FEM Calculations of Coulomb Two Center Problem

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Abstract
An algorithm for solving of the boundary value problem for the discrete spectrum of a two-center Coulomb system is presented. The energy and separation constant eigenvalues and the corresponding eigenfunctions are calculated by the secant method on a suitable grid of the parameter, the distance between two Coulomb charges. The eigensolutions at each step of the secant method are calculated using KANTBP 5M program, which implements the finite element method in Maple.

Keywords
Coulomb two center problem, discrete spectrum, finite element method

1. Introduction

The boundary value problem (BVP) of two Coulomb centers (discrete spectrum) allows separation of variables in a prolate spheroidal coordinate system and is characterized by two eigenvalues, the energy $E(R)$ and the separation constant $\lambda(R)$, depending on a real parameter, the distance R between the centers of Coulomb charges Z_1 and Z_2. Discretization of the problem is traditionally carried out using expansions of eigenfunctions in functional series with constant coefficients, depending on R. This approach is applied in programs implemented in FORTRAN, see, e.g., [2] or in Wolfram Mathematica [3]. Of interest is an alternative discretization of this problem by the finite element method (FEM), in which polynomials of a lower degree of the order of 10 are used, in contrast to 100–200 in traditional Galerkin-type expansions. Using lower-order polynomials ensures greater resistance of the FEM computational scheme to rounding errors, i.e. it does not require the use high bit depth for arithmetic operations with floating point with an increase in the numbers of the sought eigenvalues.

The aim of the work is to develop a method and algorithm for solving the problem of two Coulomb centers with real eigenvalues of the discrete energy spectrum and the separation constant on the grid of the values of the real parameter R, the distance between the centers of Coulomb charges, using the secant method and the finite element method implemented in Maple by means of the KANTBP 5M program [1].

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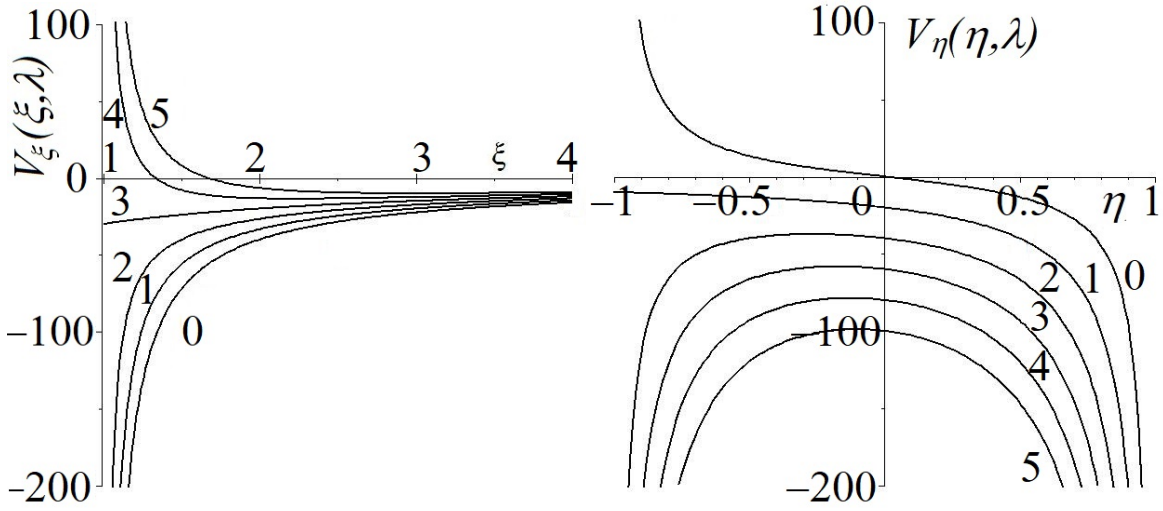

Figure 1: Potentials $V_\xi(\xi,\lambda)$ and $V_\eta(\eta,\lambda)$ at 0: λ=0; 1: λ=20; 2: λ=40; 3: λ=60; 4: λ=80; 5: λ=100.

2. Algorithm for solving the boundary value problem by the secant method and the KANTBP 5M program

In the input data file of KANTBP 5M program for solving BVPs, the ordinary second-order differential equation with variable coefficients is specified in the form [1]:

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

Therefore, we represent the equations of the two-center Coulomb problem in prolate spheroidal coordinates for the eigenfunctions $F_{n_\xi m}(\xi;R)$ and $\Phi_{n_\eta m}(\eta;R)$ in the required form

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

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

Here $\epsilon_{n_\xi}(R)=-p^2(R)$ and $\epsilon_{n_\eta}(R)=-p^2(R)$ are the eigenvalues, $V_\xi(\xi,\lambda_{n_\xi}(R))$ and $V_\eta(\eta,\lambda_{n_\eta}(R))$ are the potentials with parameters $a=(Z_1+Z_2)R$ and $b=(Z_2-Z_1)R$, $Z_2\geq Z_1$:

$$V_\xi(\xi,\lambda(R))=+\frac{\lambda(R)-a\xi}{\xi^2-1}+\frac{m^2}{(\xi^2-1)^2},\quad V_\eta(\eta,\lambda(R))=-\frac{\lambda(R)+b\eta}{1-\eta^2}+\frac{m^2}{(1-\eta^2)^2}, \tag{4}$$

depending on the separation constant $\lambda_{n_\xi}(R)=\lambda(R)$ and $\lambda_{n_\eta}(R)=\lambda(R)$ as a parameter (see Fig. 1). Note that problem (2) always has both a Coulomb discrete ($p^2>0$) and a continuous ($p^2<0$) spectrum, whereas problem (3) has only a discrete spectrum. Here the sign of λ is opposite to that of $\bar{\lambda}$ accepted in the ARSENY program [2], i.e., $\lambda(0)\geq 0$ and $\lambda=-\bar{\lambda}$. The asymptotic behavior of the solution is $F_{n_\xi m}(\xi;R)\sim(\xi^2-1)^{m/2}$ and $\Phi_{n_\eta m}(\eta;R)\sim(1-\eta^2)^{m/2}$. For zero azimuthal quantum number m=0, the eigenfunctions obey the Neumann condition:

$$\lim_{\xi\to 1}(\xi^2-1)\frac{dF_{n_\xi m}(\xi;R)}{d\xi}=0,\quad \lim_{\xi\to\xi_{max}}(\xi^2-1)\frac{dF_{n_\xi m}(\xi;R)}{d\xi}=0,\quad \lim_{\eta\to\mp 1\pm 0}(1-\eta^2)\frac{d\Phi_{n_\eta m}(\eta;R)}{d\eta}=0,$$

while for $m\neq 0$ the eigenfunctions obey the following Dirichlet and Neumann conditions:

$$F_{n_\xi m}(\xi=1;R)=0,\quad \lim_{\xi\to\xi_{max}}(\xi^2-1)\frac{dF_{n_\xi m}(\xi;R)}{d\xi}=0,\quad \lim_{\eta\to\mp 1\pm 0}(1-\eta^2)\Phi_{n_\eta m}(\eta;R)=0.$$

and the orthogonality and normalization conditions

$$\int_0^{\xi_{\max}} F_{n_\xi m}(\xi;R)F_{n'_\xi m}(\xi;R)(\xi^2-1)d\xi=\delta_{n_\xi n'_\xi},\ \int_{-1}^{1}\Phi_{n_\eta m}(\eta;R)\Phi_{n_\eta m}(\eta;R)(1-\eta^2)d\eta=\delta_{n_\eta n'_\eta}.$$

Note that the energy eigenvalues corresponding to $\epsilon_{n_\xi}(R)=-p^2(R)$ or $\epsilon_{n_\eta}(R)=-p^2(R)$ monotonically increase with increasing separation constant $\lambda(R)$ for Eq. (2) and monotonically decrease for Eq. (3), i.e., the differences $\epsilon_{n_\xi}(R)-\epsilon_{n_\eta}(R)$ monotonically increase with increasing $\lambda(R)$. This follows from Eq. (4) and is illustrated in Fig. 1. The BVP potentials have Coulomb asymptotic behavior $V_\xi(\xi\to\infty,\lambda)\to-1/\xi$, $V_\xi(\xi\to1+0,\lambda)\sim-1/(\xi-1)$, $V_\eta(\eta\to1-0,\lambda)\sim-1/(1-\eta)$, $V_\eta(\eta\to-1+0,\lambda)\sim-1/(1+\eta)$. This circumstance allows us to classify the solutions of the original problem by the number of zeros n_ξ and n_η in the variables ξ and η, respectively. Note that the discrete spectrum $\epsilon_{n_\xi}(R)=-p^2(R)$ of Eq. (2) is countable and lies in the interval $\epsilon_{n_\xi}(R)\in(\epsilon_{\min},0)$. This allows solving the problem for a given set of quantum numbers (n_ξ,n_η,m) or $(N=n_\xi+n_\eta+m+1,l=n_\eta-m,m)$ for a fixed $m\geq0$ using the initial approximation $E_{n_\xi,n_\eta,m}(0)=-(Z_1+Z_2)^2/N^2$ and $\lambda_{n_\xi,n_\eta,m}(0)=l(l+1)$ by means of the following algorithm that implements the secant method for solving equation $f(x)=0$:

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

with initial values $x^{(1)}$ and $x^{(0)}$ at $f(x)=\epsilon_{n_\xi}(\lambda;R)-\epsilon_{n_\eta}(\lambda;R)$, $x=\lambda$.

Algorithm SECANT for calculating eigenvalues and eigenfunctions of two Coulomb centers by the secant method and the KANTBP 5M program for solving BVP for Eqs. (2) and (3)
Input: Z_1, Z_2 are the problem parameters
N is the maximum number,
Ω_ξ and Ω_η are the grids for BVPs for Eq. (2) and for Eq. (3)
Output: $\lambda(R)$, $-p^2(R)$, $F_{n_\xi m}(\xi;R)$, and $\Phi_{n_\eta m}(\eta;R)$ are the solutions of BVPs for Eqs. (2) and (3)
Cycle over $n_\xi=0,...,N_{\max}$ and $n_\eta=0,...,N_{\max}-n_\xi-m-1$
Step 1 Initial approximation of interval boundaries $\lambda\in[\lambda_0,\lambda_1]$ for the first program run
Step 2 Loop by parameter $R=\{R_{\min}(\delta R)R_{\max}\}$ with step δR
Step 2.1 Reevaluation $a=(Z_1+Z_2)R$ and $b=(Z_2-Z_1)R$
Step 2.2 Calculation of the eigenvalue $\epsilon^{(0)}_{n_\xi}\equiv\epsilon_{n_\xi}$ of the BVP for Eq. (2) at $\lambda=\lambda_0$
Step 2.3 Calculation of the eigenvalue $\epsilon^{(1)}_{n_\xi}\equiv\epsilon_{n_\xi}$ of the BVP for Eq. (2) at $\lambda=\lambda_1$
Step 2.4 Calculation of the eigenvalue $\epsilon^{(0)}_{n_\eta}\equiv\epsilon_{n_\eta}$ of the BVP for Eq. (3) at $\lambda=\lambda_0$
Step 2.5 Calculation of the eigenvalue $\epsilon^{(1)}_{n_\eta}\equiv\epsilon_{n_\eta}$ of the BVP for Eq. (3) at $\lambda=\lambda_1$
Step 2.6 Calculate the energy differences for the first two approximations
$\epsilon_0:=\epsilon^{(0)}_{n_\xi}-\epsilon^{(0)}_{n_\eta}$ and $\epsilon_1:=\epsilon^{(1)}_{n_\xi}-\epsilon^{(1)}_{n_\eta}$
Step 2.7 New approximation for λ and energy difference using the formula of the secant method $\lambda=(\epsilon_1\lambda_0-\epsilon_0\lambda_1)/(\epsilon_1-\epsilon_0)$ and $\delta\epsilon=\epsilon_1-\epsilon_0$
Step 2.8 secant method: loop is executed until $|\delta\epsilon|>\delta$
Step 2.8.1 Calculation of the eigenvalue ϵ_{n_ξ} of the BVP for Eq. (2) at given λ
Step 2.8.2 Calculation of the eigenvalue ϵ_{n_η} of the BVP for Eq. (3) at given λ
Step 2.8.3 Calculating the energy difference $\epsilon:=\epsilon_{n_\xi}-\epsilon_{n_\eta}$
Step 2.8.4 Selecting the initial approximations $(\epsilon_0,\lambda_0)=(\epsilon,\lambda)$ or $(\epsilon_1,\lambda_1)=(\epsilon,\lambda)$ (they will also be used when moving to the new R)
Step 2.8.5 New approximation for λ and energy difference using the formula of the secant method $\lambda=(\epsilon_1\lambda_0-\epsilon_0\lambda_1)/(\epsilon_1-\epsilon_0)$ and $\delta\epsilon=\epsilon_1-\epsilon_0$
Step 2.8 End of loop of secant method
Step 2. End of loop by R
Step 3. Write OUTPUT: R, λ, $\epsilon_{n_\xi}\approx-p^2(R)$, $\epsilon_{n_\eta}\approx-p^2(R)$, $F_{n_\xi m}(\xi;R)$, and $\Phi_{n_\eta m}(\eta;R)$
End of cycle over n_ξ and n_η

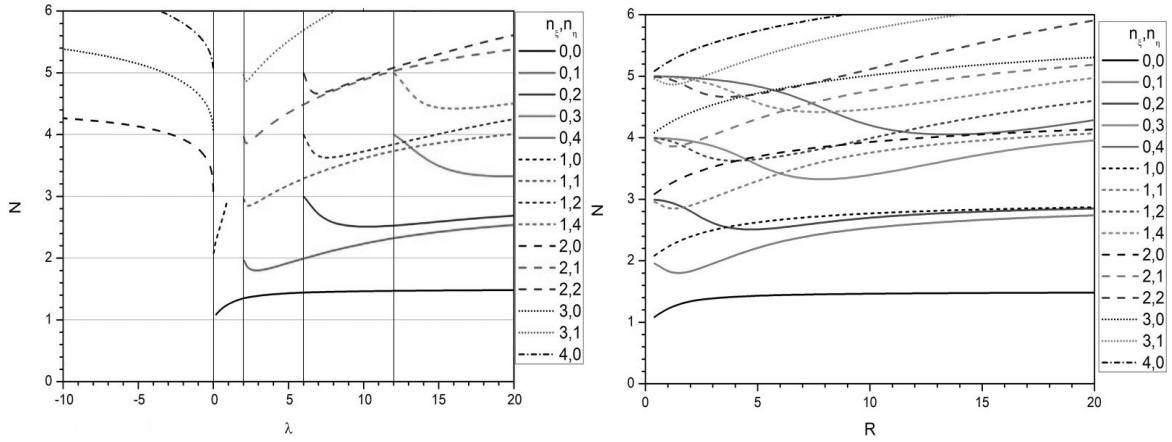

Figure 2: Effective quantum number $N \equiv N_{n_\xi,n_\eta,m}(\lambda_{n_\xi,n_\eta,m}(R))$ versus the parameter $\lambda \equiv \lambda_{n_\xi,n_\eta,m}(R)$, and $N \equiv N_{n_\xi,n_\eta,m}(R)=(Z_1+Z_2)/\sqrt{-2E_{n_\xi,n_\eta,m}(R)}$ versus the parameter R for $Z_1=1$, $Z_2=2$, and $m=0$.

As an example, we present results of the *Algorithm SECANT* calculations of a set of eigenvalues of energy $E_{n_\xi,n_\eta,m}(R)$ and parameter $\lambda_{n_\xi,n_\eta,m}(R)$ for $Z_1=1$, $Z_2=2$, $m=0$, and $N_{\max}=10$ on grids $\Omega_\xi=\{\xi_0=1, ..., \xi_i=\xi_{i-1}+0.08/\xi_{i-1}, ..., \xi_{n-1}=187.4197583, \xi_n=202.4133390\}$ and $\Omega_\eta=\{-1(0.1)1\}$ by means of program KANTBP 5M with 5-th order Hermite interpolation polynomials, which agree within 6-7 digits with those calculated by means of program ARSENY [2]. Figure 2 plots the effective quantum number $N_{n_\xi,n_\eta,m}(\lambda_{n_\xi,n_\eta,m}(R))$ as a function of the parameter λ, and $N_{n_\xi,n_\eta,m}(R)=(Z_1+Z_2)/\sqrt{-2E_{n_\xi,n_\eta,m}(R)}$ as a function of the parameter R for $Z_1=1$, $Z_2=2$, and $m=0$. Note that $N_{n_\xi,n_\eta,m}(0)=(Z_1+Z_2)/\sqrt{-2E_{n_\xi,n_\eta,m}(0)}$ at $R=0$, is equal to the value of the principal quantum number $N(0)=N=n_\xi+n_\eta+1$ of the united atom with the Coulomb charge $Z=Z_1+Z_2$, for the asymptotic energy eigenvalues $E_{Nlm}(R=0)$, and the asymptotic separation constant values $\bar{\lambda}_{lm}(R=0)=l(l+1)$, $l=n_\eta$ at $m=0$, which can be seen in the figures. Moreover, due to the separation of variables, the number of zeros n_ξ and n_η of the eigenfunctions $F_{m,n_\xi}(\xi;R)$ and $\Phi_{m,n_\eta}(\eta;R)$ is preserved for all values of the parameter R.

Note, for solving a continuous spectrum problem at a fixed value $E>0$, it is sufficient to solve eigenvalue problem for Eq. (3) and substitute a calculated eigenvalue $\lambda_{n_\xi m}$ to Eq. (2) and to solve the corresponding BVP with the mixed Neumann (or Dirichlet) and Robin boundary conditions. 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 [2].

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