Exact solutions for vibrational levels of the Morse potential

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Abstract. The vibrational levels of diatomic molecules via Morse potentials are studied by means of the system confined in a spherical box of radius ℓ. It is shown that there exists a critical radius ℓ_{cr} at which the spectrum of the usual unbounded system can be calculated to any desired accuracy. The results are compared with those of Morse's classical solution which is based on the assumption that the domain of the internuclear distance r includes the unphysical region $(-\infty, 0)$. By determining numerically exact lower and upper bounds for the energy eigenvalues of Li_2 molecule, it is deduced here that Morse's approach is perfect and gives very impressive results.

1. Introduction

The radial part of the wave equation for the nuclear motion of a diatomic molecule of nuclear masses M_1 and M_2 is the Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - l(l+1) \right] + v(r) \right\} \mathcal{R}(r) = E\mathcal{R}(r) \qquad r \in [0, \infty) \tag{1.1}$$

where $\mu = M_1 M_2 / (M_1 + M_2)$, $\hbar$ is the reduced Planck's constant, and $-l(l+1)$ denotes the eigenvalues of the angular momentum operator with $l = 0, 1, \ldots$. Purely vibrational levels of diatomic molecules, where $l = 0$, have been described by the Morse potential,

$$v(r) = D[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}] \qquad D, a, r_0 > 0 \tag{1.2}$$

for a long time [1]. A review of Morse potential problems is, however, outside the scope of this paper, and the importance of the subject for both theory and applications in quantum mechanics may be found in the literature [2–7].

Instead of the usual form of the Schrödinger equation in (1.1) it is sometimes of importance to study an enclosed quantum-mechanical system due to its various applications in several fields. A model of this type consists of truncating the infinite domain of the wavefunction, and, hence, dealing with the problem over a bounded region. It is interesting to note that such a bounded system has been used for some time as a powerful method to determine the spectrum of the usual Schrödinger equation with asymptotic boundary conditions. Actually, in the preceding articles of the present author and his co-workers, the truncated interval approach has been applied very effectively in solving both symmetrical [8, 9] and asymmetrical [9, 10] quantum problems in one dimension as well as nonseparable [11, 12] and isotropic [13, 14] potentials in two and N dimensions, respectively. More recently, Aquino [15] used the same approximation to compute the energy levels of the three-dimensional isotropic harmonic oscillator and the hydrogen atom for which the exact eigenvalues are known analytically in the unbounded interval. In fact, more accurate results

than those presented by Aquino [15] were reported in [13, 14] as well, not only for the harmonic oscillator but also for more general polynomial potentials.

In accordance with this method we consider the confined Morse potential bounded by an infinitely high potential at $r = \ell$, where the eigenvalue problem in (1.1) will be defined on a finite interval, $r \in [0, \ell]$. It is well known that the Schrödinger operator for anharmonic oscillators and well potentials possesses only a discrete spectrum with an enumerable infinite set of eigenstates. Similarly, the corresponding enclosed systems have again spectral properties of this kind. In contrast, the number of discrete states of the Morse potential is finite whereas it becomes infinite when the confinement is introduced. Thus, there is a discrepancy in the number of discrete states of the confined and nonconfined Morse potentials. This work is also motivated by this fact which makes it possible to understand whether this discrepancy affects the numerical performance of the truncated interval approach in computing the eigenvalues of the original problem.

Transforming the dependent variable from $\mathcal{R}(r)$ to $\Phi(r)/r$ and the independent variable from r to ar, we see that equation (1.1) becomes

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\mu}{\hbar^2 a^2} v(r/a) \right] \Phi(r) = \frac{\mu E}{\hbar^2 a^2} \Phi(r). \tag{1.3}$$

If we further introduce the frequency

$$\omega_0 = a\sqrt{2D/\mu} \tag{1.4}$$

of classical small vibrations about the equilibrium position $r = r_0$ and express the energy parameters in unit $\hbar\omega_0$, i.e.

$$D = \Delta\hbar\omega_0 \qquad E = \mathcal{E}\hbar\omega_0 \tag{1.5}$$

it is now more convenient to write the eigenvalue problem in the rescaled form

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + 2\Delta^2 V(r) \right] \Phi(r) = 2\Delta\mathcal{E}\Phi(r) \qquad \Phi(0) = 0 \qquad \lim_{r \to \infty} \Phi(r) = 0 \tag{1.6}$$

where

$$V(r) = e^{-2(r-ar_0)} - 2e^{-(r-ar_0)}. \tag{1.7}$$

The parameters Δ, r_0 and a will be chosen empirically, or otherwise, to characterize a specific molecule.

First of all, it is useful to briefly recall Morse's analytical solution for the interval $r \in (-\infty, \infty)$. Letting $u = e^{-(r-ar_0)}$ we transform (1.6) into the form

$$\left[-\frac{1}{2} \left(\frac{d^2}{du^2} + \frac{1}{u} \frac{d}{du} - \frac{v^2}{u^2} \right) - \frac{Z}{u} \right] \Phi(u) = \lambda\Phi(u) \qquad u \in [0, \infty) \tag{1.8}$$

with

$$v^2 = -4\Delta\mathcal{E} \qquad Z = 4\Delta^2 \qquad \lambda = -2\Delta^2 \tag{1.9}$$

where the boundary conditions again read as

$$\lim_{u \to \infty} \Phi(u) = 0 \qquad \Phi(0) = 0. \tag{1.10}$$

In fact, equation (1.8) is nothing but the two-dimensional electronic Schrödinger equation for the hydrogen atom which admits exact solutions of the form

$$\lambda = -\frac{2Z^2}{(2v + 2n + 1)^2} \tag{1.11a}$$

$$\Phi(u) = Cu^v e^{-\sqrt{-2\lambda}u} L_n^{(2v)}(2\sqrt{-2\lambda}u) \tag{1.11b}$$

for $n = 0, 1, \ldots$, where the $L_n^{(2\nu)}$ stand for the associated Laguerre polynomials, and C is some normalization constant [16]. Note that this is the two-dimensional version of the hydrogenic eigensolutions given usually in three dimensions.

The solution of (1.11a) for ν in conjunction with (1.9) gives the results

$$\nu^{(1)} = -2\Delta - (n + \tfrac{1}{2}) \qquad \nu^{(2)} = 2\Delta - (n + \tfrac{1}{2}) \tag{1.12}$$

where the positive values of ν are acceptable in order to satisfy the condition at $u = 0$. Therefore, we reject the case of $\nu^{(1)}$ and find, from the first equation in (1.9), that

$$\mathcal{E}_n = -\Delta + (n + \tfrac{1}{2})\left[1 - \frac{1}{4\Delta}(n + \tfrac{1}{2})\right] \qquad n = 0, 1, \ldots, K \tag{1.13}$$

and that

$$K = [\![2\Delta - \tfrac{1}{2}]\!] \tag{1.14}$$

assuring the discrete eigenvalues of the Morse potential lie between $-\Delta$ and zero. The positive integer $K+1$ denotes the number of bound states which is finite. Clearly, if $\Delta < \frac{1}{4}$ then the problem has no discrete eigenvalues from the viewpoint of Morse's approximation.

Morse's analytical solution so determined is quite informative on the spectral properties. Nevertheless, the inclusion of the unphysical region $-\infty < r < 0$ raises a question about the numerical performance of the simple formula in (1.13). In section 2, we present a closed formal solution in terms of the confluent hypergeometric function for the physical domain $0 \leqslant r < \infty$. Furthermore, in section 3 we formulate the Dirichlet and von Neumann boundary value problems over a truncated interval of r, $r \in [0, \ell]$, for the Schrödinger equation (1.6). In this way, we generate converging upper and lower bounds to the eigenvalues of the nonconfined system [10, 12]. The last section is devoted to the discussion of the specimen numerical applications and the concluding remarks.

2. A formal explicit analytic solution

Starting with Morse's substitution $u = e^{-(r-ar_0)}$, we rewrite equation (1.8) of the form

$$u^2\frac{d^2\Phi}{du^2} + u\frac{d\Phi}{du} - (\nu^2 - 8\Delta^2 u + 4\Delta^2 u^2)\Phi = 0 \tag{2.1}$$

in the true physical domain $e^{ar_0} \geqslant u \geqslant 0$. Introducing the linear transformation

$$\xi = 4\Delta u \qquad 4\Delta e^{ar_0} \geqslant \xi \geqslant 0 \tag{2.2}$$

and proposing a solution of the type

$$\Phi(\xi) = \xi^\nu e^{-\frac{1}{2}\xi} y(\xi) \qquad \nu > 0 \tag{2.3}$$

we find that the differential equation satisfied by $y(\xi)$ is

$$\xi\frac{d^2 y}{d\xi^2} + (2\nu + 1 - \xi)\frac{dy}{d\xi} - (\nu + \tfrac{1}{2} - 2\Delta)y = 0. \tag{2.4}$$

On the other hand, the boundary conditions imply that

$$y(4\Delta e^{ar_0}) = 0 \tag{2.5}$$

and $y(0)$ is bounded providing $\nu > 0$. Fortunately, (2.4) is the Kummer's equation [17] having a regular solution,

$$y(\xi) = C_1 F_1(\nu + \tfrac{1}{2} - 2\Delta; 2\nu + 1; \xi) \tag{2.6}$$

which remains finite at $\xi = 0$. In (2.6), C is a normalization factor, and $_1F_1(\alpha; \beta; \xi)$ denotes the confluent hypergeometric function.

The condition at $\xi = 4\Delta e^{ar_0}$ gives the relation

$$_1F_1(v + \tfrac{1}{2} - 2\Delta; 2v + 1; 4\Delta e^{ar_0}) = 0 \tag{2.7}$$

to determine proper values of v, so that the eigenvalues $\mathcal{E}$ of the problem. It should be noticed that the double inequality $-\Delta < \mathcal{E} < 0$ specifies the range of v values required. In principle, we can find a finite number of distinct roots for (2.7) such that

$$2\Delta > v_0 > v_1 > \cdots > v_n > \cdots > v_M > 0 \tag{2.8}$$

and obtain, from the first relation in (1.9), the discrete eigenvalues of the Morse potential

$$\mathcal{E}_n = -\frac{1}{4\Delta} v_n^2 \qquad n = 0, 1, \ldots, M \tag{2.9}$$

with the corresponding eigenfunctions

$$\Phi_n(\xi) = C_n \xi^{v_n} e^{-\frac{1}{2}\xi} {}_1F_1(v_n + \tfrac{1}{2} - 2\Delta; 2v_n + 1; \xi) \tag{2.10}$$

for $n = 0, 1, \ldots, M$. It is shown that (2.10) expresses an explicit analytic solution in terms of a well known special function of mathematical physics. A similar exact solution for the vibrational levels of the Morse potential was also introduced in [18]. However, the roots v_n of (2.7) cannot be obtained explicitly whose computation is a matter of numerical analysis. Actually, the confluent hypergeometric function in (2.7) is an infinite series containing rational functions of v. Perhaps it might have been truncated, or its suitable asymptotic expansions might have been used to determine the roots v_n. When the series is truncated, it seems that it is possible to reduce (2.7) to a polynomial equation in v, with very complicated coefficients depending on the potential parameters. Even in this approximation, we encounter the problem of finding the roots of a polynomial of an arbitrarily high degree, which is still not preferable to matrix diagonalization. Hence, we use the name *formal* for the eigensolutions in (2.7) and (2.10), which are not at all practical in computing the eigenvalues of the system to any desired accuracy. Further comments are given in the last section.

3. The truncated interval approach

According to the approximation mentioned in the introduction, the actual domain $r \in [0, \infty)$ of the Schrödinger equation (1.6) is truncated to $r \in [0, \ell]$, and the Dirichlet conditions $\Phi(0) = \Phi(\ell) = 0$ are taken into account. The normalized sequence of functions

$$\phi_k(r) = \sqrt{\frac{2}{\ell}} \sin \frac{k\pi}{\ell} r \qquad k = 1, 2, \ldots \tag{3.1}$$

comprises a basis over the truncated interval of r. Thus, if we expand the wavefunction into a series of the $\phi_k(r)$, the differential equation (1.6) can be converted to the matrix eigenvalue problem

$$\sum_{m=1}^{\infty} (H_{km} - 2\Delta\mathcal{E}\delta_{km})c_m = 0 \qquad k = 1, 2, \ldots \tag{3.2}$$

with

$$H_{km} = \tfrac{1}{2}k^2(\pi/\ell)^2\delta_{km} + 2\Delta^2 \int_0^\ell \phi_k(r)V(r)\phi_m(r)\,\mathrm{d}r \tag{3.3}$$

where the c_m and δ_{km} are the expansion coefficients and the Kronecker delta, respectively. The matrix representation of the potential $V(r)$ in (3.3) may be denoted by V_{km} and be evaluated analytically. Indeed, we see that

$$V_{km} = e^{2ar_0}[I_{k-m}(2) - I_{k+m}(2)] - 2e^{ar_0}[I_{k-m}(1) - I_{k+m}(1)] \tag{3.4}$$

where

$$I_j(\alpha) \equiv I_{-j}(\alpha) = \alpha\ell\left[\frac{1-(-1)^je^{-\alpha\ell}}{\alpha^2\ell^2 + j^2\pi^2}\right] \qquad j = 0, \pm 1, \pm 2, \dots. \tag{3.5}$$

The eigenvalues of (3.2) provide us upper bounds for the eigenvalues of the relevant Schrödinger equation, depending on the boundary parameter ℓ. From the physical viewpoint, as the original problem is three-dimensional we have assumed the confinement of the molecule in a sphere of radius ℓ, which is equivalent to the assumption made by Ley-Koo *et al* [2]. Nevertheless, the accuracy of the results may not always be guaranteed solely by the upper bound evaluations.

Moreover, in the case of the von Neumann boundary conditions, where $\Phi'(0) = \Phi'(\ell) = 0$, the use of the orthonormal basis

$$\varphi_1(r) = \sqrt{\frac{1}{\ell}} \qquad \varphi_k(r) = \sqrt{\frac{2}{\ell}}\cos\frac{(k-1)\pi}{\ell}r \qquad k = 2, 3, \dots \tag{3.6}$$

again leads to a standard matrix eigenvalue problem of form (3.2) yielding lower bounds to $\mathcal{E}$ [12]. Now the matrix elements are given by

$$\widehat{H}_{km} = \tfrac{1}{2}(k-1)^2(\pi/\ell)^2\delta_{km} + 2\Delta^2\widehat{V}_{km} \tag{3.7}$$

in which the contribution of the potential energy is expressible as

$$\widehat{V}_{km} = \gamma_{km}e^{2ar_0}[I_{k-m}(2) + I_{k+m-2}(2)] - 2\gamma_{km}e^{ar_0}[I_{k-m}(1) + I_{k+m-2}(1)] \tag{3.8}$$

where

$$\gamma_{km} = \sqrt{(1 - \tfrac{1}{2}\delta_{k,1})(1 - \tfrac{1}{2}\delta_{m,1})}. \tag{3.9}$$

As a matter of fact, regarding ℓ as a nonlinear optimization parameter [10, 12], we have an occasion of determining two-sided bounds to the eigenvalues of the nonconfined system and, hence, numerically exact results for the Morse potential.

In table 1, lower and upper bound energies of an electronic state of the Li_2 molecule are given in the notation of [12]. For instance, $-34.498\,785\dots7\,427\,779/8$ shows that $-34.498\,785\dots7\,427\,779 < \mathcal{E}_0 < -34.498\,785\dots7\,427\,778$. The same energy eigenvalues are calculated by means of Morse's classical solution as well, and reported in table 2 for comparison.

4. Discussion

In this paper, the vibrational energy levels for the nuclear motion of a diatomic molecule have been examined both analytically and numerically. Extremely accurate results are presented for a specimen electronic state of the Li_2 molecule only, without any loss of generality, as the other states and molecules could be treated in a similar way. By means of the lower and upper bounds formulation in section 3, the eigenvalues of the Morse potential are recorded to about 30 significant figures, showing that the truncated interval approach can be applied equally well to a problem having different spectral properties than those of anharmonic oscillators and well potentials considered in our previous studies [9, 12]. Perhaps such an accuracy may be regarded as being extreme in present day molecular spectroscopy as the

Table 1. The lower and upper bound energy eigenvalues of the Morse potential for $^7Li_2$ molecule in the $A\,^1\Sigma_u^+$ state determined by the truncated interval approach in section 3, where $\Delta = 34.997$, $r_0 = 3.10821$, and $a = 0.616$. The last column contains the results in [2] with $N = 600$ and $\ell/a = 31.74$, for comparison.

n	N	ℓ_{cr}	Lower and upper bounds to $\mathcal{E}_n$	$\mathcal{E}_n$ in [2]
0	75	3.25	−34.498 785 867 360 059 433 665 742 7779/8	−34.498 785 867 360 4677
1	78	3.25	−33.513 072 806 240 534 902 991 685 0016/5	−33.513 072 806 241 4320
2	82	3.25	−32.541 646 684 001 485 841 643 569 4488/7	−32.541 646 684 002 1528
3	85	3.30	−31.584 507 500 642 912 249 621 396 1197/6	−31.584 507 500 643 4506
4	88	3.35	−30.641 655 256 164 814 126 925 165 0141/0	−30.641 655 256 165 5102
5	90	3.40	−29.713 089 950 567 191 473 554 876 1322/1	−29.713 089 950 567 6886
6	92	3.45	−28.798 811 583 850 044 289 510 529 4738/7	−28.798 811 583 851 2790
7	95	3.50	−27.898 820 156 013 372 574 792 125 0386/5	−27.898 820 156 014 1817
8	98	3.55	−27.013 115 667 057 176 329 399 662 8282/1	−27.013 115 667 057 5088
9	101	3.60	−26.141 698 116 981 455 553 333 142 8406/5	−26.141 698 116 982 0595
10	105	3.70	−25.284 567 505 786 210 246 592 565 0771/0	−25.284 567 505 787 0984
11	108	3.75	−24.441 723 833 471 440 409 177 929 5366/5	−24.441 723 833 471 6096
12	110	3.80	−23.613 167 100 037 146 041 089 236 2201/0	−23.613 167 100 037 7494
13	114	3.85	−22.798 897 305 483 327 142 326 485 1272/1	−22.798 897 305 483 8091
14	117	3.90	−21.998 914 449 809 983 712 889 676 2578/7	−21.998 914 449 810 2718
15	119	3.95	−21.213 218 533 017 115 752 778 809 6119/8	−21.213 218 533 017 4288
16	122	4.00	−20.441 809 555 104 723 261 993 885 1901/0	−20.441 809 555 105 2090
17	124	4.05	−19.684 687 516 072 806 240 534 902 9917/6	−19.684 687 516 072 9802
18	127	4.10	−18.941 852 415 921 364 688 401 863 0171/0	−18.941 852 415 921 7014
19	131	4.20	−18.213 304 254 650 398 605 594 765 2656/5	−18.213 304 254 650 5699
20	135	4.25	−17.499 043 032 259 907 992 113 609 7381/0	−17.499 043 032 260 2215
21	138	4.30	−16.799 068 748 749 892 847 958 396 4341/0	−16.799 068 748 750 2584
22	142	4.40	−16.113 381 404 120 353 173 129 125 3537/6	−16.113 381 404 120 6413
23	145	4.45	−15.441 980 998 371 288 967 625 796 4969/8	−15.441 980 998 371 2994
24	148	4.50	−14.784 867 531 502 700 231 448 409 8637/6	−14.784 867 531 502 8206
25	150	4.60	−14.142 041 003 514 586 964 596 965 4541/0	

initial data are known up to a few figures. From the methodological point of view, however, it is important to predict the capability and limitations of an algorithm being developed.

In our tables, n is the quantum number, and N stands for the order of the truncated variational matrices in (3.3) and (3.7). The boundary parameter at which the required precision for the unbounded energies can be achieved, are denoted by ℓ_{cr} and included in table 1. It is shown from tables 1 and 2 that Morse's solution recalled in the introduction yields absolutely the correct results to the accuracy quoted. Hence Morse's original assumption of including the unphysical portion $-\infty < r < 0$ of the domain does not result in any deviation from the correct eigenvalues representing the physical domain.

The last comment is a contradiction to the conclusion of [2]. The rescaled potential parameters $\Delta = 34.997$, $r_0 = 3.108\,21$, and $a = 0.616$ used here are those of Ley-Koo *et al* [2], which clearly make a direct comparison possible. First, however, we observe surprisingly that the eigenvalues tabulated as Morse's results in [2] are inaccurate (table 2). We do not understand indeed why this is so, since the calculations can be realized by the very simple formula in (1.13). The mistake is perhaps caused by a misinterpretation, or otherwise, of the classical Morse's solution. Unfortunately, the associated remarks throughout [2] about the justification of Morse's approximation are meaningless because of this fatal error.

Secondly, we perceive that the authors of [2] are at fault in saying that 'the radius of spherical box 31.74 and matrices of 600×600 assure convergence and accuracy to the

Table 2. The energy eigenvalues of the Morse potential for $^7Li_2$ molecule in the $A\,^1\Sigma_u^+$ state evaluated from Morse's solution in equation (1.13), where $\Delta = 34.997$, $r_0 = 3.108\,21$, and $a = 0.616$. The last column contains the same calculations performed in [2].

n	$\mathcal{E}_n$ [this work]	$\mathcal{E}_n$ in [2]
0	−34.498 785 867 360 059 433 665 742 778	−34.498 786 926 269 5133
1	−33.513 072 806 240 534 902 991 685 002	−33.513 074 453 432 9139
2	−32.541 646 684 001 485 841 643 569 449	−32.541 648 329 848 3712
3	−31.584 507 500 642 912 249 621 396 120	−31.584 509 144 471 5536
4	−30.641 655 256 164 814 126 925 165 014	−30.641 656 897 302 4646
5	−29.713 089 950 567 191 473 554 876 132	−29.713 091 588 341 1006
6	−28.798 811 583 850 044 289 510 529 474	−28.798 813 217 587 4689
7	−27.898 820 156 013 372 574 792 125 039	−27.898 821 785 041 5658
8	−27.013 115 667 057 176 329 399 662 828	−27.013 117 290 703 3879
9	−26.141 698 116 981 455 553 333 142 841	−26.141 699 734 572 9385
10	−25.284 567 505 786 210 246 592 565 077	−25.284 569 116 650 2178
11	−24.441 723 833 471 440 409 177 929 537	−24.441 725 436 935 2221
12	−23.613 167 100 037 146 041 089 236 220	−23.613 168 695 427 9552
13	−22.798 897 305 483 327 142 326 485 127	−22.798 898 892 128 4204
14	−21.998 914 449 809 983 712 889 676 258	−21.998 916 027 036 6071
15	−21.213 218 533 017 115 752 778 809 612	−21.213 220 100 152 5260
16	−20.441 809 555 104 723 261 993 885 190	−20.441 811 111 476 1700
17	−19.684 687 516 072 806 240 534 902 992	−19.684 689 061 007 5462
18	−18.941 852 415 921 364 688 401 863 017	−18.941 853 948 746 6475
19	−18.213 304 254 650 398 605 594 765 266	−18.213 305 774 693 4739
20	−17.499 043 032 259 907 992 113 609 738	−17.499 044 538 848 0325
21	−16.799 068 748 749 892 847 958 396 434	−16.799 070 241 210 3161
22	−16.113 381 404 120 353 173 129 125 354	−16.113 382 881 780 3284
23	−15.441 980 998 371 288 967 625 796 497	−15.441 982 460 558 0693
24	−14.784 867 531 502 700 231 448 409 864	−14.784 868 977 543 5389
25	−14.142 041 003 514 586 964 596 965 454	

number of digits indicated'. In fact, the inspection of table 1 shows that the results in [2] are accurate only to about 11 decimal places, the last five being incorrect. Note that there is no uncertainty in our results since exact two-sided bounds are presented. Therefore, the same eigenvalues have been calculated in this study correctly up to their 30 digits by the diagonalization of at most 150×150 matrices as the parameter ℓ varies from 3.25 to 4.60, depending on n. The importance of this remark is that the crucial point of truncating the unbounded domain lies in the determination of a proper size of the confinement, which we call it the critical radius ℓ_{cr}. Since the eigenvalues, $\mathcal{E} = \mathcal{E}_n(\ell)$ say, of a confined system are asymptotic to those of the corresponding nonconfined system, one should never conclude that much better results could be accomplished for much larger values of ℓ [19]. As a typical example, we illustrate in table 3 how the value of $\ell_{cr} = 3.25$ for $\mathcal{E}_0$ can be specified by exploiting the lower and upper bounds calculations. It is shown that the same converged results for the ground-state eigenvalue are obtainable at $\ell = 3.35$ and 4.00 as well, at the cost of using higher truncation orders of 78 and 95, respectively. Therefore, $\ell_{cr} = 3.25$ may be regarded as a 'practical infinity' at which the best converged results are reached in an optimal way, and beyond which the size of the box does not play much more role any more. Obviously, ℓ_{cr} depends on the required accuracy, the state number and the potential function in question. From table 3, we see that if the required accuracy was about 25 significant figures then $\ell = 3.00$ might have been taken as a critical radius. A more detailed discussion on ℓ_{cr} can be found in [8, 13, 19].

Table 3. The rate of convergence of the lower and upper bounds to the ground-state eigenvalue of the Morse potential as a function of ℓ. The potential parameters are the same as in tables 1 and 2.

ℓ	N	Lower and upper bounds to $\mathcal{E}_0(\ell)$
2.00	20	$-34.69/06$
2.25	25	$-34.500/496$
2.50	35	$-34.498\,785\,875/59$
2.75	50	$-34.498\,785\,867\,360\,059\,70/17$
2.85	65	$-34.498\,785\,867\,360\,059\,433\,75/58$
3.00	70	$-34.498\,785\,867\,360\,059\,433\,665\,742\,95/61$
3.25	75	$-34.498\,785\,867\,360\,059\,433\,665\,742\,7779/8$
3.35	78	$-34.498\,785\,867\,360\,059\,433\,665\,742\,7779/8$
4.00	95	$-34.498\,785\,867\,360\,059\,433\,665\,742\,7779/8$

The asymptotic nature of $\mathcal{E}_n(\ell)$ explains the reason of inaccuracy in the eigenvalues computed by Ley-Koo *et al* [2]. More specifically, the selected radius of confinement 31.74 which is, in their own words, '10 or 12 times the equilibrium internuclear separation r_0 in the Morse potentials', is too large. Indeed, it does not yield wholly exact results even though a huge matrix size of 600×600 is used. This can be attributed to the fact that if ℓ is taken to be much greater than a proper value so-called ℓ_{cr}, then the matrix size required for convergence increases dramatically, and, hence, a rapid loss of precision occurs due to rounding errors [13, 19]. Consequently, the truncated interval or the confined system approach should be applied very carefully, and the confinement size ℓ has to be selected by mathematical arguments rather than the physical considerations.

Providing the von Neumann and Dirichlet problems in the box are solved exactly, we generate error bounds for the eigenvalues $\mathcal{E}$ of the original problem in the sense that

$$\mathcal{E}^-(\ell) < \mathcal{E} < \mathcal{E}^+(\ell) \tag{4.1}$$

where $\mathcal{E}^-$ and $\mathcal{E}^+$ denote the eigenvalues of the von Neumann and Dirichlet problems, respectively, which are strictly increasing and decreasing functions of ℓ [10, 12]. On the other hand, Rayleigh–Ritz-type numerical solutions of the Schrödinger equation proposed in section 3 converge correctly to the exact solutions as $N \to \infty$ for each $\ell > 0$ [20, 21]. For finite values of N, it is well known that the confirming digits between two successive approximations are acceptable as the true digits of the exact solution, where $N \to \infty$. In other words, the difference between the results of two consecutive truncation orders is a measure of the error in the determination of the exact solution. For instance, table 4 exhibits the rate of convergence of $\mathcal{E}^-$ and $\mathcal{E}^+$ as a function of the truncation order N at $\ell = 2.85$. Hence, the results for $\ell = 2.85$ in table 3 represent the true digits of the exact solution, which are recorded by way of inspecting the stable digits of the successive approximations in table 4. In general, it should be noted that the truncated matrix eigenvalues of both the von Neumann and Dirichlet problems converge from above as N increases; however, they still give lower and upper bounds on the eigenvalues of the original Morse potential problem as long as their significant figures are taken into account. Furthermore, we see from table 3 that the $N-$truncated matrix eigenvalues yield converging lower and upper bounds for increasing values of ℓ. The two bounds coincide to 30 digits as ℓ approaches ℓ_{cr}, where the last decimal points of the upper bounds are rounded up. Therefore, the double inequality in (4.1) then implies that the maximum uncertainty in our tabulated results for the critical confinement sizes is ± 1 in the last decimal points.

Table 4. The rate of convergence of the ground state eigenvalues of the von Neumann and Dirichlet problems at $\ell_{cr} = 2.85$, as a function of the truncation order N.

N	$\mathcal{E}_0^-(2.85)$	$\mathcal{E}_0^+(2.85)$
40	−34.498 785 867 343	−34.498 785 867 357
45	−34.498 785 867 360 037	−34.498 785 867 360 055
50	−34.498 785 867 360 059 412	−34.498 785 867 360 059 430
55	−34.498 785 867 360 059 433 734	−34.498 785 867 360 059 433 579
60	−34.498 785 867 360 059 433 750 885	−34.498 785 867 360 059 433 581 953
65	−34.498 785 867 360 059 433 750 893	−34.498 785 867 360 059 433 581 955

Finally, we have a few comments on the analytical solution presented in section 2. Essentially, the solution in (2.3) tends towards Morse's one, when the first parameter of the confluent hypergeometric function in (2.6) is equated to a negative integer giving the expression $\nu^{(2)}$ in (1.12) for ν. In this case, the confluent hypergeometric function reduces to Laguerre polynomials $L_n^{(2\nu)}$, and hence the solution in (2.3) satisfies the asymptotic boundary condition at $\xi \to \infty$. In other words, the treatment of the confluent hypergeometric series by setting its first parameter as a negative integer is a necessity owing to the fact that the exponential factor $\exp(-\frac{1}{2}\xi)$ in (2.3) becomes dominant as $\xi \to \infty$ if and only if $y(\xi)$ is simply a polynomial.

In the physical domain, on the other hand, ξ remains finite with the end condition in (2.5). So there is no reason and no need of making $y(\xi)$ a polynomial due to the nonexistence of an asymptotic condition at infinity. As a result, the roots ν_n of (2.7) do not satisfy exactly the relation $\nu_n + \frac{1}{2} - 2\Delta = -n$ in (1.12), which is obtained by Morse's approximation. However, it is shown from (2.9) that the parameter ν_n is closely related to the eigenvalues $\mathcal{E}_n$. Furthermore, the accuracy of Morse's solution implies evidently that the actual values of ν_n should not differ to a large extent from those of $\nu^{(2)}$ in (1.12). From this point of view, it follows then that the estimation

$$\nu_n = 2\Delta - (n + \varepsilon_n + \tfrac{1}{2}) \qquad n = 0, 1, \ldots, [\![2\Delta - \varepsilon_n - \tfrac{1}{2}]\!] \tag{4.2}$$

for the zeros of the confluent hypergeometric function in (2.7) is quite plausible, where $|\varepsilon_n| \ll 1$.

Despite the uselessness of our exact analytical solution in computing the eigenvalues, equation (4.2) now provides us a further check on the accuracy of our results in an inverse procedure. Actually, numerical experiments with very small values of ε_n, typically ranging from 10^{-25} to 10^{-40}, show that equation (2.7) can be satisfied to a very high accuracy, which clarifies once more the validity of Morse's approximation.

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