Model of Diatomic Homonuclear Molecule Scattering by Atom or Barriers

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Abstract. The mathematical model of quantum tunnelling of diatomic *homonuclear* molecules through repulsive barriers *or scattering by an atom* is formulated in the s-wave approximation. The 2D boundary-value problem (BVP) in polar coordinates is reduced to a 1D BVP for a set of second-order ODEs by means of Kantorovich expansion over the set of parametric basis functions. The algorithm for calculating the asymptotic form of the parametric basis functions and effective potentials of the ODEs at large values of the parameter (hyperradial variable) is presented. The solution is sought by matching the numerical solution in one of the subintervals with the analytical solution in the adjacent one. The efficiency of the algorithm is confirmed by comparing the calculated solutions with those of the parametric eigenvalue problem obtained by applying the finite element method in the entire domain of definition at large values of the parameter. The applicability of algorithms and software are demonstrated by the example of benchmark calculations of discrete energy spectrum of the trimer Be_3 in collinear configuration.

Keywords: Parametric boundary-value problems · Second-order ordinary differential equations · Finite element method

1 Introduction

The studies of tunnelling of bound particles through repulsive barriers revealed the effect of resonance quantum transparency of the barrier: when the cluster size is comparable with the spatial width of the barrier, one can observe enhanced barrier transparency, the mechanism of which is analogous to the mechanism of blooming of optical systems. At present this effect and its possible applications is a subject of extensive studies in different physical fields, e.g., the quantum diffusion of molecules [14,18].

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The formulation of the model of quantum tunnelling of a diatomic molecule through Gaussian barriers in the s-wave approximation is given in the form of 2D boundary-value problems in the Cartesian and polar coordinates [11,19]. Evidently, it corresponds to the scattering of a diatomic homonuclear molecule in a potential field of the third atom having infinite mass. Therefore, we can consider the tunneling of a diatomic molecule through the barriers as a limiting case of the molecule scattering by an atom, e.g., the resonance scattering of Be_2 dimer by the Be atom via the compound trimer Be_3: Be_2+Be states. Below we consider the statement of both problems and show both common and specific properties of the corresponding solutions.

In the present paper using different solutions of the auxiliary boundary-value problems with respect to the transverse variable, or the angular variable, with parametric dependence upon the *hyperradial* variable as basis functions, the 2D boundary-value problem is reduced to a system of coupled ODEs of the second order. In the Cartesian coordinates the effective potentials decrease exponentially (below the dissociation threshold) and in the polar coordinates they decrease as inverse powers of the independent variable. Therefore, in the latter case it is necessary to calculate the asymptotic expansions of matrix elements and fundamental solutions of the system of coupled ODEs. For their calculation it is necessary to develop symbolic-numeric algorithms, implemented in the Maple computer algebra system [19].

The paper is organised as follows. In Sect. 2 we give the setting of the 2D BVP. In Sect. 3 the reduction of the BVP using the Kantorovich method is executed. As an example, the eigenvalues and the hyperradial components of eigenfunctions are calculated for the model of Be_3 trimer in the collinear configuration. In Sect. 4 we present the algorithms for calculating the asymptotes of parametric basis functions in polar coordinates at large values of the parameter (hyperradial variable) and the effective potentials. In Conclusion the results and perspectives are discussed.

2 Setting of the Problem

Consider a 2D model of three identical particles with the mass M and the coordinates $x_i \in \mathbf{R}^1$, $i = 1, 2, 3$, coupled via the pair potential $\tilde{V}(|x_i - x_j|)$ $i, j = 1, 2, 3$. Performing the change of variables at cyclic permutation $(\alpha, \beta, \gamma) = (1, 2, 3)$:

$$x \equiv x_{(\alpha\beta)} = x_\alpha - x_\beta, \quad y \equiv y_{(\alpha\beta)\gamma} = \frac{x_\alpha + x_\beta - 2x_\gamma}{\sqrt{3}}, \quad x_0 = \frac{\sqrt{2}}{\sqrt{3}}(x_1 + x_2 + x_3),$$

we arrive at the Schrödinger equation for the wave function in a center-of-mass system $\{x_i \in \mathbf{R}^1 | x_1 + x_2 + x_3 = 0\}$

$$\left(-\frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial x^2} + \frac{M}{\hbar^2}(\tilde{V}(x, y) - \tilde{E})\right) \Psi(y, x) = 0. \tag{1}$$

In the case of a diatomic molecule with identical nuclei coupled via the pair potential $\tilde{V}(|x_1 - x_2|)$ and moving in the external potential field $\tilde{V}^b(|x_i - x_3|)$,

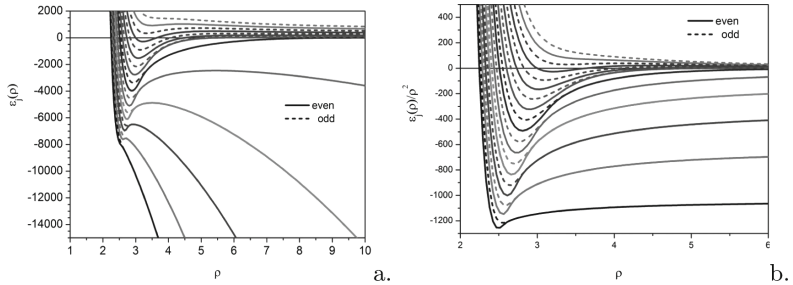

Fig. 1. The potential curves of Be_2 (in K, $1\,\mathrm{K} = 0.18\,\text{Å}^{-2}$), i.e., the energy eigenvalues depending upon the parameter ρ (in Å): a. $\varepsilon_j(\rho)$ and b. $\tilde{\varepsilon}_j = \varepsilon_j(\rho)/\rho^2$.

$i = 2, 1$ of the third atom having the infinite mass, the same Eq. (1) is valid for the variables

$$x = x_1 - x_2, \quad y = x_1 + x_2,$$

the origin of the coordinate frame being placed on the infinite-mass atom, $x_3 = 0$.

Here the potential function for a trimer with the pair potentials (below this case is referred to as Task 2),

$$\tilde{V}(x,y) = \tilde{V}(|x|) + \tilde{V}(|\frac{x-\sqrt{3}y}{2}|) + \tilde{V}(|\frac{x+\sqrt{3}y}{2}|), \tag{2}$$

or the potential function for a dimer in the field of barrier potentials (below this case is referred to as Task 3)

$$\tilde{V}(x,y) = \tilde{V}(|x|) + \tilde{V}^b(|\frac{x-y}{2}|) + \tilde{V}^b(|\frac{x+y}{2}|), \tag{3}$$

is symmetric with respect to the straight line $x = 0$ (i.e., $x_1 = x_2$), which allows one to consider the solutions of the problem in the half-plane $x \geq 0$. Using the Dirichlet or Neumann boundary condition at $x = 0$ allows one to obtain the solutions, symmetric and antisymmetric with respect to the permutation of two particles. If the pair potential possesses a high maximum in the vicinity of the pair collision point, then the solution of the problem in the vicinity of $x = 0$ is exponentially small and can be considered in the half-plane $x \geq x_{\min}$. In this case setting the Neumann or Dirichlet boundary condition at $x_{\min}$ gives only a minor contribution to the solution. The equation, describing the molecular subsystem, has the form

$$\left(-\frac{d^2}{dx^2} + \frac{M}{\hbar^2}(\tilde{V}(x) - \tilde{\varepsilon})\right)\phi(x) = 0. \tag{4}$$

We assume that the molecular subsystem has the discrete spectrum, consisting of a finite number n_0 of bound states with the eigenfunctions $\phi_j(x)$, $j = 1, n$ and eigenvalues $\tilde{\varepsilon}_j = -|\tilde{\varepsilon}_j|$, and the continuous spectrum of eigenvalues $\tilde{\varepsilon} > 0$ with

the corresponding eigenfunctions $\phi_{\tilde{\varepsilon}}(x)$. As a rule, the solution of the discrete spectrum problem for Eq. (4) can be found only numerically.

The proposed algorithm is illustrated by the example of the molecular interaction approximated by the Morse potential of Be_2 with the reduced mass $M/2 = 4.506$ Da of the nuclei [14,19]

$$V(x) = \frac{M}{\hbar^2}\tilde{V}(x), \quad \tilde{V}(x) = D\{\exp[-2(x-\hat{x}_{eq})\alpha] - 2\exp[-(x-\hat{x}_{eq})\alpha]\}. \quad (5)$$

Here $\alpha = 2.96812\,\text{Å}^{-1}$ is the potential well width, $\hat{x}_{eq} = 2.47\,\text{Å}$ is the average distance between the nuclei, and $D = 1280\,\text{K}$ ($1\,\text{K} = 0.184766$ Å^{-2},$1\,\text{Å}^{-2} = 5.412262\,\text{K}$) is the potential well depth. This potential supports five bound states [20] having the energies $\varepsilon_i = (M/\hbar^2)\tilde{\varepsilon}_i$, $i = 1, ..., n_0 = 5$ presented in Table 1. The parameter values are determined from the condition $(\tilde{\varepsilon}_2 - \tilde{\varepsilon}_1)/(2\pi\hbar c) = 277.124\,\text{cm}^{-1}$, $1\,\text{K}/(2\pi\hbar\ \text{c}) = 0.69503476\ \text{cm}^{-1}$.

To solve the discrete spectrum problem we applied the finite element method of the seventh order using the Hermitian interpolation polynomials with double nodes [12]. The grid $\{x_0, ..., x_i, ..., x_n\}$ was used to calculate the values of both the function and its derivatives.

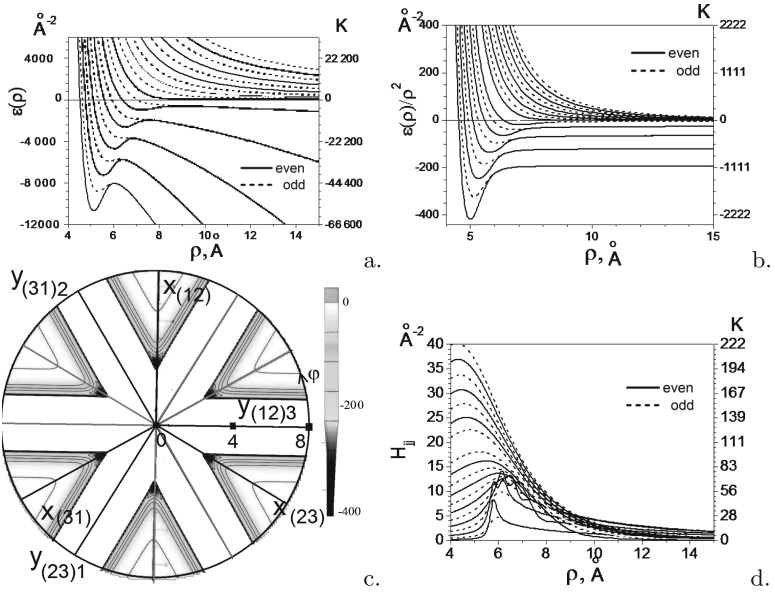

Fig. 2. Be+Be_2: The potential curves of Be_3 (in K), i.e., the energy eigenvalues depending upon the parameter ρ (in Å): a. $\varepsilon_j(\rho)$ and b. $\tilde{\varepsilon}_j = \varepsilon_j(\rho)/\rho^2$, c. the isolines of 2D potentials of Be_3 trimer, and d the diagonal effective potentials $H_{jj}(\rho)$.

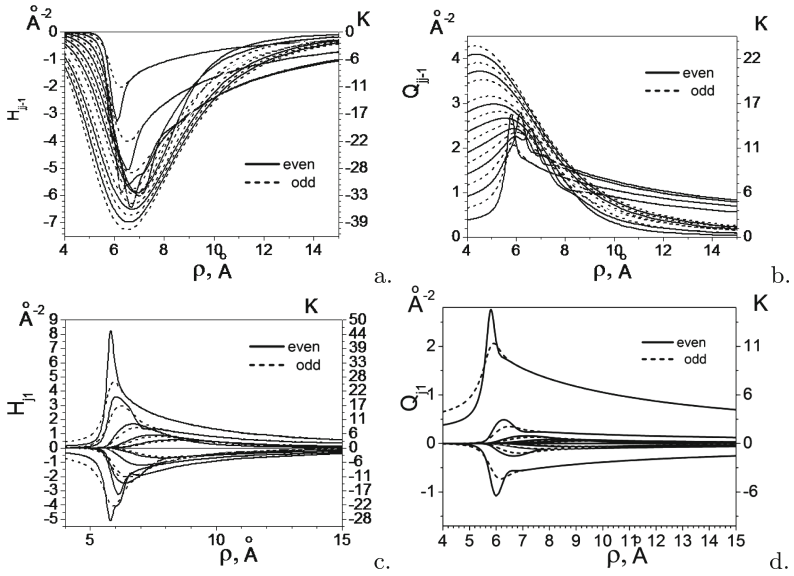

Fig. 3. The effective potentials (13) a. $H_{jj-1}(\rho)$, b. $Q_{jj-1}(\rho)$, c. $H_{j1}(\rho)$, d. $Q_{j1}(\rho)$.

3 Reduction of the BVP Using the Kantorovich Method

Using the change of variables $x = \rho \sin\varphi$, $y = \rho\cos\varphi$, we rewrite Eq. (1) in polar coordinates (ρ, φ), $\Omega_{\rho,\varphi} = (\rho \in (0, \infty), \varphi \in [0, 2\pi])$

$$\left(-\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho} - \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2} + V(\rho,\varphi) - E\right)\Psi(\rho,\varphi) = 0, \tag{6}$$

where for a trimer with pair potentials

$$V(\rho,\varphi) = V(\rho|\sin\varphi|) + V(\rho|\sin(\varphi - 2\pi/3)|) + V(\rho|\sin(\varphi - 4\pi/3)|), \tag{7}$$

and for a dimer with pair potential in the external field of barrier potentials:

$$V(\rho,\varphi) = V(\rho|\sin\varphi|) + V^b(\rho|\sin(\varphi - \pi/4)|) + V^b(\rho|\sin(\varphi + \pi/4)|). \tag{8}$$

The solution of Eq. (6) is sought in the form of Kantorovich expansion

$$\Psi_{i_o}(\rho,\varphi) = \sum_{j=1}^{j_{\max}} \phi_j(\varphi;\rho)\chi_{ji_o}(\rho). \tag{9}$$

Here $\chi_{ji_o}(\rho)$ are unknown functions and the orthogonal normalised basis functions $\phi_j(\varphi;\rho)$ in the interval $\varphi \in [0, \pi]$ are defined as eigenfunctions, corresponding to the eigenvalues of the Sturm-Liouville problem for the equation

$$\left(-\frac{d^2}{d\varphi^2}+\rho^2V(\rho,\varphi)-\varepsilon_j(\rho)\right)\phi_j(\varphi;\rho)=0,\quad \int_0^{2\pi}d\varphi\phi_i(\varphi;\rho)\phi_j(\varphi;\rho)=\delta_{ij}. \tag{10}$$

Table 1. The discrete spectrum energies of dimer Be_2 and the binding energy $E^b=-(E-E^a)$ of even (e) and odd (o) states of trimer Be_3 counted of $E^a=\tilde{\varepsilon}_1=-193.06\,\text{Å}^{-2}=-1044\,\text{K}$ dimer energy Be_2 calculated in grid $\Omega_\rho=4.1(20)7(10)10$.

$-\tilde{\varepsilon}_1$=1044.879 649 K	$E^b_{1,e}=196.02\,\text{Å}^{-2}=1060.86\,\text{K}$	$E^b_{1,o}=107.52\,\text{Å}^{-2}=581.90\,\text{K}$
$-\tilde{\varepsilon}_2$=646.157 093 K	$E^b_{2,e}=142.37\,\text{Å}^{-2}=770.51\,\text{K}$	$E^b_{2,o}=67.41\,\text{Å}^{-2}=364.84\,\text{K}$
$-\tilde{\varepsilon}_3$=342.791 979 K	$E^b_{3,e}=93.95\,\text{Å}^{-2}=508.50\,\text{K}$	$E^b_{3,o}=34.60\,\text{Å}^{-2}=187.28\,\text{K}$
$-\tilde{\varepsilon}_4$=134.784 305 K	$E^b_{4,e}=52.77\,\text{Å}^{-2}=285.63\,\text{K}$	$E^b_{4,o}=11.79\,\text{Å}^{-2}=63.83\,\text{K}$
$-\tilde{\varepsilon}_5$=22.134 073 K	$E^b_{5,e}=32.32\,\text{Å}^{-2}=174.95\,\text{K}$	$E^b_{5,o}=0.8\,\text{Å}^{-2}=4.4\,\text{K}$
	$E^b_{6,e}=22.31\,\text{Å}^{-2}=120.75\,\text{K}$	
	$E^b_{7,e}=5.14\,\text{Å}^{-2}=27.87\,\text{K}$	

For the problems under consideration the potential function $V(\rho,\varphi)$ depending on the parameter ρ can be defined as follows.

Task 1. The case of one pair potential in the intervals $\varphi\in(0,2\varphi_\alpha)$ ($\varphi_\alpha=\pi/3$, $\pi/4$ or $\pi/2$) $V(\rho,\varphi)=V(\rho\sin\varphi)$.
Task 2. The case of three pair potentials (7), in the interval $\varphi\in(0,2\varphi_\alpha=\pi/3)$.
Task 3. The case of one pair potential and two penetrable or almost impenetrable barrier potentials (8), in the interval $\varphi\in(0,\varphi_\alpha=\pi/2)$ or in the intervals $\varphi\in(0,\varphi_\alpha=\pi/4-\epsilon)$ and $\varphi\in(\varphi_\alpha=\pi/4-\epsilon,\pi/2)$, $0<\epsilon\ll\pi/4$.

The solutions symmetric with respect to the permutation of two particles satisfy the Neumann boundary condition at $\varphi=0$ and $\varphi=2\varphi_\alpha$, while the antisymmetric ones satisfy the Dirichlet boundary condition. If the pair potential possesses a high peak in the vicinity of the pair collision point, then the solution of the problem (6) will be considered in the half-plane $\Omega_{\rho,\varphi}=(\rho\in(\rho_{\min},\infty),\varphi\in[\varphi_{\min}(\rho),2\varphi_\alpha-\varphi_{\min}(\rho)])$ with the Neumann or Dirichlet boundary condition. Since the potential of the boundary-value problem (10) is symmetric with respect to $\varphi=\varphi_\alpha$, the even $\phi_j(\varphi;\rho)=\phi_j(2\varphi_\alpha-\varphi;\rho)$ and odd $\phi_j(\varphi;\rho)=-\phi_j(2\varphi_\alpha-\varphi;\rho)$ solutions, satisfying the Neumann or the Dirichlet boundary condition respectively, will be considered separately in the interval $\varphi\in[\varphi_{\min}(\rho),\varphi_\alpha]$.

The system of coupled ODEs in the Kantorovich form has the form

$$\left[-\frac{1}{\rho}\frac{d}{d\rho}\rho\frac{d}{d\rho}+\frac{\varepsilon_i(\rho)}{\rho^2}-E\right]\chi_{ii_o}(\rho)+\sum_{j=1}^{j_{\max}}W_{ij}(\rho)\chi_{ji_o}(\rho)=0, \tag{11}$$

$$W_{ij}(\rho)=H_{ji}(\rho)+\frac{1}{\rho}\frac{d}{d\rho}\rho Q_{ji}(\rho)+Q_{ji}(\rho)\frac{d}{d\rho}. \tag{12}$$

The effective potentials $Q_{ij}(\rho) = -Q_{ji}(\rho)$, $H_{ij}(\rho) = H_{ji}(\rho)$ are given by the integrals calculated using the above symmetry on reduced intervals $\varphi \in [0, \varphi_\alpha]$:

$$Q_{ij}(\rho) = -\int_0^{\varphi_\alpha} d\varphi \phi_i(\varphi;\rho) \frac{d\phi_j(\varphi;\rho)}{d\rho}, H_{ij}(\rho) = \int_0^{\varphi_\alpha} d\varphi \frac{d\phi_i(\varphi;\rho)}{d\rho} \frac{d\phi_j(\varphi;\rho)}{d\rho}. \quad (13)$$

For Task 3 the effective potentials $\hat{W}_{ij}(\rho) = W_{ij}(\rho) + V^b_{ij}(\rho)$ are sums of $W_{ij}(\rho)$, calculated using the potential curves and the parametric basis functions of Task 1, and the integrals of barrier potentials $V^b_{ij}(\rho)$ mutiplied by the basis functions

$$V^b_{ij}(\rho) = \int_0^{\varphi_\alpha} d\varphi \phi_i(\varphi;\rho)(V^b(\rho \sin(\varphi - \pi/4)) + V^b(\rho \sin(\varphi + \pi/4)))\phi_j(\varphi;\rho).$$

As an example, we calculated the parametric basis functions of BVP (10) and the effective potentials (13) for the models of Be_2 dimer and Be_3 trimer in collinear configuration using the programme ODPEVP [1]. The results are shown in Figs. 1, 2, and 3. For this model the eigenvalues and the hyperradial components of 2D eigenfunctions of the BVP for the set of ODEs (11) were calculated using the program KANTBP [12]. The discrete energy spectrum of the dimer Be_2 and a set of the binding energies of the trimer Be_3 is shown in Table 1, and the components of the trimer eigenfunctions (9) are shown in Fig. 4.

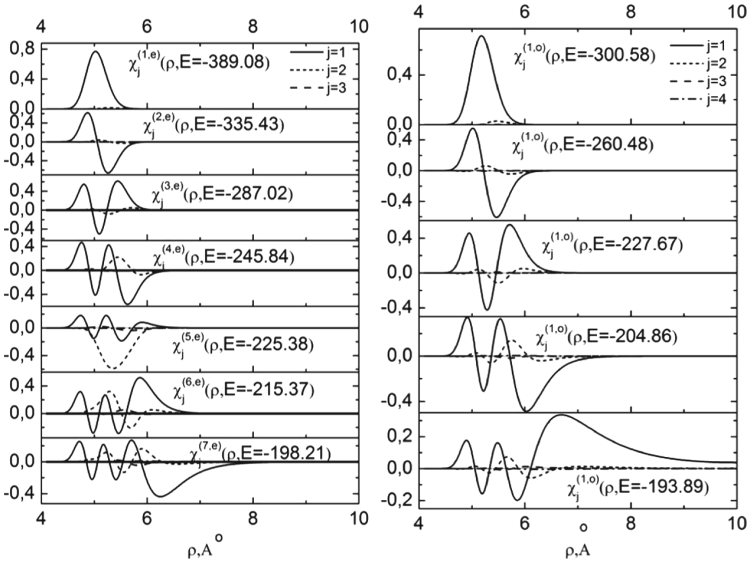

Fig. 4. Components $\chi_j^{i,\sigma=e,o}(\rho, E) \equiv \chi_j^{(i)}(\rho)$ of even (e) and odd (o) bound states with total energy E in $Å^{-2}$.

4 Asymptotes of the Parametric Basis Functions

In polar coordinates at large ρ the width of the potential well decreases with the growth of ρ. This fact allows the linearisation of the argument $\rho\sin\varphi - \hat{x}_{eq} \to \rho(\varphi - \arcsin(\hat{x}_{eq}/\rho))$ at $|x-\hat{x}_{eq}|/\rho \ll 1$ in the expression for the potential function $V(\rho\sin\varphi)$ and the reformulation of Eq. (10) in the interval $\varphi = (0, \varphi_\alpha)$ as

$$\left(-\frac{\partial^2}{\partial\varphi^2} + \rho^2 V(\rho\varphi) - \varepsilon_j(\rho)\right)\phi_j(\varphi;\rho) = 0. \tag{14}$$

By the change of variables $x = \rho\varphi$ this equation is reduced to Eq. (4).

The cluster eigenfunctions of the lower part of discrete spectrum $\varepsilon_j(\rho) < 0$ are known to be localised in the potential well and exponentially small beyond it. Therefore, the solutions of the BVP for Eq. (14) of Task 1 are determined from the solutions of the BVP for Eq. (4) $\varepsilon_j(\rho) = \rho^2\tilde{\varepsilon}_j$, $\phi_j(\varphi = x/\rho;\rho) = \sqrt{\rho}\phi_j(x)$, $j = 1, ..., n_0$. Provided that the solution of the BVP was earlier calculated in Cartesian coordinates on the grid $\{x_0 = 1.7665, ..., x_i, ..., x_{7999} = 9.7655\}$ by means of the program KANTBP 4M using FEM with the interpolating Hermite polynomials of the fifth order and double nodes, the solution in polar coordinates on the grid $\varphi_i = (x_i + \frac{x_{eq}^3}{6\rho^2})/\rho$ is recalculated as

$$\phi_{j;i}^{0;h\varphi}(\rho) = \phi_j^h(\varphi_i;\rho) = \sqrt{\rho}\phi_{j;i}^{0;hx}, \quad \phi_{j;i}^{1;h\varphi}(\rho) = \left.\frac{\phi_j^h(\varphi;\rho)}{d\varphi}\right|_{\varphi=\varphi_i} = \rho\sqrt{\rho}\phi_{j;i}^{1;hx}. \tag{15}$$

Let us calculate the solution of the problem at large ρ

$$\left(-\frac{\partial^2}{\partial\varphi^2} + \rho^2 V(\rho\sin\varphi) - \varepsilon_j(\rho)\right)\phi_j(\varphi;\rho) = 0. \tag{16}$$

Using the new variable x' defined as $\varphi = x'/\rho$, $x' = \rho\arcsin(x/\rho)$ we get

$$\left(-\frac{\partial^2}{\partial x'^2} + V(\rho\sin(x'/\rho)) - \frac{\varepsilon_j(\rho)}{\rho^2}\right)\phi_j(x';\rho) = 0. \tag{17}$$

In the argument of the potential we add and subtract x' and expand the potential in Taylor series in the vicinity of x', $V(\rho\sin(x'/\rho)) = V(x' + (\rho\sin(x'/\rho) - x')) = V(x') + \frac{dV(x')}{dx'}(\rho\sin(x'/\rho) - x') + \frac{1}{2}\frac{d^2V(x')}{dx'^2}(\rho\sin(x'/\rho) - x')^2 + O(\rho^{-6}) = V(x') - \frac{1}{\rho^2}\frac{x'^3}{6}\frac{dV(x')}{dx'} + \frac{1}{\rho^4}\left(\frac{x'^5}{120}\frac{dV(x')}{dx'} + \frac{x'^6}{36}\frac{d^2V(x')}{dx'^2}\right)$. Then

$$\left(-\frac{\partial^2}{\partial x'^2} + V(x') - \frac{V^{(1)}(x')}{\rho^2} + \frac{V^{(2)}(x')}{\rho^4} - \frac{\varepsilon_j(\rho)}{\rho^2}\right)\phi_j(x';\rho) = 0, \tag{18}$$

$$\langle\phi_i(\rho)|\phi_j(\rho)\rangle \equiv \int_{x'_0}^{x'_{\max}} dx'(\phi_i(x';\rho)\phi_j(x';\rho) = \delta_{ij}. \tag{19}$$

For the Morse potential (5) the corrections to the potential are expressed as

$$V^{(1)}(x') \equiv \frac{x'^3}{6}\frac{dV(x')}{dx'} = \frac{D\alpha x'^3}{3}\{\exp[-2(x'-\hat{x}_{eq})\alpha] - 2\exp[-(x'-\hat{x}_{eq})\alpha]\}$$

$$V^{(2)}(x') \equiv \left(\frac{x'^5}{120}\frac{dV(x')}{dx'} + \frac{x'^6}{72}\frac{d^2V(x')}{dx'^2}\right)$$

$$= \frac{D\alpha x'^5}{180}\{(10\alpha x' - 3)\exp[-2(x'-\hat{x}_{eq})\alpha] - (5\alpha x' - 3)\exp[-(x'-\hat{x}_{eq})\alpha]\}$$

We seek the solution in the form of the power series using the second-order perturbation theory

$$\phi_j(x';\rho) = \phi_j^{(0)}(x') + \frac{\phi_j^{(1)}(x')}{\rho^2} + \frac{\phi_j^{(2)}(x')}{\rho^4}, \quad \frac{\varepsilon_j(\rho)}{\rho^2} = E_j^{(0)} + \frac{E_j^{(1)}}{\rho^2} + \frac{E_j^{(2)}}{\rho^4} \tag{20}$$

that yields the recurrence set of nonuniform ODEs

$$\left(L - E_j^{(0)}\right)\phi_j^{(0)}(x') = 0, \quad L = -\frac{\partial^2}{\partial x'^2} + V(x'),$$

$$\left(L - E_j^{(0)}\right)\phi_j^{(1)}(x') + \left(V^{(1)}(x') - E_j^{(1)}\right)\phi_j^{(0)}(x') = 0,$$

$$\left(L - E_j^{(0)}\right)\phi_j^{(2)}(x') + \left(V^{(1)}(x') - E_j^{(1)}\right)\phi_j^{(1)}(x') + \left(V^{(2)}(x') - E_j^{(2)}\right)\phi_j^{(0)}(x') = 0.$$

The first- and second-order corrections of the eigenfunctions satisfy the relations

$$\langle\phi_i^{(0)}(x')|\phi_j^{(0)}(x')\rangle \equiv \int_{x_0'}^{x'_{\max}} dx'(\phi_i^{(0)}(x')\phi_j^{(0)}(x') = \delta_{ij},$$

$$\langle\phi_j^{(0)}(x')|\phi_j^{(1)}(x')\rangle = 0, \quad \langle\phi_j^{(1)}(x')|\phi_j^{(1)}(x')\rangle + 2\langle\phi_j^{(0)}(x')|\phi_j^{(2)}(x')\rangle = 0.$$

and corrections of the eigenvalues are determined by integrals

$$E_j^{(1)} = \langle\phi_j^{(0)}|V^{(1)}(x')|\phi_j^{(0)}\rangle, \quad E_j^{(2)} = \langle\phi_j^{(0)}|V^{(2)}(x')|\phi_j^{(0)}\rangle + \langle\phi_j^{(0)}|V^{(1)}(x')|\phi_j^{(1)}\rangle.$$

Substituting (20) into the effective potentials $Q_{ij}(\rho)$ and $H_{ij}(\rho)$ defined by

$$Q_{ij}(\rho) = -\langle\phi_i(\rho)|\frac{\partial}{\partial\rho}|\phi_j(\rho)\rangle + Q_{ij}^{(0)}, \quad Q_{ij}^{(0)} = -\langle\phi_i(\rho)|\frac{x}{\rho}\frac{\partial}{\partial x} + \frac{1}{2\rho}|\phi_j(\rho)\rangle, \tag{21}$$

$$H_{ij}(\rho) = K_{ij}(\rho) - \frac{\partial Q_{ij}(\rho)}{\partial\rho}, \quad K_{ij}(\rho) = -\langle\phi_i(\rho)|(\frac{\partial}{\partial\rho} + \frac{x}{\rho}\frac{\partial}{\partial x} + \frac{1}{2\rho})^2|\phi_j(\rho)\rangle,$$

$$H_{ij}(\rho) = \langle\frac{\phi_i(\rho)}{\partial\rho}|\frac{\partial\phi_j(\rho)}{\partial\rho}\rangle + \frac{2}{\rho}\langle(-\frac{1}{2} - x\frac{\partial}{\partial x})\phi_i(\rho)|\frac{\partial\phi_j(\rho)}{\partial\rho}\rangle + H_{ij}^{(0)}(\rho), \tag{22}$$

$$H_{ij}^{(0)}(\rho) = \frac{1}{\rho^2}\langle\frac{\partial\phi_i(\rho)}{\partial x}|x^2|\frac{\partial\phi_j(\rho)}{\partial x}\rangle - \frac{1}{4\rho^2}\langle\phi_i(\rho)|\phi_j(\rho)\rangle, \tag{23}$$

we arrive at the required asymptotic expansions for cluster states, $i, j = 1, ..., n_0$:

$$Q_{ij}(\rho) = \frac{Q_{ij}^{(1)}}{\rho^1} + \frac{Q_{ij}^{(3)}}{\rho^3} + O(\rho^{-5}), \quad H_{ij}(\rho) = \frac{H_{ij}^{(2)}}{\rho^2} + \frac{H_{ij}^{(4)}}{\rho^4} + O(\rho^{-6}). \quad (24)$$

Remark. The effective potentials $E_j^{(1)} + H_{jj}^{(0)} = (1/4)\rho^{-2}$ lead to asymptotic cluster fundamental solutions of the ODEs (11), defined by the Bessel functions $J_{1/2}(\sqrt{-E+\varepsilon_j}\rho)$, $j = 1, ..., n_0$, while for pseudostates the asymptotic fundamental solutions of the ODEs are $J_m(\sqrt{E}\rho)$ with integer $m = (j - n_0) = 1, 2, ...$

The eigenfunctions of pseudostates $\varepsilon_j(\rho) \geq 0$, $(j-n_0) = 1, 2, ...,$, are localized in out of the potential well. Then the (n_0-1)-th node is located at the boundary of the potential well. Here and below we consider the case of $\varphi_\alpha = \pi/2$ illustrated by Fig. 5. From this fact the estimate of the eigenvalues for pseudostates $\varepsilon_j(\rho) \approx (j-n_0)^2$ follows, namely, the eigenvalues of the corresponding BVPs in Cartesian coordinates, $\varepsilon_j = \varepsilon_j(\rho)/\rho^2$, will be a small quantity (see Fig. 1b). Then the numerical values of the function $B(\varphi_i; \rho) = B(x_i)$ and its derivative $B'(\varphi_i; \rho) = \rho B'(x_i)$ on the specified grid $\Omega_\varphi = \{\varphi_1 = \varphi_0, ..., \varphi_i = x_i/\rho, ..., \varphi_N = \varphi_\varepsilon\}$ in the polar system of coordinates are determined via the values of the function $B(x_i)$ and its derivative $B'(x_i)$ on the grid $\Omega_x = \{x_1 = x_0, ..., x_i, ..., x_N = x_\varepsilon\}$, found in the form of the power series of small parameter ε_n:

$$B_j(x_i) = B_i^{(0)} + B_i^{(1)}\varepsilon_n + B_i^{(2)}\varepsilon_n^2, \quad B'_j(x_i) = b_i^{(0)} + b_i^{(1)}\varepsilon_n + b_i^{(2)}\varepsilon_n^2, \quad (25)$$

using the Runge-Kutta method, in which the third power of unknown ε_n and the higher ones are neglected. The expansion coefficients $B_i^{(k)} \equiv B_i^{(k)}(x_i)$ and $b_i^{(k)} \equiv b_i^{(k)}(x_i)$, $k = 0, 1, 2$, calculated at the grid nodes x_i for the potential (5) are presented in Fig. 6. One can see that in the vicinity of the potential well the corrections to the eigenfunctions are small, and at $x > 6$ they become essential. The coefficient $b_i^{(0)}$, the derivative of the wave function with $\varepsilon_n = 0$, becomes constant for $x > 5.5$. From these observations the condition for choosing x_ε follows. The interval $\varphi_0 \leq \varphi \leq \pi/2$ is divided into two subintervals by the point $\varphi_\varepsilon = x_\varepsilon/\rho$: $\varphi_0 < \varphi \leq \varphi_\varepsilon$ and $\pi/2 > \varphi > \varphi_\varepsilon$. In the calculations the point x_ε was chosen from the condition $|V(x > x_\varepsilon)| < \varepsilon$, where ε is a preassigned number, and the left-hand boundary of the interval $\varphi_0 = 0$. In the case of a high barrier, at the pair collision point, when the eigenfunctions in its vicinity are close to zero, the left boundary of the interval changes, $\varphi_0 = x_0/\rho > 0$. The eigenfunctions $\phi_j(\varphi; \rho)$ are calculated in the form

$$\phi_j(\varphi;\rho) = \begin{cases} A_j(\rho)B_j(\varphi;\rho), & \varphi_0 \leq \varphi \leq \varphi_\varepsilon, \\ C_j(\rho)\sqrt{\frac{2}{\pi}}\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}(\sqrt{\varepsilon_j(\rho)}(\varphi - \pi/2)), & \varphi_\varepsilon < \varphi \leq \pi/2, \end{cases} \quad (26)$$

$$2\int_{\varphi_0}^{\pi/2} d\varphi(\phi_n(\varphi;\rho))^2 = 1. \quad (27)$$

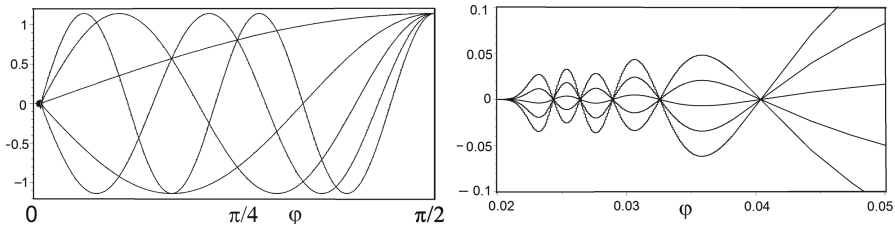

Fig. 5. Eigenfunctions $\phi_j(\varphi;\rho)$ corresponding to the eigenvalues $\varepsilon_j(\rho) \geq 0$ of the even pseudostates $j = n+1 = 6, ..., 10$ at $\rho = 100$.

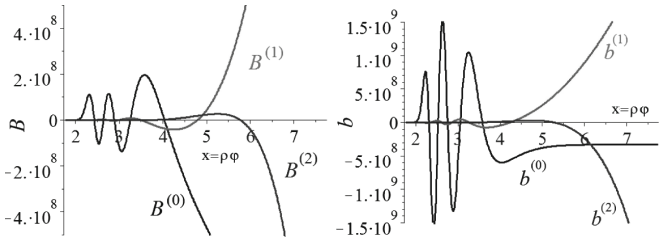

Fig. 6. Expansion coefficients $B_i^{(k)}$ and $b_i^{(k)}$, $k = 0, 1, 2$, calculated at the nodes x_i.

Here $A_j(\rho)$ and $C_j(\rho)$ are the normalisation factors, and $B(\varphi;\rho)$ is determined from the numerical solution $B(x)$ in Cartesian coordinates using the transformation $\varphi = x/\rho$. From the continuity of the eigenfunctions and their derivatives,

$$\phi_n(\varphi_\varepsilon - 0;\rho) = \phi_n(\varphi_\varepsilon + 0;\rho), \frac{d\phi_n}{d\varphi}(\varphi_\varepsilon - 0;\rho) = \frac{d\phi_n}{d\varphi}(\varphi_\varepsilon + 0;\rho), \tag{28}$$

we get the equation for the eigenvalue $\varepsilon_n(\rho)$:

$$\left\{\begin{matrix}\tan(\sqrt{\varepsilon_n(\rho)}(\varphi_\varepsilon - \frac{\pi}{2})) & \text{even } n \\ -\cot(\sqrt{\varepsilon_n(\rho)}(\varphi_\varepsilon - \frac{\pi}{2})) & \text{odd } n\end{matrix}\right\} - \frac{\sqrt{\varepsilon_n(\rho)}}{R} = 0, \quad R = \frac{B_n'(\varphi_\varepsilon;\rho)}{B_n(\varphi_\varepsilon;\rho)} = \frac{\rho B_n'(x_\varepsilon)}{B_n(x_\varepsilon)}. \tag{29}$$

The solution $\varepsilon_n(\rho)$ ($\varepsilon_n = \varepsilon_n(\rho)/\rho^2$) of the derived equation is sought in the form of a power series

$$\varepsilon_n(\rho) = n^2 + \varepsilon_n^{(1)}\rho^{-1} + \varepsilon_n^{(2)}\rho^{-2} + O(\rho^{-3}). \tag{30}$$

Substitute (25) into (29), and then substitute (30) into the resulting equation. Expanding both sides of the equation in inverse powers of ρ and neglecting the terms, containing the third and higher powers of $1/\rho$, we arrive at the system of linear equations, from which the expansion coefficients $\varepsilon_n^{(1)}$ and $\varepsilon_n^{(2)}$, and then the coefficients $A_n(\rho)$ and $C_n(\rho)$ are determined. Since the values of the function $B_n(\varphi;\rho)$ and its derivative $B_n'(\varphi;\rho)$ on the grid Ω_φ are known, for the

calculation of the first integral we use the quadrature formula of the Newton-Cotes type. The second integral is calculated analytically using the expansion (30). We have the analytical expression in the interval $\varphi_\varepsilon(\rho) < \varphi \le \pi/2$, and the explicit dependence of its values upon the parameter ρ on the grid Ω_φ. For the considered potential (5) we get the asymptotes of the potential curves at $n = j - n_0$:

$$\varepsilon_n(\rho)\rho^{-2} = n^2\rho^{-2} + 4.50520671n^2\rho^{-3} + 15.22266564n^2\rho^{-4} + O(\rho^{-5}). \quad (31)$$

Table 2. Convergence of the expansion (31) at $\rho = 50$ and the numerical results (NUM).

n^2	1.00000000	4.00000000	9.00000000	16.00000000
$+\varepsilon_n^{(1)}/\rho$	1.09010413	4.36041653	9.81093720	17.44166614
$+\varepsilon_n^{(2)}/\rho^2$	1.09619320	4.38477280	9.86573880	17.53909120
NUM	1.09614800	4.38462804	9.86554769	17.53908477

The calculated eigenvalues in comparison with the numerical solution obtained by means of the program ODPEVP [1] are presented in Table 2. The described algorithm is implemented in the Maple system. The asymptotic expansions, obtained using it at $\rho = 50$, coincide with the numerical solution given by the finite element method to 4–5 significant digits for the eigenvalues and to 3–4 significant digits for the eigenfunctions. The asymptotes of the effective potentials (13) between the states $n_1 = i - n_0$ and $n_2 = j - n_0$ of the same parity at $n_0 = 5$, $i, j = n_0 + 1, ...$ have the form:

$$Q_{n_1n_2}(\rho) = \frac{2.27}{\rho^2}\frac{n_2n_1}{(n_1^2-n_2^2)} + \frac{5.14}{\rho^3}\frac{n_2n_1}{(n_1^2-n_2^2)} + O(\frac{1}{\rho^4}),$$
$$H_{n_1n_2}(\rho) = \frac{10.27}{\rho^4}\frac{n_2n_1(n_1^2+n_2^2)}{(n_1^2-n_2^2)^2} + \frac{68.20}{\rho^5}\frac{n_2n_1((n_1^2-n_2^2)^2+0.68(n_1^2+n_2^2))}{(n_1^2-n_2^2)^2} + O(\frac{1}{\rho^6}),$$
$$H_{n_1n_1}(\rho) = (0.64 + 2.11n_1^2)\frac{1}{\rho^4} + (2.91 - 10.03n_1^2)\frac{1}{\rho^5} + O(\frac{1}{\rho^6}). \quad (32)$$

Using (15), (20) and (26) we get the asymptotic expansions for $Q_{ij}(\rho)$ and $H_{ij}(\rho)$ between the cluster states $i = 1, ..., n_0$ and pseudostates $(j - n_0) = 1, 2, ...,$

$$Q_{ij}(\rho) = \frac{Q_{ij}^{(5/2)}}{\rho^{5/2}} + \frac{Q_{ij}^{(7/2)}}{\rho^{7/2}} + O(\rho^{-9/2}),\ H_{ij}(\rho) = \frac{H_{ij}^{(7/2)}}{\rho^{7/2}} + \frac{H_{ij}^{(9/2)}}{\rho^{9/2}} + O(\rho^{-11/2}). \quad (33)$$

5 Conclusion

The model for quantum tunneling of a diatomic molecule through repulsive barrier is formulated as a 2D boundary-value problem for the Schrödinger equation.

This problem is reduced using the Kantorovich expansions to the boundary-value problem for a set of second-order ordinary differential equations with the third-type boundary conditions. The symbolic-numeric algorithms are proposed and implemented in Maple to evaluate the asymptotic expansions (20), (32), (24) and (33) of the parametric BVP eigensolutions and the effective potentials $W_{ij}(\rho)$ in inverse powers of ρ, used for calculation of the asymptotes of the fundamental solutions of the system of second-order ODEs at large values of ρ [19].

The proposed approach can be applied to the analysis of quantum transparency effect, quantum diffusion of molecules Be_2 and the Efimov effect [5–8,21] in Be+Be_2 scattering using modern theoretical and experimental results [13,15–17] and algorithms and programs [1–4,9,10,12].

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