

Numerov

A code for calculating and exploring the fine structure of rotation-vibration spectra of diatomic molecules

SeyedAbdolreza Sadjadi and Shant Shahbaziyan

ssadjadi@hku.hk , chemist_shant@yahoo.com

I. Version History

First Release: Jan 26, 2004

Language: Fortran90

Compiled for: WindowsX

This is a modified version of **Joel Tellinghuisen** Q-basic code (J.Chem.Edu,66,51(1986)).

The present version of Numerov code is compatible with “**FIT1D code**”. The latter is a program for least square fitting of one independent variable problems to Taylor series. FIT1D has been written by **Kirk A. Peterson** (Department of Chemistry, Washington State University, Pullman, WA 99164-4630). It can be downloaded as the windows *.exe file from this webpage by the permission granted to us by Kirk A. Peterson.

II. What Does Numerov do?

For diatomic molecules the one-dimensional Schrödinger equation (following equation) can be solved using Cooley-Numerov's numerical method.

$$\frac{\partial^2 P_R(R)}{\partial R^2} + \left\{ \frac{-2\mu}{\hbar^2} E_{gr}^e(R) + \frac{J(J+1)}{R^2} \right\} P_R(R) + \frac{2\mu}{\hbar^2} E^{rv} = 0$$

$J = 0$ are the vibrational levels without the effect of rotation

$J \neq 0$ coupling between rotation and vibration

$E_{gr}^e(R)$ = The energy of electronic ground state

E^{rv} = Rotational - Vibrational energy

$P_R(R)$ = Wave function

For the given mathematical form of $E_{gr}^e(R)$, J value and initial guess on E^{rv} value, **Numerov** calculates the accurate E^{rv} , P(R) and the corresponding vibration quantum number. The vibration quantum number is determined by counting the number of nodes in wave function P(R). $E_{gr}^e(R)$ is calculated by fitting the points on the potential energy profile to the Taylor series of expansion using **FIT1D** code. Numerov has simple input file structure and the input file is constructed automatically by “**FIT1D**” code.

For full derivation of this formula please download the **BO-approximation.pdf** file from our webpage.

III. Input file

We have designed an easy to use and self descriptive input file. Following is the sample of the input file for CO molecule.

```
R1 (Angst) , R2 (Angst) , Step number
J0
E0 (cm-1) , THRESHOLD
Reduced Mass
  2.0978260438      Re
-112.7501433344
  .0000000000
  .7665965301
-  .9132372992
  .7299311471
-  .4810099645
  .2345935681
-  .1002931439
  .1201338762
-  .1293026271
  .0529214198
  .0000729902
-  .0017347118
-  .0019026997
  .0006118660
```

R1 is the left hand limit and **R2** is the right hand limit of search outside the classical region of potential energy curve. Both are in unit of Angstrom.

Step Number is the number of points in numerical calculations.

J0 is the quantum number for desired rotational energy level.

E0>0 (cm^{-1}) is the initial guess of the energy value for the select rotation-vibration level.

THRESHOLD is the convergence criterion for calculating the total energy E^v

Reduced Mass (in atomic mass unit) is the reduced mass of the molecule with chosen isotopic mass for each atoms. This value is punched automatically to input file by **FIT1D**.

The following numbers in each raw are **R_e** value (equilibrium bond length) in Bohr units and potential energy constants of Taylor series of expansion.

IV. Running the Program

Numerov is executed by the following command line in the DOS shell of the Windows

```
Numerov-0.exe <filename.inp> filename.out
```

V. Output files

Our code produces five different kinds of output files, each contains useful data and helps to check the correctness of the calculations.

a) filename. out

This is the main output file contains the final results of calculations. Below is an example of data and format of this output file:

```
V=          0
J=  0.0000000000000000E+000
E(V,J)-cm-1    1213.104684514063000
-----
Bv=          1.987775564045156
```

v is the number of nodes in wavefunction. This is equal to vibrational quantum number.

J is the rotational quantum number. It is given as $J0$ in the input file.

$E(V,J)-cm^{-1}$ is the final total energy of vibration-rotation level

$Bv(cm^{-1})$ is the rotational constant for vibration quantum level v . Bv is calculated by the mathematical expansion of $E(V,J)$ as

$$E(V,J) = G_v + B_v J(J+1) - k[J(J+1)]^2 + H[J(J+1)]^3, \dots$$

b) Start. Out

This file, reprints what the program reads from its input file. It helps to check the process of reading the input data by code.

c) Potential. Out

This file contains the calculated potential energy at each point (X). X is the inter-nuclear distance (R). We used $U(R)-U(R_e)$ instead of $U(R)$, thus the $U(R)$ values in our code are rescaled to positive values.

d) Step. out

This file shows the value of (ΔE^{rv}) in unit of cm^{-1} for successive cycles.

e) Wavefunction.out

For calculated $E(V,J)$ the numerical value of normalized wavefunction $P(R)$ is printed at each R value. R values are in unit of Angstrom.