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On Testing Diatomic Vibration–Rotation Wavefunction for High Levels

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The analytic expression of the vibrational wavefunction for a diatomic Morse potential is well known but practically unused for high vibrational levels v; this is due to the fact that the Laguerre polynomials appearing in the Morse wavefunctions are difficult to handle for high v. A recurrent formula relating ψ_v to ψ_{v-1}, at any point, and independent of the Laguerre polynomials, is presented. The numerical value of ψ_v is thus easily found at any point for any level (up to the dissociation). © 1985 Academic Press, Inc.

1. INTRODUCTION

The vibration–rotation motion of a diatomic molecule is described by the wavefunction $\psi_{vJ}(r)$, where r is the internuclear distance, v is the vibration quantum number, and J is the rotational one. This wavefunction is the solution of the radial Schroedinger equation

$$\frac{d^2\psi_{vJ}(r)}{dr^2}+\left\{\frac{2\mu}{\hbar^2}\left[E_{vj}-U(r)\right]+\frac{J(J+1)}{r^2}\right\}\psi_{vJ}(r)=0 \tag{1}$$

subject to the boundary conditions

$$\psi_{vJ}(r)\xrightarrow[r\to\infty]{r\to 0} 0 \tag{2}$$

where $U(r)$ is the potential of the considered electronic state of the molecule, μ and $\hbar$ having their usual significance [1].

A well-known analytic expression of the wavefunction which corresponds to the Morse rotationless potential ($J=0$) [2], is given by

$$\psi_v^M(r)=e^{-z/2}z^{b/2}L_v^b(z) \tag{3}$$

where

$$z=ke^{-a(r-r_e)}$$

$$b=k-2v-1.$$

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k, a, r_e are constants related to the Morse potential function; $L_v^b(z)$ is the generalized Laguerre polynomial.

The Morse potential function is not considered of physical interest any more. It is commonly replaced by the numerical potential (determined by the coordinates of its turning points with suitable interpolations and extrapolations), which is determined by the well-known RKR semi-classical methods [3] or by the recent quantum methods [4–5].

The wavefunction ψ_{vJ} is thus determined by numerical integration of the Schroedinger equation. Since the earlier work of Cooley [6], many papers designed to improve the accuracy of the computed wavefunction [7–12] have been published.

To test the accuracy of a numerical method, one usually applies it to the Morse potential and compares the computed wavefunction ψ_v^c to the exact one ψ_v^M (Eq. (3)), or compares the computed eigenvalue E_v^c to the Morse exact one E_v^M given by [2]

$$E_v^M = w_e(v+\tfrac{1}{2}) - w_e x_e(v+\tfrac{1}{2})^2 \tag{4}$$

While the last test is commonly found in the literature, the "wavefunction-test" is rarely presented [6–8], and for only low vibrational levels ($0 \leqslant v \leqslant 4$).

We believe that the reason is due to the fact that the Laguerre polynomials appearing in the Morse wavefunctions ψ_v^M are difficult to handle. For most of the practical cases we have $k \sim 100$, $a \sim 1$, and $z \sim 100$ (near the equilibrium r_e); some elements of the polynomial $L_v^b(z)$ become as large as z^v. Since the elements of $L_v^b(z)$ are alternatively positive and negative, the accurate computing of these polynomials for the high values of v becomes tedious work, and the Morse wavefunction cannot be considered "exact" any more.

This difficulty is avoided by giving an expression of the Morse wavefunction ψ_v^M, that is, independent of the Laguerre polynomial and, thus, easy to handle. A recurrent formula relating ψ_v^M to ψ_0^M is presented in Section 2. A new test for the numerical methods of computing the wavefunction ψ_v is presented in Section 3. Some examples of a numerical application are given in Section 4.

2. A RECURRENT FORMULA FOR THE MORSE WAVEFUNCTION

Consider the Morse wavefunctions for v and $v-1$:

$$\psi_v(z) = e^{-z/2} z^{(k-2v-1)/2} L_v^{k-2v-1}(z)$$

$$\psi_{v-1}(z) = e^{-z/2} z^{(k-2v+1)/2} L_{v-1}^{k-2v+1}(z).$$

The ratio of these functions is

$$\frac{\psi_v}{\psi_{v-1}} = \frac{1}{z} \times \frac{L_v^{k-2v-1}}{L_{v-1}^{k-2v+1}}.$$

Using the well-known relation [13],

$$L_n^{\alpha}(z)=L_n^{\alpha+1}(z)-L_{n-1}^{\alpha+1}(z)$$

twice produces

$$L_v^{k-2v-1}=L_v^{k-2v+1}-2L_{v-1}^{k-2v+1}+L_{v-2}^{k-2v+1}. \tag{5}$$

In order to retain polynomials of order v and $v-1$ only, use the other well-known relation [13]

$$(n+1)\,L_{n+1}^{\alpha}(z)-(2n+\alpha+1-z)\,L_n^{\alpha}(z)+(n+\alpha)\,L_{n-1}^{\alpha}(z)=0 \tag{6}$$

to obtain

$$L_v^{k-2v-1}=\frac{(k-2v)\,L_v^{k-2v+1}-(k-2v-z)\,L_{v-1}^{k-2v+1}}{k-v} \tag{7}$$

and

$$\frac{\psi_v}{\psi_{v-1}}=\frac{1}{z(k-v)}\times\left[-(k-2v+z)+(k-2v)\,\frac{L_v^{k-2v+1}}{L_{v-1}^{k-2v+1}}\right].$$

In order to eliminate the Laguerre polynomial from this relation, consider

$$R_{v-1}=\frac{L_v^{k-2v+1}}{L_{v-1}^{k-2v+1}}$$

along with

$$R_v=\frac{L_{v+1}^{k-2v-1}}{L_v^{k-2v-1}}.$$

Using Eq. (7) and Eq. (5) again results in

$$R_v=\frac{k-v}{v+1}\times\frac{(k-2v-z)\,R_{v-1}-(k-2v)}{(k-2v)\,R_{v-1}-(k-2v+z)} \tag{8}$$

where $R_0=k-z$ (according to the definition of L_v^b [13]).

Finally,

$$\frac{\psi_v}{\psi_{v-1}}=\frac{1}{z(k-v)}\times[-(k-2v+z)+(k-2v)\,R_{v-1}] \tag{9}$$

with $\psi_0=e^{-z/2}z^{(k-1)/2}$ (according to Eq. (3)).

For practical reasons, it is convenient to consider the ratio

$$\phi_v(r)=\frac{\psi_v(r)}{\psi_v(r_e)}$$

or

$$\phi_v(z)=\frac{\psi_v(z)}{\psi_v(k)}=e^{-(z-k)/2}\left[\frac{z}{k}\right]^{b/2}\times\frac{L_v^b(z)}{L_v^b(k)}.$$

We deduce that:

$$\frac{\phi_v(z)}{\phi_{v-1}(z)}=\frac{\psi_v(z)}{\psi_{v-1}(z)}\times\frac{\psi_{v-1}(k)}{\psi_v(k)}$$

According to Eq. (9), we have

$$\frac{\psi_v(k)}{\psi_{v-1}(k)}=\frac{1}{k(k-v)}\times[-2(k-v)+(k-2v)\,R_{v-1}(k)]$$

and according to Eq. (8), we have

$$R_v(k)=\frac{k-v}{v+1}\times\frac{-2vR_{v-1}(k)-(k-2v)}{(k-2v)\,R_{v-1}(k)-2(k-v)};\qquad R_0(k)=0$$

and

$$\frac{\phi_v(z)}{\phi_{v-1}(z)}=\frac{k}{z}\times\frac{k-2v+z-(k-2v)\,R_{v-1}(z)}{2(k-v)-(k-2v)\,R_{v-1}(k)}$$

with

$$\phi_0(z)=e^{-(z-k)/2}\left[\frac{z}{k}\right]^{(k-1)/2}.$$

The two functions $\psi_v(z)$ and $\phi_v(z)$ differ only by a multiplicative constant, and both represent the unnormalized Morse wavefunction. However the function $\phi_v(z)$ presents an advantage, since $\phi_0(z)$ does not contain the term $z^{(k-1)/2}$ appearing in $\psi_0(z)$. This term might be large ($\sim 10^{100}$) and present numerical difficulties.

3. THE TESTING OF A NUMERICAL METHOD

Some well-known numerical methods seek to compute the eigenvalue E_v and the eigenfunction ψ_v simultaneously. A simple scheme of some of these methods can be presented as follows:

(i) A trial value $\tilde{E}$ of E_v is given; trial initial values $\tilde{\psi}(r_0)$ and $\tilde{\psi}'(r_0)$ at an "origin r_0" are given.

(ii) The differential equation (1) is replaced by convenient difference equations, and the solution $\psi(\tilde{E}; r)$ is computed.

(iii) This solution is accepted as the eigenfunction $\psi_v(r)$, if the boundary conditions (2) are numerically verified (the trial value $\tilde{E}$ is then the required eigenvalue E_v).

(iv) If the boundary conditions are not satisfied, other trial values are used, and the steps (i), (ii), (iii) are repeated until E converges (or ψ converges).

The numerical algorithm is tested by applying it to a model potential (like the Morse function). As mentioned above, the agreement between the computed eigenvalue E_v^c and the Morse exact one E_v^M is the usual test of this treatment. This test confirms the validity of the difference equations and their numerical solution.

It is possible to test only the difference equations. This is possible if, for a model potential, the exact eigenvalue and the exact initial values of the solution, as well as the exact theoretical value of the solution at any point, are available.

The Morse potential function is adequate for this purpose, for the following reasons:

(i) The exact eigenvalue is known (Eq. (4)).

(ii) The exact initial values $\psi_v(r_e)$ and $\psi_v'(r_e)$ are known at r_e (minimum of the potential) (see Appendix).

(iii) The exact theoretical value of the solution $\psi_v(r)$ is known at any point (Eqs. (8), (9)).

This test is of particular interest when high accuracy is required for the wavefunction, particularly for high levels.

4. NUMERICAL APPLICATION

Examples of the numerical application to the present work are given for the Morse potential function already used by Johnson [9], where the constants are

$$w_e = 1000,$$

$$w_e x_e = 8,$$

$$\frac{2\mu}{\hbar^2} = 0.296594629.$$

The reason for this choice is the large number of possible vibrational levels ($v = 60$).

The difference equations to be tested are fifth order Runge–Kutta [14]. These equations contain the initial values $\psi(r_0)$, $\psi'(r_0)$ and their use here may show the efficiency of the test presented in Section 3 better than the commonly used Numerov difference equation [15].

In Table I we give the value $\psi_v^c(x)$ computed for the given potential and for $v = 20$ at several values of $x = r - r_e$. This computation is repeated for five mesh sizes h varying between 0.005 and 0.001 Å. For each value of x the computed

TABLE I

Values of the Vibration Wavefunction $\psi_v(x)$

	x (Å)		
h (Å)	0.3	0.6	0.9
0.005	−3.837 769 2	4.642 565 1	3.398 926 3
0.004	−3.841 135 9	4.647 982 5	3.382 090 2
0.003	−3.842 582 7	4.650 325 8	3.373 743 8
0.002	−3.843 062 7	4.651 109 9	3.370 527 8
0.001	−3.843 160 1	4.651 270 9	3.369 762 7
Exact	−3.843 164 8	4.651 280 3	3.369 717 1

Note. Computed by Runge–Kutta difference equations (with several step-sizes h) and compared, at several points, to the exact value given by Eq. (8) (Johnson model potential [9], $v = 20$).

wavefunctions ψ_v^c are compared to the "exact" value ψ_v^M calculated from the recurrent formula Eq. (8). All computations were done on the TI 980A computer.

In Tables II and III results are given for $v = 40$ and $v = 60$, respectively.

For all these examples, as well as for other levels and other potentials, the exact wavefunction ψ_v^M is the limit of the computed one when the mesh size h decreases.

We conclude that this test "measures" the accuracy of the difference equations used for the numerical integration of the radial Schroedinger equation.

TABLE II

Values of the Vibration Wavefunction $\psi_v(x)$

	x (Å)		
h (Å)	0.3	0.6	0.9
0.005	0.919 573 0	−0.125 727 7	−0.716 300 1
0.004	0.918 320 1	−0.117 785 1	−0.709 317 8
0.003	0.917 493 1	−0.113 841 9	−0.705 629 9
0.002	0.917 104 8	−0.112 327 5	−0.704 138 3
0.001	0.916 997 9	−0.111 969 7	−0.703 769 7
Exact	0.916 990 0	−0.111 945 9	−0.703 744 5

Note. Computed by Runge–Kutta difference equations (with several step-sizes h) and compared, at several points, to the exact value given by Eq. (8) (Johnson model potential [9], $v = 40$).

TABLE III

Values of the Vibration Wavefunction $\psi_v(x)$

	x (Å)		
h (Å)	0.3	0.6	0.9
0.005	−1.072 092 6	−1.163 160 0	0.686 600 1
0.004	−1.074 339 6	−1.168 627 8	0.701 922 1
0.003	−1.075 071 7	−1.170 698 4	0.709 036 4
0.002	−1.075 220 9	−1.171 273 9	0.711 606 4
0.001	−1.075 225 9	−1.171 363 1	0.712 178 7
Exact	−1.075 226 7	−1.171 366 4	0.712 214 5

Note. Computed by Runge–Kutta difference equations (with several step-sizes h) and compared, at several points, to the exact value given by Eq. (8) (Johnson model potential [9], $v=60$).

APPENDIX: EXACT INITIAL VALUES FOR THE MORSE VIBRATIONAL WAVEFUNCTION

At any point r, the Morse vibrational wavefunction is given by

$$\psi_v(r)=e^{-z/2}z^{(k-2v-1)/2}L_v^{k-2v-1}(z),$$

where $z=ke^{-a(r-r_e)}$.

Its logarithmic derivative is

$$\frac{1}{\psi_v(r)}\times\frac{d\psi_v(r)}{dr}=a\left[\frac{z-(k-2v-1)}{2}-\frac{z}{L_v^{k-2v-1}(z)}\times\frac{dL_v^{k-2v-1}(z)}{dz}\right].$$

Take the origin at $r=r_e$ $(z=k)$, and for the unnormalized wavefunction arbitrary $\psi_v(r_e)=1$, we find

$$\psi_v'(r_e)=a\left[\frac{1}{2}+v-\frac{k}{L_v^{k-2v-1}(k)}\frac{d}{dz}L_v^{k-2v-1}(k)\right].$$

We found previously [16] a recurrent formula relating $\psi_v'(r_e)$ to $\psi_{v-1}'(r_e)$. This formula is obtained by considering

$$Y_v=\frac{k}{L_v^{k-2v-1}(k)}\times\frac{d}{dz}L_v^{k-2v-1}(k)-v.$$

By using the well-known relation [13]

$$z\frac{dL_n^{\alpha}(z)}{dz}=nL_n^{\alpha}(z)-(n+\alpha)L_{n-1}^{\alpha}(z)$$

we get:

$$Y_v = -(k-v-1)\, L_{v-1}^{k-2v-1}(k)/L_v^{k-2v-1}(k)$$

and

$$Y_{v-1} = -(k-v)\, L_{v-2}^{k-2v+1}(k)/L_{v-1}^{k-2v+1}(k).$$

Relations (5) and (6) are used as many times as necessary, to find a relation between Y_v and Y_{v-1} independent of the Laguerre polynomial. We finally get

$$Y_v = -v(k-v) \times \frac{2Y_{v-1} + k - 2v}{(k-2v)\, Y_{v-1} - 2v(k-v)}$$

with

$$Y_0 = 0$$

and

$$\psi_v'(r_e) = a[\tfrac{1}{2} - Y_v].$$

The initial values of the Morse wavefunction are thus deduced for any level v without any approximation.

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