FEM Solver Coulomb Two Center Problem

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Outline

Abstract

The finite element method (FEM) solver for the two-center Coulomb problem with discrete and continuous spectrum in prolate spheroidal coordinates under separation independent variables is presented.
The eigenvalues of energy and separation constant of discrete spectrum and the eigenfunctions or separation constant and phase shift of continues spectrum of energy and the eigenfunctions of the boundary problems for the quasiradial and quasiangular equations are calculated by the finite element method KANTBP 5M program implemented in Maple on a grid of the parameter, the distance between the Coulomb centers.
The required difference of pair of eigenvalues of energy of discrete spectrum of quasiradial and quasiangular equations are calculated with a given accuracy by the iteration second method with respect to the required separation constant.
Benchmark calculations agree with etalon calculations by programs that implement alternative methods in FORTRAN within a required accuracy.

1D Problem statement

Self-adjoint system of second-order ODE for unknowns $\Phi(z)$ by z in the region $z \in \Omega_z = (z^{\min}, z^{\max})$

$$\left(-\frac{1}{f_B(z)}\frac{d}{dz}f_A(z)\frac{d}{dz} + V(z) - E\right)\Phi(z) = 0.$$

$f_B(z) > 0$ $f_A(z) > 0$, $V(z)$ are real or complex-valued coefficients from the Sobolev space $\mathcal{H}_2^{s\geq 1}(\Omega)$.
All coefficients are continuous (or piecewise continuous) functions that have derivatives up to the order of $\kappa^{\max} - 1 \geq 1$ in the domain $z \in \bar{\Omega}_z$.

The boundary conditions:

$$\text{(I)}: \qquad \Phi(z^t) = 0, \quad t = \min \text{ and/or } \max,$$

$$\text{(II)}: \qquad \lim_{z\to z^t} f_A(z)\frac{d}{dz}\Phi(z) = 0, \quad t = \min \text{ and/or } \max,$$

$$\text{(III)}: \qquad \lim_{z\to z^t} \frac{d}{dz}\Phi(z) = R(z^t)\Phi(z^t), \quad t = \min \text{ and/or } \max.$$

Problem 1. For bound or metastable states

Case of the real potentials and real eigenvalues E: $E_1 \leq E_2 \leq ... \leq E_{N_o}$

$$\langle \Phi_m | \Phi_{m'} \rangle = \int_{z^{\min}}^{z^{\max}} f_B(z) (\Phi^{(m)}(z))^* \Phi^{(m')}(z) dz = \delta_{mm'}.$$

Case of the complex potentials and complex eigenvalues $E = \Re E + \imath \Im E$: $\Re E_1 \leq \Re E_2 \leq ... \leq \Re E_{N_o}$,

The eigenfunctions $\mathbf{\Phi}_m(z)$ obey the normalization and orthogonality conditions

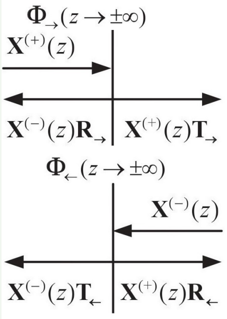
$$(\Phi_m | \Phi_{m'}) = \int_{z^{\min}}^{z^{\max}} f_B(z) \Phi^{(m)}(z) \Phi^{(m')}(z) dz = \delta_{mm'}.$$

J.G. Muga, J.P. Palao, B. Navarro, I.L. Egusquiza Complex absorbing potentials Physics Reports 395 (2004) 357–426

A.A. Gusev et al,Symbolic-numeric solution of boundary-value problems for the Schrodinger equation using the finite element method: scattering problem and resonance states, Lecture Notes in Computer Science 9301 (2015) 182–197.

Problem 2. The scattering problem

"incident wave + outgoing waves" asymptotic form



$$\Phi_{\rightarrow}(z\rightarrow\pm\infty) = \begin{cases} X_{\rm min}^{(\rightarrow)}(z) + X_{\rm min}^{(\leftarrow)}(z)R_{\rightarrow}, & z\rightarrow-\infty \\ X_{\rm max}^{(\rightarrow)}(z)T_{\rightarrow} + X_{\rm max}^{(c)}(z)T^{c}_{\rightarrow}, & z\rightarrow+\infty \end{cases}$$

$$\Phi_{\leftarrow}(z\rightarrow\pm\infty) = \begin{cases} X_{\rm min}^{(\leftarrow)}(z)T_{\leftarrow} + X_{\rm min}^{(c)}(z)T^{c}_{\leftarrow}, & z\rightarrow-\infty \\ X_{\rm max}^{(\leftarrow)}(z) + X_{\rm max}^{(\rightarrow)}(z)R_{\leftarrow}, & z\rightarrow+\infty \end{cases}$$

$\Phi_{\rightarrow}(z)$, $\Phi_{\leftarrow}(z)$ are the solutions
$X_{\rm min}^{(\rightarrow)}(z)$, $X_{\rm min}^{(\leftarrow)}(z)$ are open channel asymptotic solutions at $z\rightarrow-\infty$,
$X_{\rm max}^{(\rightarrow)}(z)$, $X_{\rm max}^{(\leftarrow)}(z)$ are open channel asymptotic solutions at $z\rightarrow+\infty$,
$R_{\rightarrow}$, $R_{\leftarrow}$ are the reflection amplitudes,
$T_{\rightarrow}$, $T_{\leftarrow}$ are the transmission amplitudes,
$X_{\rm min}^{(c)}(z)$, $X_{\rm max}^{(c)}(z)$ are closed channel solutions,
$T^{c}_{\rightarrow}$, $T^{c}_{\leftarrow}$, are auxiliary coefficients.

Problem 2. The scattering problem

Wronskian conditions

$$\mathbf{Wr}(X^{(\mp)}(z), X^{(\pm)}(z)) = \pm 2\imath, \;\; \mathbf{Wr}(X^{(\pm)}(z), X^{(\pm)}(z)) = 0$$

$$\mathbf{Wr}(a(z), b(z)) = a(z)\frac{db(z)}{dz} - \frac{da(z)}{dz}b(z).$$

For real-valued potentials

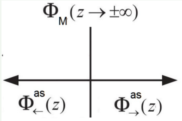
$$T^*_{\rightarrow}T_{\rightarrow} + R^*_{\rightarrow}R_{\rightarrow} = 1,$$
$$T^*_{\leftarrow}T_{\leftarrow} + R^*_{\leftarrow}R_{\leftarrow} = 1,$$
$$T_{\rightarrow} = T_{\leftarrow}.$$

For real-valued potentials the scattering matrix is symmetric and unitary, for complex potentials it is only symmetric

$$\mathbf{S} = \begin{pmatrix} R_{\rightarrow} & T_{\leftarrow} \\ T_{\rightarrow} & R_{\leftarrow} \end{pmatrix}, \qquad \mathbf{S}^{\dagger}\mathbf{S} = \mathbf{S}\mathbf{S}^{\dagger} = 1.$$

Problem 3. The metastable state pr. with complex e.v. $E = \Re E + \imath \Im E$:

Asymptotic form



$$\Phi_{\rightarrow}(z \to \pm\infty) = \begin{cases} X_{\min}^{(\leftarrow)}(z) O_{\leftarrow} + X_{\min}^{(c)}(z) O^{c}_{\leftarrow}, & z \to -\infty \\ X_{\max}^{(\rightarrow)}(z) O_{\rightarrow} + X_{\max}^{(c)}(z) O^{c}_{\rightarrow}, & z \to +\infty \end{cases}$$

Robin (Siegert) BC

$$\text{(III)}: \quad \lim_{z \to z^t} \frac{d}{dz} \Phi(z) = R(z^t) \Phi(z^t), \quad t = \min \text{ and/or } \max$$

$$R(z^t) = \left(\lim_{z \to z^t} \frac{d}{dz} \left(X_t^{(\leftrightarrows)}(z), X_t^{(c)}(z) \right) \right) \left(X_t^{(\leftrightarrows)}(z), X_t^{(c)}(z) \right)^{-1}$$

Orthonormalization conditions

$$(\Phi_m | \Phi_{m'}) = \int f_B(z) \Phi^{(m)}(z) \Phi^{(m')}(z) dz = \delta_{mm'}.$$

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Finite Element Method

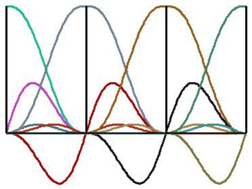
BVP → problem of determination of stationary points of the variational functional

$$\int_{z_{\min}}^{z_{\max}} \left(\frac{d\Phi(z)}{dz_i} f_A(z) \frac{d\Phi(z)}{dz} + f_B(z)\Phi(z)(V(z)-E)\Phi(z) \right) dz$$

$$+\Phi(z_{\min})R(z_{\min})\Phi(z_{\min}) - \Phi(z_{\max})R(z_{\max})\Phi(z_{\max})$$

Exp. of sol. over the basis of local functions $N_\mu^g(z)$

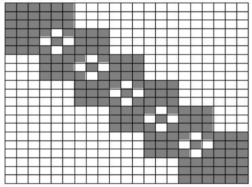
$$\Phi(z) = \sum_{\mu=0}^{L-1} \Phi_\mu^h N_\mu^g(z). \qquad (*)$$



After subst. (*) into a variational functional and minimizing it, we obtain the generalized AEP

$$\mathbf{A}^p \boldsymbol{\xi}^h - \varepsilon^h \mathbf{B}^p \boldsymbol{\xi}^h = 0.$$

$\mathbf{A}^p$ is the stiffness matrix;
$\mathbf{B}^p$ is the positive definite mass matrix;



The statement of Coulomb Two Center Problem

The stationary Schrödinger equation for the two Coulomb center problem

$$\left[-\frac{1}{2}\triangle_{\mathbf{r}} - \frac{Z_1}{r_1} - \frac{Z_2}{r_2} - E\right]\Psi(\mathbf{r};R) = 0, \qquad \mathbf{r}=\{x,y,z\} \in \mathcal{R}^3$$

R is the distance between the Coulomb centers,
Z_1 and Z_2 are charges
r_1 and r_2 are the distances from the electron to the first and the second center,
E are eigenvalues of electron energy: $E = E(R) < 0$ of discrete spectrum and $E \geq 0$ of continues one.

prolate spheroidal coordinates $\mathbf{r}=\{\xi,\eta,\varphi\}$

$$x = \frac{R}{2}\sqrt{(\xi^2-1)(1-\eta^2)}\cos\varphi, \quad y = \frac{R}{2}\sqrt{(\xi^2-1)(1-\eta^2)}\sin\varphi, \quad z = \frac{R}{2}\xi\eta,$$

$$1 \leq \xi < \infty, \quad -1 \leq \eta \leq 1, \quad 0 \leq \varphi < 2\pi,$$

$$r_1 = \frac{R}{2}(\xi+\eta), \quad r_2 = \frac{R}{2}(\xi-\eta), \quad dv = (R/2)^3(\xi^2-\eta^2)d\xi d\eta d\varphi$$

$$\triangle_{\mathbf{r}} = \frac{4}{R^2(\xi^2-\eta^2)}\left[\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial}{\partial\eta} + \frac{(\xi^2-\eta^2)}{(\xi^2-1)(1-\eta^2)}\frac{\partial^2}{\partial\varphi^2}.\right]$$

The separation of the variables

$$\Psi(\mathbf{r};R) = \Psi_m(\xi,\eta;R)\exp(\pm\imath m\varphi)/\sqrt{2\pi}, \quad m = 0, 1, \cdots, \tag{1}$$
$$\Psi_m(\xi,\eta;R) = \Psi_{n_\xi n_\eta m}(\xi,\eta;R) = F_{n_\xi n_\eta m}(\xi;R)\Phi_{n_\xi n_\eta m}(\eta;R)$$

The BVP for system of ODEs

$$\left[-\frac{1}{\xi^2-1}\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi}-\epsilon(R)+\frac{\lambda(R)-a\xi}{\xi^2-1}+\frac{m^2}{(\xi^2-1)^2}\right]F_{n_\xi n_\eta m}(\xi;R)=0, \tag{2}$$
$$\left[-\frac{1}{1-\eta^2}\frac{d}{d\eta}(1-\eta^2)\frac{d}{d\eta}-\epsilon(R)-\frac{\lambda(R)+b\eta}{1-\eta^2}+\frac{m^2}{(1-\eta^2)^2}\right]\Phi_{n_\xi n_\eta m}(\eta;R)=0. \tag{3}$$

$\epsilon(R)=-p^2(R)$ are the eigenvalues, $\lambda(R)$ the separation constant, n_ξ and n_η are number of zeros of $F_{n_\xi n_\eta m}(\xi;R)$ and $\Phi_{n_\xi n_\eta m}(\eta;R)$ connected to principal $N = n_\xi + n_\eta + m + 1$ and azimuthal $l = n_\eta + m$ quantum numbers, $a=(Z_1+Z_2)R$, $b=(Z_2-Z_1)R$.

FEM algebraic problem

$$\mathbf{A}_1^p\boldsymbol{\xi}^h - \epsilon^h\mathbf{B}_1^p\boldsymbol{\xi}^h + \lambda^h\mathbf{C}_1^p\boldsymbol{\xi}^h = 0,$$
$$\mathbf{A}_2^p\phi^h - \epsilon^h\mathbf{B}_2^p\phi^h - \lambda^h\mathbf{C}_2^p\phi^h = 0.$$

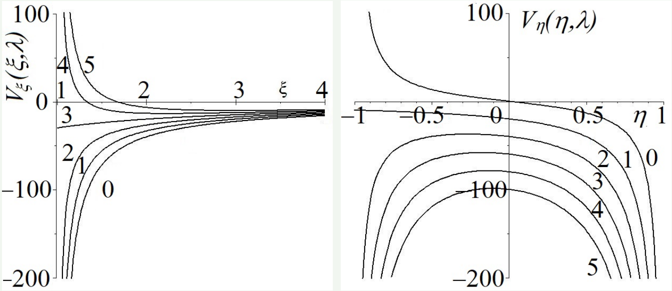
Discrete spectrum. Reformulation of the problem

The BVP for system of ODEs

$$\left[-\frac{1}{\xi^2-1}\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi}-\epsilon_{n_\xi}(R)+\frac{\lambda(R)-a\xi}{\xi^2-1}+\frac{m^2}{(\xi^2-1)^2}\right]F_{n_\xi m}(\xi;R)=0, \qquad (4)$$

$$\left[-\frac{1}{1-\eta^2}\frac{d}{d\eta}(1-\eta^2)\frac{d}{d\eta}-\epsilon_{n_\eta}(R)-\frac{\lambda(R)+b\eta}{1-\eta^2}+\frac{m^2}{(1-\eta^2)^2}\right]\Phi_{n_\eta m}(\eta;R)=0. \qquad (5)$$

Here $\epsilon_{n_\xi}(R)=-p^2(R)$ and $\epsilon_{n_\eta}(R)=-p^2(R)$ are the eigenvalues



Potentials of BVPs (4) and (5) at $m=0$ versus λ marked by 0: $\lambda=0$; 1: $\lambda=20$; 2: $\lambda=40$; 3: $\lambda=60$; 4: $\lambda=80$; 5: $\lambda=100$.

Discrete spectrum. The secant method

The equation

$$f(x)=0, \quad f(x){=}\epsilon_{n_\xi}(\lambda;R){-}\epsilon_{n_\eta}(\lambda;R), \quad x{=}\lambda.$$

The secant method for solving equation $f(x){=}0$

$$x^{(s+1)}{=}[f(x^{(s)})x^{(s-1)}{-}f(x^{(s-1)})x^{(s-1)}]/[f(x^{(s)}){-}f(x^{(s-1)})], \quad s{=}1,2,\ldots$$

with initial values $x^{(1)}$ and $x^{(0)}$ for given R

The Algorithm

Input: Z_1, Z_2, R, m, n_ξ, n_η, $\delta=10^{-7}$ is the tolerance, Ω_ξ and Ω_η are the grids

Output: $\lambda(R)$, $\epsilon_{n_\xi}(\lambda;R){=}\epsilon_{n_\eta}(\lambda;R){=}{-}p^2(R)$, $F_{n_\xi n_\eta m}(\xi;R)$, and $\Phi_{n_\xi n_\eta m}(\eta;R)$

Step 1 Initial approximation of interval boundaries $\lambda\in[\lambda_0,\lambda_1]$

Step 2 FEM calc. $\epsilon^{(0)}_{n_\xi}{\equiv}\epsilon_{n_\xi}(\lambda_0;R)$, $\epsilon^{(1)}_{n_\xi}{\equiv}\epsilon_{n_\xi}(\lambda_1;R)$, $\epsilon^{(0)}_{n_\eta}{\equiv}\epsilon_{n_\eta}(\lambda_0;R)$, $\epsilon^{(1)}_{n_\eta}{\equiv}\epsilon_{n_\eta}(\lambda_1;R)$;

Step 3 $\epsilon_0:={\epsilon^{(0)}_{n_\xi}}{-}\epsilon^{(0)}_{n_\eta}$, $\epsilon_1:={\epsilon^{(1)}_{n_\xi}}{-}\epsilon^{(1)}_{n_\eta}$, $\lambda{=}(\epsilon_1\lambda_0{-}\epsilon_0\lambda_1)/(\epsilon_1{-}\epsilon_0)$, $\delta\epsilon{=}\epsilon_1{-}\epsilon_0$;

Step 4 secant method: loop is executed until $|\delta\epsilon|>\delta$

Step 4.1 FEM calc. $\epsilon_{n_\xi}{\equiv}\epsilon_{n_\xi}(\lambda;R)$, $\epsilon_{n_\eta}{\equiv}\epsilon_{n_\eta}(\lambda;R)$, $\epsilon:={\epsilon_{n_\xi}}{-}\epsilon_{n_\eta}$

Step 4.2 Select $(\epsilon_0,\lambda_0){=}(\epsilon,\lambda)$ or $(\epsilon_1,\lambda_1){=}(\epsilon,\lambda)$ by sign of ϵ

Step 4.3 New approximation $\lambda{=}(\epsilon_1\lambda_0{-}\epsilon_0\lambda_1)/(\epsilon_1{-}\epsilon_0)$, $\delta\epsilon{=}\epsilon_1{-}\epsilon_0$

Step 4 End of loop of secant method

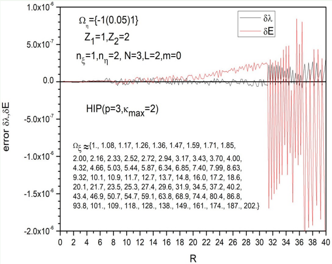
End

Discrete spectrum. Results

Separation constants $\lambda(R)$ and eigenvalues $p(R)^2$ calculated for $R=10$, $Z_1=1$ and $Z_2=2$ and $m=0$ using the TERM and KANTBP 5M program and their differences.

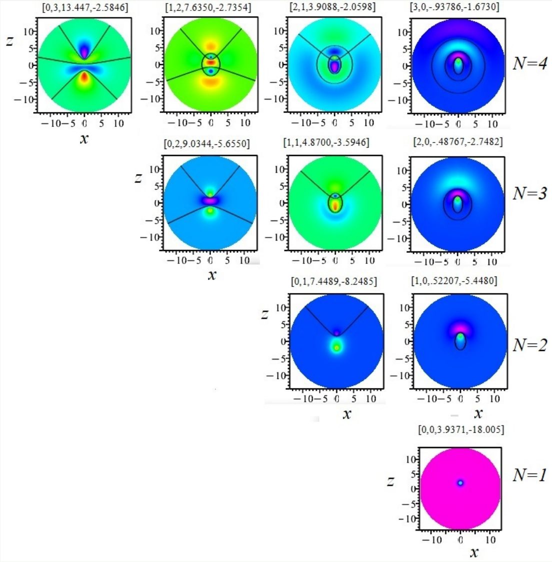
		TERM		KANTBP 5M				
n_ξ	n_η	$\lambda(R)$	$p^2(R)$	$-\lambda(R)$	$-p^2_{n_\xi}(R)$	$-p^2_{n_\eta}(R)$	$\delta\lambda(R)$	$\delta p^2(R)$
0	0	-9.97499	105.00071	9.97499	-105.00072	-105.0007	-6.0E-07	-5.7E-06
0	8	-73.58715	2.83101	73.58715	-2.83101	-2.831	-1.0E-07	-2.6E-09
8	0	5.30544	2.19296	-5.30544	-2.19296	-2.19295	-1.4E-06	-4.7E-08
8	1	-3.09148	1.94442	3.09145	-1.94442	-1.94437	-3.0E-05	-8.5E-07

Gusev, A. A., Solov'ev, E. A., and Vinitsky, S. I.: ARSENY: A program for computing inelastic transitions via hidden crossings in one-electron atomic ion–ion collisions with classical description of nuclear motion, Comput. Phys. Commun. 286, 108662 (2023)

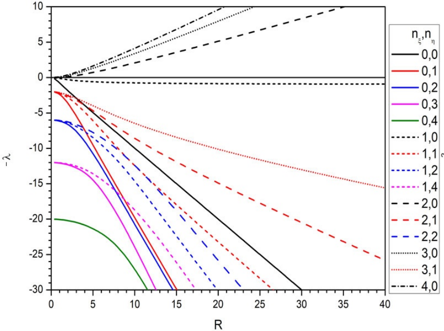


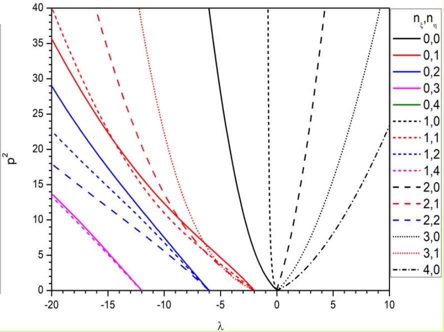
Differences of the functions of the separation constant $\delta\lambda(R) = \lambda^{(SK)}(R) - \lambda^{(T)}(R)$ and energy $\delta E(R) = E^{(SK)} - E^{(T)}$ depending on the parameter R, for $Z_1 = 1$ and $Z_2 = 2$ and $m = 0$, calculated using the secant method algorithm and the KANTBP 5M program, and the TERM (T) procedure

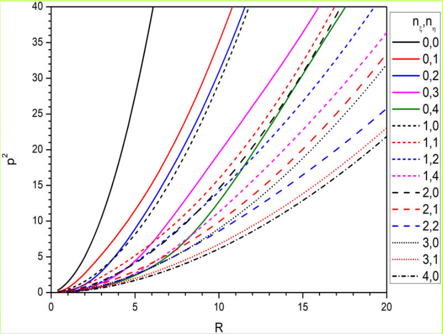
Discrete spectrum. The eigenfunctions $\Psi_{n_\xi n_\eta m}(\xi,\eta,R)$ in xz plane for $N=n_\xi+n_\eta+m+1\le 4$ at $R=4$, $m=0$ labelled by $[n_\xi,n_\eta,\lambda(R),\epsilon(R)]$



Discrete spectrum. Results







The dependence among p^2, λ and R.

Continuous spectrum. Reformulation of the problem

The BVP for system of ODEs

$$\left[-\frac{1}{\xi^2-1}\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi}-\epsilon(R)+\frac{\lambda(R)-a\xi}{\xi^2-1}+\frac{m^2}{(\xi^2-1)^2}\right]F_{n_\eta m}(\xi;R)=0, \qquad (6)$$

$$\left[-\frac{d}{d\eta}(1-\eta^2)\frac{d}{d\eta}-\lambda(R)-(1-\eta^2)\epsilon(R)+b\eta+\frac{m^2}{(1-\eta^2)}\right]\Phi_{n_\eta m}(\eta;R)=0. \qquad (7)$$

The logarithmic derivative $\mathcal{R}(\xi)$ in the Robin BC is determined using asymptotes of the radial Coulomb spheroidal function (RCSF) $F_{km}(\xi;R))$ or regular $\mathcal{F}_l(\gamma,\rho)=N_c(f)F_l(\gamma,\rho)$ and irregular $\mathcal{G}_l(\gamma,\rho)=N_c(f)F_l(\gamma,\rho)$ asymptotes of Coulomb functions at $\rho=c\xi$ and $\gamma=-a/2c=-(Z_1+Z_2)/k$

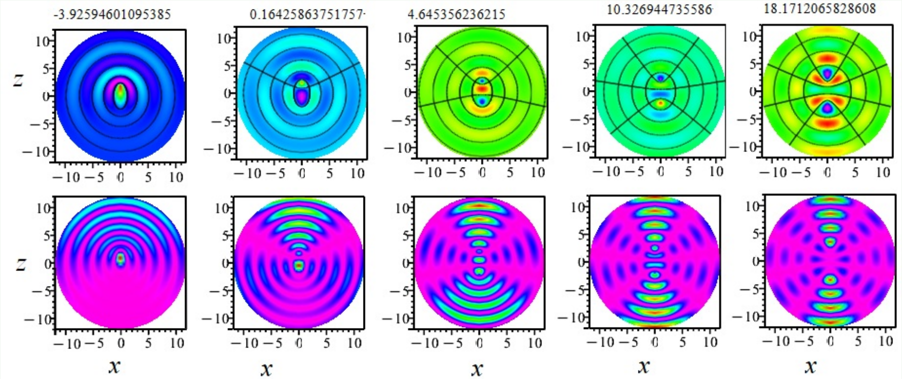
$$F^{as}_{flm}(\xi;R)=\hat{\mathcal{R}}^-_l(\gamma,\rho))-\hat{\mathcal{R}}^+_l(\gamma,\rho)S_l,\ S_l=\exp(\imath 2\delta^{(s)}_{lm}(k)), \qquad (8)$$

$$\hat{\mathcal{R}}^\pm_l(\gamma,\rho))=\mathcal{R}^\pm_l(\gamma,\rho))A^\pm(\rho;p),\ A^\pm(\rho;p)=\left(1+\sum_{n=1}^{p}\frac{a^\pm_n}{\rho^n}\right),$$

$$\mathcal{R}^\pm_l(\gamma,\rho\to\infty)=\frac{N_c(f)}{(c\xi)}\exp(\pm\imath\theta(\xi)),\ \theta(\xi)=c\xi-\gamma\ln(2c\xi)-l\frac{\pi}{2}+\delta^{(C)}_l(Z/k),$$

where $a^\pm_n$ is coefficients of the function $A^\pm(p,\rho)$ determining from recurrence relations obtained by substitution of the $\hat{\mathcal{R}}^\pm_l(\gamma,\rho))$ to Eq. (6) at $\xi\gg 1$.

Continuous spectrum. Results



The Real part of continuum spectrum eigenfunctions $\Psi_{n_\eta m}(\xi, \eta, R, k)$ (upper panel) and probability density $(R/2)^3(\xi^2 - \eta^2)|\Psi_{n_\eta m}(\xi, \eta, R, k)|^2$ (lower panel) in xz plane at $E = 2k^2 = 2$, $R = 4$, $m = 0$ with the separation constant $\lambda(R)$ from $n_\eta = 0$ (left) till $n_\eta = 4$ (right)

Resume

- It was shown that presented algorithm and program SECANT for calculating a pair of real valued eigenvalues and eigenfunctions at $N \leq 10$ of the two Coulomb centers system by the secant method, which call as a subroutine the KANTBP 5M program for FEM solving BVPs for Eqs. (2) and (3)provides a good agreement with the etalon results obtained by ARSENY program with the required accuracy of the order of $10^{-6} - 10^{-7}$, that is accepted in the current applications.
- Evidently, the algorithm and program SECANT can also used to call as a subroutine the some other programs for solving BVPs for Eqs. (2) and (3),for example as well as some other CAS.
- For solving a continuous spectrum problem at a fixed value $E > 0$, it is sufficient to solve eigenvalue problem for Eq. and substitute a calculated eigenvalue $\lambda_{n_\xi m}$, and to solve the corresponding BVP for with the mixed Neumann (or Dirichlet) and Robin boundary conditions using asymptotes like and only the KANTBP 5M program.
- The algorithm SECANT can be also applied to calculate the series of branching points R_c sought for in the complex plane of distance R and the hidden crossings of complex energy curves $E_{n_\xi,n_\eta,m}(R)$ following the corresponding algorithms of ARSENY program.

THANK YOU FOR YOUR ATTENTION