



Evangelos Miliordos [†]

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ROVIB is a manifold of routines calculating the energies and the wavefunctions of the rovibrational levels of a diatomic molecule. Currently, only bound potential energy curves can be used for the construction of the wavefunctions. The method employed for the solution of the rovibrational Schrödinger equation is iterative and based on the Numerov technique as described elsewhere.[1] The resulting energy levels are utilised for the extraction of the rovibrational constants of the diatomic molecule in question. Originally, the code was written in FORTRAN90, but a graphics user interface (GUI) enviroment allows the simple manipulation of the input and output data.

[†] Contact information: emiliord@gmail.com

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1. INTRODUCTION

The Hamiltonian operator (in spherical polar coordinates) of two nuclei moving in the field of the electrons surrounding them is

$$(1) \quad \hat{H} = \left\{ -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{1}{r^2} \frac{\hat{\mathcal{L}}^2(\theta, \phi)}{\hbar^2} \right] + U(r) \right\} \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

where $\hat{\mathcal{L}}$ is the operator of the angular momentum, depending on the zenith angle θ and azimuthal angle ϕ of the bond vector, with respect to the laboratory frame of reference. The variable r is the bond distance, and $U(r)$ the potential energy due to the electrons. Setting the wavefunction to be a product containing the spherical harmonics, i.e.

$$(2) \quad \Psi(r, \theta, \phi) = Y_{J, m_J}(\theta, \phi) \frac{R_{v, J}(r)}{r}$$

we finally obtain

$$(3) \quad \frac{d^2}{dr^2} R_{v, J}(r) = \left\{ \frac{J(J+1)}{r^2} + \frac{2\mu[U(r) - E_{v, J}]}{\hbar^2} \right\} R_{v, J}(r)$$

The effective potential inside the curly brackets will be written as $G_J(r)$. Presently, this radial equation is solved numerically. First we assume that at some point r_0 , much smaller than the equilibrium bond length, $R_{v, J}(r_0)$ is practically zero, and then we divide the r -space in small parts separated by a constant length, say δr . So, we have the distances $r_1, r_2, \dots, r_{n-1}, r_n, r_{n+1}, \dots$ two consecutive of them differing by δr , i.e. $r_{n+1} - r_n = \delta r$. Next, we expand the wavefunction at r_n in Taylor series. Keeping the terms up to δr^4 in the Taylor expansion, and using equation 3 we obtain

$$(4) \quad R_{n+1}^{v, J} = \frac{2R_n^{v, J} - R_{n-1}^{v, J} + \frac{5}{6}G_n^J R_n^{v, J} \delta r^2 + \frac{1}{12}G_{n-1}^J R_{n-1}^{v, J} \delta r^2}{1 - \frac{1}{12}G_{n+1}^J \delta r^2}$$

where $R_n^{v, J} = R_{v, J}(r_n)$ and $G_n^J = G_J(r_n)$. In this way, if we knew the exact energy value $E_{v, J}$, we would be able to calculate $R_{n+1}^{v, J}$ from $R_{n-1}^{v, J}$ and $R_n^{v, J}$. We do know that at very small r distances the wavefunction nullifies. Arbitrarily we set this point to be r_0 , and that at r_1 the radial function $R_1^{v, J}$ to be 0.0001. The latter value will be precisely determined upon normalizing the final wavefunction. Conclusively, if we know the energy, we can readily get the wavefunction.

Now, assuming an energy value, we may construct the wavefunction, and observe its shape. Setting energy equal to the equilibrium energy we get a non-integrable function (see the black line of figure 1), while going towards the ground state energy the resulting function resembles the well known Gaussian-like shape of the wavefunction (see the dark and light gray lines of figure 1). Around the exact energy the wavefunction at distances larger than the equilibrium, where it is expected to vanish, reveals a strange behavior. At slightly lower (than the exact) energy in this region suddenly turns to positive infinity (dark grey line), whereas at slightly larger energy it bears an additional node and then goes to negative infinity (light grey line). Someone has to pinpoint the energy where this transition occurs, and this energy will be the exact one. Increasing even more the energy, the additional node moves to shorter distances and a second crest emerges (see the magenta and red lines). Again, at energies close to the exact energy of the first excited state, the

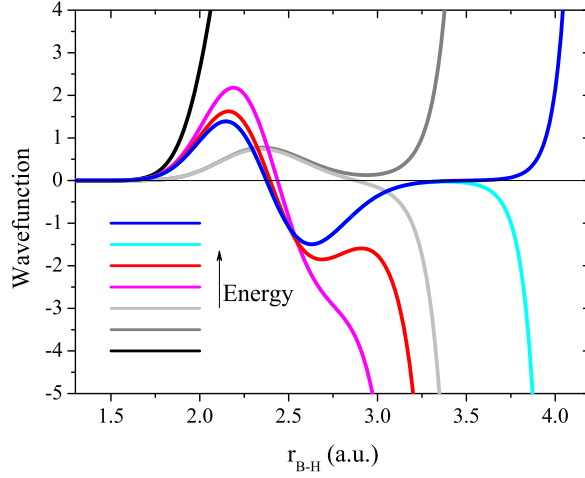


FIGURE 1. Eigenfunctions obtained at several energies ranging from the equilibrium energy to a little higher than the first excited state of BH.

same strange behavior is observed. The closer we go towards the exact energy from below, the longer the distance where the wavefunction turns to negative infinity becomes (see cyan line). Similarly, the closer we go towards the exact energy from above, the longer the distance where the additional node takes place becomes (see blue line). Practically, the present code tries to find two energy values, one with the additional node and one with the sudden turning point, that do not differ by a certain amount (the wanted accuracy level), and gives their average value.

Once we get the energy levels $E_{v,J}$, we can fit them in the energy expansion in terms of $(v + \frac{1}{2})$ and $J(J+1)$, and obtain the corresponding spectroscopic parameters.

$$(5) \quad E_{v,J} = \sum_{i,j=0}^{\infty} c_{i,j} \left(v + \frac{1}{2} \right)^i [J(J+1)]^j$$

The most common among them are $c_{0,0} = E_e$, $c_{1,0} = \omega_e$, $c_{2,0} = -\omega_e x_e$, $c_{3,0} = \omega_e y_e$, $c_{4,0} = \omega_e z_e$, $c_{0,1} = B_e$, $c_{1,1} = -\alpha_e$, $c_{2,1} = \gamma_e$, $c_{3,1} = \delta_e$, $c_{0,2} = D_e$, and $c_{1,2} = \beta_e$.

Alternatively, these constants may be estimated through the multiple derivatives of the potential curve at r_e (Dunham analysis). The formulas employed in the current code are

$$(6) \quad \begin{aligned} \omega_e &= \sqrt{\frac{U''(r_e)}{\mu}} & B_e &= \frac{\hbar^2}{2\mu r_e^2} & D_e &= \frac{4B_e^3}{\omega_e^2} \\ \alpha_e &= -\frac{2B_e^2}{\omega_e} \left[\frac{2B_e r_e^3 U'''(r_e)}{\hbar \omega_e^2} + 3 \right] & \omega_e x_e &= \frac{B_e^2 r_e^4}{4\hbar \omega_e^2} \left[\frac{10B_e r_e^2 [U'''(r_e)]^2}{3\hbar \omega_e^2} - U^{IV}(r_e) \right] \end{aligned}$$

The derivatives are calculated upon fitting a region of the curve into a polynomial.

2. INSTALLATION

Installation of ROVIB is extremely easy. Just unzip all files and folders included in the *rovib.zip* you are given in a folder of your convenience; create a new folder under *C:\Program Files*, for instance. Then, if you wish you can create a shortcut on your desktop: right click on *rovib.exe* → *Send To* → *Desktop*. The current version works under *WindowsXP*; the proper function under *WindowsVista* or *Windows7* is not guaranteed.

3. GUI DESCRIPTION

When you invoke the program, the following form will appear

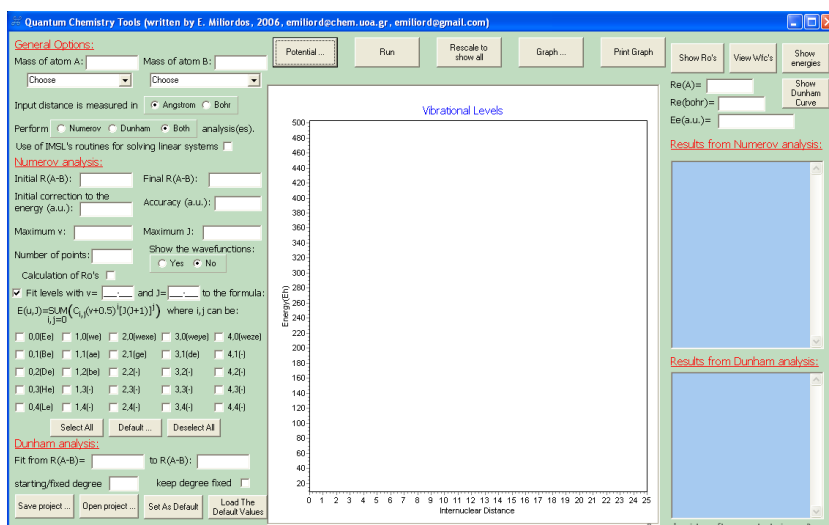


FIGURE 2. Initial form appearing when the program is executed.

There are a lot of blanks to fill in, dictating the code what to do. The default values for these blanks can be loaded by clicking on the button *Load the default values* in the bottom left corner. Optionally, you may change the default values by clicking on the *Set as default* button next to the former one.

First, we will describe the first column on the left starting from the *General options* block. There, you can give the mass of the two atoms presented as A and B, by either writing them in the white boxes, or by selecting the corresponding isotope from the boxes right below them. If the isotope you want is absent in these lists, you can add it by hand (see section 4). Then, you must declare in what units the distances you give are. Energy values must always be in atomic units. Next, you choose which method you would like to apply (Numerov, Dunham, or both). Finally, there are two ways for the code to solve the linear systems of equations that arise; the first one is related to the IMSL library, and the second one is part of ROVIB. Normally, there is no difference in the results between the two options.

We turn, now, to the *Numerov analysis* block. First you specify the region to which equation 4 should be applied (*Initial R(A-B)* and *Final R(A-B)*). We suggest that these two values must be equal to the first and last distance of the

given potential energy curve. Initially the code evaluates the number of nodes at energy equal to $(v + 1/2)\omega_e$ obtained through the second derivative at r_e . If it is lower than v , then it enhances the energy by, say, δE , whereas if it is more than $v + 1$, then the energy is decreased. This is repeated until the code finds two energies E_1 (with v nodes) and E_2 (with $v + 1$ nodes) revealing the strange behavior described previously (see figure 1). After this point, it takes the average energy value E_{av} of E_1 and E_2 and counts its nodes. Next, it replaces the energy (E_1 or E_2) having the same number of nodes (compared to E_{av}) with E_{av} . This iteration goes on until the difference between E_1 and E_2 is lower than E_{acc} . The *initial correction to the energy* box corresponds to δE and generally must not be changed from the default value of 0.01. A greater value may accelerate the initial estimate of E_1 and E_2 , but it decelerates the estimate of the exact energy, and vice versa. The next box (*Accuracy*) is E_{acc} in a.u. (default = 10^{-7}). This means that the final energy will be $\pm E_{acc}$ away from the exact value. *Maximum v* and *maximum J* are the maximum values for the corresponding quantum numbers of the energy levels to be calculated. *Number of points* is related to the number of points the region from *Initial R(A-B)* to *Final R(A-B)* should be divided (default=1000). Then two options about the appearance of the wavefunctions and the calculation of $r_0 = \langle \Psi | r | \Psi \rangle$ for every energy level follow. Finally, if the box in front of *Fit levels* is checked, the energy levels with v and J in the range specified in the boxes that follow will be fitted to equation 5. The code keeps the terms with i, j determined by the checked boxes right below. The buttons *Select All*, *Default ...*, and *Deselect All* are related to the latter boxes.

The last block of this column is the *Dunham analysis*. Here you may specify the region to be fitted in a polynomial, and the order of the polynomial. If the *keep degree fixed* is not checked, the code will try to find which degree matches best.

Just above the chart, there are five buttons. By clicking the first one (*Potential ...*) an additional box appears, where you must give the computed points of the potential energy curve. These points will be fitted in splines, so that the final curve will be constructed. Please do not leave blank lines, and each line must contain only one r followed by its energy. In addition, the distances must be given in ascending order, otherwise an error message will occur. By clicking the second one (*Run*) the fortran code will be activated, and the rovibrational Schrödinger equation is being solved. Note that the label of the *Run* button converts to *Stop*. Usually, the whole process takes only a few seconds, and when the code finishes gracefully, a message appears on your screen showing the total time. If your job continues for more than a couple of minutes, then something is wrong with the parameters you entered, and the fortran code runs with no reason, or there is a bug in the code. Anyhow, the fortran process must be terminated by clicking again the *Run* or *Stop* button. If it does not work (and ROVIB slows down your PC), then you must kill the *rv.exe* process through the windows task manager (not the *rovib.exe* one). The next button rescales the chart, so that you can see the whole curve. This applies when you have already zoomed in the chart (see below). The *Graph ...* button offers the chance to you to change the colors of the resulting graph, the ranges of the axes, or their labels (see figure 3). This is done with the help of a new panel emerging on your screen. The last button (*print graph*) prints the graph using the default printer.

The remaining objects on this form carry only results. After a successful calculation, you can see the fitted potential energy curve (in black), the energy levels, and optionally the wavefunctions (in red). Upon dragging your mouse (with the left click down) you may zoom in, while right click of your mouse shows a pop-up menu with the following options: *Print graph*, *Copy to clipboard*, *Properties*, *Enable zoom*, *Enable position finder*. The first one is equivalent to the corresponding button. The second one copies the graph to clipboard, so that you can paste it to some other program (like MSword). The third one does exactly what the button *Graph* does. The last two options are interdependent, and they define what the left click of your mouse to do. When the last option is enabled, then upon clicking on the graph you get the (x,y) coordinates at the point clicked.

The last column provides all of the numerical results. There are four buttons, with the use of which you can see the numerical values of $r_{v,J} = \langle \Psi_{v,J} | r | \Psi_{v,J} \rangle$, or the wavefunctions at each r value, the accurate energy values, and the Dunham polynomial function highlighted on the graph. The rest boxes show the spectroscopic results obtained from either the Numerov or the Dunham analysis.

4. ADVANCED OPTIONS

There are a couple of things that you can do aside from the GUI interface. After a successful run, the FORTRAN code produces some txt files inside the folder *temp*, under the folder where ROVIB is installed. There you can find all results, including wavefunctions, energies, expectation values, in a format more appropriate for further programming.

Also, in the installation folder you can find a file called *amass.txt*. This file contains the entries for the isotopes to be shown in GUI. There you can add your own entries, but it must be done in the appropriate way. Each atom's isotopes must be separated by some others' with a blank line. Then, each entry must occupy two lines: the first will be reflected in GUI, and the second is the mass corresponding to this isotope. See the picture below.

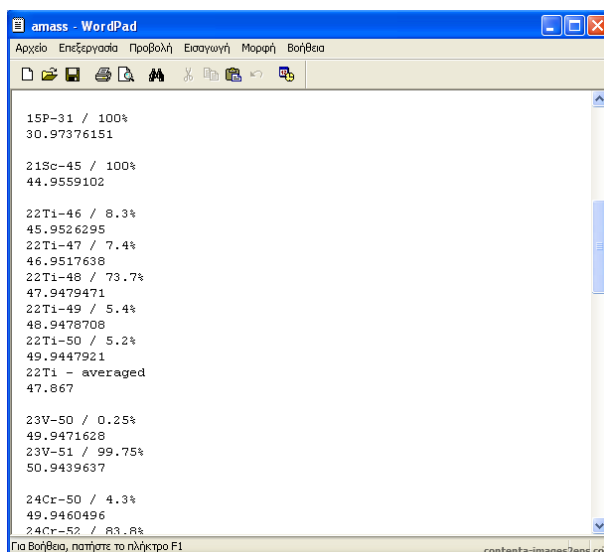


FIGURE 3. A part of the file *amass.txt*.

5. EXAMPLE

In this section we cite an example based on the ground state $X^1\Sigma^+$ of ^{11}BH . The input parameters, and the final picture of ROVIB are shown in figure 4 (please zoom in, if necessary).

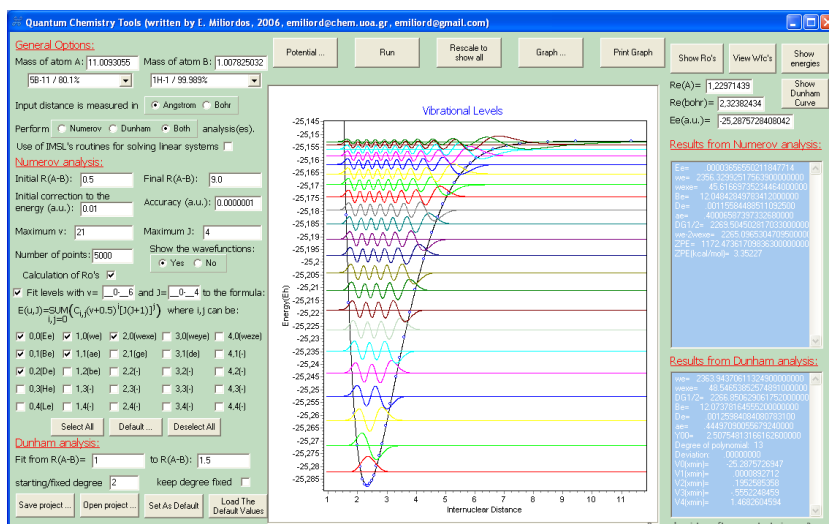


FIGURE 4. Final picture of GUI after the calculation of the 22 vibrational energy levels of the ground state $X^1\Sigma^+$ of ^{11}BH .

Presently, we perform a Numerov analysis, calculating the first 22 vibrational levels ($v = 0 - 21$) with $J = 0 - 4$. If you ask higher v or J level to be found, there will be an error message, indicating that the next level belongs to the continuum. Next, we fit the levels with $v = 0 - 6$ and $J = 0 - 4$ into the energy expansion of equation 5. At the same time, the points of the potential energy curve between 1.0 and 1.5 Å are fitted in the best possible polynomial, which seems to be of degree 13 (see *Results from Dunham analysis*). The spectroscopic parameters obtained from both methods are in good agreement. Note that the values of the spectroscopic constants depend (strongly sometimes) on the selected levels to be fitted, and the terms kept in equation 5. So, someone must be careful when comparisons with the experimental results are made. You must try to simulate the experimental data, and use the same energy levels, and spectroscopic parameters, if possible.

However, the experimental spectral lines, and those predicted by a high level of theory must be very close to each other. In our example we used aug-cc-pV5Z basis sets centered on both atoms, applying the iMRCISD methodology, as implemented in MOLPRO.[2] We used 44 different internuclear distances r ranging from 0.5 to 9.0 Å, but usually a much smaller number (around 20) is more than enough. Our energy values are included in the MSeExcel file *BHexample.xls* in the installation folder, along with the resulting energies and predicted spectral lines, as compared with the experimental ones. From Table 1 you can see the remarkable agreement between theory and experiment, validating the *power* of ROVIB.

TABLE 1. Results on ^{11}BH at the aug-cc-pV5Z/MRCISD level of theory.

Δv	J	$J \rightarrow J + 1$		$J \rightarrow J - 1$	
		theory	expt[3]	theory	expt[3]
0 \rightarrow 1	0	2292.41	2292.02		
	1	2314.44	2313.96	2245.78	2245.60
	2	2335.55	2335.01	2221.24	2221.17
	3	2355.79	2355.15	2195.95	2195.98
	4	2375.06	2374.35	2169.90	2170.04
	5	2393.35	2392.58	2143.14	2143.39
	6	2410.66	2409.82	2115.70	2116.06
	7	2426.93	2426.04	2087.61	2088.09
	8			2058.91	2059.49
1 \rightarrow 2	0	2196.25	2195.79		
	1	2217.46	2216.92	2151.27	2151.01
	2	2237.82	2237.19	2127.59	2127.42
	3	2257.27	2256.55	2103.15	2103.08
	4	2275.78	2274.99	2077.99	2078.01
	5	2293.34	2292.48	2052.11	2052.24
	6	2309.95	2308.99	2025.57	2025.80
	7	2325.52	2324.50	1998.39	1998.73
2 \rightarrow 3	2	2141.65	2141.58		
	3	2160.32	2160.17	2011.84	2012.33
	4	2178.11	2177.87	1987.52	1988.11
	5	2194.96	2194.63	1962.53	1963.20
	6	2210.83	2210.43	1936.87	1937.62
	7	2225.70	2225.25	1910.58	1911.43

6. KNOWN ISSUES

We would like to bring to your attention the following issues

- *Initial R(A-B)* and *Final R(A-B)* must be inside the range of the given energy calculations.
- The energy levels to be fitted must be a subtotal of the calculated energy levels.
- The *Open project . . .* and *Save project . . .* buttons may not work properly, and it will be fixed in later versions.

REFERENCES

- [1] I. N. Levine, *Quantum Mechanics*, 5th edition; Prentice Hall Inc., Upper Saddle River, New Jersey, USA, 2000.
- [2] MOLPRO, version 2006.1, a package of *ab initio* programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel and G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer and M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni and T. Thorsteinsson, see <http://www.molpro.net>.
- [3] F. S. Pianalto, L. C. O'Brien, P. C. Keller, and P. F. Bernath, *J. Mol. Spectrosc.* **129**, 348 (1988).