = h^2 y_k^{(4)} + O(h^6). \quad (1.5)$$

Now, we multiply (1.5) by the factor $h^2/12$ and subtract it from (1.4), which leads to the integration formula

$$z_{k-1} - 2z_k + z_{k+1} = h^2 y_k^{(2)},$$

where

$$z_k := y_k - \frac{h^2}{12} y_k^{(2)} = \left[1 - \frac{h^2}{12} (V_k - E) \right] y_k. \quad (1.6)$$

Finally, if we replace $y_k^{(2)}$ by means of the differential equation (1.1), the integration formula may be written in the form

$$-z_{k-1} + \left(2 + \frac{h^2(V_k - E)}{1 - \frac{h^2}{12}(V_k - E)} \right) z_k - z_{k+1} = 0, \quad (1.7)$$

where an error term achieves the order of $O(h^6)$.

1.2 Numerov-Cooley method

Finite difference method for the case of exact eigenvalue.

Let us deal with the case of finding eigenfunction of linear differential operator $-\frac{d^2}{dx^2} + V(x)$, when an exact eigenvalue E is given. The integration formula (1.7) can be expressed by the system of equations

$$\mathbf{M}Z = 0,$$

where 0 is a null vector, $Z = (z_0, \dots, z_n)^T$, and \mathbf{M} is the symmetric matrix with the only non-zero elements

$$M_{(k-1)k} = M_{k(k+1)} = 1, \\ M_{kk} = - \left(2 + \frac{h^2(V_k - E)}{1 - \frac{h^2}{12}(V_k - E)} \right), \quad k = 0, 1, \dots, N.$$

The tridiagonal matrix algorithm for solving $\mathbf{MZ} = 0$ can be found in almost all textbooks on numerical analysis (*e.g.* [5], [6]), and we do not present it here.

Iterative method for eigenvalue approximation.

Let E_0 denote an estimate of the eigenvalue of the linear differential operator $-\frac{d^2}{dx^2} + V(x)$ defined in $L^2(\mathbb{R}, dx)$. Our task is to find accurate eigenvalue E .

The solution of Eq. (1.1) may be subjected to boundary conditions at the limit points a, b of the interval $\langle a, b \rangle$ in \mathbb{R} . We use the following conditions:

$$y_0(x_0) = y_0(x_n) = 0, \quad (1.8a)$$

$$y_0(x_1), y_0(x_{n-1}) = \text{a small arbitrary number.} \quad (1.8b)$$

The method of integration consists of integrating y_0^{out} outward from x_0 to some point x_m , $m = 1, \dots, N - 1$, and y_0^{in} inward from x_n to the crossing point x_m , using starting values (1.8) and integration formula (1.7). Since (1.1) is homogenous in y , the resulting values $y_0(x_k)$ on the grid points may be replaced by

$$y_0(x_i) \equiv \frac{c}{1 - \frac{h^2}{12}(V_i - E)} \frac{y_0^{out}(x_i)}{y_0^{out}(x_m)}, \quad i = 0, \dots, m,$$

and by

$$y_0(x_j) \equiv \frac{c}{1 - \frac{h^2}{12}(V_j - E)} \frac{y_0^{in}(x_j)}{y_0^{in}(x_m)}, \quad j = N + 1, \dots, m$$

such that $z_0(x_m) = c$, where the non-zero constant c is usually taken $c \equiv 1$.

Further in the text we omit writing subscript 0 of $y_0(x_k)$ or $z_0(x_k)$, corresponding to E_0 .

When integrating with the trial value E_0 , all the equations of (1.7), except for the m th, are satisfied. We put

$$F(E_0) := -z_{m-1} + \left(2 + \frac{h^2(V_m - E_0)}{1 - \frac{h^2}{12}(V_m - E_0)} \right) z_m - z_{m+1} \quad (1.9)$$

which represents the difference between 0 at the right hand side of (1.7) and calculated value in m th step. Hereinafter we attempt to find an iteration scheme for giving precision to the trial eigenvalue E_0 . If we set $F(E_0) = 0$, the problem arises how to calculate zero of the function $F(E)$. For that purpose we apply the Newton-Raphson method (see *e.g.* [7], [8])

$$E_1 = E_0 - D(E_0),$$

where the correction term is

$$D(E_0) = \frac{F(E_0)}{F'(E_0)}.$$

The next terms of iteration sequence are calculated from the recurrent formula

$$E_{k+1} = E_k - \frac{F(E_k)}{F'(E_k)}.$$

It is necessary to assume $F'(E_k) \neq 0$ in each step. We prove below that this condition is fulfilled and moreover, we provide the exact formula for the first derivative of F . Thenceforth let the vector-matrix formulation of equations (1.7) for $k = 0, 1, \dots, m-1, m+1, \dots, N$, and (1.9) be expressed as

$$\mathbf{M}Z = F,$$

where \mathbf{M} is a matrix rearranged such that its first row corresponds to the m th equation, and Z is a vector, with the first element matching the m th variable, i.e. $Z = (c, z_a)^T$ and $F = (F(E_0), 0)^T$. In other words

$$\begin{pmatrix} M_{11} & M_{a1}^T \\ M_{a1} & \mathbf{M}_{aa} \end{pmatrix} \begin{pmatrix} c \\ z_a \end{pmatrix} = \begin{pmatrix} F(E_0) \\ 0 \end{pmatrix},$$

i.e.

$$M_{11}c + M_{a1}^T z_a = F(E_0), \quad (1.10a)$$

$$M_{a1}c + \mathbf{M}_{aa} z_a = 0. \quad (1.10b)$$

Differentiating (1.10a) and (1.10b) with respect to E_0 and using the notation $\mathbf{M}' = \frac{d}{dE_0}\mathbf{M}$ we have

$$M'_{11}c + (M'_{a1})^T z_a + M_{a1}^T z'_a = F'(E_0), \quad (1.11a)$$

$$M'_{a1}c + \mathbf{M}'_{aa} z_a + \mathbf{M}_{aa} z'_a = 0. \quad (1.11b)$$

It is unfavourable, that the term containing z'_a occurs in $F'(E_0)$. To cancel it, we need to execute these rearrangements: Transposing and multiplying (1.10b) by z'_a from the right, and multiplying (1.11b) by z_a^T from the left, we obtain the following equations

$$cM_{a1}^T z'_a + z_a^T \mathbf{M}_{aa}^T z'_a = 0, \quad (1.12)$$

$$cz_a^T M'_{a1} + z_a^T \mathbf{M}'_{aa} z_a + z_a^T \mathbf{M}_{aa} z'_a = 0. \quad (1.13)$$

Since \mathbf{M}_{aa} is symmetric, subtracting (1.13) from (1.12) we get

$$cM_{a1}^T z'_a = cz_a^T M'_{a1} + z_a^T \mathbf{M}'_{aa} z_a.$$

We now can replace the problematic term $M_{a1}^T z'_a$ in (1.11a) resulting in

$$F'(E_0) = cM'_{11} + (M'_{a1})^T z_a + z_a^T M'_{a1} + \frac{1}{c} z_a^T \mathbf{M}'_{aa} z_a.$$

It is obvious from the above given form of \mathbf{M} that the matrix \mathbf{M}' is diagonal and with elements

$$\mathbf{M}'_{kk} = \frac{d}{dE_0} \left(2 + \frac{h^2(V_k - E_0)}{1 - \frac{h^2}{12}(V_k - E_0)} \right) = -\frac{h^2}{\left(1 - \frac{h^2}{12}(V_k - E_0)\right)^2}$$

and thus

$$F'(E_0) = \frac{1}{c^2} M'_{11} + \frac{1}{c} z_a^T \mathbf{M}'_{aa} z_a = \frac{1}{c} Z^T \mathbf{M}' Z. \quad (1.14)$$

Consequently, by means of (1.6) we conclude that

$$F'(E_0) = \frac{1}{c} \sum_{k=0}^n \mathbf{M}'_{kk} z_k^2 = -\frac{h^2}{c} \sum_{k=0}^n y_0^2(x_k),$$

and the correction formula is of the final form

$$D(E_0) = \frac{cF(E_0)}{h^2 \sum_{k=0}^n y_0^2(x_k)} = c \frac{h^{-2}(-z_{m-1} + 2z_m - z_{m+1}) + (V_m - E_0)y_m}{\sum_{k=0}^n y_0^2(x_k)}.$$

The convergence of the above numerical procedure is considered in [9] in details.

Chapter 2

Modifications of Numerov-Cooley method for accurate computations of the Schrödinger equation

2.1 Exponentially fitted method

Again, we consider the equation (1.1) with nonsingular potential $V(x)$

$$y''(x) = f(x)y(x), \quad f(x) = V(x) - E, \quad x \in \langle a, b \rangle \quad (2.1)$$

and general two-step differential scheme that solves it

$$a_0 y(x+h) + a_1 y(x) + a_2 y(x-h) = h^2 [b_0 y''(x+h) + b_1 y''(x) + b_2 y''(x-h)] \quad (2.2)$$

(putting $a_j \equiv a_j(h)$, $b_j \equiv b_j(h)$, $j = 0, 1, 2$)

with the special values of weights coming from Numerov method [1]

$$a_0 = a_2 = 1, \quad a_1 = -2, \quad b_0 = b_2 = \frac{1}{12}, \quad b_1 = \frac{5}{6}, \quad (2.3)$$

which provide the equation

$$y(x+h) - 2y(x) + y(x-h) = h^2 \left[\frac{1}{12} y''(x+h) + \frac{5}{6} y''(x) + \frac{1}{12} y''(x-h) \right].$$

The method (2.2) is associated with the error operator

$$\mathcal{L}[y(x); h] = \sum_{j=0}^2 a_j y(x - (j-1)h) - h^2 \sum_{j=0}^2 b_j y''(x - (j-1)h)$$

which with (2.3) annihilates, (i.e. the method integrates exactly) any linear combination of the functions

$$S_0 \equiv \{1, x, x^2, x^3, x^4, x^5\} \quad (2.4a)$$

We denote $\bar{f} \equiv \bar{V} - E$, where \bar{V} is some constant approximating $V(x)$ over some elementary range of width $2h$. The standard Numerov method integrates only polynomial whose degree is as high as possible, and therefore we would like to extend the method to the cases of higher level scheme based on the sets

$$S_1 \equiv \{1, x, x^2, x^3, e^{\pm\sqrt{\bar{f}}x}\}, \quad (2.4b)$$

$$S_2 \equiv \{1, x, e^{\pm\sqrt{\bar{f}}x}, x e^{\pm\sqrt{\bar{f}}x}\}, \quad (2.4c)$$

$$S_3 \equiv \{e^{\pm\sqrt{\bar{f}}x}, x e^{\pm\sqrt{\bar{f}}x}, x^2 e^{\pm\sqrt{\bar{f}}x}\}. \quad (2.4d)$$

Theorem 1. If we use the previous notation S_i for the sets of solutions (2.4) of the two-step differential scheme (2.2), then for $i = 0, 1, 2, 3$ it holds $a_0 = a_2$ and $b_0 = b_2$.

Proof. It is noticeable that the equation (2.2) is invariant under a group of transformations $x \rightarrow -x$ (reflection), $x \rightarrow x + \Delta x$ (translation).

Introducing the solution $y(x) = x^l$ and $y(x) = (-x)^l$, $l = 0, 1, \dots, 5$ into (2.2)

$$\begin{aligned} a_0(x+h)^l + a_1 x^l + a_2(x-h)^l \\ = h^2 l(l-1)[b_0(x+h)^{l-2} + b_1 x^{l-2} + b_2(x-h)^{l-2}], \end{aligned}$$

$$\begin{aligned} a_0(-x+h)^l + a_1(-x)^l + a_2(-x-h)^l \\ = h^2 l(l-1)[b_0(-x+h)^{l-2} + b_1(-x)^{l-2} + b_2(-x-h)^{l-2}] \end{aligned}$$

and subsequently subtracting one of these two equations from the second one, we get:

$$\begin{aligned} (a_0 - a_2)(x+h)^l - (a_0 - a_2)(x-h)^l \\ = h^2 l(l-1)[(b_0 - b_2)(x+h)^{l-2} - (b_0 - b_2)(x-h)^{l-2}]. \end{aligned}$$

Common factoring the left and right hand side of this equation and using binomial formula, we have

$$\begin{aligned} (a_0 - a_2) \sum_{k=0}^l \binom{l}{k} (x^k h^{l-k} - x^k (-h)^{l-k}) \\ = h^2 l(l-1)(b_0 - b_2) \sum_{k=0}^{l-2} \binom{l-2}{k} (x^k h^{l-2-k} - x^k (-h)^{l-2-k}). \end{aligned}$$

Carrying out easy rearrangements yields

$$\begin{aligned} (a_0 - a_2) \sum_{k=0}^l \binom{l}{k} (1 - (-1)^{l-k}) x^k h^{-k} \\ = l(l-1)(b_0 - b_2) \sum_{k=0}^{l-2} \binom{l-2}{k} (1 - (-1)^{l-k}) x^k h^{-k}. \end{aligned}$$

Now, we compare the coefficients at $(1 - (-1)^{l-k})x^k h^{-k}$ for $k = 0, 1, \dots, l$, accordingly:

$$\begin{aligned} k = 0 : & \quad (a_0 - a_2) \binom{l}{0} = l(l-1)(b_0 - b_2) \binom{l-2}{0}, \\ k = 1 : & \quad (a_0 - a_2) \binom{l}{1} = l(l-1)(b_0 - b_2) \binom{l-2}{1}, \\ & \quad \vdots \\ k = l : & \quad (a_0 - a_2) \binom{l}{l} = 0. \end{aligned}$$

From the last row (the case of $k = l$) it is obvious, that it must hold $a_0 = a_2$, which implies $b_0 = b_2$ from the first row ($k = 0$). Introducing the solutions

$$y(x) = x^l \exp(\pm \sqrt{\bar{f}} x) \quad \text{and} \quad y(x) = (-x)^l \exp(\pm \sqrt{\bar{f}} (-x)), \quad l = 0, 1, 2$$

into the equation (2.2), and using binomial formula, we receive the following system of equations:

$$\begin{aligned} & a_0(x+h)^l \exp(\pm \sqrt{\bar{f}}(x+h)) + a_1 x^l \exp(\pm \sqrt{\bar{f}} x) \\ & + a_2(x-h)^l \exp(\pm \sqrt{\bar{f}}(x-h)) = h^2 \sum_{k=0}^2 \binom{2}{k} \left[b_0 \frac{d^k}{dx^k} (x+h)^l \frac{d^{2-k}}{dx^{2-k}} \exp(\pm \sqrt{\bar{f}}(x+h)) \right. \\ & \left. + b_1 \frac{d^k}{dx^k} x^l \frac{d^{2-k}}{dx^{2-k}} \exp(\pm \sqrt{\bar{f}} x) + b_2 \frac{d^k}{dx^k} (x-h)^l \frac{d^{2-k}}{dx^{2-k}} \exp(\pm \sqrt{\bar{f}}(x-h)) \right], \quad (2.5) \end{aligned}$$

$$\begin{aligned} & a_0(-x+h)^l \exp(\pm \sqrt{\bar{f}}(-x+h)) + a_1 (-x)^l \exp(\pm \sqrt{\bar{f}}(-x)) \\ & + a_2(-x-h)^l \exp(\pm \sqrt{\bar{f}}(-x-h)) = h^2 \sum_{k=0}^2 \binom{2}{k} \left[b_0 \frac{d^k}{dx^k} (-x+h)^l \frac{d^{2-k}}{dx^{2-k}} \exp(\pm \sqrt{\bar{f}}(-x+h)) \right. \\ & \left. + b_1 \frac{d^k}{dx^k} (-x)^l \frac{d^{2-k}}{dx^{2-k}} \exp(\pm \sqrt{\bar{f}}(-x)) + b_2 \frac{d^k}{dx^k} (-x-h)^l \frac{d^{2-k}}{dx^{2-k}} \exp(\pm \sqrt{\bar{f}}(-x-h)) \right]. \end{aligned}$$

We reduce and perform (2-k)th derivative and thus the system of equations is simplified into

$$\begin{aligned} & a_0(x+h)^l \exp(\pm \sqrt{\bar{f}} h) + a_1 x^l + a_2(x-h)^l \exp(\pm \sqrt{\bar{f}}(-h)) \\ & = h^2 \sum_{k=0}^2 \binom{2}{k} (\pm \sqrt{\bar{f}})^{2-k} \left[b_0 \frac{d^k}{dx^k} (x+h)^l \exp(\pm \sqrt{\bar{f}} h) + b_1 \frac{d^k}{dx^k} x^l \right. \end{aligned}$$

$$\begin{aligned}
& + b_2 \frac{d^k}{dx^k} (x-h)^l \exp(\pm \sqrt{\bar{f}}(-h)) \Big], \\
& a_0 (x-h)^l \exp(\pm \sqrt{\bar{f}} h) + a_1 x^l + a_2 (x+h)^l \exp(\pm \sqrt{\bar{f}}(-h)) \\
& = h^2 \sum_{k=0}^2 \binom{2}{k} \left(\pm \sqrt{\bar{f}} \right)^{2-k} (-1)^{2-k} \left[b_0 \frac{d^k}{dx^k} (x-h)^l \exp(\pm \sqrt{\bar{f}} h) + b_1 \frac{d^k}{dx^k} x^l \right. \\
& \quad \left. + b_2 \frac{d^k}{dx^k} (x+h)^l \exp(\pm \sqrt{\bar{f}}(-h)) \right].
\end{aligned}$$

Subtracting second equation from the first one and carrying out easy rearrangements we obtain the following form

$$\begin{aligned}
& ((x+h)^l - (x-h)^l) [a_0 \exp(\pm \sqrt{\bar{f}} h) - a_2 \exp(\pm \sqrt{\bar{f}}(-h))] \\
& = 4h^2 (\pm \sqrt{\bar{f}}) b_1 \frac{d}{dx} x^l + h^2 \bar{f} ((x+h)^l - (x-h)^l) [b_0 \exp(\pm \sqrt{\bar{f}} h) - b_2 \exp(\pm \sqrt{\bar{f}}(-h))] \\
& \quad + 2h^2 (\pm \sqrt{\bar{f}}) \left(\frac{d}{dx} (x+h)^l + \frac{d}{dx} (x-h)^l \right) [b_0 \exp(\pm \sqrt{\bar{f}} h) + b_2 \exp(\pm \sqrt{\bar{f}}(-h))] \\
& \quad + h^2 \underbrace{\left(\frac{d^2}{dx^2} (x+h)^l - \frac{d^2}{dx^2} (x-h)^l \right)}_{=0 \quad \forall l=0,1,2} [b_0 \exp(\pm \sqrt{\bar{f}} h) - b_2 \exp(\pm \sqrt{\bar{f}}(-h))].
\end{aligned}$$

We compare the coefficients at $\exp(\pm \sqrt{\bar{f}} h)$ and $\exp(\pm \sqrt{\bar{f}}(-h))$, by which we obtain the system of equations

$$\begin{aligned}
\exp(\pm \sqrt{\bar{f}} h) : \quad & a_0 ((x+h)^l - (x-h)^l) = b_0 h^2 \bar{f} ((x+h)^l - (x-h)^l) \\
& \quad + 2b_0 h^2 (\pm \sqrt{\bar{f}}) \left(\frac{d}{dx} (x+h)^l + \frac{d}{dx} (x-h)^l \right), \\
\exp(\pm \sqrt{\bar{f}}(-h)) : \quad & -a_2 ((x+h)^l - (x-h)^l) = -b_2 h^2 \bar{f} ((x+h)^l - (x-h)^l) \\
& \quad + 2b_2 h^2 (\pm \sqrt{\bar{f}}) \left(\frac{d}{dx} (x+h)^l + \frac{d}{dx} (x-h)^l \right).
\end{aligned}$$

We sum up these two equations resulting in particular forms for $l = 0, 1, 2$.

$$\begin{aligned}
l = 0 : \quad & 0 = 0, \\
l = 1 : \quad & (a_0 - a_2) = \bar{f} h^2 (b_0 - b_2) + 2h (\pm \sqrt{\bar{f}}) (b_0 + b_2), \\
l = 2 : \quad & (a_0 - a_2) = \bar{f} h^2 (b_0 - b_2) + 2h (\pm \sqrt{\bar{f}}) (b_0 + b_2).
\end{aligned}$$

The second and third equations are identical. They provide a pair of equations which differ only in the sign at $\sqrt{\bar{f}}$.

$$(a_0 - a_2) = \bar{f}h^2(b_0 - b_2), \text{ which holds } \forall \bar{f}.$$

Hence $a_0 = a_2$, and $b_0 = b_2$.

The first equation does not supply the above-mentioned condition for symmetry of the coefficients, however we show that this condition is to be fulfilled also for the case of $y(x) = x^l \exp(\pm\sqrt{\bar{f}}x)$, $l = 0$.

If we substitute the solutions

$$y(x) = \exp(\pm\sqrt{\bar{f}}x) \quad \text{a} \quad y(x) = \exp(\pm\sqrt{\bar{f}}(-x))$$

into Eq. (2.2), we get the following system of equations:

$$\begin{aligned} & a_0 \exp(\pm\sqrt{\bar{f}}h) + a_1 + a_2 \exp(\pm\sqrt{\bar{f}}(-h)) \\ &= \bar{f}h^2 \left[b_0 \exp(\pm\sqrt{\bar{f}}h) + b_1 + b_2 \exp(\pm\sqrt{\bar{f}}(-h)) \right], \end{aligned}$$

$$\begin{aligned} & a_2 \exp(\pm\sqrt{\bar{f}}h) + a_1 + a_0 \exp(\pm\sqrt{\bar{f}}(-h)) \\ &= \bar{f}h^2 \left[b_2 \exp(\pm\sqrt{\bar{f}}h) + b_1 + b_0 \exp(\pm\sqrt{\bar{f}}(-h)) \right], \end{aligned}$$

Subsequently subtracting the second equation from the first one and after simplifying, the equation becomes

$$\begin{aligned} & (a_0 - a_2) \left(\exp(\pm\sqrt{\bar{f}}h) - \exp(\pm\sqrt{\bar{f}}(-h)) \right) \\ &= \bar{f}h^2(b_0 - b_2) \left(\exp(\pm\sqrt{\bar{f}}h) - \exp(\pm\sqrt{\bar{f}}(-h)) \right), \end{aligned}$$

which provides the formula

$$(a_0 - a_2) = \bar{f}h^2(b_0 - b_2), \quad \forall \bar{f}.$$

Hence $a_0 = a_2$, and $b_0 = b_2$. □

With no loss in generality we take in Eq.(2.2) $a_0 = a_2 = 1$ thus we read

$$y(x+h) + a_1 y(x) + y(x-h) = h^2 [b_0 y''(x+h) + b_1 y''(x) + b_0 y''(x-h)]. \quad (2.6)$$

According to the paper [3] we denote $Z \equiv \bar{f}h^2$, and define for $n = 1, 2, \dots$

$$\begin{aligned} R^+(n, Z) &= \exp(n\sqrt{Z}) + \exp(-n\sqrt{Z}), \\ R^-(n, Z) &= \exp(n\sqrt{Z}) - \exp(-n\sqrt{Z}). \end{aligned}$$

If we use $y(x) = \exp(\pm\sqrt{f}x)$ in Eq.(2.6), we come to the following equation

$$a_1 + R^+(1, Z) = b_0 Z R^+(1, Z) + b_1 Z. \quad (2.7)$$

Similarly, with $y(x) = x \exp(\pm\sqrt{f}x)$ and using formula (2.5), we get

$$\begin{aligned} a_1 x + x R^+(1, Z) + h R^-(1, Z) &= Z [b_1 x + b_0 x R^+(1, Z) + b_0 h R^-(1, Z)] \\ &\quad + 2\sqrt{Z}h [b_1 + b_0 R^+(1, Z)], \end{aligned}$$

which gives together with (2.7) the expression for $R^-(1, Z)$,

$$R^-(1, Z) = b_0 [2\sqrt{Z}R^+(1, Z) + ZR^-(1, Z)] + 2b_1\sqrt{Z}. \quad (2.8)$$

Finally, if we use $y(x) = x^2 \exp(\pm\sqrt{f}x)$ and (2.5), we have

$$\begin{aligned} a_1 x^2 + x^2 R^+(1, Z) + 2xh R^-(1, Z) + h^2 R^+(1, Z) \\ = Z [b_1 x^2 + b_0 x^2 R^+(1, Z) + 2b_0 xh R^-(1, Z) + b_0 h^2 R^+(1, Z)] \\ + 4\sqrt{Z}h [b_1 x + b_0 x R^+(1, Z) + b_0 h R^-(1, Z)] + h^2 [2b_1 + 2b_0 R^+(1, Z)], \end{aligned}$$

which results after the substitution of (2.7) and (2.8) in

$$R^+(1, Z) = b_0 [ZR^+(1, Z) + 2R^+(1, Z) + 4\sqrt{Z}R^-(1, Z)] + 2b_1. \quad (2.9)$$

Equations (2.7), (2.8), and (2.9) perform a linear algebraic system for the three unknown variables a_1 , b_0 , and b_1 . By means of simple algebraic calculations and expressions

$$R^+(n, Z)R^-(n, Z) = R^-(2n, Z), \quad R^\pm(n, Z)R^\pm(n, Z) = R^\pm(2n, Z) \pm 2$$

we can find out that

$$\begin{aligned} a_1(Z) &= -2 - \frac{A(Z)}{D(Z)}, \\ b_0(Z) &= \frac{B_0(Z)}{D(Z)}, \\ b_1(Z) &= \frac{B_1(Z)}{D(Z)}, \end{aligned}$$

where

$$\begin{aligned}
D(Z) &= \frac{1}{8\sqrt{Z}} \left(3R^-(1, Z) + \sqrt{Z}R^+(1, Z) \right), \\
B_0(Z) &= \frac{1}{8\sqrt{Z}^3} \left(\sqrt{Z}R^+(1, Z) - R^-(1, Z) \right), \\
B_1(Z) &= \frac{1}{8\sqrt{Z}^3} \left(R^-(2, Z) + \sqrt{Z}R^+(2, Z) - 6\sqrt{Z} \right), \\
A(Z) &= -\frac{1}{8\sqrt{Z}} \left(6R^-(1, Z) + 2\sqrt{Z}R^+(1, Z) - 3R^-(2, Z) + \sqrt{Z}R^+(2, Z) - 6\sqrt{Z} \right).
\end{aligned} \tag{2.10}$$

On the computer programming purposes, we apply the Taylor series expansion for all the terms in (2.10)

$$\begin{aligned}
D(Z) &= \frac{3}{8\sqrt{Z}} \sum_{k=0}^{\infty} \frac{1}{k!} \sqrt{Z}^k (1 - (-1)^k) + \frac{1}{8} \sum_{k=0}^{\infty} \frac{1}{k!} \sqrt{Z}^k (1 + (-1)^k) \\
&= \frac{3}{4} \sum_{k=0}^{\infty} \frac{1}{(2k+1)!} \sqrt{Z}^{2k} + \frac{1}{4} \sum_{k=0}^{\infty} \frac{1}{(2k)!} \sqrt{Z}^{2k} \\
&= \sum_{k=0}^{\infty} \frac{k+2}{2(2k+1)!} Z^k, \\
B_0(Z) &= \frac{1}{8Z} \sum_{k=0}^{\infty} \frac{1}{k!} \sqrt{Z}^k (1 + (-1)^k) - \frac{1}{8\sqrt{Z}^3} \sum_{k=0}^{\infty} \frac{1}{k!} \sqrt{Z}^k (1 - (-1)^k) \\
&= \frac{1}{4Z} \sum_{k=0}^{\infty} \frac{1}{(2k)!} Z^k - \frac{1}{4Z} \sum_{k=0}^{\infty} \frac{1}{(2k+1)!} Z^k \\
&= \frac{1}{4Z} \sum_{k=0}^{\infty} \frac{2k}{(2k+1)!} Z^k = \frac{1}{Z} \sum_{k=1}^{\infty} \frac{k}{2(2k+1)!} Z^k \\
&= \sum_{k=0}^{\infty} \frac{k+1}{2(2k+3)!} Z^k,
\end{aligned}$$

$$\begin{aligned}
B_1(Z) &= \frac{1}{8\sqrt{Z}^3} \sum_{k=0}^{\infty} \frac{1}{k!} 2^k \sqrt{Z}^k (1 - (-1)^k) + \frac{1}{8Z} \sum_{k=0}^{\infty} \frac{1}{k!} 2^k \sqrt{Z}^k (1 + (-1)^k) - \frac{3}{4Z} \\
&= \frac{1}{4Z} \sum_{k=0}^{\infty} \frac{1}{(2k+1)!} 2^{2k+1} Z^k + \frac{1}{4Z} \sum_{k=0}^{\infty} \frac{1}{(2k)!} 2^{2k} Z^k - \frac{3}{4Z} \\
&= \frac{1}{4Z} \left[\left(\sum_{k=0}^{\infty} \frac{2k+3}{(2k+1)!} 2^{2k} Z^k \right) - 3 \right] = \frac{1}{4Z} \sum_{k=1}^{\infty} \frac{2k+3}{(2k+1)!} 2^{2k} Z^k \\
&= \sum_{k=0}^{\infty} \frac{2k+5}{2(2k+3)!} 2^{2k} Z^k,
\end{aligned}$$

$$\begin{aligned}
A(Z) &= -\frac{3}{4\sqrt{Z}} \sum_{k=0}^{\infty} \frac{1}{k!} 2^k \sqrt{Z}^k (1 - (-1)^k) - \frac{1}{4} \sum_{k=0}^{\infty} \frac{1}{k!} \sqrt{Z}^k (1 + (-1)^k) \\
&\quad + \frac{3}{8\sqrt{Z}} \sum_{k=0}^{\infty} \frac{1}{k!} 2^k \sqrt{Z}^k (1 - (-1)^k) - \frac{1}{8} \sum_{k=0}^{\infty} \frac{1}{k!} 2^k \sqrt{Z}^k (1 + (-1)^k) + \frac{3}{4} \\
&= -\frac{3}{2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)!} Z^k - \frac{1}{2} \sum_{k=0}^{\infty} \frac{1}{(2k)!} Z^k + \frac{3}{4} \sum_{k=0}^{\infty} \frac{1}{(2k+1)!} 2^{2k+1} Z^k \\
&\quad - \frac{1}{4} \sum_{k=0}^{\infty} \frac{1}{(2k)!} 2^{2k} Z^k + \frac{3}{4} \\
&= -\sum_{k=0}^{\infty} \frac{k+2}{(2k+1)!} Z^k + \sum_{k=0}^{\infty} \left(\frac{5}{2} - k \right) \frac{1}{(2k+1)!} 2^{2k-1} Z^k + \frac{3}{4} \\
&= -\sum_{k=3}^{\infty} \frac{k+2}{(2k+1)!} Z^k - \sum_{k=3}^{\infty} \left(k - \frac{5}{2} \right) \frac{1}{(2k+1)!} 2^{2k-1} Z^k \\
&= -Z^3 \sum_{k=0}^{\infty} \frac{1}{(2k+7)!} [k+5+16(2k+1)2^{2k}] Z^k.
\end{aligned}$$

Incorporating these expansions into the iteration scheme (2.2) we obtain

$$\begin{aligned}
&D(Z) y(x+h) - [2D(Z) + A(Z)] y(x) + D(Z) y(x-h) \\
&= h^2 [B_0(Z) f(x+h) y(x+h) + B_1(Z) f(x) y(x) + B_0(Z) f(x-h) y(x-h)].
\end{aligned}$$

Now we discretise the equation under the independent variable. It holds that

$$\begin{aligned}
&[D(Z_n) - B_0(Z_n) f(x_{n+1}) h^2] y(x_{n+1}) - [2D(Z_n) + A(Z_n) + B_1(Z_n) f(x_n) h^2] y(x_n) \\
&+ [D(Z_n) - B_0(Z_n) f(x_{n-1}) h^2] y(x_{n-1}) = 0,
\end{aligned}$$

where we take $Z_n \equiv f(x_n) h^2$. If we use the previous notation $y_n = y(x_n)$ we achieve

$$\begin{aligned}
&[D(Z_n) - B_0(Z_n) Z_{n+1}] y_{n+1} - [2D(Z_n) + A(Z_n) + B_1(Z_n) Z_n] y_n \\
&+ [D(Z_n) - B_0(Z_n) Z_{n-1}] y_{n-1} = 0,
\end{aligned}$$

which can be easily rewritten, under notation $D_n = D(Z_n)$, into the short version of the main equation

$$[D_n - (B_0)_n Z_{n+1}]y_{n+1} - [2D_n + A_n + (B_1)_n Z_n]y_n + [D_n - (B_0)_n Z_{n-1}]y_{n-1} = 0.$$

By that we derive the coefficients of integration scheme

$$\begin{aligned} W_{nn+1} &:= D_n - (B_0)_n Z_{n+1}, \\ W_{nn} &:= -[2D_n + A_n + (B_1)_n Z_n], \\ W_{nn-1} &:= D_n - (B_0)_n Z_{n-1}, \end{aligned}$$

representing the three elements in n th row of the tridiagonal matrix \mathbf{W} . Further, we find more accurate eigenvalue by means of Numerov-Cooley method described above, such that for certain $m \in \{1, \dots, N-1\}$ it holds $y_m = 1$. However, then

$$F(E_0) = W_{mm+1}(E_0)y_{m+1} + W_{mm}(E_0)y_m + W_{mm-1}(E_0)y_{m-1} \neq 0.$$

We differentiate the elements of matrix \mathbf{W} with respect to E_0

$$\begin{aligned} W'_{nn+1} &= W'_{nn-1} = (B_0)_n h^2, \\ W'_{nn} &= (B_1)_n h^2, \end{aligned}$$

where we use the notation $\mathbf{W}' = \frac{d}{dE_0}\mathbf{W}$. According to (1.14) it holds

$$F'(E_0) = Y^T \mathbf{W}' Y,$$

which one may interpret as

$$\begin{aligned} F'(E_0) &= \sum_{n=1}^{N-1} \left(y_n W'_{nn+1} y_{n+1} + y_n W'_{nn} y_n + y_n W'_{nn-1} y_{n-1} \right) \\ &= h^2 \sum_{n=1}^{N-1} y_n \left((B_0)_n y_{n+1} + (B_1)_n y_n + (B_0)_n y_{n-1} \right). \end{aligned}$$

Now, we are able to calculate the correction term $D(E_0)$ using the Newton-Raphson method, i.e.

$$D(E_0) = \frac{F(E_0)}{F'(E_0)}.$$

2.2 Raptis-Allison method

The one-dimensional radial Schrödinger equation has the form

$$y''(x) = \left[\frac{L(L+1)}{x^2} - E + U(x) \right] y(x), \quad x \geq 0. \quad (2.11)$$

We call the term $L(L+1)/x^2$ (L is a positive integer) *the centrifugal potential*, and the function $U(x)$ *the potential*. In molecular physics usually $U(x) \rightarrow 0$ much faster than the term $L(L+1)/x^2$ so the latter is the dominant term for values of x greater than R . In the so-called asymptotic region where the potential $U(x)$ is negligible, Eq. (2.11) is effectively reduced to

$$y''(x) = \left[\frac{L(L+1)}{x^2} - E \right] y(x).$$

One boundary condition being $y(0) = 0$ and the other condition, which depends on the physical model, being imposed at large x . Based on the sign of the energy E there are two main categories of problems. In the case of positive energy (i.e. $E = k^2 > 0$) we have a phase shift problem, forasmuch as in the range of large values of the independent variable the solution of the Schrödinger equation exhibits sinusoidal behaviour. The latter case (i.e. $E < 0$) giving an eigenvalue problem as the solution displays decreasing exponential behaviour.

The method investigated in this section is an extension of the well known Numerov method which can be written,

$$\left(1 - \frac{1}{12}h^2 f_{n+1}\right) y_{n+1} - \left(2 + \frac{10}{12}h^2 f_n\right) y_n + \left(1 - \frac{1}{12}h^2 f_{n-1}\right) y_{n-1} = 0,$$

where h is the interval size and

$$f_n = \frac{L(L+1)}{x_n^2} - E + U(x_n).$$

Consider the two-step formula (2.6) and the associated operator \mathcal{L} annihilating the polynomials $1, x$ belong to sets $S_i, i = 0, 1, 2$. Thus the coefficients $a_j, j = 0, 1, 2$ are subjected to the condition $a_0 + a_1 + a_2 = 0$. On the basis of deliberation elucidated in the previous section we choose $a_0 = 1$ with no loss of generality and further we know $a_0 = a_2$. Expanding the error operator

$$\mathcal{L}[y(x); h] = y(x+h) - 2y(x) + y(x-h) - h^2[b_0 y''(x+h) + b_1 y''(x) + b_2 y''(x-h)]$$

in a Taylor series we have

$$\mathcal{L}[y(x); h] = [1 - (b_0 + b_1 + b_2)]h^2 y''(x) + (b_0 - b_2)h^3 y'''(x) + O(h^4).$$

Condition $b_0 + b_1 + b_2 = 1, (b_0 = b_2)$ gives accuracy of $O(h^4)$. Following the method of Raptis and Allison [2, 4] to derive their method in the form

$$y_{n+1} - 2y_n + y_{n-1} = h^2[b_0(h)y''_{n+1} + (1 - 2b_0(h))y''_n + b_0(h)y''_{n-1}], \quad (2.12)$$

where the coefficient is determined such that the method (2.12) integrates exactly certain desired linearly independent functions of set $S_i, i = 0, 1$, i.e. we now require

that the appropriate functional \mathcal{L} integrates exactly $e^{\pm\omega x}$. The case of *real* ω (setting $\omega = k \neq 0$) corresponds to our demand for the method (2.12) to be exact for any linear combination of the functions

$$1, x, x^2, x^3, e^{\pm kx},$$

the coefficient, which would be most appropriate to integrate the bound state problem, is

$$b_0(h) = \frac{(1 - e^{kh})^2 - (kh)^2 e^{kh}}{(kh)^2 (1 - e^{kh})^2}.$$

In the case of *pure imaginary* ω (setting $\omega = ik \neq 0$), i.e., we want the corresponding functional to annihilate the functions

$$1, x, x^2, x^3, \sin kx, \cos kx,$$

the coefficient, which would be most appropriate to integrate the scattering problem, is

$$b_0(h) = \frac{(kh)^2 - 2(1 - \cos kh)}{2(kh)^2 (1 - \cos kh)}. \quad (2.13)$$

For small values of kh a better representation of (2.13) is

$$b_0(h) = \frac{(kh)^2 - 4 \sin^2(\frac{1}{2}kh)}{4(kh)^2 \sin^2(\frac{1}{2}kh)},$$

or the Taylor expansion

$$b_0(h) = \frac{1}{12} \left[1 + \frac{(kh)^2}{20} + \frac{(kh)^4}{504} + O(h^6) \right]$$

for smaller values of h . In the limit as $k \rightarrow 0$ the coefficients go over into the Numerov's ones. Thus, we can express the recursion formula for both cases as

$$[1 - h^2 b_0(h) f_{n+1}] y_{n+1} - [2 + h^2 (1 - 2b_0(h)) f_n] y_n + [1 - h^2 b_0(h) f_{n-1}] y_{n-1} = 0.$$

Chapter 3

Numerical illustration

In this section we present some numerical results to illustrate the methods derived in the previous two chapters. Consider the system has a spherically symmetric potential and the incident motion is assumed to be in the z direction, angular momentum is conserved, the radial part of the wave function satisfies one-dimensional equations

$$-\frac{\hbar^2}{2M} \left[\frac{d^2}{dx^2} + \frac{2}{x} \frac{d}{dx} + V(x) \right] R(x) = ER(x), \quad x \geq 0, \quad (3.1)$$

where

$$V(x) = \frac{\hbar^2}{2M} \frac{L(L+1)}{x^2} + U(x).$$

By substituting $R(x) = y(x)/x$ equation (3.1) is simplified to

$$-\frac{\hbar^2}{2M} y''(x) + (V(x) - E) y(x) = 0. \quad (3.2)$$

3.1 Scattering problem

In the case of positive energy $E = k^2$, corresponding to elastic scattering under a potential $V(x)$ the Schrödinger equation may conveniently be written in the reduced form

$$y''(x) + (k^2 - V(x)) y(x) = 0, \quad (3.3)$$

where

$$k^2 = \frac{2M}{\hbar^2} E, \quad V(x) = \frac{L(L+1)}{x^2} + \frac{2M}{\hbar^2} U(x).$$

The solution of Eq. (3.3) has the asymptotic form (i.e. for $\rightarrow \infty$) [10]

$$y(x) \simeq D [\sin(kx - L\pi/2) + \tan \delta_L \cos(kx - L\pi/2)], \quad (3.4)$$

where δ_L is the real scattering phase shift of the L th partial wave induced by the potential $V(x)$. The value of $\tan \delta_L$ may be computed using the formula

$$\tan \delta_L = \frac{y(x_2) \sin(kx_1 - L\pi/2) - y(x_1) \sin(kx_2 - L\pi/2)}{y(x_1) \cos(kx_2 - L\pi/2) - y(x_2) \cos(kx_1 - L\pi/2)} \quad (3.5)$$

for x_1 and x_2 distinct points in the asymptotic region such that x_2 is the right-hand end point of the interval of integration and $x_1 = x_2 - h$. The term $L\pi/2$ in (3.4) is conventional.

In order to perform numerical calculations for the wave scattering phase shifts and the scattering length we adopt the widely used Lennard-Jones potential given by

$$V(x) = 500\left(\frac{1}{x^{12}} - \frac{1}{x^6}\right) + \frac{L(L+1)}{x^2}.$$

As a test of the numerical accuracy we consider the numerical integration for a case $E = 1.0$ and for each integer value of angular momentum L from 0 to 10. The numerical integration procedure runs from initial point $x_0 = 0.01$ to x_{max} such that we are demanding the factor $V(x)$ in (3.3) is sufficiently small compared with k^2 . The phase shifts δ_L for each L were obtained from the asymptotic behaviour of the wave function $y(x) \propto \sin(kx - L\pi/2 + \delta_L)$, using the algorithm of (3.5). For comparison purposes in our numerical illustration we use Numerov's method (labeled as method /0/) and the exponentially fitted method of Raptis and Allison (labeled as method /1/), which are considered in the previous chapters. The results obtained for various values of steplengths and the number of steps are summarized in the Table 3.1.

Table 3.1: Computed phase shifts using the method of Numerov /0/ and the exponentially fitted method of Raptis and Allison /1/: [a] $h = 0.01$, no. of points 10^7 , [b] $h = 0.04$, no. of points 10^7 , [c] $h = 0.04$, no. of points $5 \cdot 10^6$, [d] $h = 0.02$, no. of points 10^7 .

Method /0/, $k = 1.0, x_0 = 0.01$				
L	[a]	[b]	[c]	[d]
0	0.15442518	0.15704467	0.15597793	0.15451798
1	1.23289633	1.23552034	1.23445611	1.23298494
2	-1.42964904	-1.42693453	-1.42799377	-1.42956431
3	0.78327355	0.78577374	0.78472201	0.78333214
4	0.12597337	0.12803924	0.12699750	0.12598851
5	0.03680488	0.03882412	0.03779488	0.03679449
6	0.01493305	0.01690712	0.01589288	0.01489265
7	0.00712904	0.00905031	0.00805358	0.00705362
8	0.00393496	0.00579622	0.00481948	0.00381954
9	0.00246857	0.00426231	0.00330808	0.00230815
10	0.00176119	0.00347991	0.00255068	0.00155077

Method /1/, $k = 1.0, x_0 = 0.01$				
L	[a]	[b]	[c]	[d]
0	0.15442286	0.15490815	0.15490816	0.15445118
1	1.23289423	1.23338377	1.23338627	1.23291808
2	-1.42965114	-1.42907176	-1.42906426	-1.42963121
3	0.78327145	0.78363771	0.78365271	0.78326531
4	0.12597129	0.12590576	0.12593076	0.12592184
5	0.03680280	0.03669071	0.03672821	0.03672782
6	0.01493097	0.01477373	0.01482623	0.01482598
7	0.00712696	0.00691693	0.00698694	0.00698696
8	0.00393288	0.00366285	0.00375285	0.00375288
9	0.00246649	0.00212896	0.00224146	0.00224149
10	0.00175911	0.00134658	0.00148408	0.00148411

The solutions of the equation (3.3), where $V(x)$ corresponds to the Lennard-Jones potential for the following range of values of L : $L = 0, 5, 10$, are illustrated on the following figures 3.1, 3.2 and 3.3. The solid line indicates the calculated solution, dotted line represents the asymptotic solution with computed phase shift δ_L and dashed line is illustrative of the asymptotic solution with zero phase shift.

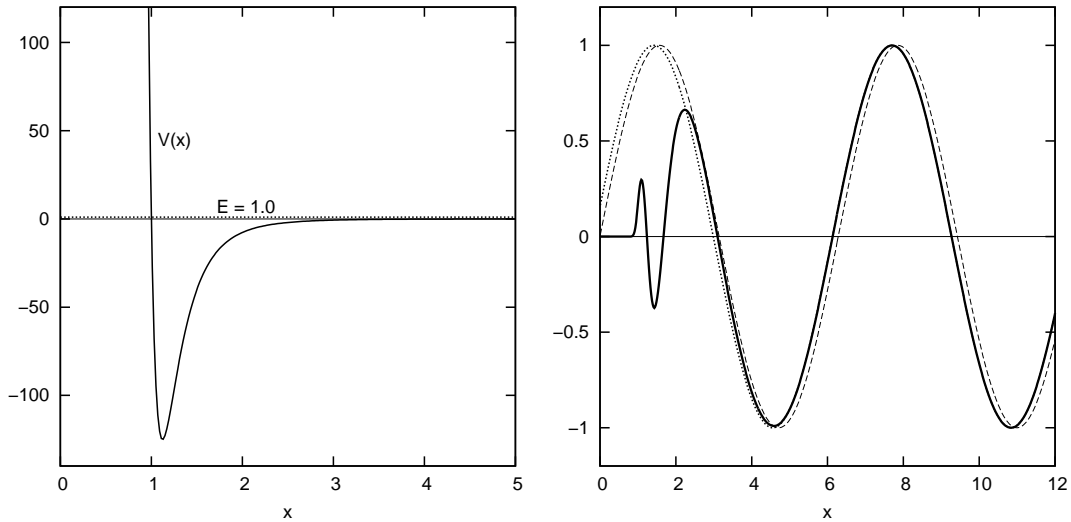


Figure 3.1: Plot of the L - J potential $V(x)$ for angular momentum $L = 0$ and the corresponding wave function with its asymptotic form. The solid line indicates the calculated solution, dotted line represents the asymptotic solution with computed phase shift δ_L and dashed line is illustrative of the asymptotic solution with zero phase shift.

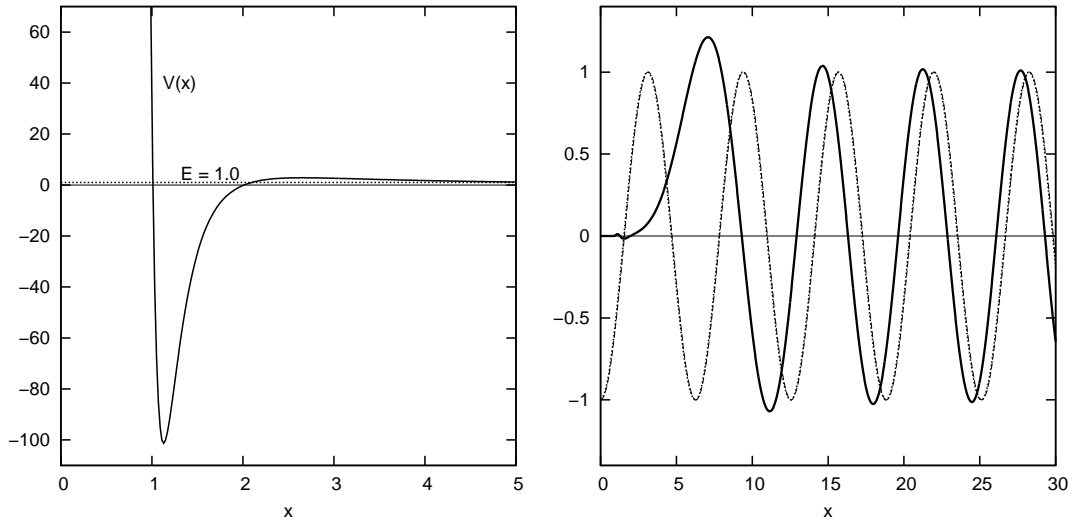


Figure 3.2: Plot of the L - J potential $V(x)$ for angular momentum $L = 5$ and the corresponding wave function with its asymptotic form. The solid line indicates the calculated solution, dotted line represents the asymptotic solution with computed phase shift δ_L and dashed line is illustrative of the asymptotic solution with zero phase shift.

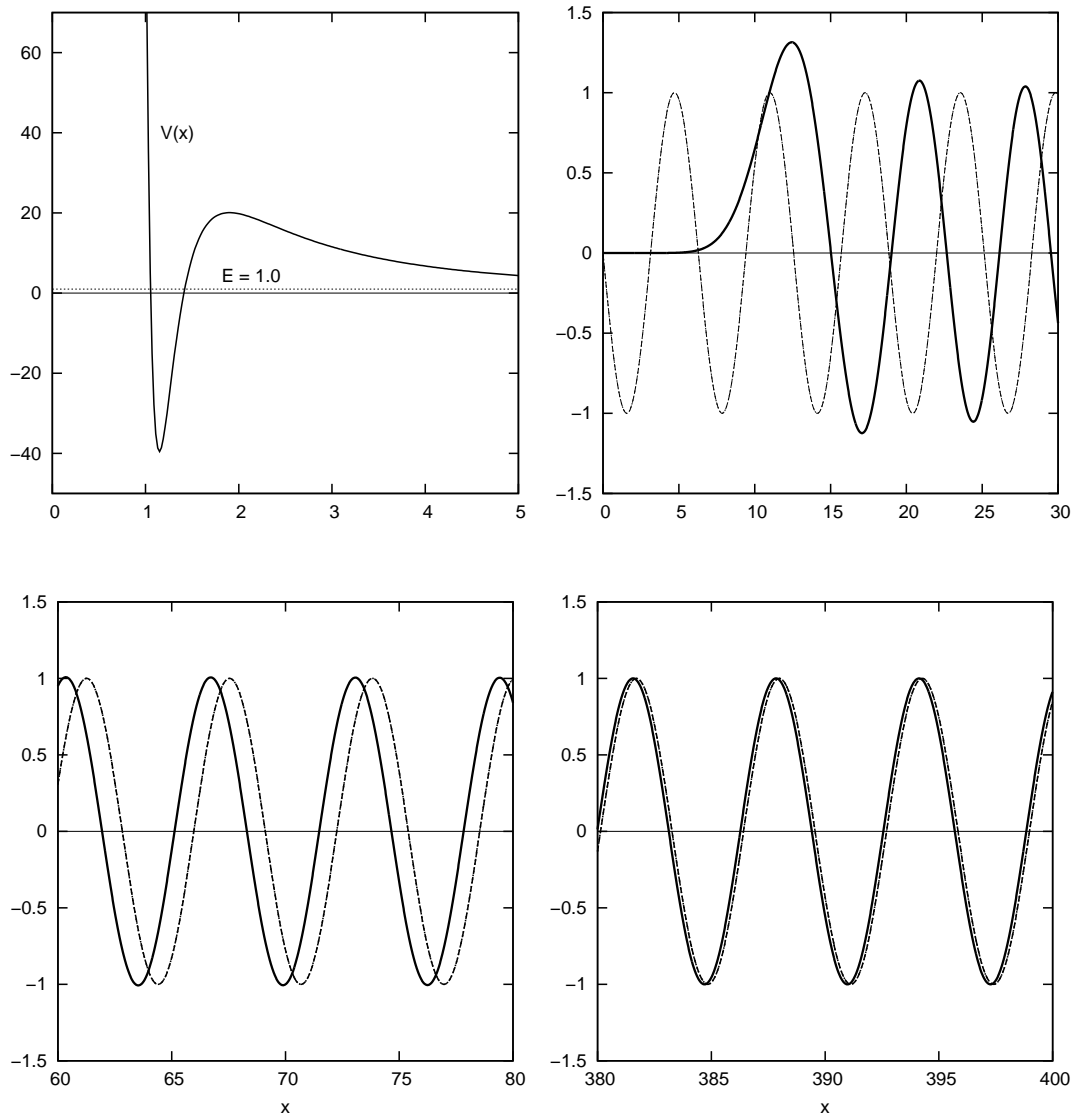


Figure 3.3: Plot of the L - J potential $V(x)$ for angular momentum $L = 10$ and the corresponding wave function with its asymptotic form. The solid line indicates the calculated solution, dotted line represents the asymptotic solution with computed phase shift δ_L and dashed line is illustrative of the asymptotic solution with zero phase shift.

3.2 The bound-state problem

We investigate here the case of negative energies in Eq. (3.2) with zero centrifugal term., i.e. $L = 0$ and with given boundary conditions. In order to solve the problem we apply the numerical integration strategy, which has been proposed by Cooley [9] and discussed above combined with the Numerov method or exponentially fitted method of Raptis and Allison. For this problem we take the Morse potential given by the expression

$$U(x) = D(1 - e^{-a(x-r_e)})^2 - D$$

with the parameters $r_e = 1.9975$, $a = 0.711248$, $D = 188.4355$. (Figure 3.4) All calculated bound-states are presented in Table 3.2 as well as the dependence of eigenvalues on the integration step and chosen method.

Table 3.2: Computed eigenvalues for Morse potential using the method of Numerov /0/ and the exponentially fitted method of Raptis and Allison /1/: [a] $h = 0.05$, no. of points 801, [b] $h = 0.025$, no. of points 1601, [c] $h = 0.005$, no. of points 8001, [d] $h = 0.0025$, no. of points 16001.

Method /0/, TOL 10^{-8} , $x_0 = 0.01$				
n	[a]	[b]	[c]	[d]
0	-178.79858410	-178.79854245	-178.79853968	-178.79853968
1	-160.28370068	-160.28344441	-160.28342741	-160.28342738
2	-142.78091804	-142.78011571	-142.78006254	-142.78006246
3	-126.29032770	-126.28856202	-126.28844510	-126.28844493
4	-110.81192389	-110.80878287	-110.80857509	-110.80857478
5	-96.34562794	-96.34077333	-96.34045249	-96.34045201
6	-82.89131054	-82.88452532	-82.88407729	-82.88407662
7	-70.44881185	-70.44002894	-70.43944948	-70.43944861
8	-59.01795928	-59.00727348	-59.00656903	-59.00656798
9	-48.59858294	-48.58624846	-48.58543594	-48.58543473
10	-39.19052880	-39.17694443	-39.17605018	-39.17604884
11	-30.79366937	-30.77935356	-30.77841176	-30.77841035
12	-23.40791198	-23.39347018	-23.39252065	-23.39251923
13	-17.03320456	-17.01929115	-17.01837685	-17.01837548
14	-11.66953898	-11.65681603	-11.65598036	-11.65597911
15	-7.31695186	-7.30604711	-7.30533119	-7.30533012
16	-3.97552278	-3.96698933	-3.96642933	-3.96642850
17	-1.64537010	-1.63964997	-1.63927481	-1.63927425
18	-0.32664416	-0.32403831	-0.32386764	-0.32386739

Method /1/, TOL 10^{-8} , $x_0 = 0.01$				
n	[a]	[b]	[c]	[d]
0	-178.79889873	-178.79856237	-178.79853972	-178.79853968
1	-160.28499058	-160.28352598	-160.28342754	-160.28342739
2	-142.78362504	-142.78028669	-142.78006282	-142.78006248
3	-126.29451112	-126.28882592	-126.28844553	-126.28844496
4	-110.81732058	-110.80912290	-110.80857563	-110.80857481
5	-96.35190242	-96.34116823	-96.34045312	-96.34045205
6	-82.89795148	-82.88494283	-82.88407796	-82.88407666
7	-70.45545899	-70.44044643	-70.43945014	-70.43944865
8	-59.02424091	-59.00766765	-59.00656966	-59.00656802
9	-48.60409686	-48.58659414	-48.58543650	-48.58543476
10	-39.19519499	-39.17723673	-39.17605065	-39.17604887
11	-30.79728394	-30.77957979	-30.77841212	-30.77841037
12	-23.41060696	-23.39363874	-23.39252092	-23.39251925
13	-17.03506972	-17.01940774	-17.01837704	-17.01837549
14	-11.67062080	-11.65688360	-11.65598047	-11.65597910
15	-7.31753486	-7.30608350	-7.30533124	-7.30533011
16	-3.97578317	-3.96700557	-3.96642936	-3.96642849
17	-1.64545888	-1.63965550	-1.63927481	-1.63927425
18	-0.32664992	-0.32403867	-0.32386764	-0.32386739

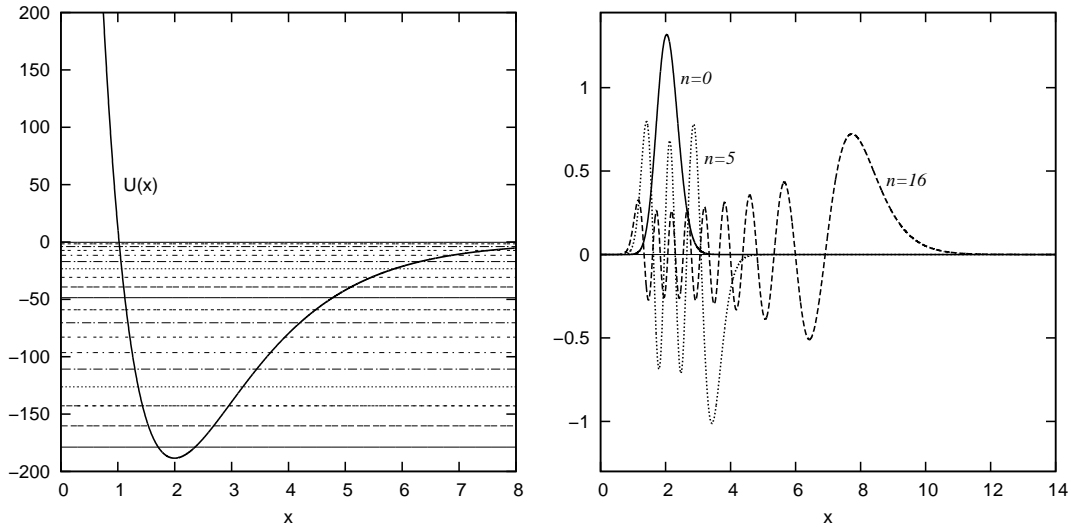


Figure 3.4: Plot of the Morse potential $U(x)$ with its bound states, and wave functions $y(x)$ for $n = 0, 5, 16$.

3.3 Scattering length

We mentioned that the collisional properties of identical bosonic particles at low energies are determined by the s-wave scattering, and expressed in terms of one

parameter - the scattering length a_s . The actual value of the scattering length is determined by potential energy $U(r)$ of atom-atom interaction. The radial Schrödinger equation for the s partial wave at zero energy is reduced to

$$-\frac{\hbar^2}{2M} \frac{d^2\chi(r)}{dr^2} + U(r)\chi(r) = 0$$

with the boundary condition $\chi(0) = 0$. Then a_s can be found from the linear asymptotic behaviour of $\chi(r)$ at large distances as

$$a_s = -\frac{C_2}{C_1},$$

where

$$\chi(r) \sim C_1 r + C_2 \quad \text{for } r \rightarrow \infty.$$

Zero energy collision of Na_2 molecules in the $a^3\Sigma_u^+$ state gives the scattering length for $U(r)$ [11] of $67.107a_0$ (a_0 is the Bohr radius).

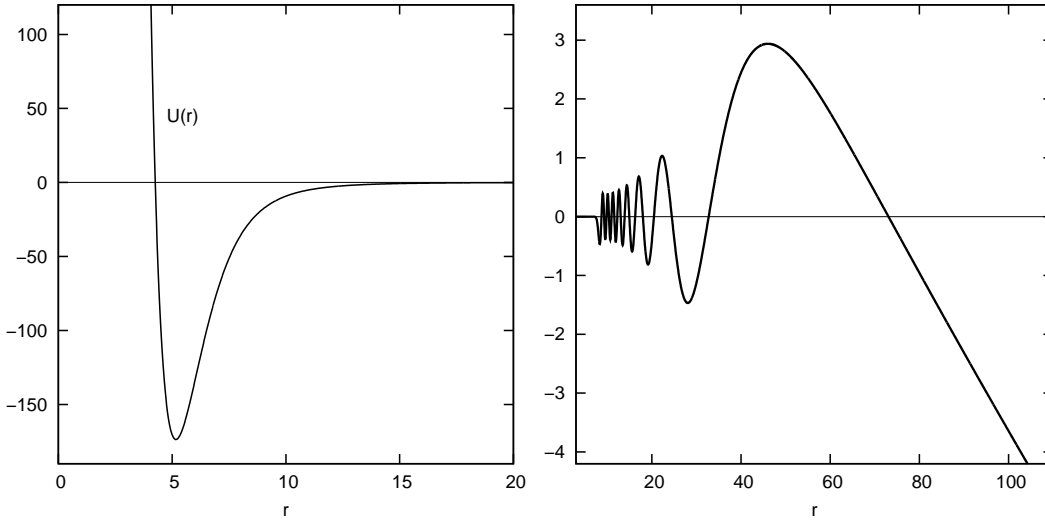


Figure 3.5: Plot of the real interatomic interaction potential $U(r)$ for triplet Na_2 , and respective zero energy wave function.

Appendix A

```
*****
*
*   BoundInt
*   " " " " " " " " " "
*
*
*
* IN: NU1, L, EO
*
* OUT: YB
*
* LOCAL: J, N, Z, Z2, H2, T, A, B, BETA0, BETA1, G, AMPL
*         M, NC, NU1, NU, P1, P2, P3, SS, T1, EE
*
* USES: QUAD
*
*   SUBROUTINE BoundInt(NU1,L,EO,IRMAX)
*
*       include 'glob.f'
*
* Local variables
*
*   INTEGER J, N, M, NC, NU1, NU, L, IRMAX
*   DOUBLE PRECISION Z, Z2, H2, T, EE, EO
*   DOUBLE PRECISION A, B(MAX_PT,2), P1, P2, P3, SS, U(MAX_PT)
*   DOUBLE PRECISION BETA0, BETA1, DBE, G(MAX_PT), AMPL, QUAD
*   DOUBLE PRECISION uLHO, uLJ, uWS, uM
*
*
*
*   NU = NU1-1
*   H2 = h**2
*   EE = EO
*   NC = 1
```

```

      A = -2.D0
*
* Potential inicialization
*
      DO N = 1, IRMAX
      IF (POT .EQ. 0) THEN
        U(N) = uLHO(X(N))
      ELSEIF (POT .EQ. 1) THEN
        U(N) = uLJ(X(N))
      ELSEIF (POT .EQ. 2) THEN
        U(N) = uWS(X(N))
      ELSEIF (POT .EQ. 3) THEN
        U(N) = uM(X(N))
      ENDIF
      VB(N) = U(N) + DBLE((L*(L+1))/X(N)**2)
      ENDDO
*
* Coefficients for the S0 method
*
      IF (MET .EQ. 0) THEN
        BETA0 = 1.d0 / 12.d0
      ENDIF
*
* Coefficients for the S1 method
*
      IF (MET .EQ. 1) THEN
        Z = DSQRT(-EE) * h
        Z2 = Z**2
        IF (Z.LE.0.01d0) THEN
          T = Z2/20.d0 + Z2*Z2/504.d0 + Z2*Z2*Z2/14400.d0
          BETA0 = (1.d0 + T)/ 12.d0
        ELSE
          T = DEXP(Z)
          BETA0 = ((1.d0-T)**2 - Z2*T)/Z2/(1.d0-T)**2
        ENDIF
      ENDIF
*
* The second coefficient
*
      BETA1 = 1.d0 - 2.d0*BETA0
*
* Recursion coefficients
*
      DO N = 1, IRMAX
        B(N,1) = H2 * BETA0
        B(N,2) = H2 * BETA1

```



```

        ENDDO
*
* Boundary conditions for the bound wavefunction
*
1900    YB(1) = 0.D0
        YB(2) = H2/DABS(VB(2)-EE+1.d0)
C      YB(2) = 0.0000001D0

        IF ((-1)**NU.EQ.1) THEN
            YB(IRMAX-1) = H2/DABS(VB(IRMAX-1)-EE+1.d0)
            YB(IRMAX) = H2/DABS(VB(IRMAX)-EE+1.d0)
            write(*,*) (-1)**NU, 1, YB(IRMAX-1), YB(IRMAX)
        ELSE
            YB(IRMAX-1) = -H2/DABS(VB(IRMAX-1)-EE+1.d0)
            YB(IRMAX) = -H2/DABS(VB(IRMAX)-EE+1.d0)
            write(*,*) (-1)**NU, -1, YB(IRMAX-1), YB(IRMAX)
        ENDIF
*
* Generalized potential function
*
        DO N = 1, IRMAX
            FB(N) = VB(N) - EE
        ENDDO
*
* Forward calculation of the bound wavefunction
*
        N = 2
2000    IF ((YB(N) .LT. YB(N-1)) .OR. (N .GT. IRMAX/2)) THEN
            M = N
        ELSE
            P1 = (B(N,2) * FB(N) - A) * YB(N)
            P2 = (B(N,1) * FB(N-1) - 1.D0) * YB(N-1)
            P3 = 1.D0 - B(N,1) * FB(N+1)
            YB(N+1) = (P1 + P2) / P3
            IF (DABS(YB(N+1)) .GT. 200.D0) THEN
                DO J = 1, N+1
                    YB(J) = YB(J) / YB(N+1)
                ENDDO
            ENDIF
            N = N + 1
            GOTO 2000
        ENDIF
*
* Forward normalization
*
        DO N = 1, M

```

```

        YB(N) = YB(N) / YB(M)
    ENDDO
*
* Backward calculation of the bound wavefunction
*
    DO N = IRMAX-1, M+1, -1
        P1 = (B(N,2) * FB(N) - A) * YB(N)
        P2 = (B(N,1) * FB(N+1) - 1.DO) * YB(N+1)
        P3 = 1.DO - B(N,1) * FB(N-1)
        YB(N-1) = (P1 + P2) / P3
        IF (DABS(YB(N-1)) .GT. 200.DO) THEN
            DO J = IRMAX, N-1, -1
                YB(J) = YB(J) / YB(N-1)
            ENDDO
        ENDIF
    ENDDO
*
* Backward normalization
*
    DO N = IRMAX, M, -1
        YB(N) = YB(N) / YB(M)
    ENDDO
*
* Calculation of the energy correction
*
    SS = 0.DO
    DO N = 2, IRMAX-1
        SS = SS + YB(N)*((YB(N-1) + YB(N+1))*B(N,1) + YB(N)*B(N,2))
    ENDDO

    P1 = (A - B(M,2) * FB(M)) * YB(M)
    P2 = (1.DO - B(M,1) * FB(M-1)) * YB(M-1)
    P3 = (1.DO - B(M,1) * FB(M+1)) * YB(M+1)
    DBE = (P1 + P2 + P3) / SS
*
* Decision on another iteration
*
    IF ((DABS(DBE) .GT. EPS) .AND. (NC .LT. 50)) THEN
        NC = NC + 1
        EE = EE - DSIGN(1.d0,DBE)*MIN(DABS(DBE),10.d0)
        WRITE(OUT,*) 'YES', DBE, M, NC, EE, E0
        GOTO 1900
    ELSE
        WRITE(OUT,*) 'NO', DBE, M, NC, EE, E0
    ENDIF
*

```

```

* End of the integration
*
*
* Normalization of the bound wavefunction
*
      DO N = 1, IRMAX
        G(N) = YB(N)*YB(N)
      ENDDO
*
      AMPL = QUAD(IRMAX,h,G)
*
      DO N = 1, IRMAX
        YB(N) = YB(N) / DSQRT(AMPL)
        write(13,*) X(N), YB(N), VB(N), EE
      ENDDO
*
* End of the BoundInt subroutine
*
      RETURN
      END

*
*
*****
*
*   Quadrature
*   """"""""
*
* IN: NMAX, STEP, G
*
* OUT: QUAD
*
* LOCAL: N, SUM
*
      FUNCTION QUAD(NMAX,STEP,G)
*
      include 'glob.f'

*
* Local variables
*
      INTEGER N, NMAX
      DOUBLE PRECISION SUM, STEP, G(MAX_PT), QUAD
*
* Calculation of the integral

```

```

*
    SUM=0.d0
    DO N=5,NMAX-4
        SUM=SUM+G(N)
    ENDDO
    SUM=SUM+17.d0*(G(1)+G(NMAX-0))/48.d0
    SUM=SUM+59.d0*(G(2)+G(NMAX-1))/48.d0
    SUM=SUM+43.d0*(G(3)+G(NMAX-2))/48.d0
    SUM=SUM+49.d0*(G(4)+G(NMAX-3))/48.d0

    QUAD = STEP*SUM
*
* End of the QUAD function
*
    RETURN
    END

*****
*
* The Lennard-Jones potential
*
    FUNCTION uLJ(x)
    DOUBLE PRECISION x,uLJ
    uLJ = 500.d0*(1/x**12.d0 - 1/x**6.d0)
    END FUNCTION uLJ
*
* The Woods-Saxon potential
*
    FUNCTION uWS(x)
    DOUBLE PRECISION x, uWS, q
    q = DEXP((x - 7.d0)/0.6d0)
    uWS = - 50.d0/(1 + q) - 50.d0/0.6 * q/(1 + q**2)
    END FUNCTION uWS
*
* The Morse potential
*
    FUNCTION uM(x)
    DOUBLE PRECISION x, uM
    PARAMETER (D = 188.4355d0, a = 0.711248d0, rel = 1.9975d0)
    uM = D*(1 - DEXP(-a*(x - rel)))**2.0d0 - D
    END FUNCTION uM
*
*The potential of one-dimensional harmonic oscillator
*
    FUNCTION uLHO(x)
    DOUBLE PRECISION x, omega, uLHO

```

```
PARAMETER (omega = 50.d0)
uLHO = (omega**2)*(x**2) - 200.d0
END FUNCTION uLHO
*****
```



```

*
DO N = 1, NMAX
  IF (POT .EQ. 0) THEN
    U(N) = uLHO(X(N))
  ELSEIF (POT .EQ. 1) THEN
    U(N) = uLJ(X(N))
  ELSEIF (POT .EQ. 2) THEN
    U(N) = uWS(X(N))
  ELSEIF (POT .EQ. 3) THEN
    U(N) = uM(X(N))
  ENDIF
  V(N) = U(N) + DBLE(L*(L+1))/X(N)**2
  F(N) = V(N) - EE
  A(N) = 0.d0
  B(N) = 0.d0
  Y(N) = 0.d0
ENDDO

*
* Boundary conditions for the wavefunction
*
Y(1) = 0.D0
Y(2) = H2/DABS(V(2)-EE+1.d0)
C   Y(2) = 0.0000001D0
*
* Coefficients for the Numerov method
*
IF (MET .EQ. 0) THEN
  BETA0 = 1.D0 / 12.D0
ENDIF

*
* Coefficients for the Raptis & Allison
* A. Raptis & A. C. Allison: CPC 14, 1-5 (1978)
* J. Mohamed: CPC 20, 309-320 (1980)
*
IF (MET .EQ. 1) THEN
  Z = DSQRT(EE) * h
  Z2 = Z**2
  IF (Z.LE.0.01d0) THEN
    T = Z2/20.d0 + Z2*Z2/504.d0 + Z2*Z2*Z2/14400.d0
    BETA0 = (1.d0 + T)/ 12.d0
  ELSE
    T = DSIN(Z/2.d0)**2
    BETA0 = (Z2 - 4.d0*T)/4.d0/Z2/T
  ENDIF
ENDIF
ENDIF

```

```

*
* The second coefficient
*
      BETA1 = 1.d0 - 2.d0*BETA0
*
* Coefficients for the recursion
*
      DO N = 1, NMAX
        B(N) = 1.d0 - H2 * BETA0 * F(N)
        A(N) = 2.d0 + H2 * BETA1 * F(N)
      ENDDO

*
* Forward calculation of the wavefunction
*
      DO N = 2, NMAX-1
        Y(N+1) = (A(N) * Y(N) - B(N-1) * Y(N-1)) / B(N+1)
        IF (DABS(Y(N+1))) .GT. 200.DO) THEN
          DO J = 1, N+1
            Y(J) = Y(J) / Y(N+1)
          ENDDO
        ENDIF
      ENDDO

*
* Normalization of the wavefunction
*
      DO N = 1, NMAX
        IF (Y(N) .GT. NORM) THEN
          NORM = Y(N)
        ENDIF
      ENDDO

      DO N = 1, NMAX
        Y(N) = Y(N)/NORM
        write(21,*) X(N), Y(N), V(N)
      ENDDO

*
* End of the integration
*
      RETURN
      END
*

```



```

*
*****
*
*   Normalizator
*   """"""""""
*
*
*
* IN: NMAX, X, Y, E, L
*
* OUT: Y, CDL, SDL, TDL
*
* LOCAL: N, T, S1, S2, C1, C2, AMPL
*

      SUBROUTINE ContNorm()

      include 'globcon.f'

*
* Local variables
*
      INTEGER N
      DOUBLE PRECISION T0, T1, T2, S1, S2, C1, C2, TDL, DL, D
      DOUBLE PRECISION EE, YC(MAX_PT), ARG(MAX_PT)
*
*
*
      EE = E
      T0 = DSQRT(EE)
      T1 = T0*X(NMAX-1) - PI*L/2.d0
      T2 = T0*X(NMAX) - PI*L/2.d0
      S1 = DSIN(T1)
      S2 = DSIN(T2)
      C1 = DCOS(T1)
      C2 = DCOS(T2)

*
* Calculation of the phase shift
*
      TDL = (Y(NMAX)*S1 - Y(NMAX-1)*S2)/(-Y(NMAX)*C1 + Y(NMAX-1)*C2)
      DL = DATAN(TDL)
*
* Analytical formula
*
      DO N = 1, NMAX

```

```

        ARG(N) = TO*X(N) - PI*L/2.d0
        D = (Y(NMAX) - DSIN(ARG(NMAX))) / DCOS(ARG(NMAX))
        YC(N) = D * (DSIN(ARG(N)) + TDL*DCOS(ARG(N)))
        write(31,*) X(N), YC(N)
    ENDDO

    write(41,100) DL
100    FORMAT(F20.8)

        write(OUT,*) X(NMAX-1), X(NMAX), TO, E, DL

*
* End of the Normalization subroutine
*
        RETURN
        END
*
*
*****

```

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Prohlášení

Prohlašuji, že jsem svou bakalářskou práci vypracovala samostatně a použila jsem pouze podklady uvedené v příloženém seznamu.

Nemám žádný důvod proti užití tohoto školního díla ve smyslu §60 Zákona č. 121/2000 Sb., o právu autorském, o právech souvisejících s právem autorským a o změně některých zákonů (autorský zákon).

Declaration

I declare that I wrote my bachelor thesis independently and exclusively with the use of cited bibliography.

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Praha, June 28, 2009

Lucie Augustovičová