Application of Finite Element Method Programs to the Calculation of Vibration–Rotation States of a Diatomic Beryllium Molecule

1st A.A. Gusev
Joint Institute for Nuclear Research
Dubna, Moscow Region, Russia
gooseff@jinr.ru

2nd O. Chuluunbaatar
Joint Institute for Nuclear Research
Dubna, Moscow Region, Russia
Institute of Mathematics
National University of Mongolia
Ulaanbaatar, Mongolia

3rd S.I. Vinitsky
Joint Institute for Nuclear Research
Dubna, Moscow Region, Russia
RUDN University
Moscow, Russia
vinitsky@theor.jinr.ru

4th V.L. Derbov
N.G. Chernyshevsky Saratov
National Research State University
Saratov, Russia

5th A. Góźdź
Institute of Physics
University of M. Curie-Skłodowska
Lublin, Poland

6th P.M. Krassovitskiy
Joint Institute for Nuclear Research
Dubna, Moscow Region, Russia
Institute of Nuclear Physics
Almaty, Kazakhstan

7th I. Filikhin
Department of Mathematics
and Physics
North Carolina Central University
Durham, USA

8th A.V. Mitin
Moscow Institute of Physics and Technology
Dolgoprudny, Moscow Region, Russia
Chemistry Department
Lomonosov Moscow State University
Moscow, Russia
Joint Institute for High Temperatures of RAS
Moscow, Russia

Abstract—A computational scheme of the finite element method (FEM) is presented that allows the solution of the eigenvalue problem for a SOODE with the known potential function using the ODPEVP and KANTBP 4M programs that implements FEM in the Fortran and Maple, respectively. Numerical analysis of the solution using the KANTBP 4M program is performed for the SOODE exact solvable eigenvalue problem. The discrete energy eigenvalues and eigenfunctions are analyzed for vibrational and rotational states of the diatomic beryllium molecule solving the eigenvalue problem for the SOODE numerically with the table-valued potential function approximated by interpolation Lagrange and Hermite polynomials and its asymptotic expansion for large values of the independent variable specified as Fortran function. The efficacy of the programs is demonstrated by the calculations of twelve eigenenergies of vibrational bound states with the required accuracy, in comparison with those known from literature, and the vibrational-rotational spectrum of the diatomic beryllium molecule.

Index Terms—eigenvalue problem, second-order ordinary differential equation, finite element method, Programs ODPEVP, KANTBP 4M, diatomic beryllium molecule, vibration–rotation states

I. INTRODUCTION

The study of mathematical models, describing waveguide problems, spectral and optical properties of diatomic molecular systems, reduces to the solution of a boundary-value problem (BVP) for an elliptic equation of the Schrödinger type [1], [2]. After the separation of angular variables, this equation reduces to a second order ordinary differential equation (SOODE) with variable coefficients and the independent variable belonging to the semiaxis $r \in (0, +\infty)$. In this equation the potential function is numerically tabulated on a non-uniform grid in a finite interval of the independent variable values [3]–[5].

To formulate the BVP on the semiaxis, the potential function should be continued beyond the finite interval using the additional information about the interaction of atoms comprising the diatomic molecule at large distances between them. The leading term of the potential function at large distances is given by the van der Waals interaction, inversely proportional to the sixth power of the independent variable with the constant, determined from theory and experimental data [6]–[8].

So, it is necessary to make an appropriate approximation of the tabulated potential function and to match the asymptotic expansion of the potential function with its tabulated numerical values (within the accuracy of their calculation) at a suitable sufficiently large value of the independent variable.

The development of technique for solving the above class of eigenvalue problems for the SOODE using the programs ODPEVP [9] and KANTBP 4M [10] implementing the FEM [11] in the Fortran and Maple respectively, constitutes the

subject of the present paper.

The efficacy of the programs is demonstrated by the calculations of twelve eigenenergies of vibrational bound states with the required accuracy, in comparison with those known from literature, and the vibrational-rotational spectrum of the diatomic beryllium molecule.

The structure of the paper is following. In section 2 setting of the BVP for the SSODE is given. In section 2.1 a reduction of the BVP to an algebraic problem is done. In section 2.2 numerical analysis of benchmark calculations by means of KANTBP 4M program of an exact solvable eigenvalue problem for the SSODE is presented. In section 3 the discrete energy eigenvalues and eigenfunctions are analyzed for vibrational and rotational states of the diatomic beryllium molecule solving the eigenvalue problem for the SOODE numerically. The table-valued potential function approximated by interpolation Lagrange and Hermite polynomials and its asymptotic expansion for large values of the independent variable is specified as Fortran function in Appendix. In section 4 summary and perspectives of applications the FEM program are given.

II. SETTING OF THE PROBLEM

The mathematical model describing the spectral and optical characteristics of molecular systems is formulated as a BVP for the SOODE for the unknown function $\Phi(r)$ of the independent variable $r \in \Omega[r^{\min}, r^{\max}]$:

$$(D - E)\,\Phi(r) = \left(-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + V(r) - E\right)\Phi(r) = 0. \quad (1)$$

Here $V(r)$ is a real-valued function from the Sobolev space $\mathcal{H}_2^{s \geq 1}(\Omega)$, providing the existence of nontrivial solutions obeying the boundary conditions (BCs) of the first (I) (Dirichlet), second (II) (Neumann), or third (III) kind at the boundary points of the interval $r \in [r^{\min}, r^{\max}]$ at the given value of $\mathcal{R}(z^t)$:

$$(\mathrm{I}): \qquad \Phi(r^t) = 0, \quad t = \min \text{ or } \max, \quad (2)$$

$$(\mathrm{II}): \qquad \lim_{r \to r^t} r^2 \frac{d\Phi(r)}{dr} = 0, \quad t = \min \text{ or } \max, \quad (3)$$

$$(\mathrm{III}): \qquad \lim_{r \to r^t} r^2 \frac{d\Phi(r)}{dr} = \mathcal{R}(r^t)\Phi(r^t), \; t = \min \text{ or } \max. (4)$$

The calculation of the approximate solution $\Phi(r) \in \mathcal{H}_2^{s \geq 1}(\bar{\Omega})$ of the BVP (1)–(4) is executed by means of the FEM using the symmetric quadratic functional [11]

$$\Xi(\Phi, E, r^{\min}, r^{\max}) = \Pi(\Phi, E) \quad (5)$$

$$-\Phi(r^{\max})\mathcal{R}(r^{\max})\Phi(r^{\max}) + \Phi(r^{\min})\mathcal{R}(r^{\min})\Phi(r^{\min}),$$

$$\Pi(\Phi, E) = \int_{r^{\min}}^{r^{\max}} \left[\frac{d\Phi(r)}{dr}\frac{d\Phi(r)}{dr} + \Phi(r)(V(r) - E)\Phi(r)\right]r^2 dr.$$

For the bound-state problem the set of M eigenvalues of the energy E_m: $E_1 \leq E_2 \leq \ldots \leq E_M$ and the corresponding set of eigenfunctions $\Phi(r) \equiv \{\Phi_m(r)\}_{m=1}^M$ is calculated in the

space $\mathcal{H}_2^2$ for the SOODE (1). The functions obey the BCs of the first, second or third kind at the boundary points of the interval $r \in [r^{\min}, r^{\max}]$ and the orthonormalization condition

$$\langle \Phi_m | \Phi_{m'} \rangle = \int_{r^{\min}}^{r^{\max}} \Phi_m(r)\Phi_{m'}(r)r^2 dr = \delta_{mm'}. \quad (6)$$

Thus, to solve the discrete spectrum problem on an axis or semiaxis, the initial problem is approximated by the BVP in the finite interval $r \in [r^{\min}, r^{\max}]$ with the BCs of the first, second, or third kind with the given $\mathcal{R}(r^t)$, dependent or independent of the unknown eigenvalue E, and the set of approximated eigenvalues and eigenfunctions is calculated.

A. Reduction to an algebraic problem

Let us construct a discrete representation of the solution $\Phi_m(r)$ of the problem (1)–(4), reduced to the variational functional (5) on the finite-element mesh

$$\Omega_{h_j(r)}^p[r^{\min}, r^{\max}] = [r_0 = r^{\min}, r_1, ..., r_{np-1}, r_{np} = r^{\max}]. \quad (7)$$

The solution $\Phi_m^h(r) \approx \Phi_m(r)$ is sought in the form of expansion in basis functions $N_\mu^g(r)$ in the interval $r \in \Delta = \cup_{j=1}^n \Delta_j = [r^{\min}, r^{\max}]$:

$$\Phi_m^h(r) = \sum_{\mu=0}^{L-1} \Phi_{m;\mu}^h N_\mu^g(r), \quad \Phi_m^h(r_l) = \Phi_{m;l}^h, \quad (8)$$

where $L = pn + 1$ is the number of the basis functions $N_\mu^g(r)$ and the desired coefficient $\Phi_{m;\mu}^h$ which at $\mu = l$ are values of the function $\Phi_m^h(r)$ at each node $r = r_l$ of the mesh $\Omega_{h_j(r)}^p[r^{\min}, r^{\max}]$. The basis functions $N_\mu^g(r)$ are piecewise continuous polynomials of the order p in the corresponding subinterval $r \in \Delta_j = [r_j^{\min} \equiv r_{(j-1)p}, r_j^{\max} \equiv r_{jp}]$ constructed using the Lagrange interpolation polynomials (LIP) or Hermite ones [11].

The substitution of the expansion (8) into the variational functional (5) reduces the BVP (1)–(4) to the generalized algebraic problem for the set of the eigenvalues E_m and the eigenvectors $\mathbf{\Phi}_m^h = \{\Phi_{m;\mu}^h\}_{\mu=0}^{L-1}$:

$$(A - E_m^h B)\mathbf{\Phi}_m^h = 0. \quad (9)$$

Here A and the positive definite matrix B are the symmetric stiffness and mass matrices, respectively, with the dimension $L \times L$, where $L = \kappa^{\max}(np + 1)$.

Theoretical estimates of the difference between the exact solution $\Phi_m(z) \in \mathcal{H}_2^2$ and the numerical one $\Phi_m^h(r) \in \mathbf{H}^1$ by the norm $\mathbf{H}^0$ evaluate the convergence of the eigenvalues and eigenfunctions of the order $2p$ and $p + 1$, respectively [11]:

$$|E_m^h - E_m| \leq c_1 h^{2p}, \quad \left\|\Phi_m^h(r) - \Phi_m(r)\right\|_0 \leq c_2 h^{p+1}, \quad (10)$$

where $h = \max_{1 < j < n} h_j$ is the maximal step $h_j = r_{j+1} - r_j$ of the mesh (7), $c_1 \equiv c_1(E_m) > 0$ and $c_2 \equiv c_2(E_m) > 0$ are independent of the step h, the norm $\mathbf{H}^0$ being defined as

$$\left\|\Phi_m^h(r) - \Phi_m(r)\right\|_0 = \left(\int_{r^{\min}}^{r^{\max}} r^2 dr (\Phi_m^h(r) - \Phi_m(r))^2\right)^{1/2}. \quad (11)$$
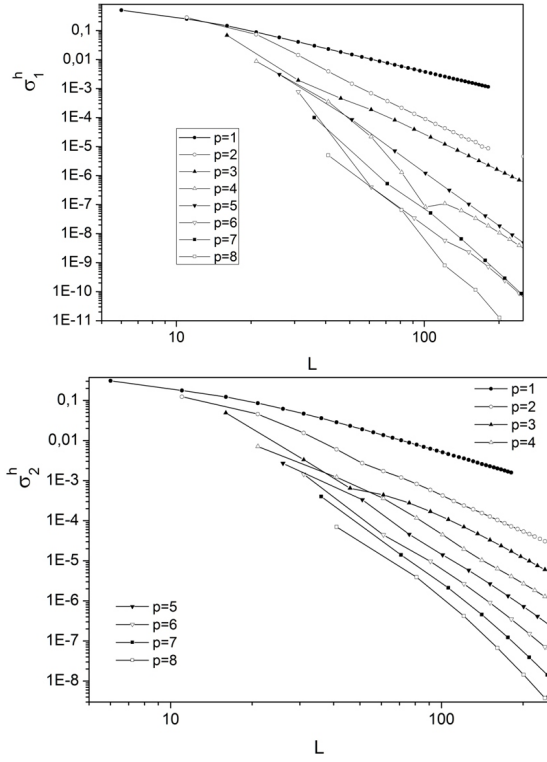
Fig. 1. Absolute errors $\sigma_1^h = |E_2^{exact} - E_2^h|$ and $\sigma_2^h = \max_{r \in \Omega^h(r)} |\Phi_2^{exact}(r) - \Phi_2^h(r)|$ of the second eigenvalue and eigenfunction of the BVP (1)–(4) as functions of the dimension $L = 5n_g p + 1$ of the algebraic eigenvalue problem, calculated with the LIP from the first ($p = 1$) to the eighth ($p = 8$) order. The left ends of the curves correspond to the mesh with one finite element between two nodes. i.e., $\Omega = \{0(2n_g)1(2n_g)5(n_g)20\}$ с $n_g = 1$, where the number n_g of finite elements between two nodes is indicated in parentheses.

Since in the programs KANTBP 4M the integration in each finite element is performed using expansion of potential $V(r)$ by, in general, interpolation Hermite polynomials (IHPs) with multiplicities of nodes κ^{max} that leads to quadrature formula [10], [11]

$$\int_{r_j^{min}}^{r_j^{max}} r^2 dr N_{L_1}(r, r_j^{min}, r_j^{max}) V(r) N_{L_2}(r, r_j^{min}, r_j^{max})$$
$$= \sum_{r=0}^{p} \sum_{\kappa=0}^{\kappa_{max}-1} V^{(\kappa)}(r_{(j-1)p+r}) V_{l_1;l_2;\kappa^{max}r+\kappa}(r_j^{min}, r_j^{max})), \quad (12)$$

where $V_{l_1;l_2;l_3}(r^{min}, r^{max})$ are determined by the integrals with IHPs

$$V_{l_1;l_2;l_3}(r_j^{min}, r_j^{max}) =$$
$$\int_{r_j^{min}}^{r_j^{max}} r^2 dr N_{l_1}(r, r_j^{min}, r_j^{max}) N_{l_2}(r, r_j^{min}, r_j^{max}) N_{l_3}(r, r_j^{min}, r_j^{max}). \quad (13)$$

The obtained expression will be exact for polynomial potentials of the order smaller than p. Generally this decomposition
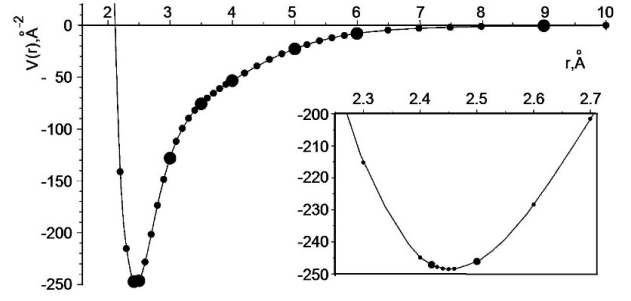

Fig. 2. The potential $V(r)$ (Å^{-2}) of the beryllium diatomic molecule as a function of r (Å) obtained by interpolating the tabulated values (points in the subintervals, the boundaries of which are larger-size points) by means of the fifth-order LIPs.

leads to numerical eigenfunctions and eigenvalues with the accuracy of the order about $p + 1$.

The estimation of the error is carried out using the maximal norm, i.e., the maximal absolute value of the error of the eigenfunctions $\Phi_m^h(r)$ and eigenvalues E_m^h in the interval $r \in \Omega^h(r)$:

$$\sigma_1 = |E_m^h - E_m| \leq c_1(E_m) h^{p+1},$$
$$\sigma_2 = \max_{r \in \Omega^h(r)} |\Phi_m^h(r) - \Phi_m(r)| \leq c_2(E_m) h^{p+1}. \quad (14)$$

In the program ODPEVP the integrals are calculated by the Gauss integration rule with $2p + 1$ nodes and held the theoretical estimations (10).

Since the eigenfunctions of the discrete spectrum exponentially decrease, $\Phi_m^{as}(r) \sim \exp(-\sqrt{-E_m}r)/r$, at $r \to +\infty$, the initial problem is reduced to a BVP for bound state in the finite interval with the Neumann conditions at the boundary points r^{min} and r^{max} of the interval and the normalization condition (6).

B. Benchmark calculations

The original bound state problem is formulated in the infinite interval $r \in (0, +\infty)$ for the Schrödinger equation (1) with the potential function inverse proportional to the square of hyperbolic cosine $V(r) = \frac{-\lambda(\lambda-1)}{\cosh(r)^2}$, where $\lambda > 1$. The eigenvalues E_m^{exact} and eigenfunctions $\Phi_m^{exact}(r) = r^{-1}\chi_m^{exact}(r)$ of this problem, normalized by the condition (6) at $r^{min} \to 0$ and $r^{max} \to +\infty$, are known in the analytical form. For the chosen $\lambda = 11/2$, the BVP has two discrete spectrum solutions with eigenvalues $-E_m = 49/4, 9/4$.

The calculations were performed in the finite interval $r \in [r^{min}, r^{max}]$ with the Neumann boundary conditions (3) on the quasi-uniform mesh $\Omega = \{0 (2n_g) 1 (2n_g) 5 (n_g) 20\}$, where in parentheses the number of finite elements between two nodes is indicated, the dimension L is expressed in terms of the number n_g and the order of LIP p as $L = 5n_g p + 1$. Figure 1 shows the dependence of the absolute errors (14) of the second state ($m = 2$) depending on the dimension L of the algebraic eigenvalue problem (9) for finite element schemes with LIP of different order p. In double logarithmic scale the plots of the error starting from a certain number L
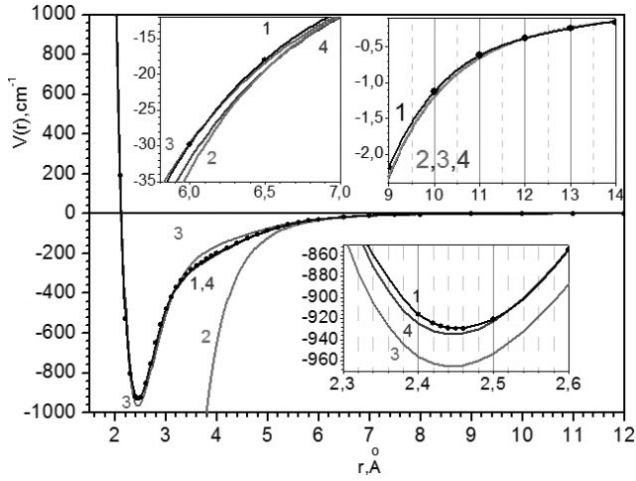
Fig. 3. The MEMO potential function $V(r)$ (points and line 1 [3]), the asymptotic expansion $V_{as}(r)$ of the MEMO function (line 2, [6]), the analytical forms of the potential function $V_{an}(r)$ (line 3 [7] and line 4 [8]). r is given in Å, $V_*(r)$ in cm^{-1}.
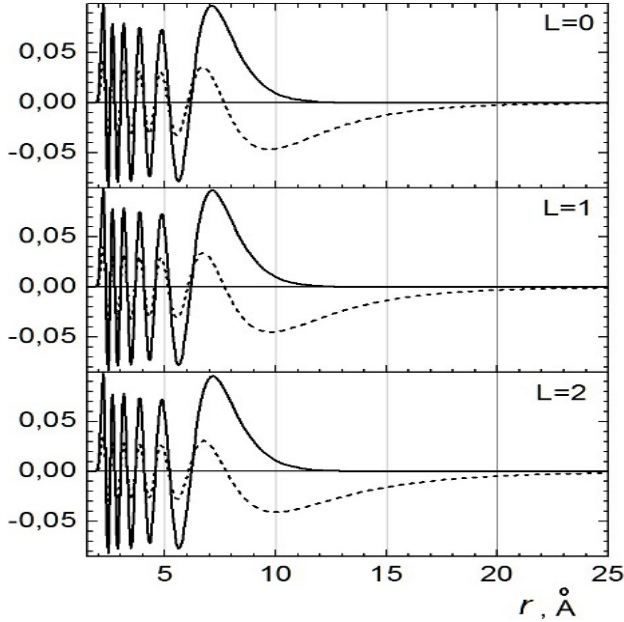

Fig. 4. The 11-th $\chi_{10L}(r) = r\Phi_{10L}(r)$ (solid curves) 12-th $\chi_{11L}(r) = r\Phi_{11L}(r)$ (dashed curves) eigenfunctions vs. r of the vibrational-rotational spectrum of beryllium diatomic molecule at $L = 0, 1, 2$: $E_{v=10;L=0} = -4.41$, $E_{v=10;L=1} = -4.21$, $E_{v=10;L=2} = -3.82$; $E_{v=11;L=0} = -0.325$, $E_{v=11;L=1} = -0.245$ and $E_{v=11;L=2} = -0.096$ (in cm^{-1}).

are close to straight lines with different slope, corresponding to the theoretical estimates of the approximation order $p + 1$ of the approximate eigenfunctions and eigenvalues (14) using the LIP with different p.

III. BERYLLIUM DIATOMIC MOLECULE

In quantum chemical calculations, the effective potentials of interatomic interaction are presented in the form of numerical tables calculated with limited accuracy and defined

TABLE I
THE EIGENVALUES OF VIBRATIONAL ENERGY $-E_{vL=0}$ (IN CM^{-1}) OF THE BERYLLIUM DIATOMIC MOLECULE CALCULATED BY THE PROGRAMS KANTBP 4M [10] AND ODPEVP [9] IMPLEMENTED FEM (FEM), AB INITIO MEMO CALCULATION [3], THEORETICAL (EMO) AND EXPERIMENTAL (EXP) RESULTS [4], SYMMETRY-ADAPTED PERTURBATION THEORY (SAPT) [5] , AND THE MORSE-LONG RANGE (MLR) FUNCTION AND CHEBYSHEV POLYNOMIAL EXPANSION (CPE) [8], D_e IS THE ABSOLUTE ENERGY AT THE DISSOCIATION LIMIT IN cm^{-1}, r_e IS THE EQUILIBRIUM INTERNUCLEAR DISTANCE IN Å.

v	FEM	MEMO	EMO	Exp	SAPT	MLR&CPE
r_e	2.4534	2.4534	2.4535	2.4536	2.443	2.445
D_e	929.804	929.74	929.74	929.7±2	938.7	934.8&935.0
0	806.07	806.48	806.5	807.4	812.4	808.1510
1	583.57	584.32	583.8	584.8	590.1	585.2340
2	408.73	408.88	408.7	410.3	414.8	410.7319
3	288.36	288.61	288.3	289.3	292.1	289.7314
4	211.18	211.42	211.1	212.6	214.5	213.0654
5	154.16	154.38	154.1	155.9	157.3	156.3536
6	107.15	107.34	107.1	108.6	109.8	109.1202
7	68.35	68.51	68.3	69.7	70.7	70.1719
8	37.80	37.92	37.7	39.2	40.0	39.6508
9	16.33	16.43	15.8	17.5	18.1	17.9772
10	4.41	4.40	3.1	4.8	5.3	5.3187
11	0.326	0.27		0.5		0.5175

on a nonuniform mesh of nodes in a finite domain of interatomic distance variation. However, for a number of diatomic molecules the asymptotic expressions for the effective potentials are calculated analytically for sufficiently large distances between the atoms. The equation for the diatomic molecules in a crude adiabatic approximation, commonly referred to as Born–Oppenheimer approximation (BO), has the form

$$\left(-\frac{\hbar^2}{2mDa\text{Å}^2}\left(\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\right)+\tilde{V}_L(\tilde{r})-\tilde{E}_{vL}\right)\tilde{\Phi}_{vL}(\tilde{r})=0, \quad (15)$$

where $\tilde{V}_L(\tilde{r}) = \tilde{V}(\tilde{r})+\frac{\hbar^2}{2mDa\text{Å}^2}\frac{L(L+1)}{r^2}$, L is a quantum number of the total angular momentum, $\hbar^2/(2Da)=1.685762920\cdot10^{-7}$ Å, the reduced mass of beryllium is $m=M/2=4.506$, $\tilde{r}=r$ Å, the effective potential is $\tilde{V}(\tilde{r})$ in atomic units $aue=0.002194746314$ Å^{-1}, the energy is $\tilde{E}_{vL}$ cm^{-1}.

The BVP (1)–(4) was solved for the equation (15) where the variable r is specified in (Å), and the effective potential $V(r) = (2mDa\text{Å}^2 aue/\hbar^2)\tilde{V}(r\text{Å})= 58664.99239\tilde{V}(r\text{Å})\text{Å}^{-2}$ and the desired value of energy $E_{vL}=(2mDa\text{Å}^2/\hbar^2)\tilde{E}_{vL}$ in Å^{-2}, $\tilde{E}_{vL}=(1/0.2672973729)E_{vL}$ cm^{-1}.

In Ref. [3] the potential $V(r)$ (see Fig. 2) is given by the BO-PRC potential function marked as MEMO tabular values $\{V^M(r_i)\}_{i=1}^{76}$. So, in the interval $r \in [r_1 = 1.5, r_{46} = 9]$ the potential $V(r)$ was approximated in subintervals $r \in [r_{5k-4}, r_{5k+1}]$, $k = 1, ..., 9$ by the fifth-order interpolation Lagrange polynomials of the variable r. In the interval $r \in [r_{match} = 14, \infty)$ the asymptotic behavior $V_{as}(r)=58664.99239\tilde{V}_{as}(r)$ at large r is given by the expansions [6]

$$\tilde{V}_{as}(r)=-\left(\frac{214(3)}{Z^6}+\frac{10230(60)}{Z^8}+\frac{504300}{Z^{10}}\right), \quad (16)$$

where $Z = r/0.52917$. In the subinterval $r \in [r_{46} = 9, r_{match} = 14]$ we consider the approximation of the potential

$V(r)$ by the fourth-order interpolation Hermite polynomial using the values of the potential $V(r)$ at the points $r = \{r_{46} = 9, r_{47} = 10, r_{48} = 11\}$ and the values of the asymptotic potential $V_{as}(r)$ and its derivative $dV_{as}(r)/dr$ at the point $r = r_{match} = 14$. This approximation is specified in Å^{-2} as REAL*8 FUNCTION VPOT(R) of the variable R in (Å) (see Appendix).

For comparison Fig. 3 plots the above potential function $V(r)$, its asymptotic expansion $V_{as}(r)$, and the analytical potential functions $\tilde{V}_{an}(r)$ in a.u. proposed in Ref. [7]:

$$\tilde{V}_{an}(r) = A\exp(-bZ) + d\exp(-eZ - fZ^2)$$
$$- \sum_{n=3}^{8}\left(\left(1 - \exp(-bZ)\sum_{k=0}^{2n}\frac{(bZ)^k}{k!}\right)\frac{C(2n)}{Z^{2n}}\right), \qquad (17)$$

where $A = 21.7721$, $b = 1.2415$, $d = -4.3224$, $e = 0.5891$, $f = 0.0774$, $Z = r/0.52917$, $C(6) = 214$, $C(8) = 10230$, $C(10) = 504300$, $C(2i) = (C(2i-2)/C(2i-4))^3 C(2i-6)$, $i = 6, 7, 8$, and r is given in Å. One can see that the MEMO potential function $V(r)$ has a minimum $-D_e(\text{FEM}) = V(r_e) = 929.804$ cm^{-1} at the equilibrium point $r_e = 2.4534$ Å and displaces above the analytic potential function $V_{an}(r)$ in the vicinity of this point, $-D_e(\text{Sheng}) = V_{an}(r_e) = -948.3$ cm^{-1} and the MLR&CPE potential functions [8] $-D_e(\text{MLR}) = 934.8$, $-D_e(\text{CPE}) = 935.0$ at $r_e = 2.445$, while the analytical potential function $V_{an}(r)$ is located above the MEMO and MLR&CPE potential functions in the interval $r \in (3.2, 6.1)$, i.e. to the left of the interval $r \in (6.1, \infty)$, where the considered potentials tend to the dominated asymptotic potential $V_{as}(r)$. In the calculation presented below, we used the asymptotic expansion $V_{as}(r)$, Eq. (16) with which the matching of the tabulated potential $V(r)$ and the asymptotic potential $V_{as}(r)$ was executed at $r = r_{match} = 14$ using REAL*8 FUNCTION VPOT(R) of the variable R in (Å) (see Appendix). The BVP (1) was solved on the finite element mesh $\Omega_1 = \{1.50\ (n_g)\ 2.00\ (n_g)\ 2.42\ (n_g)\ 2.50\ (n_g)\ 3.00\ (n_g)\ 3.50\ (n_g)\ 4.00\ (n_g)\ 5.00\ (n_g)\ 6.00\ (n_g)\ 9.00\ (n_g)\ 14.00\ (n_g)\ 19.00\ (n_g)\ 24.00\ (n_g)\ 29.00\ (n_g)\ 38.00\ (n_g)\ 48.00\ (6n_g)\ r^{max} = 78.00\}$ with Neumann BCs. In each of the subintervals (except the last one) the potential $V(r)$ was approximated by the LIP of the fifth order, and $n_g = 4$ finite elements were used. The last integrand was divided into $6n_g$ finite elements and the potential $V(r)$ was replaced with its asymptotic expansion. In the solution of the BVP at all finite elements of the mesh the local functions were represented by the fifth-order LIP. Table I presents the results of using FEM programs KANTBP 4M and ODPEVP to calculate twelve energy eigenvalues of beryllium diatomic molecule. Note, that our calculation was performed using the program that implements the Numerov method on the mesh (0,100) for twelve levels with the mesh spacing 0.02 with Dirichlet BCs for $\chi_{vL}(r) = r\Phi_{vL}(r)$, which differs from the FEM results in Table I only in the last significant digit. The table shows the eigenvalues calculated with ab initio modified (MEMO) expanded Morse oscillator (EMO) potential function [3]. In
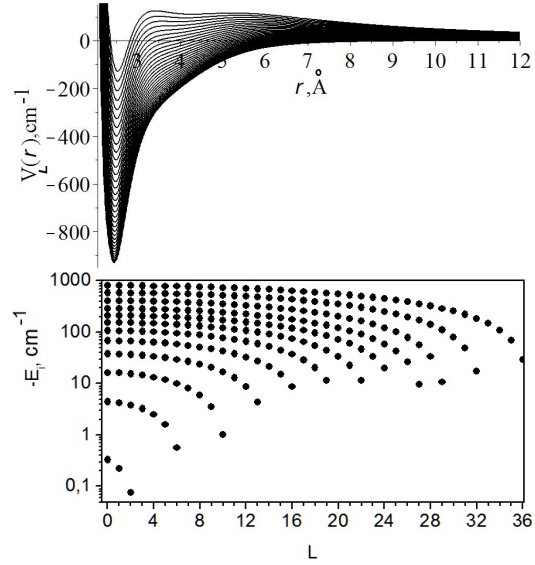

Fig. 5. Potential functions $V_L(r)$ (in cm^{-1}) vs r (in Å) at $L = 0, ..., 36$ and rotational-vibrational spectrum E_{vL} (in cm^{-1}) of the beryllium diatomic molecule vs L at.

contrast to the original EMO function, which was used to describe the experimental (Exp) vibrational levels [4], it has not only the correct dissociation energy, but also describes all twelve vibrational energy levels with the RMS error smaller than 0.4 cm^{-1}. The table also shows the results of recent calculation using the Morse long-range (MLR) function and Chebyshev polynomial expansion (CPE) alongside with the EMO potential function [8]. The main attention in the optimization of the MLR and CPE functions was focused on their correct long-range behavior displayed in Fig. 3. However, there are some problems with the quality of the MLR and CPE potential curves [3]. As a consequence, one can see from the table, that the MLR and CPE results provide *a lower estimate* while FEM and MEMO results give *an upper estimate* for the discrete spectrum of the diatomic beryllium molecule.

Fig. 5 displays potential functions $V_L(r)$ from $L = 0$ till $L = 36$ that support $36 + 33 + 30 + 28 + 25 + 23 + 20 + 17 + 14 + 11 + 7 + 3 + 1 = 248$ vibrational–rotational levels or $12 + 12 + 12 + 11 + 11 + 11 + 11 + 10 + 10 + 10 + 10 + 9 + 9 + 9 + 8 + 8 + 8 + 7 + 7 + 7 + 6 + 6 + 6 + 5 + 5 + 4 + 4 + 4 + 3 + 3 + 2 + 2 + 2 + 1 + 1 + 1 + 1 = 248$ rotational-vibrational levels. The Fig. 5 shows also the rotational-vibrational spectrum E_{vL} (in cm^{-1}) of the beryllium diatomic molecule vs L. One can see that potentials $V_L(r)$ at $L = 1$ and $L = 2$ supports 12 vibrational energy levels.

CONCLUSION

We present the computational finite element scheme for the solution of the BVP for the SOODE with variable coefficients using the programs KANTBP 4M and ODPEVP. The numerical analysis of the solution of the benchmark eigenvalue problem for the SOODE is given.

The discrete energy eigenvalues and eigenfunctions are analyzed for vibrational–rotational states of the diatomic beryl-

lium molecule by solving the eigenvalue problem for the SOODE numerically with the table-valued potential function approximated by interpolation Lagrangian and Hermite polynomials and its asymptotic expansion for large values of the independent variable specified as Fortran function.

The efficacy of the programs is demonstrated by the calculations of twelve eigenenergies of the vibrational bound states of the diatomic beryllium molecule with the required accuracy in comparison with those known from literature, as well as the vibrational-rotational spectrum.

New high accuracy *ab initio* calculations of the tabulated potential function will be useful for further study of the vibrational-rotational spectrum and scattering problems.

The results and the presented FEM programs with interpolation Hermite polynomials that preserve the derivatives continuity of the approximate solutions can be applied in the analysis of spectra of diatomic molecules and waveguide problems by solving the eigenvalue and scattering problems in the closed–coupled channel method.

REFERENCES

[1] Gevorkyan M.N., Kulyabov, D.S., Lovetskiy, K.P., Nikolaev, N.E., Sevastianov, A.L., Sevastianov, L.A.: Guided modes of a planar gradient waveguide. Mathematical Modelling and Geometry 5, 1–20 (2017)

[2] Greene, C.H., Giannakeas, P., Pérez-Ríos, J.: Universal few-body physics and cluster formation, Rev. Mod. Phys. 89, 035006–1–66 (2017)

[3] Mitin, A.V.: Unusual chemical bonding in the beryllium dimer and its twelve vibrational levels. Chem. Phys. Lett. 682, 30–33 (2017)

[4] Merritt, J.M., Bondybey, V.E., Heaven, M.C.: Beryllium dimer – caught in the act of bonding. Science 324 (5934), 1548–1551 (2009)

[5] Patkowski, K., Špirko, V., Szalewicz, K.: On the Elusive Twelfth Vibrational State of Beryllium Dimer. Science **326**, 1382–1384 (2009); Supporting Online Material www.sciencemag.org/cgi/content/full/326/5958/1382/DC1

[6] Porsev, S.G., Derevianko, A.: High-accuracy calculations of dipole, quadrupole, and octupole electric dynamic polarizabilities and van der Waals coefficients C 6, C 8, and C 10 for alkaline-earth dimers. JETP, **102**, 195–205 (2006)

[7] Sheng, X.W., Kuang, X.Y., Li, P., Tang, K.T.: Analyzing and modeling the interaction potential of the ground-state beryllium dimer. Physical Review A 88, 022517 (2013)

[8] Meshkov, V.V., Stolyarov, A.V., Heaven, M.C., Haugen, C., LeRoy, R.J.: Direct-potential-fit analyses yield improved empirical potentials for the ground $X^1\Sigma_g^+$ state of Be_2. J. Chem. Phys. 140, 064315–1–8 (2014); ftp://ftp.aip.org/epaps/journ_chem_phys/E-JCPSA6-140-046406/Band_Constants.txt

[9] Chuluunbaatar, O., Gusev, A.A., Vinitsky, S.I., Abrashkevich, A.G.: ODPEVP: A program for computing eigenvalues and eigenfunctions and their first derivatives with respect to the parameter of the parametric self-adjoined Sturm-Liouville problem. Comput. Phys. Commun. 181, 1358–1375 (2009).

[10] Gusev, A.A., Hai, L.L.,Chuluunbaatar, O., Vinitsky, S.I.: KANTBP 4M - program for solving boundary problems of the self-adjoint system of ordinary second-order differential equations. http://wwwinfo.jinr.ru/programs/jinrlib/kantbp4m/indexe

[11] Gusev, A.A., Chuluunbaatar, O., Vinitsky, S.I., Derbov, V.L., Gozdz, A., Hai, L.L., Rostovtsev, V.A.: Symbolic-numerical solution of boundary-value problems with self-adjoint second-order differential equation using the finite element method with interpolation Hermite polynomials. Lecture Notes in Computer Science 8660, 138–154 (2014)

APPENDIX

```fortran
REAL*8 FUNCTION VPOT(R)
REAL*8 R
 IF ( R .LT. 0.200D1) THEN
 VPOT = -25773.7109044290317516659D0*R
#+45224.0477977149109075999D0
#+11630.1409366263902691980D0*(R-1.50D0)**5
#-21410.9944579041874319967D0*(R-1.50D0)**3
#-6655.69301415296537793622D0*(R-1.50D0)**4
#+37646.6374905803929755811D0*(R-1.50D0)**2
 ELSEIF ( R .LT. 0.242D1) THEN
 VPOT = -3104.29731660146789925758D0*R
#+6567.96677835187237746414D0
#+145901.637557436977844389D0*(R-2.00D0)**5
#+70890.0501932798636244675D0*(R-2.00D0)**3
#-178091.891722217850289831D0*(R-2.00D0)**4
#-5215.01465840480348371833D0*(R-2.00D0)**2
 ELSEIF ( R .LT. 0.250D1) THEN
 VPOT = -87.4623224249792247412537D0*R
#-35.4722493028120322541662D0
#-5122452.98252855176907985D0*(R-2.42D0)**5
#-37267.2557427451395256506D0*(R-2.42D0)**3
#+767538.576723810368564874D0*(R-2.42D0)**4
#+1940.26376259904725429059D0*(R-2.42D0)**2
 ELSEIF ( R .LT. 0.300D1) THEN
 VPOT =95.5486415932416181588138D0*R
#-485.009680038558034254034D0
#-559.791178882855959174489D0*(R-2.50D0)**5
#-2399.49666698491294179656D0*(R-2.50D0)**3
#+2045.36781464380745875587D0*(R-2.50D0)**4
#+1039.16158144865749926292D0*(R-2.50D0)**2
 ELSEIF ( R .LT. 0.350D1) THEN
 VPOT = 181.680445623994493034163D0*R
#-673.209766066617684340488D0
#-42.1375729651804208384176D0*(R-3.00D0)**5
#+154.527717281912104793036D0*(R-3.00D0)**3
#-2.64421453511851874413350D0*(R-3.00D0)**4
#-224.971347436273044312400D0*(R-3.00D0)**2
 ELSEIF ( R .LT. 0.400D1) THEN
 VPOT = 58.2170634592331667146628D0*R
#-279.496863252389085774320D0
#+16.3002196867918408302045D0*(R-3.50D0)**5
#+60.2807956755861261238267D0*(R-3.50D0)**3
#-47.2260081876105825000000D0*(R-3.50D0)**4
#-47.2940696984941697748181D0*(R-3.50D0)**2
 ELSEIF ( R .LT. 0.500D1) THEN
 VPOT =37.5433740382779941025814D0*R
#-203.532767180257088384326D0
#+1.57933446805903445309567D0*(R-4.00D0)**5
#+2.06536720797980643219389D0*(R-4.00D0)**3
#-3.90913978185322013018878D0*(R-4.00D0)**4
#-6.72175482977376484481239D0*(R-4.00D0)**2
 ELSEIF ( R .LT. 0.600D1) THEN
 VPOT = 22.4749425088812799926950D0*R
#-135.176802468861661924475D0
#-1.74632723645421934973176D0*(R-5.00D0)**5
#-1.13910625636659500093584D0*(R-5.00D0)**3
#+3.46551546383436915312500D0*(R-5.00D0)**4
#-8.23297658169947934799179D0*(R-5.00D0)**2
 ELSEIF ( R .LT. 0.900D1) THEN
 VPOT = 8.25446369250102969043326D0*R
#-57.5068241812660846645295D0
#+0.262554831228983391666862D-1*(R-6.00D0)**5
#+1.52595797003340802069435D0*(R-6.00D0)**3
#-.302331762133111382686686D0*(R-6.00D0)**4
#-4.49546478165576415777827D0*(R-6.00D0)**2
 ELSEIF ( R .LT. 0.1400D2) THEN
 VPOT = 11.3859412349923766803961369372260*R
#-37.6833040378197826988899968642231D0
#-1.30369881127054011757584016618490*R**2
#+0.66754675480363307334180101286140-1*R**3
#-0.12861577375486918213137485397657D-2*R**4
 ELSE
 Z=R/0.52917D0
 VPOT = -( 214.D0/Z**6+10230.D0/Z**8
# +504300.D0/Z**10)
 VPOT =58664.99239D0*VPOT
 RETURN
 END
```