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Article

Analysis of the accuracy of calculations using Duo and Level diatomic nuclear motion programs

Irina I. Mizus [a,b], Lorenzo Lodi [c,b], Jonathan Tennyson [c], Nikolai F. Zobov [b], Oleg L. Polyansky [c,b,*]

[a] Holon Institute of Technology, Golomb Street, 52, Holon, 5810201, Israel
[b] Institute of Applied Physics, Russian Academy of Sciences, 46 Ulyanov Street, Nizhny Novgorod, 603950, Russia
[c] Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

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ABSTRACT

Analysis of the accuracy of two programs widely-used for computing ro-vibrational spectra of diatomic molecules, namely Duo and Level, is presented. Using model systems for which analytic results are available it is shown that compared to Level, Duo gives similar or usually higher accuracy for line intensities, and is accurate for calculations of bound state energies and corresponding wavefunctions. Furthermore, Duo provides matrix elements accurate to about 10^{-4}–10^{-5}% relative to the analytic values, which is sufficient for developing of accurate methods for experimental determination of some macroscopic gas features, such as pressure, concentration, temperature, and so on; this level of accuracy can only be achieved with Level by significantly increasing the number of grid points in the calculation.

1. Introduction

Spectroscopic measurements of transition frequencies (line positions) of gaseous molecules can provide, in favourable conditions, some of the most accurate measurements in the whole of science, with relative uncertainties as low as a few parts in 10^{-12}. Even leaving aside such extreme accuracy, standard laboratory set-ups can routinely provide line positions of rotation-vibrational lines in the infrared (IR), microwave and optical region with relative uncertainties of a few parts in 10^{-9}, a level of accuracy that at present can be matched by *ab initio* theory only for diatomic molecules with two [1] or possibly three [2] electrons.

The situation is very different for line intensities, for which the level of accuracy achievable by both experiments and theory is much lower, typically in the range 1%–20%. Nevertheless, over the past twenty years or so it has become possible in some cases to obtain line intensities with an accuracy better than 1% [3]. Such as accuracy is required for several applications including monitoring of the Earth's atmosphere [4] and might be necessary for the analysis of the atmospheres of the exoplanets. Very recently agreement between experiment and theory for some CO_2 lines to a level better than 0.01% has been reported for the first time [5]. Very accurate line intensity determination has a number of potential applications in metrology, for example for new standards of temperature [6], pressure [7] and isotopic composition [8], although these may requires accuracies one or even two orders of magnitude higher than presently possible.

For calculations with sub-percent accuracy it has generally been assumed that the existing variational nuclear motion programs used to solve the Schrödinger equation for the rotation-vibration line positions and intensities, such as [9], can compute line intensities to better than 0.1% accuracy. However, if we are aiming accuracies of 0.01% or even 0.001% for experiment and theory, the accuracy of the calculation for a given potential energy surface (PES) and dipole moment surface (DMS) has to be better than these thresholds. Only in this case will the final accuracy of the calculations be determined by the accuracy of the underlying PES and DMS, and unaffected by the nuclear motion calculations. In such situations tests of the accuracy of existing programs becomes necessary. Exactly solvable problems provide a natural basis for testing the accuracy achievable in practical computations.

In this paper we consider diatomic molecules; there are two reasons for this. Firstly, the analysis of exactly solvable one-dimensional problems is much simpler, than the ones for polyatomic molecules. Secondly, such one-dimensional models can closely resemble real molecules, such as for example CO; the CO molecule will be used in metrological studies, such as the studies of the pressure standards [10, 11].

We present a careful analysis of the computational accuracy of two diatomic program packages – the recently developed program Duo [12], and the more mature code Level (version 16) [13]; both of these packages are widely used for computing spectra and spectroscopic

* Corresponding author at: Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom.
E-mail address: o.polyansky@ucl.ac.uk (O.L. Polyansky).

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features of diatomic molecules. Indeed Level has been used to build a high accuracy model for H_2 [14]. Our analysis was performed using three simple cases: (i) a quantum harmonic oscillator system; (ii) an artificial Morse oscillator quantum system; and (iii) CO represented as Morse oscillator. We call a system "artificial" if the parameters are not based on those for an actual molecule and is considered just a simple benchmark quantum problem, which can be solved analytically.

The intensity of an absorption line for a multipole transition operator depends on matrix elements of the form

$$M_{mn}^{(l)} = \left\langle m \left| (r - r_e)^l \right| n \right\rangle, \tag{1}$$

where m, n are vibrational quantum numbers of the system, l is an integer, and $r - r_e$ is the displacement from equilibrium separation (r_e). The transition intensity is proportional to the squared absolute value of the matrix element: $I \sim \left| M_{mn}^{(l)} \right|^2$ with $l = 1$ for an electric dipole transition and $l = 2$ for an electric quadrupole, which is why the accuracy of such matrix element calculations is important. Indeed it has been established that particular care is needed when computing the intensity of high overtones bands [15,16].

We show that for the three test cases listed above Duo gives similar or even higher accuracy for transition intensities and corresponding matrix elements than Level, and a more than satisfactory accuracy of calculations for bound state energies and corresponding wavefunctions. This paper is organised as follows. In the next section we briefly discuss the differences between the two codes considered here. Section 3 describes the analytic basis for calculations of bound state energies, wavefunctions and matrix elements for the three quantum systems considered. In Section 4 we perform a careful comparison of analytic results with the corresponding values computed with Duo and Level, and with the experimental values when possible. The Section 5 summarizes our findings and concludes the paper.

2. General comparison of Duo and Level

Level is a widely-used program with a long and distinguished history, and one might wonder why there was a need for a new program for the spectroscopy of diatomic molecules. It is therefore perhaps worthwhile to spend a few words comparing some general differences between Level [13] and Duo [12].

In terms of functionalities, the main difference between the two programs is that Level is designed for computing rotational-vibrational levels originating from isolated spin–singlet electronic states, while Duo can deal with virtually any situation. Level is written with a focus on the usual $^1\Sigma^{\pm}$ electronic terms, and it cannot deal with interactions between different electronic states at all; as a result, Level is usually inadequate for describing the spectra of open-shell molecules. Conversely, Duo is a very general program which allows for the inclusion many kinds of couplings between different electronic terms [17] including recently hyperfine interactions [18], and therefore can be used to treat all types of diatomic molecules. Duo also implements rather sophisticated strategies to fit curves (energy curves and coupling curves) to experimental data, which Level does via an auxiliary program Dpotfit [19]. Level can be used to treat long-lived, quasibound states, see Doss et al. [20] for example; Duo has also been adapted to treat near-dissociation continuum problems including quasibound states [21]. Duo has also been adapted to simulate bound–free (photodissociation) spectra [22] and has been recently extended to compute quadrupole transition intensities [23].

Next, we note that Level is written in FORTRAN77, while Duo uses the much more modern Fortran2003. This fact may be considered irrelevant from the point of view of the final user, but from a developers' point of view Duo is written in a way that reflects modern programming best practices and, it is hoped, this fact makes Duo easier to read, maintain and extend. Another technical difference is that, although both programs use text-based input files, Level uses an old-fashioned column-based format, while Duo a more modern and user-friendly one. All calculations were performed using standard double precision arithmetic within the Intel Fortran compiler of version 19.1.3.304 using the Intel Maths Kernel Library (MKL) on a workstation with an Intel Xeon E5-4640 processor running CentOS Linux 7.

Importantly for the comparisons of this paper, Level and Duo are based on different algorithms for solving the one-dimensional Schrödinger equation, namely Numerov's method and the sinc discrete variable representation (DVR) method. Both algorithms have their pros and cons, but the basic point, as demonstrated below, is that Duo's algorithm provides *much* faster convergence than Level's. We discuss these difference in more detail in the next subsection.

2.1. Numerical method used for the vibrational Schrödinger equation

Level uses Numerov's method, which has a long and distinguished history in solving the one-dimensional Schrödinger equation, while Duo is based on the sinc DVR approach. A useful general discussion which introduces both the Numerov and sinc DVR approaches in a common theoretical framework can be found in Refs. [24,25]. In the following we only make a few remarks without any aim at completeness. The Numerov method takes its name from the Russian astronomer Boris Numerov, who introduced it in the 1920s for astronomical calculations [26,27]. Specifically, Numerov's method is a convenient way to discretise a second-order ordinary differential equations (ODEs) of the form $y''(x) = f(x, y)$, i.e. when the first-derivative term is not present.

The Numerov formula is a three-point recurrence relation which, given the value of y at two adjacent points, predicts a value for y at the successive (or preceding) grid point. The Schrödinger equation can be written in the form

$$\psi''(x) = f(x)\psi(x), \quad \text{with} \quad f(x) = \frac{2m}{\hbar^2}\left[V(x) - E\right], \tag{2}$$

meaning that the Numerov method can be used to propagate the value of $\psi(x)$ from two initial values. Because the value of the energy E is unknown, for solving the Schrödinger equation the Numerov method has to be accompanied by a strategy to find E. This often consists of a so-called "shooting" approach: an initial value for E is guessed, and the function $\psi(x)$ is computed for all grid points; then it is checked if the guessed value of E is too high or too low, and a new, improved value of E is generated, and so on. One particularly efficient strategy was introduced in 1961 by Cooley [28] and then implemented in 1963 by Cashion [29], so that the whole method is sometimes called Numerov-Cooley or Numerov-Cooley-Cashion. In the same year Cashion and Zare produced a document for internal use at the Lawrence Berkeley National Laboratory, reporting not only a description of the method but also the full listing of the Fortran code of the program [30]. This program can be considered as the direct ancestor of today's version of Level, which is also based on the Numerov-Cooley method. One advantage of the Numerov-Cooley method is that it requires very little memory, which was probably a very important consideration in those early years. The calculation of each eigenvalue/eigenvector pair can be computed independently and the amount of memory needed is, for a grid with N points, of the order of N units of floating-point storage (typically 4 or 8 bytes). If one recomputes the value of the potential whenever necessary without storing it in memory the memory requirements can be reduced much further, down to a handful of bytes. The error in the computed eigenvalues in Numerov-based approaches is $O(h^4)$ (h being the grid step size), which is usually acceptably fast, both in terms of computational effort and for containing the numerical round-off error. To expand on this last point, in the Numerov formula there are factors of the type $y_i - y_{i-1}$, and for $h \to 0$ the calculation of these is subject to greater and greater round-off error. A more detailed analysis shows that the round-off error increases as h^2; as a result, when working with finite precision, the error for Numerov-Cooley method is given by the sum of two terms: $A/h^4 + Bh^2$. This implies that, when doing calculations with a fixed precision (e.g., double precision

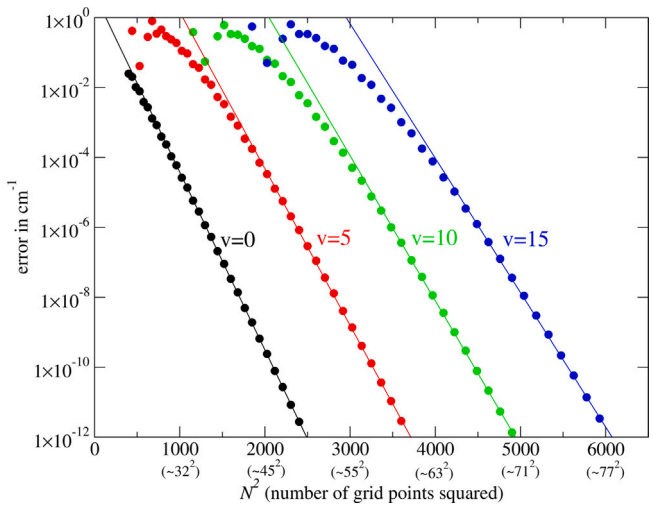

Fig. 1. Convergence of energy levels of a harmonic oscillator using Duo and a uniform grid ($r_{\min}$ and $r_{\max}$ are kept fixed). The straight-line behaviour indicates that the logarithm of error depends linearly on N^2, which implies a convergence of the $\exp(-\alpha/h^2)$ type.

numbers) there is an optimal minimal grid step size h_{opt}, and using a smaller grid size will result in greater error because of round-off. Finally, the computational effort scales proportionally to the number of points $O(N)$.

The method used by Duo is the sinc DVR. This method is sometimes also called Colbert-Miller DVR, because these two authors derived it in a much-cited paper from 1992 [31]. However, essentially the same method had been independently derived and applied to the Schrödinger equation by Guardiola and Ros [24] and by Lund and Riley [32] in 1984, and closely related methods were already known in the mathematical literature [33]. A description of this method from the point of view of the discrete-variable-representation (DVR) approach can be found in the article by Littlejohn et al. [34] and in the book by Tannor [35]. In this approach, the Schrödinger equation is transformed into a standard matrix eigenvalue/eigenvector problem, with a real symmetric matrix of size $N \times N$. On the one hand this involves a much larger memory usage of the order of N^2, as the matrix has to be stored (although one can reduce memory use by recomputing matrix elements whenever needed). In practice this has ceased to be a problem for this kind of applications in the late-1980s, as the typical memory usage was of the order of 0.1 to 2 MB, which is totally negligible on any modern machine. Typical algorithms to find the full spectrum of dense matrices generally scale as N^3, which is much steeper than the N of the Numerov method. However, this is more than compensated by the *much* faster rate of convergence of the sinc method, for which errors are expected to scale at least as fast as $\exp(-\alpha/h^a)$, with α in the range 1–2, which is much faster than the A/h^4 of Numerov's method. So for high enough accuracy the sinc DVR method will always provide faster convergence, both with respect to the number of grid points and to compute time. As an example Fig. 1 reports convergence speed of Duo for several levels of a harmonic oscillator, revealing super-exponential convergence of the type $\exp(-\alpha/h^2)$.

3. Analytic calculations

As a benchmark for analyzing the computational accuracy of Duo and Level, analytic calculations were performed for three cases simple quantum systems. Their details are described below.

3.1. Quantum harmonic oscillator

As a specific example of a one-dimensional harmonic quantum oscillator, we consider an artificial system with a harmonic potential

$$V(r) = \frac{1}{2} k_s (r - r_e)^2, \tag{3}$$

with equilibrium distance $r_e = 3$ Å, force constant $k_s = 50\,000\ \text{cm}^{-1}/\text{Å}^2$, and mass of each atom set to $m_0 = 3.371525838831536$ Da, which ensures that the harmonic frequency $\nu_0 = \sqrt{\frac{2k_s}{m_0}}$ is exactly $1000.0000\ \text{cm}^{-1}$, and the bound state energies of the system are just half-integer numbers multiplied by $1000.0000\ \text{cm}^{-1}$: $500\ \text{cm}^{-1}$, $1500\ \text{cm}^{-1}$, $2500\ \text{cm}^{-1}$, etc.

The expression for the corresponding wavefunctions is well-known:

$$\psi_n(x) = \frac{1}{\sqrt{2^n\, n!\, \sqrt{\pi} a}} \exp\left(-\frac{x^2}{2a^2}\right) H_n\left(\frac{x}{a}\right), \tag{4}$$

where $a = \sqrt{\frac{2\hbar}{m_0 \omega_0}} \approx 0.14142$ Å in our case, ω_0 is an angular harmonic frequency, $\omega_0 = 2\pi\nu_0$, $x = r - r_e$, and H_n are Hermite polynomials. General expressions for the (m, n) matrix element of a potential function x^j were obtained by Wilcox [36]:

$$\langle m|x^j|n\rangle = \sum_{k=b}^{m} \frac{\alpha^{-j}\, j!\, \sqrt{m!\, n!}}{k!(m-k)!(n-k)!\, 2^w\, w!}, \tag{5}$$

where b is zero or $\frac{1}{2}(m+n-j)$, whichever is larger, $w = k + \frac{1}{2}(j-m-n)$, and $\alpha = \sqrt{m_0\omega_0/\hbar} = \sqrt{2}/a \approx 10.000\ \text{Å}^{-1}$. Here it is assumed that (i) $n \geq m$ as the operator is Hermitian so $\langle m|x^j|n\rangle = \langle n|x^j|m\rangle$; (ii) $m+n-j$ must be even to assure that b is integer else the matrix element is zero; and (iii) there is a well-known selection rule for the harmonic oscillator system that $\langle m|x^j|n\rangle$ vanishes unless $j \geq n-m$. From (ii) and (iii) one can conclude that $n-m$ must be even if j is even, and vice versa.

Assuming that $m+n-j = 2l$, where l is integer, and introducing a summation index $i = 0, 1, 2, 3, \ldots$ we obtain $b = l$ if $l > 0$ and 0, otherwise; $k = b + i = l + i$ for $l > 0$ and $k = i$ for $l \leq 0$; and $w = b + i - l = i$ for $l \geq 0$ and $w = i - l$, otherwise. To ensure that condition (iii) is satisfied l must be $\leq m$.

Thus, we can rewrite the expression for $\langle m|x^j|n\rangle$ as:

$$\langle m|x^j|j+2l-m\rangle = \sum_{i=0}^{m-l} \frac{\alpha^{-j}\, j!\, \sqrt{m!\,(j+2l-m)!}}{(l+i)!\,(m-l-i)!\,(j+l-m-i)!\, 2^i\, i!}, \tag{6}$$

if $0 \leq l \leq m$, and

$$\langle m|x^j|j+2l-m\rangle = \sum_{i=0}^{m} \frac{\alpha^{-j}\, j!\, \sqrt{m!\,(j+2l-m)!}}{i!\,(m-i)!\,(j+2l-m-i)!\, 2^{i-l}\,(i-l)!}, \tag{7}$$

if $l < 0$. From Eq. (6) one can obtain a simple expression for an important special case, when $n = m + j$, and thus $l = m \geq 0$:

$$\begin{aligned}\langle m|x^j|m+j\rangle &= \frac{\alpha^{-j}\, j!\, \sqrt{m!\,(m+j)!}}{m!\, j!} \\ &= \alpha^{-j} \sqrt{(m+1)(m+2)\ldots(m+j-1)(m+j)}.\end{aligned} \tag{8}$$

For the matrix element $\langle m-j|x^j|m\rangle$ we can use the substitution $t = m - j$ to show that

$$\begin{aligned}\langle m-j|x^j|m\rangle = \langle t|x^j|t+j\rangle &= \alpha^{-j} \sqrt{(t+1)(t+2)\ldots(t+j-1)(t+j)} \\ &= \alpha^{-j} \sqrt{m(m-1)\ldots(m-j+2)(m-j+1)}.\end{aligned} \tag{9}$$

To compare Duo and Level calculations, we consider $j = 1$, 2 and 3. Therefore, we need the following expressions for the non-zero matrix elements:

- $j = 1$; then $n - m$ must be odd, too, and we have a single case which satisfies the selection rule $j \geq n - m$, namely: $n = m + 1$, for which we obtain:

$$\langle m|x|m+1\rangle = \langle m+1|x|m\rangle = \alpha^{-1}\sqrt{m+1}. \tag{10}$$

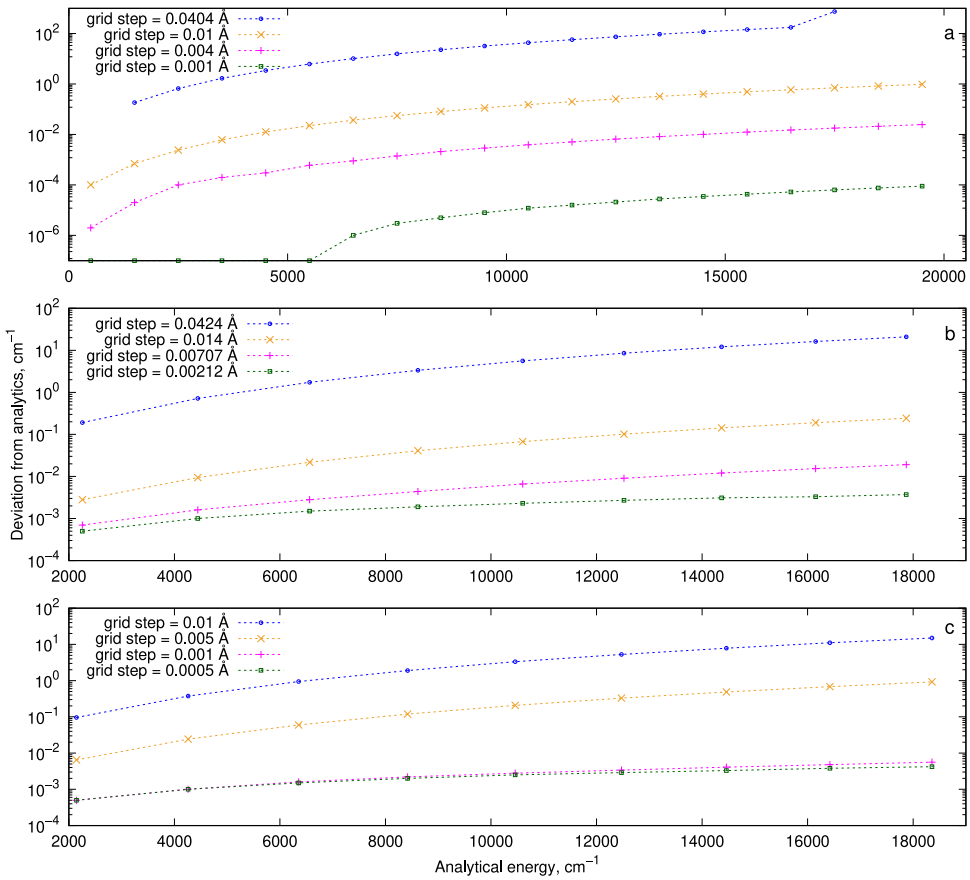

Fig. 2. Convergence of LEVEL energy levels as a function of grid step for three systems: a – for the artificial harmonic oscillator, b – for the artificial Morse oscillator, and c – for the CO molecule.

- $j = 2$; here $n - m$ must be even and can be equal to 0 or 2. For $n - m = 2$ we have:

$$\langle m|x^2|m+2\rangle = \langle m+2|x^2|m\rangle = \alpha^{-2}\sqrt{(m+1)(m+2)}. \tag{11}$$

When $n = m$, we have $l = m - 1$, and for the case $n = m = 0$ the value $l = -1 < 0$, so we should apply Eq. (7); it is easy to show that in this case $\langle 0|x^2|0\rangle = \alpha^{-2}$. If $n = m > 0$, then $l \geq 0$, and applying Eq. (6):

$$\langle m|x^2|m\rangle = \sum_{i=0}^{1} \frac{2\alpha^{-2} m!}{(m+i-1)!\,(1-i)!^2\, 2^i\, i!} = \alpha^{-2}(2\,m+1);$$

combining both cases gives

$$\langle m|x^2|m\rangle = \alpha^{-2}(2\,m+1). \tag{12}$$

- $j = 3$; here $n - m$ must be odd and can be equal to 1 or 3. For $n = m + 3$ we have:

$$\langle m|x^3|m+3\rangle = \langle m+3|x^3|m\rangle = \alpha^{-3}\sqrt{(m+1)(m+2)(m+3)}. \tag{13}$$

When $n = m + 1$, again $l = m - 1$. Acting as above for $j = 2$ gives the final non-zero matrix elements:

$$\langle m|x^3|m+1\rangle = \langle m+1|x^3|m\rangle = 3\alpha^{-3}(m+1)^{3/2}. \tag{14}$$

3.2. Quantum Morse oscillator

The Morse potential is very popular for modeling simple anharmonic diatomic potentials and is expressed as [37]:

$$V(r) = D_e\left(1 - \exp\left(-a(r - r_e)\right)\right)^2, \tag{15}$$

where r_e is the equilibrium distance, D_e is the dissociation energy, and a is a scaling factor. Bound state energies of a diatomic can be predicted with satisfactory accuracy using a Morse potential which gives a simple well-known expression for its energy levels [37]:

$$E_n = \hbar\omega_e\left(\left(n+\frac{1}{2}\right) - x_e\left(n+\frac{1}{2}\right)^2\right), \tag{16}$$

where n is the vibrational quantum number, ω_e is the harmonic frequency, and x_e is an anharmonicity factor, which can be expressed as $x_e = \frac{\omega_e}{4D_e}$.

The expression for the corresponding wavefunctions is also well-known [37]:

$$\psi_n(y) = N_n\,\exp(-y/2)\,y^{\beta/2}\,L_n^{\beta}(y), \tag{17}$$

where $y = A\exp(-a(r - r_e))$, $A = 1/x_e$, $\beta = A - 2n - 1$, the normalisation constant is expressed through Γ functions as:

$$N_n = \left(\frac{a\,\beta\,n!}{\Gamma(A-n)}\right)^{1/2},$$

and $L_n^{\beta}(y)$ are generalised Laguerre polynomials [38]:

$$L_n^{\beta}(y) = \sum_{i=0}^{n} \frac{(-1)^i\,\Gamma(\beta+n+1)}{i!\,(n-i)!\,\Gamma(\beta+i+1)}\,y^i.$$

A general procedure for obtaining analytic (n, m) matrix elements of function x^j for the Morse oscillator was derived by Rong et al. [39] on the basis of calculations by Sage [40]. This procedure is carried out in two steps. First, the matrix elements of y^{λ} are calculated as:

$$\langle \nu+m|y^{\lambda}|m\rangle = \frac{N_0\,N_{\nu}}{a}\sum_{i=0}^{m} \times \frac{\Gamma(A+\lambda-m-\nu-i-1)\Gamma(i-\lambda+1)\Gamma(i-\lambda+\nu+1)}{\Gamma(i+\nu+1)\Gamma(m-i+1)\Gamma(i+1)\Gamma(1-\lambda+\nu)\Gamma(1-\lambda-\nu)}, \tag{18}$$

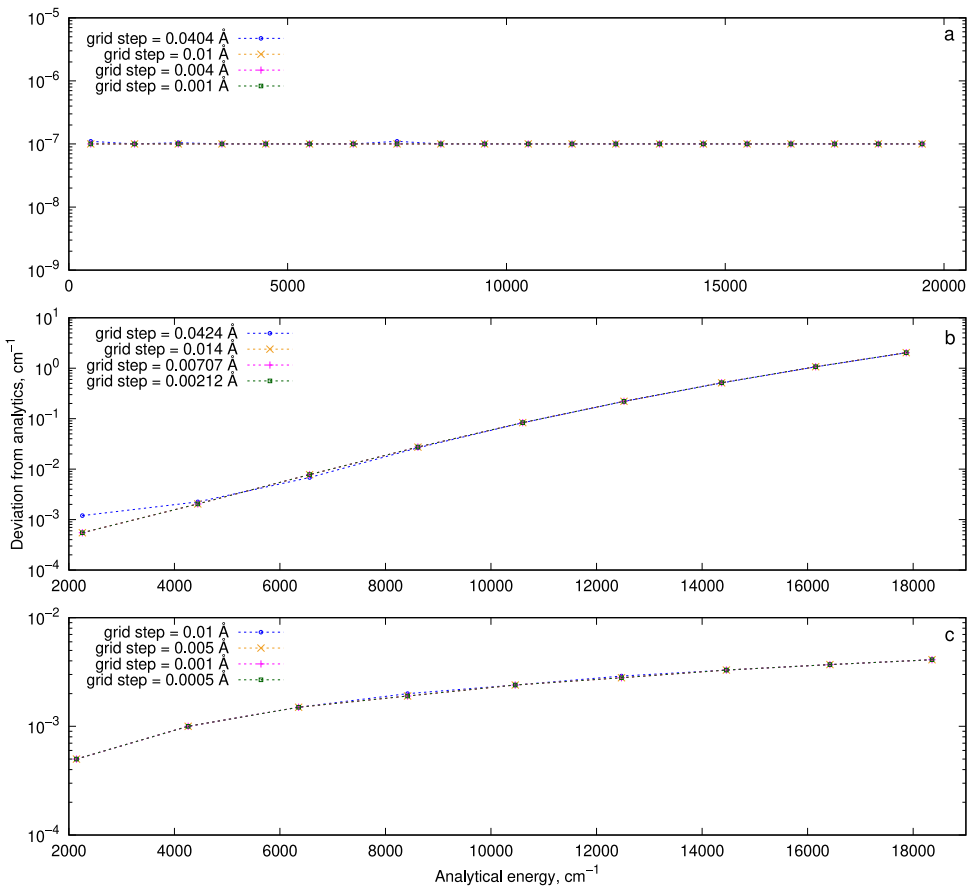

Fig. 3. Convergence of Duo energy levels as a function of the grid step for three quantum systems: a – for the artificial harmonic oscillator, b – for the artificial Morse oscillator, and c – for the CO diatomic.

where $\nu = n - m \geq 0$ and λ is an integer parameter. In the second step, the matrix elements of $x^j = (r - r_e)^j$ are calculated using the relationship:

$$x^j = \frac{(-1)^j}{a^j} \frac{d^j}{d\lambda^j} \left(\frac{y}{A}\right)^\lambda \Bigg|_{\lambda=0}. \tag{19}$$

For comparison with calculations using Duo and Level, we consider Morse potentials with $1 \leq j \leq 6$, $m = 0$ and $n = \nu$, $0 \leq n \leq 9$. In this case we have the following expression for the matrix element of y^λ:

$$\langle n|y^\lambda|0\rangle = \sqrt{\frac{(A-1)(A-2n-1)\,n!}{\Gamma(A)\Gamma(A-n)}} \times \frac{\Gamma(A+\lambda-n-1)\Gamma(1-\lambda)\Gamma(n+1-\lambda)}{\Gamma(n+1)\Gamma(1-\lambda+n)\Gamma(1-\lambda-n)}. \tag{20}$$

To obtain the matrix element of x^j, we apply the derivative procedure of Eq. (19):

$$\langle n|x^j|0\rangle = \frac{(-1)^j}{a^j} \frac{d^j}{d\lambda^j} \left(\frac{\langle n|y^\lambda|0\rangle}{A^\lambda}\right)\Bigg|_{\lambda=0}. \tag{21}$$

The resulting Eqs. (20) and (21) are, however, rather computationally expensive to evaluate. The equations for the matrix elements $\langle n|x^j|0\rangle$, which are cheaper to compute, but also less compact, are given by Eqs. (33)–(47) of Rong et al. [39].

Below we consider two Morse oscillator systems with different parameters:

1. An artificial Morse oscillator quantum system
   For this case we chose the following parameters: the mass of each atom $m_0 = 1.00$ Da, the dissociation energy $D_e = 40\,000\,\text{cm}^{-1}$, the scaling factor $a = 1.0\,\text{Å}^{-1}$, the equilibrium distance $r_e = 2.0$ Å. The harmonic frequency can be obtained from a simple expression: $\omega_e = 2a\sqrt{\frac{D_e}{m_0}} \approx 2322.5942\,\text{cm}^{-1}$, the anharmonicity factor $x_e = \frac{\omega_e}{4D_e} \approx 0.014516$, and $A = 1/x_e \approx 68.8885$.
2. Vibrations of the CO molecule represented by a Morse oscillator
   For CO we used parameters due to Nasser et al. [41]: the reduced mass $\mu = 6.8562086$ Da, the dissociation energy $D_e = 90\,540.574\,\text{cm}^{-1}$, the scaling factor $a = 2.299397\,\text{Å}^{-1}$, the equilibrium distance $r_e = 1.1283$ Å. Thus, the harmonic frequency can be obtained as $\omega_e = a\sqrt{\frac{2D_e}{\mu}} \approx 2169.8111\,\text{cm}^{-1}$, the anharmonicity factor $x_e = \frac{\omega_e}{4D_e} \approx 0.0059913$, and $A = 1/x_e \approx 166.9096$.

4. Comparison with computed data

Here we present the results of calculations using Duo and Level for vibrational energies, wavefunctions and some matrix elements in three cases considered above, and compare them with our results of analytic calculations. In order to make such a comparison valid, the fully converged calculations have to be performed by both programs. The choice of the grids of both programs has been made in such a way, that the further improvement had no influence on the value of highest energy considered down to at least $10^{-3}\,\text{cm}^{-1}$ or 7 to 8 significant figures.

4.1. Quantum harmonic oscillator

The parameters chosen for the artificial harmonic oscillator system we consider ensure that its bound state energies are just half-integer

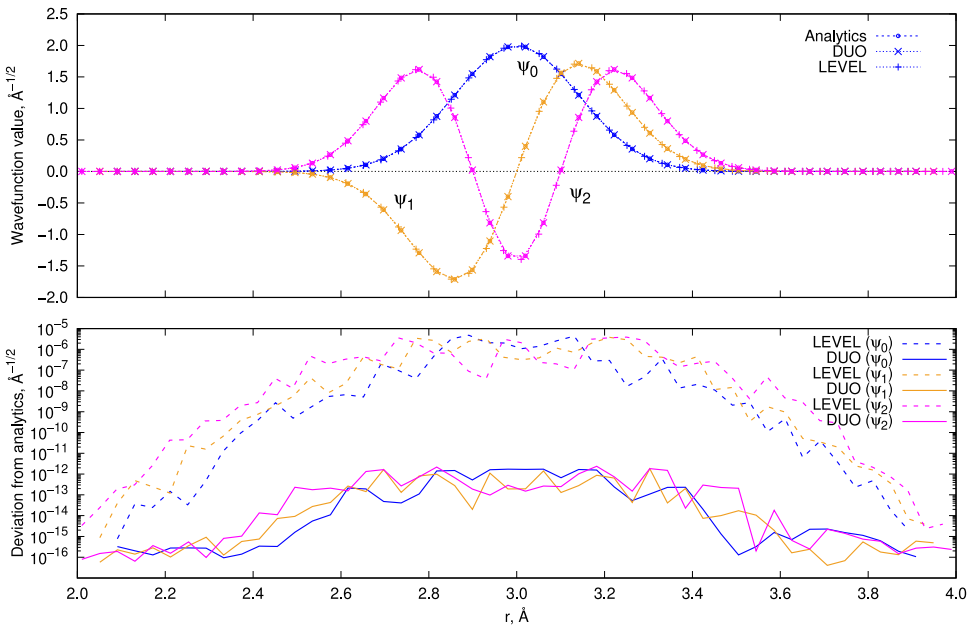

Fig. 4. Comparison of analytic wavefunctions with computed ones for an artificial harmonic oscillator. The upper plot shows computed and calculated wavefunctions for the three lowest vibrational states as a function of an internuclear distance; the lower plot gives the absolute difference between the computed results from the analytic ones.

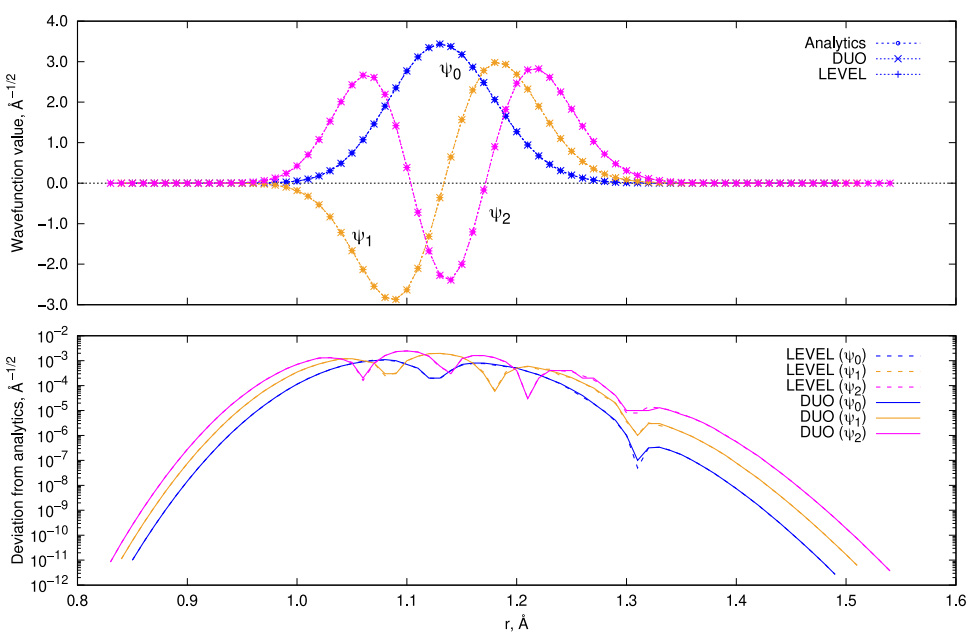

Fig. 5. Comparison of the analytic wavefunctions with the computed ones for CO represented by a Morse oscillator. The upper plot shows computed and calculated wavefunctions for the three lowest vibrational states as a function of an internuclear distance; the lower plot gives the absolute difference between the computed results from the analytic ones.

numbers multiplied by 1000.0000 cm^{-1}: 500 cm^{-1}, 1500 cm^{-1}, 2500 cm^{-1}, etc. Our computations used equidistant grids spanning $R_{min} = 1$ to $R_{max} = 5$ Å: for Duo a step of $h = 0.0404$ Å (100 grid points) was used, while for Level $h = 0.001$ Å (4000 grid points) was used.

Comparison of energies

Figs. 2 and 3 show that the 20 lowest energies computed using Duo coincide with the theoretical ones at least up to the sixth decimal place, while Level shows this accuracy only up to 5500 cm^{-1}; for higher bound states its accuracy becomes worse gradually and reaches about 10^{-4} cm^{-1} for the energy level with the vibrational quantum number $n = 19$. Besides, to achieve convergence with eigenvalue convergence parameter 10^{-6} cm^{-1}, we had to reduce the Level step size by a factor of 40 compared with the one used in the Duo calculations, and to add trial energies to Level's input data as we did not manage to calculate all the bound states of the harmonic oscillator system using Level without this manual intervention.

Comparison of wavefunctions

The main goal of this work is to clarify if Duo or Level can provide an accuracy of at least 0.0001% while computing of intensities for small diatomics, that is of great importance for experimental needs at the moment. From this point of view, all the comparisons of wavefunctions performed in this work have rather an illustrative purpose, which is needed to ensure that not only intensities, but eigenfunctions and energies can be obtained with satisfactory accuracy, as well. That is

Table 1
Comparison of analytic matrix harmonic oscillator elements $\langle m|x|n\rangle$ with ones computed using Duo and Level. $\delta_{\text{Duo/Level}} = \left|\left|\langle m|x|n\rangle_{\text{Duo/Level}}\right| - \left|\langle m|x|n\rangle_{\text{an}}\right|\right| / \left|\langle m|x|n\rangle_{\text{an}}\right| \times 100$, % is the relative percentage deviation of the Duo/Level results from the analytic ones.

n	m	$\langle m\|x\|n\rangle_{\text{an}}$, Å	δ_{Duo}, %	δ_{Level}, %
1	0	0.1000000	0.0	1.6×10^{-7}
2	1	0.1414214	1.7×10^{-7}	7.6×10^{-7}
3	2	0.1732051	1.4×10^{-7}	1.0×10^{-6}
4	3	0.2000000	0.0	1.0×10^{-6}
5	4	0.2236068	1.1×10^{-7}	8.5×10^{-7}
6	5	0.2449490	1.1×10^{-7}	6.2×10^{-7}
7	6	0.2645751	4.2×10^{-8}	7.9×10^{-8}
8	7	0.2828427	1.7×10^{-7}	1.1×10^{-7}
9	8	0.3000000	0.0	1.4×10^{-7}
10	9	0.3162278	6.3×10^{-9}	1.8×10^{-7}
11	10	0.3316625	1.2×10^{-8}	2.2×10^{-7}
12	11	0.3464102	1.4×10^{-7}	2.6×10^{-7}
13	12	0.3605551	1.2×10^{-7}	3.1×10^{-7}
14	13	0.3741657	8.6×10^{-8}	3.7×10^{-7}
15	14	0.3872983	9.8×10^{-8}	4.2×10^{-7}
16	15	0.4000000	0.0	4.8×10^{-7}
17	16	0.4123106	1.1×10^{-7}	5.5×10^{-7}
18	17	0.4242641	6.8×10^{-8}	6.2×10^{-7}
19	18	0.4358899	8.0×10^{-8}	6.9×10^{-7}
20	19	0.4472136	1.1×10^{-7}	7.6×10^{-7}

why we limit ourselves to only considering of a few lowest stable states of the quantum systems.

Fig. 4 compares analytic and computed wavefunctions for the quantum harmonic oscillator system. The analytic wavefunctions of the three lowest vibrational states were calculated using Eq. (4). Their computed versions were obtained using Duo and Level.

However, there is a difference in the treatment normalization between these two packages. The Duo eigenvectors are normalized so that the sum of squares of the DVR points gives unity. Thus, to obtain the data shown in the Figs. 4, 5 and the Fig. 1 from the Supplementary material we had to multiply the Duo results by $c_{\text{Duo}} = 1/\sqrt{h}$, where h is the step size. We also adjusted the sign of the Duo wavefunctions so the overall phase coincided with the analytic ones.

Fig. 4 shows that all the computed wavefunctions coincide with the analytic ones within 10^{-5} Å$^{-1/2}$, which is about 5×10^{-4} % of the amplitudes. The accuracy of Duo is much better (up to six to seven orders of magnitude) than Level, and almost reaches the floating point numerical accuracy. All the Duo and analytic results coincide within 10^{-6} % for almost all grids considered, while Level shows generally much worse accuracy.

Comparison of matrix elements

A comparison between analytic and computed matrix elements $\langle m|x|n\rangle$, $\langle m|x^2|n\rangle$ and $\langle m|x^3|n\rangle$ is shown in Tables 1, 2, and in Table VIII of the Supplementary materials, respectively. These off-diagonal matrix elements have a phase ambiguity due to the arbitrary overall phase of the bra and ket wavefunctions. These signs do not effect intensity calculations and we present only (unsigned) absolute values. The tables contain data for the vibrational quantum numbers up to 20. Our calculations show that the relative deviations of the Duo results from the analytic ones is less than 5×10^{-7} % for all matrix elements. Meanwhile, the accuracy of the matrix elements obtained using Level is often much worse, with the relative deviations δ_{Level} being up to 10^{-4} % and in some cases larger than the ones of Duo by two to three orders of magnitude.

4.2. Artificial Morse oscillator

Our computations used equidistant grids spanning 0.3 to 4.5 Å with h = 0.0424 Å (100 grid points) in Duo and h = 0.0021 Å (about 2000 grid points) in Level to solve for the Morse potential with the parameters listed first in Section 3.2. As this case has appeared to be rather similar to the one from the following section, the detailed consideration of it one can find in the Supplementary material.

Table 2
Comparison of analytic harmonic oscillator matrix elements $\langle m|x^2|n\rangle$ with ones computed with Duo and Level. $\delta_{\text{Duo/Level}} = \left|\left|\langle m|x^2|n\rangle_{\text{Duo/Level}}\right| - \left|\langle m|x^2|n\rangle_{\text{an}}\right|\right| / \left|\langle m|x^2|n\rangle_{\text{an}}\right| \times 100$, % is the relative percentage deviation of the Duo/Level results from the analytic ones.

n	m	$\langle m\|x^2\|n\rangle_{\text{an}}$, Å	δ_{Duo}, %	δ_{Level}, %
0	0	0.01000000	0.0	2.9×10^{-6}
2	0	0.01414214	1.4×10^{-7}	4.2×10^{-7}
1	1	0.03000000	0.0	3.0×10^{-6}
3	1	0.02449490	1.2×10^{-7}	9.5×10^{-6}
2	2	0.05000000	0.0	2.7×10^{-6}
4	2	0.03464102	1.4×10^{-7}	1.3×10^{-5}
3	3	0.07000000	0.0	2.0×10^{-6}
5	3	0.04472136	1.1×10^{-7}	1.4×10^{-5}
4	4	0.09000000	0.0	8.0×10^{-7}
6	4	0.05477226	9.1×10^{-8}	5.5×10^{-6}
5	5	0.11000000	0.0	8.1×10^{-7}
7	5	0.06480741	3.1×10^{-8}	4.8×10^{-6}
6	6	0.13000000	0.0	1.4×10^{-7}
8	6	0.07483315	5.3×10^{-8}	2.7×10^{-8}
7	7	0.15000000	0.0	1.9×10^{-7}
9	7	0.08485281	4.7×10^{-8}	3.5×10^{-8}
8	8	0.17000000	0.0	2.5×10^{-7}
10	8	0.09486833	1.1×10^{-8}	6.3×10^{-8}
9	9	0.19000000	0.0	3.2×10^{-7}
11	9	0.10488088	1.7×10^{-7}	7.6×10^{-8}
10	10	0.21000000	0.0	4.0×10^{-7}
12	10	0.11489125	6.1×10^{-8}	9.6×10^{-8}
11	11	0.23000000	0.0	4.9×10^{-7}
13	11	0.12489996	2.4×10^{-8}	1.2×10^{-7}
12	12	0.25000000	0.0	5.8×10^{-7}
14	12	0.13490738	2.7×10^{-7}	1.4×10^{-7}
13	13	0.27000000	0.0	6.8×10^{-7}
15	13	0.14491377	3.2×10^{-7}	1.7×10^{-7}
14	14	0.29000000	0.0	7.9×10^{-7}
16	14	0.15491933	9.7×10^{-8}	2.0×10^{-7}
15	15	0.31000000	0.0	9.1×10^{-7}
17	15	0.16492423	1.2×10^{-8}	2.3×10^{-7}
16	16	0.33000000	0.0	1.0×10^{-6}
18	16	0.17492856	8.6×10^{-8}	2.7×10^{-7}
17	17	0.35000000	0.0	1.2×10^{-6}
19	17	0.18493242	4.9×10^{-8}	3.0×10^{-7}
18	18	0.37000000	0.0	1.3×10^{-6}
20	18	0.19493589	5.1×10^{-8}	3.4×10^{-7}
19	19	0.39000000	0.0	1.5×10^{-6}
20	20	0.41000000	0.0	1.6×10^{-6}

4.3. CO as a Morse oscillator

As above, to achieve convergence in the Level calculations to 10^{-6} cm^{-1}, we had to reduce the grid step size by a factor of 20 compared to the sinc DVR grid used by Duo. Thus, during these computations, equidistant grids between 0.8 and 3.79 Å used h = 0.01 Å (300 grid points) in Duo and h = 0.0005 Å (about 6000 grid points) in Level; the Morse potential (15) used a set of parameters given as the second list in Section 3.2.

Comparison of energies

A comparison of the energies computed using Duo and Level with the analytic energies and the available experimental data for the CO diatomic is given in the Table 3. The table shows that both packages obtain energies of the lowest 9 bound states for a CO diatomic with a relative accuracy of about 2×10^{-5} % for each state. The deviations of both Duo and Level results from the observed energies below 10 500 cm^{-1} are the same, as well, within 0.07 % which is a reflection of the accuracy of the Morse potential curve used for this study.

Comparison of wavefunctions

Fig. 5 compares the analytic and computed wavefunctions for CO and shows that all the computed wavefunctions coincide with the analytic ones within 0.01 Å$^{-1/2}$, which is about 0.25% of amplitudes.

Table 3
Comparison of the computed using Duo and Level CO diatomic energies with the analytic ones $E_{an} = E_n - E_0$ (bound state energies E_n were calculated using Eq. (16)) and the available experimental data E_{obs}. Here $\Delta_i^{an/obs} = E_i - E_{an/obs}$ is the absolute difference between the computed and the calculated/observed energies, and $\delta_i = |E_i - E_{an}|/E_{an} \times 100$, % is the relative percentage deviation of the computed result from the analytic values. The absolute deviations from the experimental data are shown in the last column and are almost equal for Duo and Level.

n	E_n, cm^{-1}	E_{an}, cm^{-1}	E_{obs}, cm^{-1}	Δ^{an}_{Duo}, cm^{-1}	δ_{Duo}, %	Δ^{an}_{Level}, cm^{-1}	δ_{Level}, %	Δ^{obs}, cm^{-1}
0	1081.6555							
1	3225.4668	2143.8112	2143.2714	−0.0005	2.37×10^{-5}	−0.0005	2.43×10^{-5}	−0.5393
2	5343.2782	4261.6226	4260.0625	−0.0010	2.35×10^{-5}	−0.0010	2.36×10^{-5}	−1.5591
3	7435.0897	6353.4342	6350.4394	−0.0015	2.34×10^{-5}	−0.0015	2.29×10^{-5}	−2.9933
4	9500.9014	8419.2459	8414.4698	−0.0020	2.32×10^{-5}	−0.0020	2.34×10^{-5}	−4.7741
5	11 540.7133	10 459.0578	10 452.2228	−0.0024	2.31×10^{-5}	−0.0025	2.35×10^{-5}	−6.8325
6	13 554.5253	12 472.8698		−0.0029	2.29×10^{-5}	−0.0029	2.32×10^{-5}	
7	15 542.3376	14 460.6820		−0.0033	2.28×10^{-5}	−0.0033	2.29×10^{-5}	
8	17 504.1499	16 422.4944		−0.0037	2.26×10^{-5}	−0.0038	2.30×10^{-5}	
9	19 439.9625	18 358.3069		−0.0041	2.25×10^{-5}	−0.0042	2.30×10^{-5}	

Table 4
Comparison of analytic matrix elements of CO $\langle n|x|0\rangle$, calculated using Eqs. (20) and (21), with the ones computed using Duo and Level. $\Delta_i = \left|\left|\langle n|x|0\rangle_i\right| - \left|\langle n|x|0\rangle_{an}\right|\right|$ is the absolute difference between the computed and the calculated values, and $\delta_i = \Delta_i / \left|\langle n|x|0\rangle_{an}\right| \times 100$, % is the relative percentage deviation of the computed results from the analytic ones.

n	$\langle n\|x\|0\rangle_{an}$, Å	Δ_{Duo}, Å	δ_{Duo}, %	Δ_{Level}, Å	δ_{Level}, %
0	3.9254×10^{-3}	9.500×10^{-10}	2.42×10^{-5}	9.50×10^{-10}	2.4201×10^{-5}
1	3.3763×10^{-2}	4.060×10^{-9}	1.20×10^{-5}	4.06×10^{-9}	1.2025×10^{-5}
2	-1.8590×10^{-3}	4.550×10^{-10}	2.45×10^{-5}	4.55×10^{-10}	2.4475×10^{-5}
3	1.6765×10^{-4}	6.180×10^{-11}	3.69×10^{-5}	5.18×10^{-11}	3.0898×10^{-5}
4	-1.9700×10^{-5}	9.600×10^{-12}	4.87×10^{-5}	3.70×10^{-12}	1.8782×10^{-5}
5	2.7690×10^{-6}	1.696×10^{-12}	6.12×10^{-5}	1.80×10^{-12}	6.4860×10^{-5}
6	-4.4549×10^{-7}	3.288×10^{-13}	7.38×10^{-5}	1.47×10^{-12}	3.2948×10^{-4}
7	7.9870×10^{-8}	6.902×10^{-14}	8.64×10^{-5}	8.37×10^{-13}	1.0482×10^{-3}
8	-1.5676×10^{-8}	1.544×10^{-14}	9.91×10^{-5}	3.81×10^{-13}	2.4314×10^{-3}
9	3.3253×10^{-9}	3.697×10^{-15}	1.11×10^{-4}	2.11×10^{-13}	6.3470×10^{-3}

Table 5
Comparison of analytic CO matrix elements $\langle n|x^2|0\rangle$, calculated using Eqs. (20) and (21), with the ones computed using Duo and Level. $\Delta_i = \left|\left|\langle n|x^2|0\rangle_i\right| - \left|\langle n|x^2|0\rangle_{an}\right|\right|$ is the absolute difference between the computed and calculated values, and $\delta_i = \Delta_i / \left|\langle n|x^2|0\rangle_{an}\right| \times 100$, % is the relative percentage deviation of the computed results from the analytic ones.

n	$\langle n\|x^2\|0\rangle_{an}$, Å	Δ_{Duo}, Å	δ_{Duo}, %	Δ_{Level}, Å	δ_{Level}, %
0	1.1588×10^{-3}	2.840×10^{-10}	2.45×10^{-5}	2.84×10^{-10}	2.4507×10^{-5}
1	4.4314×10^{-4}	1.617×10^{-10}	3.65×10^{-5}	1.62×10^{-10}	3.6489×10^{-5}
2	1.5827×10^{-3}	3.760×10^{-10}	2.38×10^{-5}	3.76×10^{-10}	2.3757×10^{-5}
3	-2.1475×10^{-4}	7.740×10^{-11}	3.60×10^{-5}	7.84×10^{-11}	3.6508×10^{-5}
4	3.0840×10^{-5}	1.494×10^{-11}	4.84×10^{-5}	1.37×10^{-11}	4.4553×10^{-5}
5	-4.9220×10^{-6}	2.995×10^{-12}	6.08×10^{-5}	1.89×10^{-12}	3.8501×10^{-5}
6	8.6693×10^{-7}	6.361×10^{-13}	7.34×10^{-5}	4.61×10^{-13}	5.3188×10^{-5}
7	-1.6657×10^{-7}	1.427×10^{-13}	8.57×10^{-5}	2.77×10^{-13}	1.6612×10^{-4}
8	3.4553×10^{-8}	3.406×10^{-14}	9.8572×10^{-5}	1.7676×10^{-13}	5.1156×10^{-4}
9	-7.6730×10^{-9}	8.535×10^{-15}	1.1123×10^{-4}	7.6745×10^{-14}	1.0002×10^{-3}

Between 1.05 and 1.40 Å the analytic and computed results coincide within 0.1%, and within 1% for almost all grid points in the whole range considered. The deviations of the Level and Duo results from the calculated ones are close to each other.

Comparison of matrix elements

The comparison between the absolute values of analytic and computed matrix elements $\langle n|x^j|0\rangle$, where $1 \le j \le 6$ and $0 \le n \le 9$, for the CO diatomic is shown in Tables 4, 5, and Tables IX–XII in the Supplementary materials, respectively.

The Tables show that relative deviations of the Duo results from the analytic ones are nearly independent of j and n, and are within 1.25×10^{-4} %, and are less than 0.0001% for the majority of cases, while for Level these deviations are similar or larger, with a maximum value of about 0.006%. Level and Duo show similar results for most cases, except for high vibrational quantum number, n, with $j \le 3$, where the accuracy of Level becomes worse.

Comparison of Einstein A coefficients

Finally, we present a comparison of Einstein A coefficients and the corresponding transition frequencies ν for CO computed with Duo and Level, which is given in Table XIII in the Supplementary materials and Table 6. The computations for Table XIII used equidistant grids between 0.8 and 1.8 Å with $h = 0.005$ Å in Duo (200 grid points) and $h = 0.0005$ Å in Level (2000 grid points). The computations for Table 6 were aimed to make the same comparison for some transitions from the near-dissociation spectrum of the CO molecule and used equidistant grids between 0.8 and 3.0 Å with $h = 0.0005$ Å in Duo (4400 grid points) and $h = 0.0001$ Å in Level (22 000 grid points). All the calculations used the very accurate semi-empirical W1216 potential of Coxon and Hajigeogiou [42] with quintic splines interpolation and a dipole moment surface, which approximates a set of 7220 dipole points with an average accuracy 0.0002 a.u. We note that the near-dissociation comparison has rather an evaluative character because it involves extrapolating the W1216 potential. To achieve good convergence in the Level calculations, with the eigenvalue convergence parameter 10^{-6} cm^{-1}, we had to reduce a grid step by a factor of 10 for Table XIII, and by a factor of 5 for Table 6 compared to the one used in Duo.

Table XIII from the Supplementary materials shows that the transition frequencies computed using Duo agree with the ones obtained using Level within 0.1%, and in most cases much better, up to 4.4×10^{-7} %. Einstein A coefficients agree to within 0.02%. Thus, both packages show close agreement for computed Einstein A coefficients. This result also shows that the limited accuracy of the dipole moment fit used in our calculations does not significantly influence the agreement between the intensities computed by Duo and Level.

At the same time, Table 6 shows almost the same level of agreement between the Duo and Level near-dissociation results for transition frequencies; however, the Einstein A coefficients agree only to within 91 %, which still is not too bad for near-dissociation spectrum calculations, especially when one accounts for the extrapolation nature of the underlying potential.

4.4. Convergence features of Level

It is worth highlighting here some specific features of calculations using Level we encountered during this work. First of all, to obtain similar levels of convergence with Duo and Level, we had to use a grid step h in Level 5 to 40 times smaller than one used in Duo for all three systems. The convergence for bound state energies using Level and Duo as a function of the grid step is shown in Figs. 2 and 3, respectively. While making Figs. 2 and 3, we first used the same step size in Level as in Duo, and then reduced it until convergence was reached. Fig. 2 shows that the accuracy of Level results obtained with the step size equal to Duo's gives results up to six orders of magnitude worse than the accuracy of the final calculation, and in the artificial harmonic oscillator case the calculation of some bound state energies even resulted in explicit divergence in Level with the Duo grid step.

Table 6
Comparison of Einstein coefficients A and corresponding transition frequencies ν for some lines from the CO diatomic near-dissociation spectrum computed with the Duo and Level packages. Here vibrational and rotational quantum numbers (n, J) and (n'', J'') label the upper and lower levels, correspondingly, $\Delta_A = A_{Duo} - A_{Level}$ is the difference between the computed A values, $\Delta_\nu = \nu_{Duo} - \nu_{Level}$ – the difference between the computed ν values, $\delta_A = |\Delta_A| / A_{Duo} \times 100$, % is the relative deviation between the computed A coefficients in percentage, and $\delta_\nu = |\Delta_\nu| / \nu_{Duo} \times 100$, % is the analogous relative deviation between the computed ν coefficients in percentage.

$\Delta J(J'')$	$n' - n''$	ν_{Duo}, cm^{-1}	A_{Duo}, s^{-1}	Δ_ν, cm^{-1}	Δ_A, s^{-1}	δ_ν, %	δ_A, %
R(13)	61 – 2	80 001.903605	4.120×10^{-7}	3.036×10^{-1}	-1.406×10^{-8}	3.795×10^{-4}	3.412×10^{0}
P(23)	62 – 2	80 100.546284	7.632×10^{-8}	1.826×10^{0}	-4.545×10^{-8}	2.280×10^{-3}	5.955×10^{1}
P(19)	62 – 2	80 301.024211	7.014×10^{-8}	1.274×10^{0}	3.156×10^{-8}	1.587×10^{-3}	4.499×10^{1}
R(18)	62 – 2	80 401.217850	2.864×10^{-9}	1.438×10^{0}	2.607×10^{-9}	1.788×10^{-3}	9.103×10^{1}
P(14)	62 – 2	80 500.265853	5.797×10^{-7}	5.059×10^{-1}	6.002×10^{-8}	6.284×10^{-4}	1.035×10^{1}
R(23)	63 – 2	80 700.076858	1.722×10^{-7}	4.387×10^{0}	8.943×10^{-8}	5.436×10^{-3}	5.192×10^{1}
R(12)	59 – 1	80 900.548577	1.112×10^{-6}	4.858×10^{-2}	-3.200×10^{-8}	6.005×10^{-5}	2.876×10^{0}
P(12)	63 – 2	81 105.082192	3.401×10^{-6}	6.122×10^{-1}	2.563×10^{-7}	7.548×10^{-4}	7.536×10^{0}
P(23)	57 – 0	81 200.999582	3.933×10^{-8}	3.958×10^{-2}	4.540×10^{-10}	4.875×10^{-5}	1.154×10^{0}
R(2)	63 – 2	81 300.178064	3.481×10^{-6}	-1.194×10^{-2}	-6.821×10^{-8}	1.468×10^{-5}	1.959×10^{0}
P(15)	60 – 1	81 400.368177	1.714×10^{-6}	1.482×10^{-1}	-3.236×10^{-8}	1.820×10^{-4}	1.888×10^{0}
P(13)	57 – 0	81 603.230040	1.164×10^{-7}	4.000×10^{-5}	1.841×10^{-9}	4.902×10^{-8}	1.582×10^{0}
R(28)	58 – 0	81 701.624491	4.217×10^{-8}	7.449×10^{-2}	-1.819×10^{-10}	9.117×10^{-5}	4.314×10^{-1}
P(28)	62 – 1	81 900.269509	1.396×10^{-6}	1.790×10^{0}	-5.088×10^{-8}	2.185×10^{-3}	3.644×10^{0}
P(15)	61 – 1	82 005.167752	1.843×10^{-6}	3.078×10^{-1}	-2.282×10^{-8}	3.753×10^{-4}	1.238×10^{0}
P(16)	58 – 0	82 200.477745	1.888×10^{-7}	3.774×10^{-2}	9.400×10^{-11}	4.592×10^{-5}	4.979×10^{-2}
P(13)	58 – 0	82 301.241575	2.061×10^{-7}	1.157×10^{-2}	9.300×10^{-10}	1.406×10^{-5}	4.513×10^{-1}
P(32)	60 – 0	82 601.892908	1.843×10^{-7}	2.629×10^{-1}	-5.521×10^{-9}	3.183×10^{-4}	2.996×10^{0}
P(7)	62 – 1	82 800.324410	1.665×10^{-6}	1.441×10^{-2}	-1.617×10^{-8}	1.740×10^{-5}	9.713×10^{-1}
R(19)	63 – 1	83 004.102892	1.303×10^{-6}	3.563×10^{0}	3.000×10^{-11}	4.292×10^{-3}	2.303×10^{-3}
R(24)	60 – 0	83 202.499635	2.361×10^{-7}	4.396×10^{-1}	-8.818×10^{-9}	5.284×10^{-4}	3.735×10^{0}
P(9)	63 – 1	83 300.762986	1.225×10^{-6}	1.830×10^{-1}	-1.900×10^{-10}	2.197×10^{-4}	1.550×10^{-2}
P(3)	63 – 1	83 401.058078	1.329×10^{-6}	-2.192×10^{-2}	-1.282×10^{-8}	2.629×10^{-5}	9.650×10^{-1}
P(26)	61 – 0	83 600.570540	2.571×10^{-7}	9.005×10^{-1}	-1.626×10^{-8}	1.077×10^{-3}	6.327×10^{0}
R(14)	64 – 1	83 700.961951	9.132×10^{-7}	4.322×10^{0}	4.963×10^{-8}	5.164×10^{-3}	5.435×10^{0}
R(22)	61 – 0	83 900.278168	2.340×10^{-7}	8.882×10^{-1}	-1.507×10^{-8}	1.059×10^{-3}	6.441×10^{0}
P(8)	65 – 1	84 304.844515	5.120×10^{-7}	9.245×10^{-1}	3.445×10^{-8}	1.097×10^{-3}	6.729×10^{0}
R(2)	65 – 1	84 400.326604	3.707×10^{-7}	2.660×10^{-2}	3.604×10^{-9}	3.152×10^{-5}	9.722×10^{-1}
R(21)	62 – 0	84 513.757607	1.681×10^{-7}	1.818×10^{0}	-2.009×10^{-8}	2.151×10^{-3}	1.195×10^{1}
R(19)	62 – 0	84 606.507734	1.464×10^{-7}	1.588×10^{0}	-1.756×10^{-8}	1.877×10^{-3}	1.199×10^{1}
R(27)	63 – 0	84 700.414030	1.714×10^{-7}	3.674×10^{0}	-3.181×10^{-8}	4.338×10^{-3}	1.856×10^{1}
P(24)	63 – 0	84 814.477867	1.121×10^{-7}	4.298×10^{0}	-2.704×10^{-8}	5.067×10^{-3}	2.413×10^{1}
P(9)	62 – 0	84 900.030626	6.823×10^{-8}	8.063×10^{-2}	-3.278×10^{-9}	9.497×10^{-5}	4.804×10^{0}
R(4)	62 – 0	85 002.712268	4.969×10^{-8}	2.268×10^{-3}	-1.042×10^{-9}	2.668×10^{-6}	2.098×10^{0}
P(16)	63 – 0	85 216.311809	3.800×10^{-8}	1.712×10^{0}	-1.099×10^{-8}	2.009×10^{-3}	2.893×10^{1}
R(15)	63 – 0	85 301.218107	4.007×10^{-8}	2.078×10^{0}	-1.188×10^{-8}	2.436×10^{-3}	2.964×10^{1}
P(10)	63 – 0	85 417.225372	1.519×10^{-8}	2.954×10^{-1}	-3.265×10^{-9}	3.458×10^{-4}	2.150×10^{1}
P(6)	63 – 0	85 503.972031	9.186×10^{-9}	1.203×10^{-2}	-9.357×10^{-10}	1.407×10^{-5}	1.019×10^{1}
P(5)	65 – 0	86 502.767930	4.014×10^{-8}	9.793×10^{-2}	4.389×10^{-9}	1.132×10^{-4}	1.093×10^{1}
R(0)	65 – 0	86 548.314535	2.481×10^{-8}	-1.547×10^{-2}	4.754×10^{-10}	1.787×10^{-5}	1.916×10^{0}

As a direct consequence, Level is significantly less computationally efficient than Duo. For instance, while computing Einstein A coefficients, Duo obtained the results shown in the Table XIII of the Supplementary materials data several times faster then Level did (about 0.5 s. versus about 1.6 s. on average) using the same parameters except for the step size. In the case of near-dissociation calculations this difference increases even more, reaching about 1 min. 49 s. versus about 16.5 s. on average, i.e. Duo showed about 6.6 times better performance than Level did.

A second feature of the Level is the complexity of choosing input parameters which lead to the converged results. Sometimes use of trial energies or pointwise input type of potentials is necessary. Duo does not have such problems making it easier to use.

As a short summary, our calculations do not show that Level has drastically worse accuracy in calculations for real molecules, in comparison with Duo. Actually, Level performs really badly only in the case of the artificial harmonic oscillator, which is the least physical system tested here. However, its accuracy improves when the system specified becomes more complex. The main practical disadvantage of Level is its poor performance due to use of the Numerov method; furthermore, Duo is much more convenient and intuitive to use.

5. Conclusions

This paper addresses questions about the accuracy for which solutions can be obtained for various parameters in diatomic nuclear motion calculations. Such questions have become important because of the need to perform rovibrational spectral calculations for diatomics (and other molecules) allow with accuracies of 0.001% or better. In particular, our comparisons show that Duo [12] can compute intensities with an accuracy of about 10^{-4}–10^{-5} % compared to analytic values for a benchmark CO calculation; this accuracy is sufficient for experimental needs for example for determining macroscopic gas properties. For the artificial harmonic and Morse oscillators these deviations were typically about 10^{-7}–10^{-8} % and less than 0.0004%, respectively. The accuracy of computed bound states energies and corresponding wavefunctions using Duo is also very satisfactory. Moreover, for the case of a simple harmonic oscillator, Duo can obtain results with accuracies close to the floating point limit.

The older diatomic nuclear motion package, Level [13], generally has accuracy similar or (somewhat) worse than Duo for calculating of matrix elements, Einstein A coefficients, bound state energies and their corresponding wavefunctions. The accuracy of Level is notably poorer for the harmonic oscillator, when matrix element calculations give results which are sometimes by two to three orders of magnitude less accurate than the corresponding Duo ones. Furthermore, to achieve converged calculations using Level, we had to reduce grids steps sizes by factors of between 10 and 40 compared to the ones used in Duo, and sometimes it was also necessary to make some additional adjustments to the input parameters. Nevertheless, Level still provides good accuracy for the few lowest vibrational states of all systems, and in some cases gives results that are even more accurate than Duo's ones. This

paper suggests that both Level and Duo can provide standard accuracy (from 10% to 0.1%) for line intensity calculations. Line intensities for molecules similar to those considered in this paper can be computed by these two programs by solution of the Schrödinger equation for a given DMS and PES with an accuracy of at least of 10^{-2} %.

We plan to continue to go along the path outlined in this paper in order to quantify the accuracy of existing polyatomic nuclear motion codes, in particular DVR3D [9] for triatomic molecules and WAVR4 [43] for tetratomic molecules for the calculation of line intensities. DVR3D has already been extensively used for high accuracy intensity predictions (eg [3,44]) and accuracy of these codes could be an important factor on the road towards 0.01% and even 0.001% accuracy of line intensities calculations and experiment, necessary for metrological and possibly atmospheric applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All results are presented as tables in the main text or the supplementary material. Both Level and Duo are distributed as open source codes. Level is available from http://scienide2.uwaterloo.ca/~rleroy/LEVEL16. while Duo is available form https://github.com/ExoMol/Duo.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jms.2022.111621. Extra tables of numerical results and a detailed analysis for the artificial Morse oscillator case are given as supplementary material.

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