High-precision evaluation of the Vibrational spectra of long-range molecules

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Abstract

Vibrational spectra of long-range molecules are determined accurately and to arbitrary accuracy with the Canonical Function Method. The energy levels of the 0− and 1u electronic states of the 23Na2 molecule are determined from the Ground state up to the continuum limit. The method is validated by comparison with previous results obtained by Stwalley et al. using the same potential and Trost et al. whose work is based on the Lennard-Jones potential adapted to long-range molecules.
I. INTRODUCTION

A new kind of high precision molecular spectroscopy is probing long-range forces between constituent atoms of molecules. This spectroscopy is based on using light to combine two colliding cold-trapped atoms into a tenuous molecule.

The burgeoning field of ”Photoassociation Spectroscopy” is allowing very precise measurement of lifetimes of the first excited states of Alkaline atoms and observation of retardation effects and long-range forces. It provides a means of probing accurately the weak interaction between these atoms [3].

The agreement between theory and experiment requires simultaneously a highly accurate representation of the interaction potential as well as a highly reliable method for the calculation of the corresponding energy levels.

Since our aim is directed towards the latter problem, we make use of an alternative method to evaluate the energy levels for the potential at hand instead of comparing to the experimental values in order to assess the validity of our results.

The determination of the vibrational spectra of these very tenuous molecules is extremely subtle specially for the highest levels which play an important role in photoassociation spectroscopy. Thus a careful control of accuracy is needed in order to diagonalise the Hamiltonian without losing accuracy for all energies including those close to the dissociation limit.

The magnitudes of potential energy, distance and mass values in these kinds of molecules stand several orders of magnitude above or below what is encountered in ordinary short-range molecules.

For instance, the typical intramolecular potential well depth at the equilibrium distance of about 100 $a_0$ (Bohrs), is a fraction of a cm$^{-1}$ while the reduced mass is several 10,000 electron masses. All these extreme values require special numerical techniques in order to avoid roundoffs, divergences, numerical instability and ill-conditioning during processing.

The method we use in this work adapts well to this extreme situation with the proviso of employing a series of isospectral scaling transformations we explain below.

Since accuracy and its control are of paramount importance in this work, the canonical function method (CFM) [4] is an excellent candidate because it bypasses the calculation of the eigenfunctions. This avoids losing accuracy associated with the numerical calculation specially with rapidly oscillating wave functions of highly excited states.
This method evaluates the full spectrum of the Hamiltonian, for any potential, to any desired accuracy up to the continuum limit. It has been tested successfully in long-range and short-range potentials for atomic and molecular states. It describes faithfully bound and free states and is straightforward to code.

This work is organised as follows: Section 2 is a description of the CFM and highlights the details of the method. Section 3 presents the results we obtain for the vibrational levels of the $^{23}\text{Na}_2$ molecule $0_g^-$ and $1_u$ electronic states. Section 4 is an additional validation of the method with the Lennard-Jones molecular potential used in a similar situation. We conclude in section 5.

II. THE CANONICAL FUNCTION METHOD

In this work we consider rotationless long-range diatomic molecules only. The associated Radial Schrödinger equation (RSE) is given by:

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} - V(r) + E\right)\psi(r) = 0$$

where $\mu$ is the reduced mass and $V(r)$ is the potential energy of the interacting constituent atoms.

The diagonalisation of the RSE is described mathematically as a singular boundary value problem. The prime advantage of the CFM is in turning it into a regular initial value problem.

Primarily developed by Kobeissi and his coworkers [4] the CFM, consists, essentially, in writing the general solution as a function of the radial distance $r$ in terms of two basis functions $\alpha(E; r)$ and $\beta(E; r)$ for some energy $E$.

Picking an arbitrary point $r_0$ at which a well defined set of initial conditions are chosen i.e.: $\alpha(E; r_0) = 1$ with $\alpha'(E; r_0) = 0$ and $\beta(E; r_0) = 0$ with $\beta'(E; r_0) = 1$, the RSE is solved by progressing simultaneously towards the origin and $\infty$. The effect of using different algorithms for the numerical integration will be examined in the next section.

During the integration, the ratio of the functions is monitored until saturation signaling the stability of the eigenvalue spectrum [8].

One may define two associated energy functions:

$$l^+(E) = \lim_{r \to +\infty} \frac{\alpha(E; r)}{\beta(E; r)}; \quad (2)$$

3
and:

\[ l_-(E) = \lim_{r \to 0} \frac{\alpha(E; r)}{\beta(E; r)} \]  

The eigenvalue function is defined in terms of:

\[ F(E) = l_+(E) - l_-(E) \]  

The saturation of the \( \alpha(E; r)/\beta(E; r) \) ratio as \( r \) progresses towards 0 or \( \infty \) yields a position independant eigenvalue function \( F(E) \). Its zeroes yield the spectrum of the RSE.

Generally, one avoids using the wavefunction but if one needs it, the functions \( \alpha(E; r) \) and \( \beta(E; r) \) are used to determine the wavefunction at any energy with the expression:

\[ \Psi(E; r) = \Psi(E; r_0)\alpha(E; r) + \Psi'(E; r_0)\beta(E; r) \]  

where \( \Psi(E; r_0) \) and \( \Psi'(E; r_0) \) are the wavefunction and its derivative at the start point \( r_0 \). The eigenfunctions are obtained for \( E = E_k \) where \( E_k \) is any zero of \( F(E) \).

The graph of the eigenvalue function has a typical \( \tan(|E|) \) shape versus the logarithm of the absolute value of the energy \( E \) as displayed in Fig. 1.

![Graph of the eigenvalue function](image)

**FIG. 1:** Behavior of the eigenvalue function \( F(E) \) with energy on a semi-log scale for the Vibrational spectra of the \( 0_g^- \) electronic state of the \( ^{23}\text{Na}_2 \) molecule. The vertical lines indicate the eigenvalue position. Energies are in cm\(^{-1}\).
III. VIBRATIONAL STATES OF THE $^{23}\text{Na}_2$ MOLECULE

We apply the CFM to the calculation of the vibrational energy levels of a diatomic molecule where the interaction between the atoms is given by the Movre and Pichler potential \cite{Movre1990}.

We start with the $0_g^-$ electronic state of the $^{23}\text{Na}_2$ molecule. The corresponding potential is given by:

$$ V(r) = \frac{1}{2}[(1 - 3X) + \sqrt{1 - 6X + 81X^2}] $$

where $X = C(0_g^-)/9r^3\Delta$. $r$ is the internuclear distance and the parameter $C(0_g^-)$ is such that:

$$ \lim_{r \to +\infty} V(r) \to -\frac{C_3(0_g^-)}{r^3} $$

Identification of the large $r$ limit yields the result: $C_3(0_g^-) = C(0_g^-)/3$. We have used in the calculations below $C_3(0_g^-) = 6.390$ Hartrees.$a_0^3$ like \cite{Movre1990}. The parameter $\Delta = 1.56512.10^{-4}$ Rydbergs is the atomic spin-orbit splitting. Given $C_3(0_g^-)$ and $\Delta$, the equilibrium internuclear distance is $r_e = 71.6a_0$.

We scale all energies with a factor $E_0$ (usually cm$^{-1}$) with the use of equation (1). Then we scale all distances with a typical length $L_0$ transforming the RSE appropriately. This double transformation is reflected generally in the potential coefficients preserving thus the functional form of the potential.

In order to gauge the accuracy of the spectra, we perform the integration of the RSE with two different methods: A fixed step Fourth-order Runge-Kutta method (RK4) and a Variable Step Controlled Accuracy (VSCA) method \cite{VSCA}.

The VSCA method is based on a series expansion of the potential and the corresponding solution to an order such that a required tolerance criterion is met. Ideally, the series coefficients are determined analytically to any order, otherwise loss of accuracy occurs leading quickly to numerical uncertainties as discussed later.

Table \ref{tab:results} shows the results we obtain with the RK4 method. The limitation of the RK4 method to fourth order hampers the finding of levels beyond the 33rd (see Table 1). In order to find the higher levels we have to select an algorithm that enables us to tune the accuracy well beyond the fourth order.

Pushing the accuracy within the framework of a fixed step method has the effect of reducing substantially the integration step. In order to avoid this problem, we use a variable
TABLE I: Vibrational levels for the $0^g_-$ electronic state of the $^{23}$Na$_2$ molecule as obtained with a fixed step RK4 method, Stwalley et al. results and the corresponding ratio. Levels 34-40 were not found by the RK4 method due to the precision limited to fourth order.

| Index | RK4 (cm$^{-1}$) | Stwalley et al. (cm$^{-1}$) | Ratio  |
|-------|-----------------|-----------------------------|--------|
| 1     | -1.7864563      | -1.7887                     | 1.00126|
| 2     | -1.5595812      | -1.5617                     | 1.00136|
| 3     | -1.3546211      | -1.3566                     | 1.00146|
| 4     | -1.1704091      | -1.1723                     | 1.00162|
| 5     | -1.0057168      | -1.0075                     | 1.00177|
| 6     | -0.8592746      | -0.86087                    | 1.00186|
| 7     | -0.7297888      | -0.73125                    | 1.00200|
| 8     | -0.6159592      | -0.61729                    | 1.00216|
| 9     | -0.5164938      | -0.51770                    | 1.00234|
| 10    | -0.4301231      | -0.43120                    | 1.00250|
| 11    | -0.3556114      | -0.35657                    | 1.00270|
| 12    | -0.2917683      | -0.29261                    | 1.00288|
| 13    | -0.2374567      | -0.23820                    | 1.00313|
| 14    | -0.1916004      | -0.19224                    | 1.00334|
| 15    | -0.1531898      | -0.15374                    | 1.00359|
| 16    | -0.1212858      | -0.12176                    | 1.00391|
| 17    | -9.5022481(-02) | -9.5438(-02)                | 1.00437|
| 18    | -7.3608067(-02) | -7.3940(-02)                | 1.00451|
| 19    | -5.6325397(-02) | -5.6599(-02)                | 1.00486|
| 20    | -4.2530440(-02) | -4.2754(-02)                | 1.00526|
| 21    | -3.1650256(-02) | -3.1831(-02)                | 1.00571|
| 22    | -2.3180032(-02) | -2.3323(-02)                | 1.00617|
| 23    | -1.6679434(-02) | -1.6791(-02)                | 1.00669|
| 24    | -1.1768423(-02) | -1.1854(-02)                | 1.00727|
| 25    | -8.1226859(-03) | -8.1873(-03)                | 1.00795|
| 26    | -5.4687973(-03) | -5.5165(-03)                | 1.00872|
| 27    | -3.5792655(-03) | -3.6136(-03)                | 1.00959|
| 28    | -2.2675456(-03) | -2.2916(-03)                | 1.01061|
| 29    | -1.3831324(-03) | -1.3995(-03)                | 1.01183|
step that adjusts itself to the desired accuracy, the VSCA method.

This method is powerful and flexible enough to find all the desired energy levels and allows us to find one additional level that was not detected before. It should be noted that the last three levels given by Stwalley et al. were extrapolated and not calculated. The agreement between our calculated levels and those of Stwalley et al. is quite good. We believe that the small discrepancy, increasing as we progress towards the dissociation limit, is due to a loss of accuracy associated with traditional methods in sharp contrast with the CFM.

The estimation of accuracy of the results hinges basically on two operations, integration and determination of the zeroes of the eigenvalue function $F(E)$. The superiority of the VSCA method is observed in the determination of the upper levels that are not detected by the RK4 method (see Tables 1 and 2). In addition, it is observed in the behavior of the eigenvalue ratio versus the index. While in both cases (RK4 and VSCA) the ratio increases steadily as the index increases because we are probing higher excited states, in the RK4 case it rather blows up as dissociation is approached. We use typically series expansion to order 12 in VSCA with a tolerance of $10^{-8}$. In the root search of $F(E)$, the tolerance required for a zero to be considered as an eigenvalue is $10^{-15}$. This does not imply that we disagree as strongly as 0.13%, for instance, with the Ground state value (see Tables 1 and 2) found by Stwalley et al. for the simple reason, we use a splitting energy $\Delta = 1.56512 \times 10^{-4}$ Rydbergs corresponding to an equilibrium internuclear distance $r_e = 71.6 a_0$. Stwalley et al. do not provide explicitly the value of $\Delta$ they use, and more recently Jones et al. provide a value that is slightly different.

We treat next the $1_u$ electronic state of the $^{23}$Na$_2$ molecule. This state is higher that the $0_g$ and the number of vibrational levels is smaller because the potential is shallower as displayed in Fig. 2.

The potential associated with the $1_u$ electronic state of the $^{23}$Na$_2$ molecule is a lot more involved. Its VSCA implementation is particularly difficult because of the complex functional of the potential as we explain below. Analytically, the VSCA algorithm requires performing a Taylor series expansion to any order around an arbitrary point.

This is still, numerically, an open problem for arbitrary functions and the use of LISP based symbolic manipulation techniques produces quickly cumbersome expressions. Spe-
TABLE II: Vibrational levels for the $0_g^-$ electronic state of the $^{23}$Na$_2$ molecule as obtained with Stwalley et al. results, the variable step controlled accuracy method (VSCA) method and the corresponding ratio. Levels 38, 39 and 40 of Stwalley et al. are extrapolated with LeRoy and Bernstein semi-classical formulae.

| Index | Stwalley et al. (cm$^{-1}$) | VSCA (cm$^{-1}$) | Ratio   |
|-------|----------------------------|-----------------|---------|
| 1     | -1.7887                    | -1.7864488      | 1.00126 |
| 2     | -1.5617                    | -1.5595638      | 1.00137 |
| 3     | -1.3566                    | -1.3546072      | 1.00147 |
| 4     | -1.1723                    | -1.1703990      | 1.00162 |
| 5     | -1.0075                    | -1.0057071      | 1.00178 |
| 6     | -0.86087                   | -0.8592631      | 1.00187 |
| 7     | -0.73125                   | -0.7297908      | 1.00200 |
| 8     | -0.61729                   | -0.6159534      | 1.00202 |
| 9     | -0.51770                   | -0.5164882      | 1.00235 |
| 10    | -0.43120                   | -0.4301217      | 1.00251 |
| 11    | -0.35657                   | -0.3556148      | 1.00269 |
| 12    | -0.29261                   | -0.2917693      | 1.00288 |
| 13    | -0.23820                   | -0.2374560      | 1.00313 |
| 14    | -0.19224                   | -0.1916002      | 1.00334 |
| 15    | -0.15374                   | -0.1531893      | 1.00359 |
| 16    | -0.12176                   | -0.1212854      | 1.00391 |
| 17    | -9.5438(-02)               | -9.5022588(-02) | 1.00437 |
| 18    | -7.3940(-02)               | -7.3608452(-02) | 1.00450 |
| 19    | -5.6599(-02)               | -5.6325744(-02) | 1.00485 |
| 20    | -4.2754(-02)               | -4.2530867(-02) | 1.00525 |
| 21    | -3.1831(-02)               | -3.1650591(-02) | 1.00570 |
| 22    | -2.3323(-02)               | -2.3180420(-02) | 1.00615 |
| 23    | -1.6791(-02)               | -1.6679756(-02) | 1.00667 |
| 24    | -1.1854(-02)               | -1.1768655(-02) | 1.00725 |
| 25    | -8.1873(-03)               | -8.1228816(-03) | 1.00793 |
| 26    | -5.5165(-03)               | -5.4689541(-03) | 1.00869 |
| 27    | -3.6136(-03)               | -3.5793742(-03) | 1.00956 |
| 28    | -2.2916(-03)               | -2.2676168(-03) | 1.01058 |
FIG. 2: Potential energy in cm$^{-1}$ for the $0_g$ and $1_u$ electronic states of the $^{23}$Na$_2$ molecule. The radial distance $r$ is in $a_0$ units.
cial methods based on analytical fitting expressions are needed in order to turn the series coefficients into a more manageable form.

The first step is to determine the $1_u$ electronic state of the $^{23}\text{Na}_2$ molecule by solving the Movre et al. [7] secular equation such that:

$$V(r) = \Delta \left[ -2\sqrt{Q} \cos\left(\frac{\theta - 2\pi}{3}\right) - \frac{a}{3} - 1 \right]$$

(8)

where $a=-2.6X$ and $X = C(1_u)/9r^3\Delta$. In addition, $\theta = \cos^{-1}\left(\frac{1+270X^3}{\sqrt{(1+63X^2)^3}}\right)$, and $Q = \frac{1+63X^2}{9}$.

The parameter $C(1_u)$ is such that:

$$\lim_{r \to +\infty} V(r) \to -\frac{C_3(1_u)}{r^3}$$

(9)

Identification of the large $r$ limit yields to the result: $C_3(1_u) = C(1_u)(\sqrt{7} - 2)/9$. We have used in the calculations below $C_3(1_u) = 1.383$ Hartrees, $a_0^3$ like Stwalley et al. The parameter $\Delta = 1.56512.10^{-4}$ Rydbergs is the same as for the $0_g^-$ state.

Table III displays the results we obtain with the RK4 method that cannot find more than 11 levels due to accuracy limitations.

The next results for the $1_u$ electronic state of the $^{23}\text{Na}_2$ molecule are obtained with the VSCA method as shown in table IV. We find an additional 15-th level in contrast to Stwalley et al. who found fourteen and extrapolated the last two levels.

The corresponding graph of the eigenvalue function is displayed in Fig. 3 below.

IV. LENNARD-JONES MOLECULES

We apply our methodology to the Lennard-Jones case. Our results are compared to the results obtained by Trost et al. [2]. We start with the levels obtained with the RK4 method. The energy unit is $\epsilon$ the depth of the potential well of the Asymmetric Lennard-Jones potential (ALJ):

$$V(r) = C_1\left(\frac{1}{r}\right)^\beta - C_2\left(\frac{1}{r}\right)^\alpha$$

(10)

The Asymmetric-Lennard-Jones (ALJ) depends on $C_1$ and $C_2$ yielding an equilibrium distance at $r = r_{min}$ and a potential depth of $-\epsilon$. Trost et al. [2] use the general parameterisation:

$$C_1 = \frac{\epsilon}{(\beta - \alpha)} r_{min}^\beta, \quad C_2 = \frac{\epsilon}{(\beta - \alpha)} r_{min}^\alpha$$

(11)
TABLE III: Vibrational levels for the $1_u$ electronic state of the $^{23}$Na$_2$ molecule as obtained with the RK4 method, Stwalley et al. results and the corresponding ratio. RK4 found only 11 levels and levels 15 and 16 of Stwalley et al. are found by extrapolation.

| * Index | RK4 (cm$^{-1}$) | Stwalley et al.(cm$^{-1}$) | Ratio   |
|---------|----------------|----------------------------|---------|
| 1       | 0.1319536      | 0.13212                    | 1.00126 |
| 2       | 9.0057392(-02) | 9.0192(-02)                | 1.00149 |
| 3       | 5.9472159(-02) | 5.9574(-02)                | 1.00171 |
| 4       | 3.7821597(-02) | 3.7896(-02)                | 1.00197 |
| 5       | 2.3027828(-02) | 2.3080(-02)                | 1.00227 |
| 6       | 1.3324091(-02) | 1.3359(-02)                | 1.00262 |
| 7       | 7.2562182(-03) | 7.2787(-03)                | 1.00310 |
| 8       | 3.6714971(-03) | 3.6849(-03)                | 1.00365 |
| 9       | 1.6950002(-03) | 1.7024(-03)                | 1.00437 |
| 10      | 6.9533077(-04) | 6.9904(-04)                | 1.00533 |
| 11      | 2.4102039(-04) | 2.4492(-04)                | 1.01618 |
| 12      | 6.8430(-05)    |                           |         |
| 13      | 1.3446(-05)    |                           |         |
| 14      | 1.4122(-06)    |                           |         |
| 15      | 3.8739(-08)    |                           |         |
| 16      | 1.2735(-12)    |                           |         |

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TABLE IV: Vibrational levels for the $1_u$ electronic state of the $^{23}\text{Na}_2$ molecule as obtained by Stwalley et al., the variable step controlled accuracy method (VSCA) and the corresponding ratio.

A new 15th level is obtained with the VSCA method.

| Index | Stwalley et al. (cm$^{-1}$) | VSCA (cm$^{-1}$) | Ratio |
|-------|-----------------------------|------------------|-------|
| 1     | 0.13212                     | 0.13244150       | 1.00243 |
| 2     | 9.0192(-02)                 | 9.07598688(-02)  | 1.00630 |
| 3     | 5.9574(-02)                 | 6.01645742(-02)  | 1.00991 |
| 4     | 3.7896(-02)                 | 3.83982868(-02)  | 1.01325 |
| 5     | 2.3080(-02)                 | 2.34584275(-02)  | 1.01640 |
| 6     | 1.3359(-02)                 | 1.36187753(-02)  | 1.01944 |
| 7     | 7.2787(-03)                 | 7.44243743(-03)  | 1.02250 |
| 8     | 3.6849(-03)                 | 3.77999552(-03)  | 1.02581 |
| 9     | 1.7024(-03)                 | 1.75281307(-03)  | 1.02961 |
| 10    | 6.9904(-04)                 | 7.23013793(-04)  | 1.03430 |
| 11    | 2.4492(-04)                 | 2.54856605(-04)  | 1.04057 |
| 12    | 6.8430(-05)                 | 7.18249908(-05)  | 1.04961 |
| 13    | 1.3446(-05)                 | 1.43120199(-05)  | 1.06441 |
| 14    | 1.4122(-06)                 | 1.53931042(-06)  | 1.09001 |
| 15    | 3.8739(-08)                 | 4.66022073(-09)  |       |
| 16    | 1.2735(-12)                 |                  |       |

*
FIG. 3: Behavior of the eigenvalue function $F(E)$ with energy on a semi-log scale for the $1_u$ electronic state of the $^{23}\text{Na}_2$ molecule. The vertical lines indicate the eigenvalue position. Energies are in cm$^{-1}$. 
It is scaled in such a way that the energy is expressed in units of the potential well depth $\epsilon$. When $\alpha = 6$, $\beta = 12$ we obtain $r_{\text{min}} = \sqrt[2]{\frac{C_2}{C_1}}$ and $\epsilon = \frac{C_2^2}{4C_1}$. and the radial distance is in $\sqrt[2]{\frac{\alpha}{\beta}}$ where $B$ is a reduced scaled mass given by $B = 2\mu \epsilon r_{\text{min}}^2$. Numerically Trost et al. use $B = 10^4$ which is the order of magnitude encountered in long-range molecules within the framework of their system of units. The potential energy in these units is displayed in Fig. 4. The RK4 methods yields the results displayed in Table V.

![Graph of potential energy](image.png)

**FIG. 4:** Potential energy of the Trost et al. model. The energy is in $\epsilon$ units where $\epsilon$ is the potential well depth and the radial distance is in $\sqrt[2]{\frac{\alpha}{\beta}}$ where $B$ is a scaled mass.

The accuracy limitation of the RK4 results in losing the uppermost level 24. Thus we move on to the results obtained with the superior VSCA method. All levels are obtained with the VSCA and the agreement with Trost et al. results is perfect as witnessed by the ratio values of Table 6. The eigenvalue function obtained with the VSCA method as a function of energy is displayed in Fig. 5.

**V. CONCLUSION**

The CFM is a very powerful method that enables one to find the Vibrational spectra of tenuous molecules where energies and distances are so remote from the ordinary short-range molecules case that special techniques should be developed in order to avoid numerical instabilities and uncertainties.

The VSCA integration method used gives the right number of all the levels and the variation of the eigenvalue function $F(E)$ definitely determines the total number of lev-
TABLE V: Quantum levels of a Lennard-Jones molecule in $\epsilon$ units, the depth of the potential well as obtained by the RK4 method, Trost et al. and the corresponding ratio. Only the last 24th level was missed by the RK4 method.

| * Index | RK4      | Trost et al. | Ratio    |
|---------|----------|--------------|----------|
| 1       | -0.9410450 | -0.9410460   | 1.000001 |
| 2       | -0.8299980 | -0.8300020   | 1.000005 |
| 3       | -0.7276400 | -0.7276457   | 1.000008 |
| 4       | -0.6336860 | -0.6336930   | 1.000011 |
| 5       | -0.5478430 | -0.5478520   | 1.000017 |
| 6       | -0.4698130 | -0.4698229   | 1.000021 |
| 7       | -0.3992870 | -0.3992968   | 1.000025 |
| 8       | -0.3359470 | -0.3359561   | 1.000027 |
| 9       | -0.2794670 | -0.2794734   | 1.000023 |
| 10      | -0.2295070 | -0.2295117   | 1.000021 |
| 11      | -0.1857220 | -0.1857237   | 1.000009 |
| 12      | -0.1477510 | -0.1477514   | 1.000003 |
| 13      | -0.1152270 | -0.1152259   | 0.999990 |
| 14      | -8.776970(-02) | -8.776691(-02) | 0.999968 |
| 15      | -6.498640(-02) | -6.498273(-02) | 0.999944 |
| 16      | -4.647400(-02) | -4.646991(-02) | 0.999912 |
| 17      | -3.181750(-02) | -3.181330(-02) | 0.999868 |
| 18      | -2.059000(-02) | -2.058616(-02) | 0.999814 |
| 19      | -1.235370(-02) | -1.235037(-02) | 0.999731 |
| 20      | -6.659580(-03) | -6.657024(-03) | 0.999616 |
| 21      | -3.048890(-03) | -3.047136(-03) | 0.999425 |
| 22      | -1.053690(-03) | -1.052748(-03) | 0.999106 |
| 23      | -1.645210(-04) | -1.983400(-04) | 1.205560 |
| 24      | -2.697000(-06) |           |          |

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| Index | VSCA       | Trost et al. | Ratio     |
|-------|------------|--------------|-----------|
| 1     | -0.9410443| -0.9410460   | 1.000002  |
| 2     | -0.8299963| -0.8300020   | 1.000007  |
| 3     | -0.7276415| -0.7276457   | 1.000006  |
| 4     | -0.6336915| -0.6336930   | 1.000002  |
| 5     | -0.5478480| -0.5478520   | 1.000007  |
| 6     | -0.4698206| -0.4698229   | 1.000005  |
| 7     | -0.3992947| -0.3992968   | 1.000005  |
| 8     | -0.3359533| -0.3359561   | 1.000008  |
| 9     | -0.2794718| -0.2794734   | 1.000005  |
| 10    | -0.2295109| -0.2295117   | 1.000003  |
| 11    | -0.1857222| -0.1857237   | 1.000008  |
| 12    | -0.1477498| -0.1477514   | 1.000010  |
| 13    | -0.1152247| -0.1152259   | 1.000010  |
| 14    | -8.7766358e-02| -8.7766914e-02| 1.000006  |
| 15    | -6.4982534e-02| -6.4982730e-02| 1.000003  |
| 16    | -4.6469838e-02| -4.6469911e-02| 1.000002  |
| 17    | -3.1813146e-02| -3.1813309e-02| 1.000005  |
| 18    | -2.0585953e-02| -2.0586161e-02| 1.000010  |
| 19    | -1.2350173e-02| -1.2350373e-02| 1.000016  |
| 20    | -6.6568735e-03| -6.6570240e-03| 1.000023  |
| 21    | -3.0470500e-03| -3.0471360e-03| 1.000028  |
| 22    | -1.0526883e-03| -1.0527480e-03| 1.000057  |
| 23    | -1.9832170e-04| -1.9834000e-04| 1.000092  |
| 24    | -2.6957891e-06| -2.6970000e-06| 1.000449  |
FIG. 5: Behavior of the eigenvalue function $F(E)$ with energy on a semi-log scale for the Trost et al. Lennard-Jones molecule. The vertical lines indicate the eigenvalue position. Energies are in potential depth $\epsilon$ units.
els. Generally it requires performing analytically Taylor series expansion to any order of an arbitrary potential function that might require the combination of numerical, symbolic manipulation and functional fitting techniques. Despite these difficulties, the results of the VSCA are rewarding.

The use of the RK4 and the VSCA methods jointly paves the way to a precise comparative evaluation of the accuracy of the spectra obtained. In practice, the RK4 method can be used in optimisation problems whereas the VSCA is more adapted to the direct evaluation of the spectra.

In this work, we did not consider molecular rotation, nevertheless the CFM is adapted to solve accurately Ro-Vibrational problems as well as any RSE diagonalisation problem.

The methodology we describe in this work enables one to tackle precisely weakly bound states that are of great importance in low-energy scattering of atoms and molecules and generally in Bose-Einstein condensation problems [2].

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