Solution and visualizaton in The Sturm – Liouville Problem.

1. Introduction. The regular Sturm – Liouville Problem

Many physical phenomena, both in classical mechanics & in quantum mechanics, are described mathematically by Sturm – Liouville problems (or Shrödinger problems, which are special cases of Sturm – Liouville problems).

The Sturm – Liouville Problem deals with linear ordinary homogeneous second order differential equation:

$$-(p(x)y'(x))' + q(x)y(x) = \lambda w(x)y(x), x \in (a,b) \qquad (1)$$

(a,b) — open interval, where a, b are finite

$\{p, q, w\}$ — coefficients, defined on the open interval (a, b)

λ — spectral parameter

The Sturm – Liouville Problem is defined by adding boundary conditions.

Boundary conditions depends on regular or singular classification of the end points a, b. Also they can be coupled and separated.

Eigen solution of The Sturm – Liouville Problem is a set of pairs $\{\lambda, y\}$. λ — eigenvalue, y — eigenfunction. Our goal is to obtain the eigen solution of The Sturm – Liouville Problem.

2. Two Center problem in quantum mechanics.

2.1 Shrödinger equation with Coulomb – like potential

The Shrödinger problems are special cases of Sturm – Liouville problems. One of well – known Shrödinger Problem is Two Center Problem in quantum mechanics. It's describes mathematically by Shrödinger equation with Coulomb – like potential. In atomic units $e = m = \hbar$ it can be presented as the following equation:

$$\Delta \psi(r; R) + 2\left(E - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}\right)\psi(r; R) = 0 \qquad (2)$$

Z_1 and Z_2 — two fixed nuclei

r_1 and r_2 — distances between electron and nuclei Z_1 and Z_2 correspondingly

R — distance between Z_1 and Z_2

$E = E(R)$ —energy term

Eigen solution of Two Center Problem is a set of pairs $\{E, \psi\}$. E —eigenvalue, ψ — eigenfunction. Our aim is to obtain the eigen solution of Two Center Problem.

It is well – known that the Shrödinger equation (2) is separable by using the prolate spheroidal coordinate system (ζ, η, φ), in which the x, y, z components of the electron position vector $\vec{r}$ can be written in terms of spherical coordinates as

$$x = \frac{R}{2}\sqrt{(\zeta^2 - 1)(1 - \eta^2)} \cos\varphi$$

$$y = \frac{R}{2}\sqrt{(\zeta^2 - 1)(1 - \eta^2)} \sin\varphi \qquad (3)$$

$$z = \frac{R}{2}\zeta\eta$$

Then the solution of equation (2) can be presented as the following product:

$$\psi_j = \psi_{kqm}(\xi, \eta, \varphi; R) = N_{kqm}(R)X_{mk}(\xi; R)Y_{mq}(\eta; R)e^{im\varphi} \qquad (4)$$

$$1 \le \zeta < \infty, \quad -1 \le \eta \le 1, \quad 0 \le \varphi < 2\pi$$

Here $X_{mk}(\zeta; R)$ and $Y_{mq}(\eta; R)$ stand for the two – Coulomb – center quasiradial and quasiangular wave functions, which are normalized according to

$$\int_V \psi^*_{kqm}(\xi, \eta, \varphi; R)\psi_{k'q'm'}(\xi, \eta, \varphi; R) = \delta_{kk'}\delta_{qq'}\delta_{mm'} \qquad (5)$$

$j = \{k, q, m\}$ — set of quantum numbers

k — principal quantum number

q — orbital quantum number

m — magnetic quantum number

Therefore, we have two equations with correspondingly boundary conditions:

- quasiradial equation

$$\frac{d}{d\xi}(\xi^2 - 1)\frac{d}{d\xi}X_{mk}(\xi; R) + \left[-\lambda - p^2(\zeta^2 - 1) + a\zeta - \frac{m^2}{\zeta^2 - 1}\right]X_{mk}(\xi; R) = 0 \quad (6)$$

$$|X_{mk}(1; R)| < \infty; \quad |X_{mk}(\zeta; R)| \xrightarrow{\xi \to \infty} 0; \quad \zeta \in [1, \infty)$$

- quasiangular equation

$$\frac{d}{d\eta}(1 - \eta^2)\frac{d}{d\eta}Y_{mq}(\eta; R) + \left[-\tilde{\lambda} - p^2(1 - \eta^2) + b\eta - \frac{m^2}{1 - \eta^2}\right]Y_{mq}(\eta; R) = 0 \quad (7)$$

$$\left|Y_{mq}(\pm 1; R)\right| < \infty; \quad -1 \le \eta \le +1$$

$$p_j^2 = -\frac{E_j R^2}{2} \quad (p > 0) - \quad \text{energy parameter}$$

$$a = (Z_1 + Z_2)R; \quad b = (Z_2 - Z_1)R - \text{charge parameters}$$

$$\lambda = \lambda_{mk}^{(\zeta)}(p, a); \quad \tilde{\lambda} = \lambda_{mq}^{(\eta)}(p, b) - \text{separation constatnts.}$$

$$\lambda_{mk}^{(\zeta)}(p, a) = \lambda_{mq}^{(\eta)}(p, b) \quad (8)$$

2.2 Quasiradial equation

For the quasiradial wave function we use well – known Jaffé expansion:

$$X_{mk}(\xi; R) = e^{-p\xi}(\xi^2 - 1)^{\frac{m}{2}}(\xi + 1)^\sigma \sum_{s=1}^{\infty} g_s \left(\frac{\xi - 1}{\xi + 1}\right)^s \quad (9)$$

Transformation of variable:

$$t = (\xi - 1)/(\xi + 1)$$

Transformation of singular points:

$$\zeta \to t; -1 \to +\infty; \infty \to +1$$

Transformation of interval:

$$\zeta \in [1; +\infty) \to t \in [0; 1)$$

$$\delta = \frac{a}{2p} - (m + 1)$$

$$\alpha_s g_{s+1} - \beta_s g_s + \gamma_s g_{s-1} = 0 - \text{three – terms relation between coefficients } g_s$$

$$\alpha_s = (s + 1)(s + m + 1)$$

$$\beta_s = 2s(s + 2p - \delta) - (m + \delta)(m + 1) - 2p\delta + \lambda$$

$$\gamma_s = (s - 1 - \delta)(s - m - 1 - \delta)$$

Eigenvalues of the problem are found from the condition of nullifying of the continued fraction:

$$F(p, a, \lambda) = \beta_0 - \cfrac{a_0 \gamma_1}{\beta_1 - \cfrac{a_1 \gamma_2}{\beta_2 -}} \ldots = 0 \tag{10}$$

Coefficients of three – terms relation converge for all $p > 0$:

$$\left| \frac{a_{s-1} \gamma_s}{\beta_{s-1} \beta_s} \right| \rightarrow \frac{1}{4} \left(1 - \frac{4p}{s} \right) + O\left(\frac{p^2}{s^2} \right)$$

The ratio of the series coefficients:

$$\frac{g_s}{g_{s+1}} \rightarrow 1 - 2\sqrt{\frac{p}{s}} + O\left(\frac{p}{s} \right)$$

It's provides the convergence of Jaffé expansion on the complete interval $t \in [0, 1)$ or $\zeta \in [1, +\infty)$.

2.3 Quasiangular equation

For the quasiradial wave function we use Baber – Hasse expansion:

$$Y_{mq}(\eta; R) = e^{-p\eta} \sum_{s=0}^{\infty} c_s P_{s+m}^m (\eta) \tag{11}$$

$\rho_s c_{s+1} - \chi_s g_s + \delta_s c_{s-1} = 0 -$ three – terms relation between coefficients c_s

$$\rho_s - \frac{(s+2m+1)(b-2p(s+m+1))}{2(s+m)+3}$$

$$\chi_s = (s + m)(s + m + 1) - \lambda$$

$$\delta_s = \frac{s[b+2p(s+m)]}{2(s+m)-1}$$

The ratio of succeeding series coefficients at large indexes:

$$\frac{c_{s+1}}{c_s} \rightarrow \frac{p}{s} \xrightarrow{s \to \infty} 0$$

Solution of (8) can be found from the following equation:

$$F(p, b, \lambda) = k_0 - \cfrac{\rho_0 \delta_1}{k_1 - \cfrac{\rho_1 \delta_2}{k_2 - \cdots}} \cdots = 0 \qquad (12)$$

Continuous fraction converges due to following limit:

$$\left| \frac{\rho_{s-1} \delta_s}{\chi_{s-1} \chi_s} \right| \xrightarrow{s \to \infty} \left(\frac{2p}{s} \right)^2$$

2.4 Computational procedure

The computational procedure implemented is as follows:

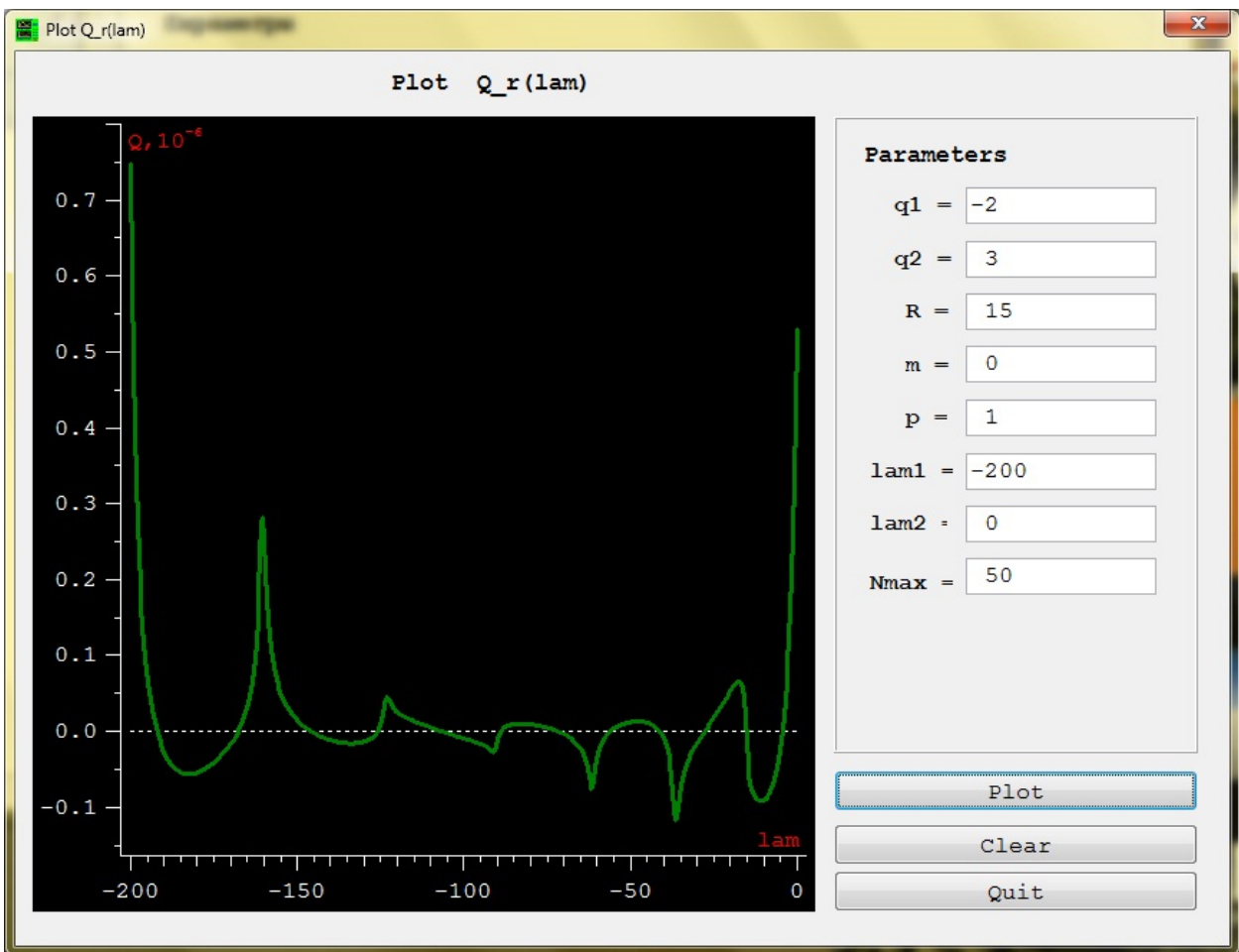- determine a set of roots of continued fractions (10) and (12) as a functions of "λ"

Fig. 1 Continued fraction (10) as a function of "λ"

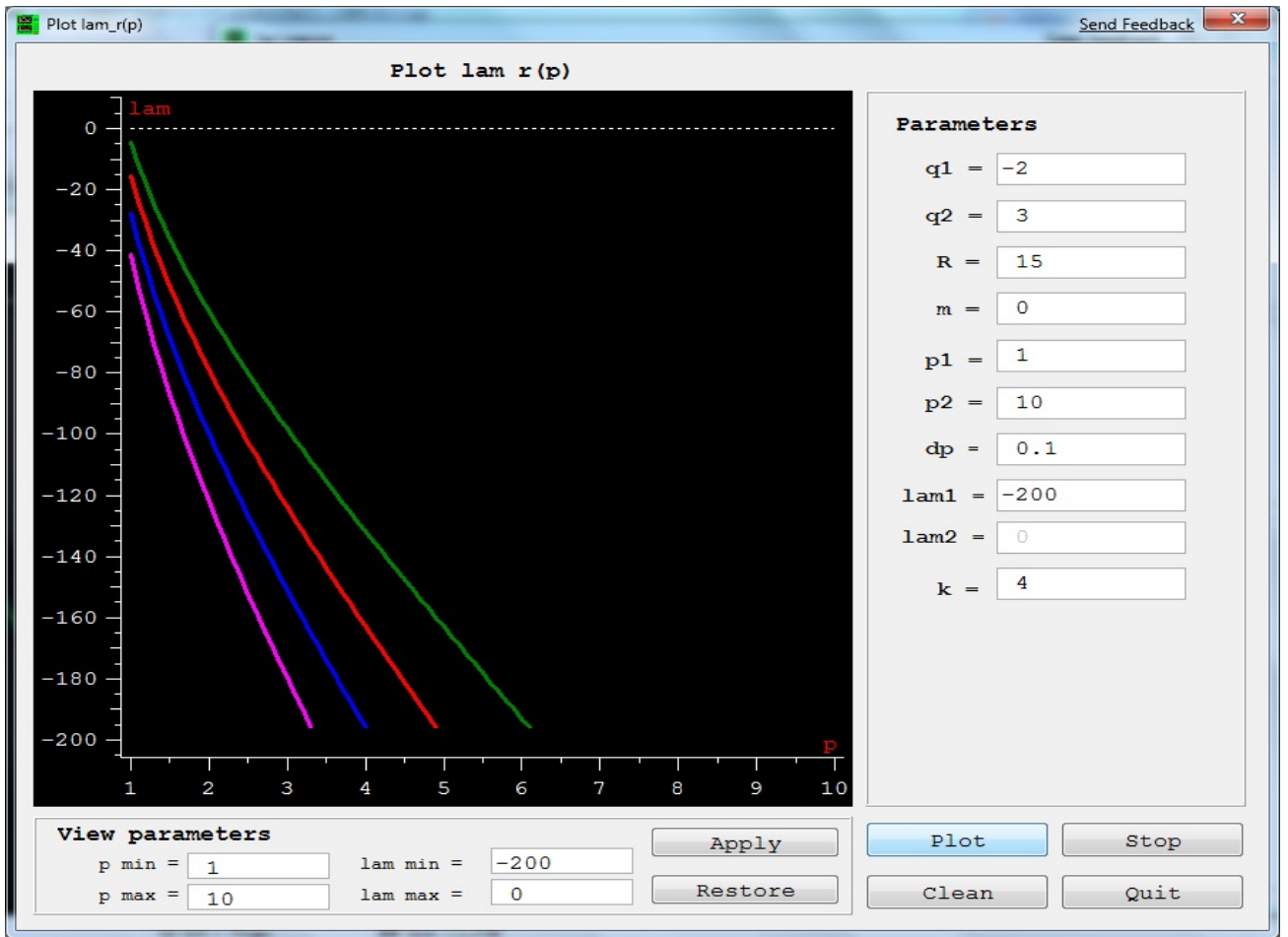- fix a root and track it's position as a function of "p"

Fig. 2 Traces of 1st, 2nd, 3rd, 4th roots of continued fraction (10)

- obtain the point of intersection of functions $\lambda_{mk}^{(\ell)}(p,a)$ and $\lambda_{mq}^{(n)}(p,b)$. This point of intersection is a solution of equation (8)

- determine eigenvalues E_j

- determine quasiradial and quasiangular wave functions by using (9) and (11)

- obtain eigenfunctions ψ_j by using (4)

3. SLEIGN2.

3.1 List of general-purpose programs

General-purpose programs for computing the eigenvalues and eigenfunctions of Sturm - Liouville problem:

- Program SLEIGN has been developed by Bailey, Gordon and Shampine ,
    programming language FORTRAN

- Code in the NAG Library has been developed by Pryce and Marletta ,
    programming   language FORTRAN

- Program SLEDGE has been developed by Fulton and Pruess ,
    programming   language FORTRAN

- Program SLEIGN2 has been developed by Bailey Everitt and Zettl ,
    programming language FORTRAN

3.2 Manual for program package SLEIGN2

To meet the needs of numerical computing techniques in SLEIGN2 was made the following assumptions:

1. The interval (a, b) of R may be bounded or unbounded

2. p, q and w are real-valued functions on (a, b)

3. p, q and w piecewise continuous on (a, b)

4. p and w strictly positive on (a, b)

Conditions on the coefficients:

    Minimal conditions:

$$p^{-1}, q, w \in L^1(a, b)$$

$$p(x), w(x) > 0$$

    Smoothness conditions:

$$p, p', q, w \in C(a, b)$$

$$p(x), w(x) > 0$$

SLP problems in SLEIGN2 are classified into various classes based on the classification of the endpoints and on whether the boundary conditions are separated (S) or coupled (C). We have the following categories:

1. R/R, Separated

2. R/R, Coupled

3. R/LCNO LCNO/R, Separated

4. R/LCNO LCNO/R, Coupled

5. R/LCO LCO/R, Separated

6. R/LCO LCO/R, Coupled

7. LCNO /LCO LCO/ LCNO LCO/ LCO, Separated

8. LCNO /LCO LCO/ LCNO LCO/ LCO, Coupled

9. LP/R LP/LCNO LP/LCO R/LP LCNO/LP LCO/LP

10. LP/LP

R – regular endpoint

LC – limit – circle endpoint

LP - limit-point

LCO - limit-circle oscillatory endpoint

LCNO - limit-circle non-oscillatory endpoint

The algorithm in SLEIGN2:

- Initial interval (a, b) is converted to interval $(-1, +1)$ in the SLEIGN2 package

- The computation procedure is implemented by   the use of Prüfer Transform.

The application of the Prüfer transformation to the Schrödinger equation leads to a nonlinear first-order differential equation. It's look like following:

$$y(x) = \rho(x)\sin\left(\theta(x)\right)$$

$$(py')(x) = \rho(x)\cos\left(\theta(x)\right)$$

Differential equation for ρ and ϑ:

$$\theta'(x) - \rho(x)^{-1}\cos^2(\theta(x)) + (\lambda w(x) - q(x))\sin^2(\theta(x))$$

$$\frac{\rho'(x)}{\rho(x)} = (p(x)^{-1} - \lambda w(x) + q(x))\sin(\theta(x))\cos(\theta(x))$$

Boundary conditions for θ:

$$\theta(a) = -arctg(A_2/A_1)$$

$$\theta(b) - \pi n = -arctg(B_2/B_1)$$

3.3 Solution in BARSIC (Business And Research Scientific Interactive Calculator)

- Numerical algorithms from SLEIGN2 remain unchanged. Subroutines of SLEIGN package (programming language FORTRAN) are compiled into 'dll' file ('so' files in case of OS Linux) and then they are called from BARSIC programs.
- Additional functions for calculation of first and second derivatives were created (It's necessary to write them in FORTRAN when SLEIGN2 is used directly)

References:

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2. J.D. Pryce "Numerical solution of Sturm-Liouville Problems" (Oxford University Press; 1993)

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6. A. Devdariani, E. Dalimier "Dipole transition-matrix elements of the one-electron heterodiatomic quasimolecules"