

CALCULATIONS OF METASTABLE AND SCATTERING STATES OF BERYLLIUM DIMER

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The computational scheme and calculation results of new rotational-vibrational metastable and scattering states for **Beryllium dimer (discrete spectrum was reported firstly in Science 324 (5934), 1548 (2009) [J.M. Merritt et al (2009)] important for the laser spectroscopy experiments** are presented. The mathematical model is formulated as a multidimensional boundary-value problem with mixed-type boundary conditions, which is reduced in the adiabatic approximation to a second-order ordinary differential equation. The solution to the problem is performed using the author's software package **KANTBP implemented as the open Fortran and Maple codes** (the libraries of programs of the journal Computer Physics Communications and JINRLIB) that implement the high-accuracy finite element method.

Beryllium diatomic molecule: the statement of problem equation

The equation for the diatomic molecules in a crude adiabatic approximation, commonly referred to as Born–Oppenheimer approximation (BO), has the form

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

where L is a quantum number of the total angular momentum, $\hbar^2/(2Da) = 1.685762920 \cdot 10^{-7} \text{\AA}$, the reduced mass of beryllium is $m = M/2 = 4.506$, $\tilde{r} = r \text{\AA}$, the effective potential is $\tilde{V}(\tilde{r})$ in atomic units $aue = 0.002194746314 \text{\AA}^{-1}$, the energy is $\tilde{E}_{vL} \text{ cm}^{-1}$.

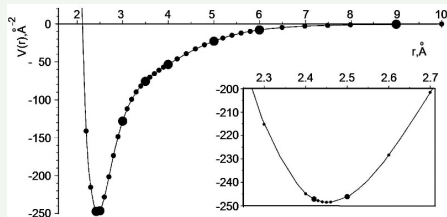
The variable r is specified in (\AA), and the effective potential

$V(r) = (2mDa\text{\AA}^2 aue/\hbar^2) \tilde{V}(r\text{\AA}) = 58664.99239 \tilde{V}(r\text{\AA}) \text{\AA}^{-2}$, and the desired value of energy $E_{vL} = (2mDa\text{\AA}^2/\hbar^2) \tilde{E}_{vL}$ in \AA^{-2} , $\tilde{E}_{vL} = (1/0.2672973729) E_{vL} \text{ cm}^{-1}$.

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

Beryllium diatomic molecule: interpolation of the tabular potential function

In Ref. [A.V. Mitin (2017)] the potential $V(r)$ 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 $r \in [r_{5k-4}, r_{5k+1}]$, $k = 1, \dots, 9$ by the fifth-order interpolation Lagrange polynomials of the variable r .



In the interval $r \in [r_{\text{match}} = 14, \infty)$ the asymptotic behavior $V_{\text{as}}(r) = 58664.99239 \tilde{V}_{\text{as}}(r)$ at large r is given by the expansions [S. G. Porsev, A. Derevianko (2006)]

$$\tilde{V}_{\text{as}}(r) = - \left(\frac{214(3)}{Z^6} + \frac{10230(60)}{Z^8} + \frac{504300}{Z^{10}} \right), \quad (2)$$

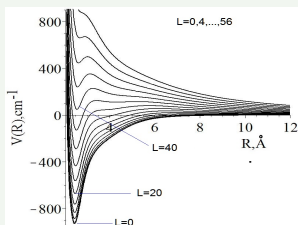
where $Z = r/0.52917$.

Beryllium Diatomic Molecule: vibrational spectrum $v = 0, \dots, 11, L = 0$

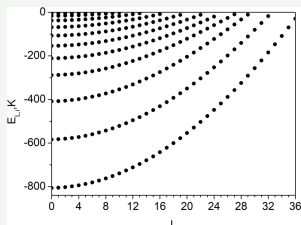
The eigenvalues of vibrational energy $-E_{vL=0}$ (in cm^{-1}) of the beryllium diatomic molecule calculated by the programs KANTBP 4M [A.A.Gusev et al (2014)] and ODPEVP [O. Chuluunbaatar et al (2009)] implemented FEM (FEM), ab initio MEMO calculation [A.V. Mitin (2017)], theoretical (EMO) and experimental (Exp) results [J.M. Merritt et al (2009)], symmetry-adapted perturbation theory (SAPT) [K. Patkowski et al (2009)], and the Morse-long range (MLR) function and Chebyshev polynomial expansion (CPE) [V. V. Meshkov, J. Chem. Phys. (2014)], Slater-type orbitals (STO) [M. Lesiuk et al (2019)], 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	STO
r_e	2.4534	2.4534	2.4535	2.4536	2.443	2.445	2.4344
D_e	929.804	929.74	929.74	929.7 \pm 2	938.7	934.8	932.2
0	806.07	806.48	806.5		812.4	808.1510	807.7
1	583.57	584.32	583.8	584.8	590.1	585.2340	584.3
2	408.73	408.88	408.7	410.3	414.8	410.7319	407.6
3	288.36	288.61	288.3	289.3	292.1	289.7314	290.4
4	211.18	211.42	211.1	212.6	214.5	213.0654	212.6
5	154.16	154.38	154.1	155.9	157.3	156.3536	156.0
6	107.15	107.34	107.1	108.6	109.8	109.1202	109.0
7	68.35	68.51	68.3	69.7	70.7	70.1719	69.7
8	37.80	37.92	37.7	39.2	40.0	39.6508	38.4
9	16.33	16.43	15.8	17.5	18.1	17.9772	17.6
10	4.41	4.40	3.1	4.8	5.3	5.3187	5.1
11	0.326	0.27			0.5	0.5175	0.21

Beryllium diatomic molecule: vibrational-rotational spectrum

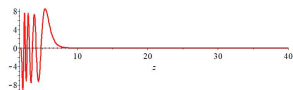
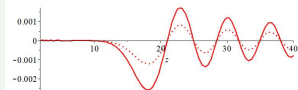


The potential function and the eigenenergies E_{vL} vs. angular momentum L of bound states of rotation-vibration spectrum of Be_2 molecule.



Scattering Problem on semiaxis:

Asymptotic form “incident wave + outgoing wave” $\Phi_{\leftarrow}(r) = X^{(\leftarrow)}(r) + X^{(\rightarrow)}(r)R$, where R is reflection amplitude $|R|^2 = 1$, $X_{\max}^{(\leftarrow)}(z)$, $X_{\max}^{(\rightarrow)}(z)$ are asymptotic solutions marked by \leftarrow or \rightarrow that means the direction of the wave.



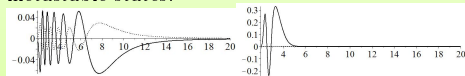
The plots of real (solid curve) and imaginary (dashed curve) parts of scattering eigenfunctions for $L = 18$ at $E = 4.7785$ ($R = 0.6367 + 0.7710i$), $E = 4.7885$ (shape resonance scattering, $R = 0.9999 + 0.0060i$), and $E = 4.7985$ ($R = 0.6467 - 0.7627i$).

Beryllium diatomic molecule: metastable states ($E = \Re E + \Im E$, $\Im E < 0$)

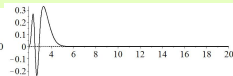
List of metastable states

L	$\Re E$	$-\Im E$	L	$\Re E$	$-\Im E$
3	0.07	9.e-3	27	22.03	3.e-17
7	0.50	5.e-4	27	45.20	0.10
8	1.47	0.09	28	6.96	2.e-20
11	1.55	1.e-5	28	35.99	5.e-6
12	4.05	0.02	28	55.00	0.16
13	5.23	0.36	29	23.51	8.e-19
14	0.08	6.e-18	29	49.66	2.e-3
15	4.60	1.e-5	29	61.47	2.e-4
16	8.99	0.01	30	11.35	4.e-21
17	13.03	0.27	30	40.05	7.e-8
18	4.78	4.e-10	30	62.55	1.e-5
19	11.51	1.e-4	31	32.62	4.e-19
20	17.99	0.03	31	56.53	1.e-4
21	6.40	5.e-13	32	52.66	8.e-8
21	23.68	0.44	33	15.02	1.e-21
22	15.49	2.e-6	34	47.64	2.e-14
23	24.44	3.e-3	35	80.25	4.e-17
23	32.61	0.73	36	111.86	1.e-13
24	11.48	1.e-12	37	11.78	4.e-18
24	32.87	0.15	38	53.59	2.e-14
25	22.99	1.e-6	39	96.16	1.e-15
25	40.35	0.61	40	139.46	1.e-15
26	7.99	5.e-20	41	183.40	3.e-15
26	34.35	1.e-3	42	227.82	4.e-15
26	45.31	0.79	43	272.33	6.e-16
			44	317.61	1.e-15

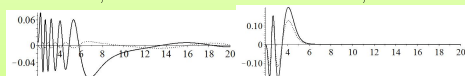
The plots of real (solid curve) and imaginary (dashed curve) parts of eigenfunctions of some metastable states.



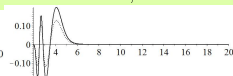
$L = 7, v = 1$



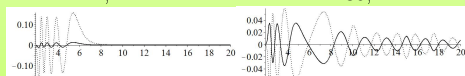
$L = 30, v = 1$



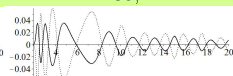
$L = 12, v = 1$



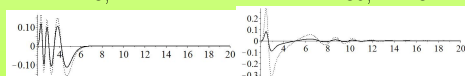
$L = 30, v = 2$



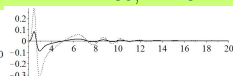
$L = 18, v = 1$



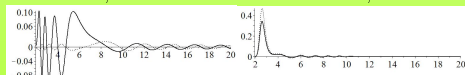
$L = 30, v = 3$



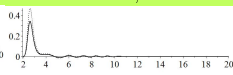
$L = 24, v = 1$



$L = 36, v = 1$



$L = 24, v = 2$



$L = 42, v = 1$

As asymptotic boundary conditions at $r = r_{\max}$ we use Siegert boundary conditions [A. J. F. Siegert (1939)]: $\Phi_*(r) \sim \exp(\pm \sqrt{E}r)$.

Conclusion

- 1 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 implemented as the open Fortran and Maple codes**. The numerical analysis of the solution of the benchmark eigenvalue problem for the SOODE is given.
- 2 The discrete energy eigenvalues and eigenfunctions are analyzed for vibrational–rotational states of the diatomic beryllium molecule reported firstly in **Science 324 (5934), 1548 (2009)** [J.M. Merritt et al (2009)] important for the laser spectroscopy experiments 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.
- 3 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 including **new rotational–vibrational metastable states**.
- 4 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**.
- 5 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.



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