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On the Numerical Integration of the Schrödinger Equation with a Double-Minimum Potential

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It is proved by analyzing the influence of a potential barrier on the wavefunction that in a manner similar to the single-minimum case the eigenvalues in a double-minimum potential can be determined accurately on the basis of the slopes of the inward and outward numerical solutions, provided that the direction of integration through the barrier is chosen properly. It is shown how the correct direction can be determined in practice. As a numerical illustration a modified Cooley method is compared with the finite-difference boundary value method and the relative advantages of both methods are discussed.

1. INTRODUCTION

It is well known that for some excited states of diatomic molecules more than one minimum can occur in the potential energy curve. Therefore the problem of solving the vibrational Schrödinger equation for bound states in a double-minimum potential is of practical interest in molecular physics. Recently this problem has been discussed by several authors [1–4] in connection with the $E, F^1\Sigma_g^+$ state of the hydrogen molecule. The potential energy curve used for the discussion in [1–3] is that computed in [5]. The vibrational energies in this potential were also computed in [5] with the aid of a slightly modified Cooley method. The modification of the method was necessary because for some vibrational levels the original Cooley procedure [6] did not converge to the proper solution. It seems that these convergence difficulties encountered in [5] gave rise to the discussion started by Lin [1].

Assuming that the difficulties reported in [5] were created by the use of the Cooley method, Lin [1] uses a variational method and Tobin and Hinze [2] a finite-difference boundary value method [7] to compute the vibrational energy levels for the E, F state of H_2. The final results of [1] and [2] are noticeably different and they differ also from the original results [5]. Truhlar and Tarara [3] demonstrated numerically that the differences are most likely due to different boundary conditions and different interpolation methods used in [1], [2], and [5]. Finally, Wicke and Harris [4] employed the three different numerical methods used in [5], [1], and [2] to compute the 16 lowest eigenvalues for an analytically given double-minimum potential and demonstrated with this example that all three methods yield practically identical results. However, it is by no means obvious that the same holds for all double-minimum

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potentials. The difficulties experienced in [5] with the Cooley method were caused by the fact that an integration of the Schrödinger equation through the classically forbidden region can add to the physically interesting solution large components of the second, linearly independent solution of the differential equation. It is obvious that a large contribution of the second solution must result in a significant change of the slope of the resulting solution. Thus, in such a case, any method that uses the slopes of the inward and outward solutions for the evaluation of the corrections to the trial eigenvalues will fail to converge.

For the case studied in [5] it has been found that it was always possible to choose the direction of integration through the classically forbidden region in such a way that the Cooley method converged, or in other words in such a way that the admixture of the nonphysical solution was small. The same method was used in [4] and again the procedure converged, but this does not prove its general applicability. Indeed, in the case of a large potential barrier one could expect a large contribution of the nonphysical solution regardless of the direction of integration. It seems that this point requires clarification.

The second important question concerns the wavefunction. Even if the numerical procedure converges, there still exists a possibility that the wavefunction is incorrect, which can result in incorrect expectation values and transition probabilities.

The above questions are quite important for applications. Therefore we thought it worthwhile to study the double-minimum problem in more detail. We hoped to understand better the origin of the numerical difficulties and to answer—at least partly—the practical questions mentioned above.

2. Properties of the Solutions Inside a Potential Barrier

By a suitable choice of the energy unit we can always write the radial Schrödinger equation as

$$\frac{d^2Y(x)}{dx^2} + [\lambda - Q(x)]\, Y(x) = 0. \tag{1}$$

The solutions are subject to the boundary conditions

$$\begin{aligned} Y(0) &= 0, \\ \lim_{x\to\infty} Y(x) &= 0, \end{aligned} \tag{2}$$

and so we deal here with a special case of the well-known (see, e.g., [8]) Sturm–Liouville problem.

To discuss some properties of arbitrary solutions of (1) we follow [8] and we introduce the polar representation:

$$\begin{aligned} Y &= r(x) \cos \phi(x), \\ Y' &\equiv dY/dx = r(x) \sin \phi(x). \end{aligned} \tag{3}$$

It can be easily shown [8] that $\phi(x)$ satisfies the equation

$$\phi' \equiv d\phi/dx = -\sin^2 \phi(x) - q(x) \cos^2 \phi(x) \tag{4}$$

with

$$q(x) = \lambda - Q(x).$$

$r(x)$ is given as

$$r(x) = r_0 \exp\left[\tfrac{1}{2} \int_{x_0}^{x} (1 - q) \sin 2\phi \, dx\right] \tag{5}$$

with r_0 and x_0 being constants.

Since (1) is homogeneous we will, without any loss of generality, assume

$$r_0 > 0,$$

which leads to

$$r(x) \geqslant 0. \tag{6}$$

Let us now investigate the solutions of (4) inside an interval $[x_1, x_2]$ defined by

$$q(x_i) = 0 \qquad \text{for } i = 1, 2$$

and (7)

$$q(x) < 0 \qquad \text{for } x \in (x_1, x_2).$$

It follows from (4) for $x \in (x_1, x_2)$:

$$\phi(x) = n\pi \Rightarrow \phi'(x) > 0$$

and (8)

$$\phi(x) = n\pi + \pi/2 \Rightarrow \phi'(x) < 0.$$

Hence for a given solution $Y(x)$ there are three mutually exclusive possibilities:

(A) There exists one and only one $x \in (x_1, x_2)$ such that

$$\phi(x) = n\pi, \qquad \text{i.e.,} \qquad Y'(x) = 0.$$

(B) There exists one and only one $x \in (x_1, x_2)$ such that

$$\phi(x) = n\pi + \pi/2, \qquad \text{i.e.,} \qquad Y(x) = 0.$$

(C) $Y(x) \neq 0$ and $Y'(x) \neq 0$ for all $x \in (x_1, x_2)$.

We note also that in the interval (x_1, x_2) both $Y = 0$ and $Y' = 0$ correspond to a minimum of $r(x)$, and there are no other extrema of $r(x)$ in the $q < 0$ region.

Let us now assume that for some fixed λ, Y and $\bar{Y} = \bar{r} \cos \bar{\phi}$ are two different solutions of (1). Thus ϕ and $\bar{\phi}$ are also two different solutions of (4) and one gets [8]

$$\phi(x) \neq \bar{\phi}(x). \tag{9}$$

From (1) we have for the Wronskian

$$Y\bar{Y}' - \bar{Y}Y' = \text{const}, \tag{10}$$

or equivalently

$$r\bar{r} \sin(\phi - \bar{\phi}) = \text{const}. \tag{11}$$

This leads to

$$\begin{aligned} \frac{\bar{r}(x)}{\bar{r}(x')} &= \frac{r(x') \sin(\phi(x') - \bar{\phi}(x'))}{r(x) \sin(\phi(x) - \bar{\phi}(x))} \\ &\geqslant \frac{r(x')}{r(x)} |\sin(\phi(x') - \bar{\phi}(x'))|. \end{aligned} \tag{12}$$

Now let $\bar{\phi}$ be such a solution that for $x' = a$

$$\phi(a) - \bar{\phi}(a) = \pi/2.$$

From (12) we have

$$\frac{\bar{r}(x)}{\bar{r}(a)} \geqslant \frac{r(a)}{r(x)} \tag{13}$$

and we conclude:

C1. If Y is such that $r(x)$ decreases in $[a, b]$ there exists always a second solution $\bar{Y}$ for which $\bar{r}(x)$ increases in $[a, b]$ at least as fast as $1/r(x)$.

In the following we will investigate the solutions in the interval $[x_1, x_2]$ defined by (7). Together with a solution $Y(x)$ we will study $\bar{Y}(x; \delta)$ defined by

$$\begin{aligned} \bar{r}(x_1) &= r(x_1), \\ \bar{\phi}(x_1; \delta) &= \phi(x_1) + \delta, \qquad |\delta| < \pi. \end{aligned} \tag{14}$$

From (4) we get

$$\bar{\phi}(x; \delta) - \phi(x) = \delta + \int_{x_1}^{x} (1 - q) \sin(\bar{\phi} + \phi) \sin(\phi - \bar{\phi})\, dx \tag{15}$$

and from (11) follows

$$\frac{\bar{\phi}(x) - \phi(x)}{\delta} > 0$$

and

$$| \bar{\phi} - \phi | < \pi.$$

By differentiating (15) with respect to δ one gets an integral equation for the derivative of $\bar{\phi}$:

$$\left(\frac{\partial \bar{\phi}}{\partial \delta}\right)_{\delta=0} = 1 - \int_{x_1}^{x} (1 - q) \sin 2\phi \left(\frac{\partial \bar{\phi}}{\partial \delta}\right)_{\delta=0} dx. \tag{16}$$

The solution of (16) reads

$$\left(\frac{\partial \bar{\phi}}{\partial \delta}\right)_{\delta=0} = \exp\left[-\int_{x_1}^{x} (1 - q) \sin 2\phi \, dx\right] \tag{17}$$

where in the second equality use has been made of (5). Thus for $| \delta |$ sufficiently small we can write

$$\Delta \equiv \bar{\phi}(x_2 ; \delta) - \phi(x_2) \simeq \left[\frac{r(x_1)}{r(x_2)}\right]^2 \delta. \tag{18}$$

We have also from (5) and (14):

$$\begin{aligned} \frac{\bar{r}(x_2)}{r(x_2)} &= \exp\left[-\int_{x_1}^{x_2} (1 - q) \sin(\bar{\phi} - \phi) \cos(\bar{\phi} + \phi) \, dx\right] \\ &\simeq \exp\left[-\delta \int_{x_1}^{x_2} (1 - q) \left(\frac{\partial \bar{\phi}}{\partial \delta}\right)_{\delta=0} \cos 2\phi \, dx\right]. \end{aligned} \tag{19}$$

It is seen from (17) that in the cases A and B mentioned above, i.e., when Y or Y' changes sign in the interval (x_1, x_2), $\partial\bar{\phi}/\partial\delta$ and $\cos 2\phi$ reach their maxima simultaneously. Therefore if $r(x)$ has a deep minimum, the integral appearing in (19) may assume quite large values.

Let now $Y(x)$ (and consequently r, ϕ) be an exact solution of the problem given by (1) and (2), and let, for definiteness, $r(x_1) \leqslant r(x_2)$. We have then from (18)

$$0 < | \Delta | \leqslant | \delta | . \tag{20}$$

Further let $\overline{Y}$ (i.e., $\bar{r}$, $\bar{\phi}$) be a numerical solution satisfying (14) and differing for $x < x_1$ from the exact solution Y only in consequence of roundings. An exact integration through the $q < 0$ region from x_1 to x_2 gives

$$\begin{aligned} \bar{\phi}(x_2) &= \phi(x_2) + \Delta, \\ \bar{r}(x_2) &= Cr(x_2), \end{aligned} \tag{21}$$

where C is given by the right-hand side of (19). Thus for $x > x_2$ $\overline{Y}$ is a numerical representation of the solution CY and satisfies the boundary conditions (2). It follows:

C2. If the exact solution inside the barier, $Q(x) > \lambda$, is such that for some $x \in (x_1, x_2)$ $r(x)$ is much less than $r(x_1)$ and $r(x_2)$ the numerical solutions are practically degenerate.

Indeed, for $C \neq 1$

$$Y_1 = \overline{Y} - Y$$

and (22)

$$Y_2 = \overline{Y} - CY$$

both satisfy (1) and (2) and are practically orthogonal. Clearly, the exact solutions are not degenerate and thus we conclude:

C3. If the conditions stated in C2 are fulfilled, the problem (1), (2) has two close eigenvalues.

It is worth noting that if (1) is replaced by a matrix equation as, e.g., in [7], the conclusions C2 and C3 follow immediately from similar theorems for the tridiagonal matrices [9].

It might be also interesting to note that C2 can be obtained directly from C1 without making use of the polar representation (3). For instance, if $Y(x)$ has a minimum inside the barrier we get the second. increasing solution as

$$Z = Y(x) \int_{x_1}^{x} Y^{-2}(t)\, dt \tag{23}$$

and we can write for $x \simeq x_1$

$$\overline{Y} = aY + bZ, \qquad a \simeq 1, \mid b \mid \ll 1.$$

For $x \simeq x_2$ we get from (23)

$$Z = CY(x) + Y(x) \int_{x_2}^{x} Y^{-2}(t)\, dt$$

with

$$C = \int_{x_1}^{x_2} Y^{-2}(t)\, dt.$$

Hence if Y has a deep minimum

$$Z \simeq CY(x) \qquad \text{for } x \simeq x_2$$

and

$$\overline{Y}(x) = (1 + C)\, Y(x).$$

Clearly, for some solutions (20) does not hold. In such a case the roles of the $x < x_1$ and $x > x_2$ regions should be interchanged; i.e., $\overline{Y}$ should be taken as a numerical representation of Y for $x > x_2$ and one should integrate through the barrier from right to left. This leads in view of (18) to:

C4. It is always possible to choose the direction of integration through the barrier in such a way that the error in the slope of the numerical solution does not increase. If $r(x_1) \leqslant r(x_2)$, the proper direction is from x_1 to x_2 and vice versa.

There are several numerical methods, as, e.g., the Cooley method [6], which compare the slopes of two solutions of (1) to determine the eigenvalues. With a given trial eigenvalue one solution $\overline{Y}_{\text{out}}$, is obtained by a numerical integration of (1) from $x = 0$ to some x_m and the other solution, $\overline{Y}_{\text{in}}$, is obtained by an inward integration from some large $x_{\max}$ to x_m. A comparison of the slopes of $\overline{Y}_{\text{out}}$ and $\overline{Y}_{\text{in}}$ at $x = x_m$ is then used to correct the trial eigenvalue. Hence due to C4 we can state:

C5. If the direction of integration through the potential barrier in a double-minimum potential is chosen properly, the barrier does not influence the accuracy of the eigenvalues computed on the basis of comparing the slopes of the inward and outward solutions of (1).

Here we should mention how one can find the correct direction of integration in practice. As is apparent from (21), it may happen that the numerical solution, $\overline{Y}$, decreases

$$| \overline{Y}(x_2)| < | \overline{Y}(x_1)|$$

and the exact one, Y, increases

$$| Y(x_2)| > | Y(x_1)|$$

while crossing the barrier. Therefore the relative magnitudes of $\overline{Y}(x_1)$ and $\overline{Y}(x_2)$ cannot be used as a reliable criterion. However, it is clear from (21) and (18) that if the eigenvalues are determined from the slopes by an iterative procedure as, e.g., that of Cooley, the process will converge only if the barrier is crossed in the proper direction. Thus if for a given direction of integration through the barrier the process converges, the resulting eigenvalue is accurate and if convergence difficulties occur for some eigenvalue one should simply change the direction of integration to achieve convergence.

Unfortunately, even if we choose the direction of integration properly, there still remains the problem of the accuracy of the wavefunction. As we have seen above, if the function has a deep minimum inside the barrier, Y_1 and Y_2 given by (22) are practically two different solutions to the same eigenvalue and any linear combination

$$\overline{Y} = aY_1 + bY_2$$

will be also a solution. So we conclude:

C6. If for a given eigenvalue practical degeneracy occurs, the wavefunction Y cannot be determined numerically in a unique way regardless of the numerical method used.

Clearly, what we mean by a "practical degeneracy" depends on various factors, as, e.g., the word length in the computer and the numerical method used. In practice one can check whether the function is accurate or not by repeating the computations with either slightly modified boundary conditions or with a slightly different integration step. If the function is sensitive to these changes it is certainly not accurate.

Unfortunately it was not possible for us to find a criterion that would give in a general case a reliable estimate of the accuracy of the wavefunction. There is no doubt, however, that it is always essential to choose the direction of integration through the barrier properly. If with an accurate eigenvalue the function is determined stepwise in the correct direction, it may be, according to C6, inaccurate, but as is seen from (21) and (22) the numerical wavefunction, $\overline{Y}$, can be written as

$$\overline{Y} = C_1 Y(x) \qquad \text{on one side of the barrier}$$

and

$$\overline{Y} = C_2 Y(x) \qquad \text{on the other side.}$$

Thus if $C_1 \neq C_2$, the function is normalized differently on both sides of the barrier but otherwise it is accurate. The situation is more serious if the direction of integration is incorrect. In such a case the numerical solution may be essentially different from the exact one because it may emerge from the barrier with a large error in the slope.

3. Numerical Illustrations and Conclusions

As we have demonstrated in Section 2 the most unfavorable conditions for a numerical integration arise when one is looking for almost degenerated eigenvalues. Therefore neither the potential used in [4] nor that from [5] can create serious difficulties if the direction of integration through the barrier is correct. To give an illustration of the numerical difficulties that one may encounter we have investigated (1) with a symmetric potential

$$Q(x) = 200\,[3(x-2)^4 - 6(x-2)^2 - 1] \tag{24}$$

and with symmetric boundary value conditions:

$$Y(0) = Y(4) = 0. \tag{25}$$

The lowest eigenvalues of this problem were computed by the bisection method as in [3, 7] and independently by the Cooley method with the direction of integration through the barrier determined in the way described in Section 2, after C5. The computations were carried out on several different computers but the word length

TABLE I

Eigenvalues $-\lambda_v$ in the Potential (24) Obtained by the Bisection and Cooley Methods

Method	$N\backslash v$	0	1	2	3
	800	751.5259462	751.5259452	656.7305754	656.7305748
	1600	751.5232212	751.5232204	656.7176856	656.7176850
Bisection	3200	751.5225394	751.5225386	656.7144648	656.7144636
	Extrapolation	751.5223121	751.5223116	656.7133912	656.7133898
Cooley	800	751.5223130	751.5223130	656.7133928	656.7133928

was in all cases equivelent to about 15 decimal significant figures. The results are presented in Table I where N denotes the number of integration points with the integration step $h = 4/N$. The extrapolation of the eigenvalues obtained by the bisection method was performed assuming

$$\lambda_h = \lambda + ah^2$$

and using the results for $N = 1600$ and $N = 3200$. The convergence threshold for the eigenvalues was 2×10^{-7} both in the bisection and Cooley methods. It is seen that in accordance with the conclusion C5 even in such a pathological case one can get as accurate results with the Cooley method as with the bisection method. And it is worth mentioning that Cooley's method is more economical in terms of computer time.

Clearly, the exact solutions $Y(x)$ of the problem given by (1), (24), and (25) are symmetric or antisymmetric with respect to $x = 2$:

$$Y(x) = \pm\, Y(4 - x), \qquad x \in [0, 2]. \tag{26}$$

However, according to our discussion at the end of Section 2, the numerical solution $\overline{Y}$ will not in general satisfy (26). Insteed we may get

$$\overline{Y}(x) \approx C\overline{Y}(4 - x), \qquad x \in [0, 2] \tag{27}$$

with $C \neq 1$. For the potential (24) this is indeed the case. The constants C derived from functions obtained by the Cooley method are presented in the last column of Table II for several vibrational levels and different numbers of integration steps. In the third column we give the convergence threshold used in the computations.

Obviously, due to symmetry, the direction of integration through the barrier is immaterial and thus the results given in Table II illustrate our conclusion C6. However, such a degeneracy as in this example is very rare in practice and therefore it is rather unlikely that one should encounter any serious difficulties with the accuracy of the wavefunction in molecular spectroscopy.

TABLE II

The Constants C as Defined by (27) Obtained with a Varying Number of Integration Points N.

	N	Convergence threshold	C
	800	2×10^{-6}	4.3×10^{4}
$v = 0$	1600	2×10^{-7}	2.9×10^{3}
	3200	2×10^{-7}	5.9×10^{1}
	800	2×10^{-6}	2.6×10^{4}
$v = 1$	1600	2×10^{-7}	9.6×10^{3}
	3200	2×10^{-7}	3.6×10^{3}
	800	2×10^{-6}	6.2×10^{2}
$v = 2$	1600	2×10^{-7}	7.6×10^{1}
	3200	2×10^{-7}	1.1×10^{0}

In most applications we have to deal with the nonsymmetric problem (1), (2) and we cannot use the symmetry of the wavefunction as an accuracy test. Therefore whenever doubts may arise one should test the stability of the solutions by varying the integration step, etc. If the direction of integration is chosen properly and the solutions are stable, they will also be accurate.

In the present work we used Cooley's method, i.e., the Numerov [10] integration formula, as an example of a step-by-step method for the determination of the solution of the differential equation (1). On the basis of Section 2 we believe that the results are qualitatively typical for any step-by-step method. However, it is clear from (19) that the magnitude of the error in the solution introduced by crossing the barrier depends strongly on the initial accuracy, δ, and thus on the integration method used.

In order to compare the modified step-by-step method of Cooley with the finite difference boundary value method of Truhlar [7] we repeated the computations of the wavefunctions using the inverse iterations as in [7]. As expected, in consequence of the degeneracy, it was not possible to get symmetric and antisymmetric functions for $v = 0$ and $v = 1$, respectively, without assuming the symmetry a priori. In this method the solutions depend on the initial symmetry of the vector but not on the direction of integration. However, this does not contradict our conclusions since the inverse iteration [9] is not a step-by-step method.

We did also some test computations of the wavefunctions corresponding to the lowest eigenvalues in the more realistic E, F-state potential of H_2. The potential was interpolated at intervals $\Delta x = 0.01$ for $0 < x \leqslant 12$ from the data of [5] by the method given in [11]. Thus we used 1200 integration points in both methods. It has been found that, e.g., for the lowest $v = 0$ eigenvalue both methods yielded the same positions ($x = 1.96$ and $x = 4.28$) of the two maxima of the wavefunction. For the relative height of the maxima, $Y(1.96)/Y(4.28)$, the inverse iteration yielded 1471 as

compared with 1474 obtained with the Cooley method. So, even without extrapolating to a vanishing integration step, the eigenfunctions are quite similar in both methods.

We hope to have demonstrated that the modified Cooley method can be used successfully for any double-minimum potential in (1). We believe that in such a case it is superior to the bisection method as used in [7] because it seems to be faster if high accuracy is required. Also in molecular applications the bisection method is not well suited for eigenvalues close to the dissociation limit since in such cases the replacement of the condition (2) by

$$Y(x_{\max}) = 0 \tag{28}$$

can lead to significant overestimates of the energies. For instance, for the hydrogen molecule E, F-state potential, computed in [5], the $v = 29$ vibrational level of H_2 is shifted up by 55 cm^{-1} if rather than (2) one assumes (28) with $x_{\max} = 12$ atomic units.

It should be noted, however, that if the potential has more than two minima, separated by high barriers, step-by-step methods may fail to converge and in such a case the method developed in [7] is superior to other methods because it is accurate and can be used without any changes for any reasonably well-behaved potential.

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