

## Optimized Calculations of Vibrational-Rotational States of Diatomic Molecules\*†

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The numerical solution of the vibrational-rotational Schrödinger equation for the bound states of diatomic molecules is discussed. A formula for starting the numerical integration at large internuclear distances, based on the requirement that the solution is bounded in all space, is given. Expressions are derived for the errors in the second derivative of the solution and the eigenvalues when the Numerov method of numerical integration is used. Based on these expressions, a method of choosing the step size is described which allows eigenvalues to be calculated to specified or optimum accuracy. Results are reported for an  $H_2$  Morse potential and an experimental  $Ar_2$  curve.

### INTRODUCTION

The quantum mechanical problem of the diatomic molecule is normally treated by the method introduced by Born and Oppenheimer [1]. They showed that usually, to a very good approximation, the wavefunction of a molecule can be written as the factored product of an electronic wavefunction and nuclear vibrational-rotational wavefunction. The electronic wavefunction is obtained as the solution to the Schrödinger wave equation for the motion of electrons in a potential field due to fixed nuclei. The eigenfunctions and eigenvalues for this potential are parametric functions of the nuclear coordinates. The energy eigenvalue

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for a given electronic state, taken as a function of the nuclear coordinates, acts as an effective potential energy in the Hamiltonian for the nuclear vibrational-rotational factor.

The validity of this approximation follows from the large nuclear masses in comparison with the electronic masses. This results in the picture of electronic motion in the presence of relatively slow moving, localized nuclei. Born and Oppenheimer assumed that nuclear motion consists of small amplitude, normal mode vibrations about an appropriate equilibrium.

The equation for the electronic motion is, of course, by itself, a formidable problem, and except for single electron cases cannot be solved exactly. It can be dealt with by a variety of variational approaches, most notably variants of the SCF (Self-Consistent Field) method. The advent of large high-speed digital computers has made possible the solution, with increasing accuracy, of these many electron problems.

Often one may be interested only in properties of the molecule at equilibrium so that it is necessary only to solve the electronic equation for this nuclear configuration. However, for many phenomena it is necessary to consider other nuclear configurations as well. This is for instance the case for a detailed understanding of band spectra. Hence one needs to determine the total wavefunction; this paper is concerned with the nuclear vibrational-rotational factor of this total wavefunction.

The numerical integration of the radial equation obtained from the nuclear vibrational-rotational equation has been treated by Cooley [2], using a uniform integration step size, and Blatt [3], using a step size which varies with internuclear distance. The use of uniform step size generally does not yield maximum efficiency and/or accuracy. A method for automatically determining an optimum variable integration mesh is clearly desirable because it eliminates the necessity of experimenting with different integration meshes and allows the numerical integration to be performed with as few points as possible to yield an acceptable accuracy in final results. Blatt's method is based on the unproven assumption that the relative error in the wavefunction at any point is the sum of the relative errors made in each integration step up to that point. Furthermore, his method requires a prior estimate of the total number of integration points to be used. A method of selecting integration points independent of such deficiencies is thus desirable.

After presenting a brief summary of the most suitable procedures for computing eigenfunctions and eigenvalues, an expression will be derived for the eigenvalue error due to the approximation of the differential equation by a difference equation. This expression is the basis for the selection of the integration step size and an estimate of eigenvalue errors.

The application of these methods will be demonstrated for the  $H_2$  Morse Potential and an experimental argon-argon potential.

## SOLVING THE DIFFERENTIAL EQUATION

In atomic units [4], the differential equation to be considered here is

$$-\frac{d^2R}{d\rho^2} + 2\mu U(\rho) R(\rho) + \frac{J(J+1)}{\rho^2} R(\rho) - 2\mu ER(\rho) = 0, \quad (1)$$

where  $\rho$  is the internuclear separation,  $\mu$  is the reduced mass of the nuclei,  $U(\rho)$  is the eigenvalue of the electronic Hamiltonian (assuming nuclear separation fixed at  $\rho$ ), with nuclear repulsion included, and  $J$  is the total angular momentum.

In the iterative procedure most commonly used to obtain eigenvalues and eigenfunctions one constructs, by numerical integration outward from sufficiently small  $\rho$ , the solution  $R_0(\rho)$  which vanishes at the origin, and by numerical integration inward from large  $\rho$ , the solution  $R_\infty(\rho)$  which vanishes as  $\rho \rightarrow \infty$ . This process is, of course, carried out for a trial value  $E$  of the energy. Each of the solutions is determined to within a normalization factor. At a suitable match point  $\rho_m$  these normalization factors can be chosen so that  $R_0(\rho_m) = R_\infty(\rho_m)$ . If we now also demand that  $R_0'(\rho_m) = R_\infty'(\rho_m)$ , this can only be satisfied for certain discrete values of  $E$ . If  $N$  is the sum of the number of nodes of  $R_0$  in the interval  $0 < \rho < \rho_m$  and the number of nodes of  $R_\infty$  in the interval  $\rho_m < \rho < \infty$ , the discrete eigenvalue  $E_N$ , whose eigenfunction has  $N$  nodes in the interval  $0 < \rho < \infty$  is approximately given by [5]

$$E_N = E + (2\mu)^{-1} \frac{d[\log R_0(\rho_m)]/d\rho - d[\log R_\infty(\rho_m)]/d\rho}{R_0^{-2}(\rho_m) \int_0^{\rho_m} R_0^2(\sigma) d\sigma + R_\infty^{-2}(\rho_m) \int_{\rho_m}^{\infty} R_\infty^2(\sigma) d\sigma}. \quad (2)$$

Using the improved eigenvalue estimate given by Eq. (2) the entire procedure is repeated until convergence has been achieved.

The integrations of  $R_0(\rho)$  and  $R_\infty(\rho)$  may be started by approximate analytic formulas derived from the differential equation (1) for sufficiently small and large  $\rho$ , respectively. If the solution is sufficiently small at the starting point, compared to its maximum value, large errors in the starting formula will have negligible effect on the final result [3]. This is always the case for  $R_0(\rho)$  since the steep nuclear repulsion term in  $U(\rho)$  causes the wavefunction to fall off rapidly as  $\rho \rightarrow 0$ . However for large  $\rho$ , particularly for values of  $E$  near the dissociation limit, the wavefunction may decay so slowly that it may not be feasible to choose the starting point where it is sufficiently small. Therefore, it seems worthwhile to discuss the starting procedures in this case.

For large  $\rho$  the potential may be expanded as

$$U(\rho) = \sum_{k=1} A_k \rho^{-k}. \quad (3)$$

The index  $k_0$  of the first nonzero term of this series depends on the nature of the dissociation products [6].

For short-range potentials ( $A_1 = 0$ ) we expect the proper solutions of Eq. (1) to be decaying exponentials [7]. However, for  $A_1 \neq 0$  (ion-ion dissociation) the asymptotic behavior of the solutions should be hydrogenic, i.e.,  $\rho^\alpha e^{-\epsilon\rho}$ . Therefore, we propose the expansion

$$R_\infty(\rho) = N_\infty \rho^\alpha e^{-\epsilon\rho} \sum_{n=0} R_\infty^{(n)} \rho^{-n}, \quad R_\infty^{(0)} = 1. \quad (4)$$

Substituting into Eq. (1) and dividing out by  $N_\infty \rho^\alpha e^{-\epsilon\rho}$  we obtain

$$\sum_{n=0} R_\infty^{(n)} \rho^{-n} \left( \sum_{m=0} C_m^{(n)} \rho^{-m} \right) = 0, \quad (5)$$

where

$$\begin{aligned} C_0^{(n)} &= -(\epsilon^2 + 2\mu E), \\ C_1^{(n)} &= 2\mu A_1 + 2\epsilon(\alpha - n), \\ C_2^{(n)} &= -(\alpha - n)(\alpha - n - 1) + 2\mu A_2 + J(J + 1), \\ C_i^{(n)} &= 2\mu A_i, \quad i > 2. \end{aligned} \quad (6)$$

Expanding, and requiring that the sum of the coefficients of the same power of  $\rho$  vanishes, we find

$$\begin{aligned} \epsilon &= \pm(-2\mu E)^{1/2}, \\ \alpha &= -\mu A_1 / \epsilon, \\ R_\infty^{(n)} &= -\sum_{i=1}^n C_{i+1}^{(n-i)} R_\infty^{(n-i)} / C_1^{(n)}. \end{aligned} \quad (7)$$

We reject the minus sign in the first of Eqs. (7) since it leads to ill-behaved solutions. The second equation shows, as expected, that, except for long-range potentials, the leading term in the solution  $R_\infty(\rho)$  is a decaying exponential. Substituting for  $\alpha$  and  $\epsilon$  in Eqs. (6) allows one to use the third of Eqs. (7) as the recursion relation to determine the coefficients  $R_\infty^{(n)}$  (with  $R_\infty^{(0)} = 1$ ).

#### NUMERICAL INTEGRATION STEP SIZE

There are several methods described in the literature for numerically integrating a differential equation of the type

$$R''(\rho) = G(\rho) R(\rho). \quad (8)$$

The simplest and most accurate method, and the one to be considered in this paper, is based on the numerical integration formula of Numerov [8]

$$\begin{aligned} \left[1 - \frac{h^2}{12} G(\rho + h)\right] R(\rho + h) - \left[2 + \frac{5}{6} h^2 G(\rho)\right] R(\rho) \\ + \left[1 - \frac{h^2}{12} G(\rho - h)\right] R(\rho - h) = 0. \end{aligned} \quad (9)$$

This formula allows one to obtain  $R(\rho + h)$  if  $R(\rho)$  and  $R(\rho - h)$  are known, or to obtain  $R(\rho - h)$  if  $R(\rho)$  and  $R(\rho + h)$  are known.

It is obvious that the accuracy of Eq. (9) in generating solutions of Eq. (8) depends on the selection of the grid points, in particular, the separation  $h$ . It is, therefore, wise to choose this separation so that the resulting solution has the required accuracy, as nearly as possible, while not requiring an excessive number of integration points.

For this purpose it is useful to determine the accuracy of the final solutions as a function of  $h$ . From Taylor Series expansion of  $R(\rho + h)$ ,  $R(\rho - h)$ ,  $R''(\rho + h)$ ,  $R''(\rho - h)$  about  $\rho$  it can be shown that [3, 9]

$$\begin{aligned} R(\rho - h) - 2R(\rho) + R(\rho + h) - (h^2/12)[R''(\rho - h) + 10R''(\rho) + R''(\rho + h)] \\ = -(1/240) h^6 R^{VI}(\rho) + \dots \end{aligned} \quad (10)$$

Equation (9) follows from Eq. (10) by neglecting the right-hand side, and using Eq. (8).

In actual practice, due to round-off the function  $R(\rho)$  generated from Eq. (9) actually satisfies

$$\begin{aligned} [1 - (h^2/12) G(\rho - h)] R(\rho - h) - [2 + (5/6) h^2 G(\rho)] R(\rho) \\ + [1 - (h^2/12) G(\rho + h)] R(\rho + h) \cong rR(\rho), \end{aligned} \quad (11)$$

where  $r$  is the approximate relative round-off error (for the IBM 7094  $r \cong 10^{-8}$ ).

If we define

$$\epsilon(\rho) = rR(\rho) + (1/240) h^6 R^{VI}(\rho), \quad (12)$$

one can show that the function  $R(\rho)$  satisfying the difference equation (11) satisfies the differential equation

$$R''(\rho) \cong G(\rho) R(\rho) + \epsilon(\rho)/h^2, \quad (13)$$

the error term being of order  $h^4$ . Using first-order perturbation theory, one may then estimate the errors of the calculated eigenvalues to be

$$\overline{\Delta E} \simeq (2\mu)^{-1} \int \left[ \left| R(\rho) \frac{1}{240} h^4 R^{VI}(\rho) \right| + \frac{rR^2(\rho)}{h^2} \right] d\rho. \quad (14)$$

We thus have a way of relating the errors made in each step of the numerical integration to the overall error in the final eigenvalue.

This result shows, as one may expect, that as  $h$  decreases, decreasing the first term in the integrand, the second term, due to round-off error, increases, a consequence of the fact that the number of numerical operations required increases. At each value of  $\rho$  the integrand in Eq. (14) has a minimum,  $Q(\rho) R^2(\rho)$ , which occurs at a value of  $h$  for which the two terms are of the same order of magnitude.

One may thus "optimize" the error by choosing  $h$  so that the magnitude of the integrand in Eq. (14) is minimized. However, in most practical cases this accuracy is not needed, since it is instead desirable to keep the eigenvalue errors smaller than some parameter  $v$ . This is conveniently accomplished by dividing the range of  $\rho$  into constant step size regions, halving or doubling the step size  $h$  as one passes from one region to the next, in such a way that

$$(2\mu)^{-1} |(1/240) h^4 R^{VI}(\rho)| < |[r/2\mu h^2 + v(\rho)] R(\rho)|, \quad (15)$$

for all  $\rho$ , where  $v(\rho)$ , a positive function, represents the desired accuracy in the computed eigenvalues where the wavefunction  $R(\rho)$  is large, but may be set at much higher values for asymptotically small or large  $\rho$ , where  $R(\rho)$  is so small that larger errors can be tolerated, since their contribution to the right-hand side of Eq. (14) is negligible.

If  $v(\rho)$  exceeds  $Q(\rho)$  in order of magnitude, or if the two are of comparable magnitude, then the desired accuracy indicated by  $v(\rho)$  would be achieved, with the round-off error term on the right-hand side of Eq. (15) being negligible in the first case, but of magnitude comparable to that of the other two terms in the second case. If  $v(\rho)$  is smaller than  $Q(\rho)$  in the region where  $R(\rho)$  is large, we of course cannot achieve the desired accuracy. However, this problem can often be corrected, since most machines offer the option of doing computations in "double precision," thus greatly reducing the round-off error, and hence the minimum achievable eigenvalue error.

## COMPUTATIONS AND RESULTS

### *Morse Potential*

A convenient potential for testing our numerical procedures is the Morse Potential [10]

$$U(\rho) = D e^{-2\beta(\rho-\rho_0)} - 2D e^{-\beta(\rho-\rho_0)}. \quad (16)$$

Its rotationless eigenvalues are given by<sup>1</sup>

$$E_N = -D[1 - \beta(2\mu D)^{-1/2}(N + \frac{1}{2})]^2. \quad (17)$$

<sup>1</sup> Although Morse solved the problem for the boundary condition  $R(-\infty) = 0$  instead of  $R(0) = 0$  the difference in resulting eigenvalues is negligible due to the steepness of the repulsive barrier for  $\rho \rightarrow 0$ .

With a computer program coded in FAP (assembly language) for use of the IBM 7094 at the University of Chicago, the eigenvalues for a Morse potential corresponding to the ground state of  $H_2$  were computed by numerical integration using a uniform step size of  $h = 0.02$  bohrs, in an integration range  $0 < \rho < 10$  bohrs. The deviations of the computed eigenvalues from those given by Eq. (17) are compared with the errors as computed by Eq. (14) in Table I, confirming the analysis of the previous section.

TABLE I

Morse Potential Results with Uniform Step Size  
 $\beta = 1.1682997^a$      $\rho_0 = 1.4$      $D = 0.1744746$      $\mu = 918.06$

$N$	$-E_N$ Integrated	$-E_N$ Analytical	Actual error ( $\times 10^6$ )	Theoretical error ( $\times 10^6$ )
0	0.16327187	0.16327187	0	5
1	0.14198150	0.14198143	7	13
2	0.12217792	0.12217775	17	23
3	0.10386112	0.10386083	29	37
4	0.08703112	0.08703065	47	55
5	0.07168785	0.07168721	64	71
6	0.05783136	0.05783054	82	87
7	0.04546158	0.04546059	99	100
8	0.03457849	0.03457741	108	108
9	0.02518208	0.02518097	111	109
10	0.01727234	0.01727128	106	105
11	0.01084931	0.01084834	97	93
12	0.00591291	0.00591214	77	75
13	0.00246323	0.00246270	53	52
14	0.00050025	0.00050000	25	25

<sup>a</sup> All quantities in atomic units.

The numerical integration was started at the origin using a power series of the form

$$R_0(\rho) = \sum_{n=1}^5 R_0^{(n)} \rho^n. \quad (18)$$

The derivation of the recursion relation for the coefficients is similar to the derivation of Eqs. (7) and will not be discussed here. In fact, it was found in earlier tests that the results are insensitive to the starting procedure used near the origin, the wavefunction being of order  $10^{-13}$  for  $H_2$ . Since the Morse potential falls off exponentially at large  $\rho$ , the expansion coefficients  $A_k$  of Eq. (3) were assumed to

vanish. The starting formulas thus obtained were found to be adequate since extending the integration range to 16 bohrs changed the highest eigenvalue, whose wavefunction at 10 bohrs is 0.04, by only  $10^{-8}$  hartrees.

The integrals in Eq. (2) were computed using Simpson's rule. Fourth differences of  $G(\rho) R(\rho)$  were used to estimate  $R^{VI}$  in Eq. (14), whose integration was carried out by the Trapezoidal Rule.

TABLE II  
H<sub>2</sub> Morse Potential Results with Optimized Step Size  
 $\Delta u = 10^{-7a}$  ( $t = 10^{-4}$ ,  $h_0 = 0.02$ )

$N$	Initial step size	No. of integration points	$-E_N$ Integrated	Error ( $\times 10^7$ )
0	0.0213	270	0.16327187	0.0
1	0.0213	270	0.14198149	0.6
2	0.0219	334	0.12217774	0.1
3	0.0219	334	0.10386084	0.1
4	0.0219	334	0.08703073	0.8
5	0.0219	334	0.07168732	1.1
6	0.0225	409	0.05783054	0.0
7	0.0225	409	0.04546062	0.3
8	0.0225	409	0.03457749	0.8
9	0.0225	409	0.02518105	0.8
10	0.0225	409	0.01727136	0.8
11	0.0231	547	0.01084828	0.6
12	0.0231	547	0.00591209	0.5
13	0.0231	547	0.00246269	0.1
14	0.0231	547	0.00049994	0.6

<sup>a</sup> All quantities in atomic units.

Next, eigenvalues were computed for this Morse Potential, for the same integration range, the integration mesh being adjusted within the program to maintain a predetermined accuracy for the eigenvalues. The results appear in Table II. When the iterative process for a given eigenvalue was close to convergence, a new set of integration points was selected using condition (15) with  $v(\rho)$  defined as follows:

$$v(\rho) = \Delta u, \quad |R(\rho)| \geq t, \\ v(\rho) = \frac{|\Delta u R(\rho)|}{t}, \quad |R(\rho)| < t. \quad (19)$$

Thus  $\Delta u$  is the specification of the accuracy to which the eigenvalues were to be computed. Increasing  $v(\rho)$  where  $|R(\rho)|$  was small allowed an increase in step size



without harming the overall accuracy in results. The parameter  $t$  determines the region over which the wavefunctions are to be computed the most accurately.

The uniform integration mesh size  $h_0$  was used to begin calculation of the first eigenvalue in the run. Then each succeeding eigenvalue was computed starting with the final mesh used for the preceding eigenvalue. To avoid unnecessary recomputation of potential curves, a new set of integration points was used only if either its eigenvalue estimate  $\overline{\Delta E}$ , or the total number of points, was significantly less than for the old mesh.

The mesh optimization was initiated by requiring that Eq. (15) be satisfied with the “=” sign at the first nonzero mesh point. In order to avoid dangerously huge step sizes, it was further required that

$$v(\rho) < 0.1 \text{ hartrees.} \quad (20)$$

To facilitate later computation of fourth differences, at least four intervals were required between step size changes.

As indicated by Table II, the desired accuracy was produced for all 15 eigenvalues. The two terms in Eq. (14) were of about equal magnitude.

#### *Diatomic Argon Experimental Curve*

Much interest has centered on the existence of stable diatomic molecules of inert gases such as argon, for which several potential curves have been proposed.<sup>2</sup> Recently Tanaka and Yoshino [11] have reported band structure in the ultraviolet absorption spectrum of argon which they attributed to transitions from six vibrational levels of the ground state of diatomic argon to various excited electronic states. Their data provides a sensitive test for proposed potential curves. To test such curves, a numerical vibrational program is needed which will carry out the numerical integration accurately and take proper account of the boundary conditions, particularly at large  $\rho$  where the wavefunctions for high vibrational states are very flat. The above described program meets these requirements.

The vibrational levels were computed for an  $\text{Ar}_2$  potential curve obtained from collision data [12] and numerically tabulated in Table III. The results appear in Table IV. A mesh, with an initial interval size of 0.038 bohrs, and consisting of less than 300 points for an integration range  $1.4 < \rho < 36$  bohrs, was found adequate to yield all eigenvalues to an accuracy of  $10^{-8}$  hartrees. The mesh optimization was initiated at  $\rho \cong 3.8$  bohrs, the first point at which  $R$  was not zero upon normalization (the minimum floating point number on the 7094 is  $\sim 10^{-38}$ ), with the same step size used from  $\rho = 1.4$  bohrs to that point. The round-off error contribution to Eq. (14) was at most  $10^{-9}$  hartrees.

<sup>2</sup> See Ref. [11] for list of papers on this subject.

TABLE III<sup>a</sup>  
Ar<sub>2</sub> Experimental Potential

$\rho^b$	$U(\rho)^c$
1.42110	$0.4527886 \times 10^1$
1.84743	$0.2333822 \times 10^1$
2.27376	$0.1198877 \times 10^1$
2.70009	0.6123605
2.98431	0.3894445
3.26853	0.2463902
3.55275	0.1548289
3.83697	$0.9643743 \times 10^{-1}$
4.12119	$0.5937867 \times 10^{-1}$
4.40541	$0.3600746 \times 10^{-1}$
4.68963	$0.2138950 \times 10^{-1}$
4.97385	$0.1234423 \times 10^{-1}$
5.25807	$0.6825844 \times 10^{-2}$
5.54229	$0.3522434 \times 10^{-2}$
5.68440	$0.2426079 \times 10^{-2}$
5.82651	$0.1596185 \times 10^{-2}$
5.96862	$0.9745518 \times 10^{-3}$
6.11073	$0.5149804 \times 10^{-3}$
6.25284	$0.1808735 \times 10^{-3}$
6.39495	$-0.5668366 \times 10^{-4}$
6.53706	$-0.2204701 \times 10^{-3}$
6.67917	$-0.3262631 \times 10^{-3}$
6.82128	$-0.3881013 \times 10^{-3}$
6.96339	$-0.4185834 \times 10^{-3}$
7.10550	$-0.4270881 \times 10^{-3}$
7.38972	$-0.4040972 \times 10^{-3}$
7.67394	$-0.3552227 \times 10^{-3}$
7.95816	$-0.3013731 \times 10^{-3}$
8.24238	$-0.2523707 \times 10^{-3}$
8.52660	$-0.2086210 \times 10^{-3}$
8.81082	$-0.1703752 \times 10^{-3}$
9.09504	$-0.1378853 \times 10^{-3}$
9.37925	$-0.1114028 \times 10^{-3}$
9.66348	$-0.9117964 \times 10^{-4}$

<sup>a</sup> Since the calculation described here was performed a revised version of this data has been reported [13].

<sup>b</sup> All quantities in atomic units.

<sup>c</sup> For  $\rho > 9.66348$ ,  $U(\rho) = -68.88\rho^{-6} - 498.45\rho^{-8}$ .

The results in Column II were obtained using fifth degree polynomials to interpolate  $U(\rho)$  between the tabulated points in Table III. The numbers in parentheses are these results minus those obtained by cubic polynomials.

TABLE IV  
Results for Experimental Ar<sub>2</sub> Potential  
 $\mu = 36420.2^a$      $h_0 = 0.02$      $\Delta u = 10^{-8}$      $t = 10^{-6}$

$N$	$E_N \times 10^4$	$\Delta G_{N+1/2} \times 10^4$	$\Delta G_{N+1/2} \times 10^4(TY)^b$
0	3.5908(-0.0015)	1.1648	1.162 ± 0.050
1	2.4260(-0.0009)	0.9026	0.948 ± 0.059
2	1.5234(-0.0005)	0.6780	0.702 ± 0.055
3	0.8454(-0.0004)	0.4336	0.478 ± 0.046
4	0.4118(-0.0001)	0.2486	0.365
5	0.1632(-0.0001)	0.1198	
6	0.0434(-0.0001)	0.0395	
7	0.0039(-0.0000)		

<sup>a</sup> All quantities in atomic units.

<sup>b</sup> Results are averages over Tanaka-Yoshino data over all measurements. Errors are standard deviations.

The integration of  $R_0$  was started, as before, by a power series in  $\rho$ . For large  $\rho$ , if we retain only the first two nonvanishing terms of Eq. (4), then from the  $\rho^{-6}$  dependence of  $U(\rho)$  (see Table III) and Eqs. (4)–(7) we obtain for  $J = 0$

$$R_\infty(\rho) = N_\infty e^{-\epsilon\rho} [1 + \mu A_6 / (5\epsilon\rho^5)]. \quad (21)$$

Since at 36 bohrs the wavefunction for  $N = 7$  had a value of more than 1/10 its maximum, the computations were carried out both with and without the  $\rho^{-5}$  term in Eq. (21). Neglect of this term is equivalent to the assumption that  $U = 0$  for large  $\rho$  while its inclusion tends to overcorrect (see Appendix). Hence the eigenvalues obtained in these two cases form upper and lower limits for the true eigenvalues. The results deviated by less than  $10^{-8}$  hartrees showing that the asymptotic starting procedure was adequate.

As can be seen from Table IV, the separations  $\Delta G_{N+1/2}$ , of the successive eigenvalues, for  $N < 4$ , deviate from those obtained by Tanaka and Yoshino by less than the experimental error of their results. The only measurement of  $\Delta G_{9/2}$  made by them is not inconsistent with our results if one takes account of the possibility that there actually may be eight vibrational levels, the highest three not being resolved spectroscopically.

#### APPENDIX

The large  $\rho$  dependence of the potential curve used was

$$U(\rho) = A_6 \rho^{-6} + A_8 \rho^{-8}, \quad (A1)$$

where

$$\begin{aligned} A_6 &= -68.88, \\ A_8 &= -498.45, \end{aligned} \tag{A2}$$

with  $U$  in hartrees and  $\rho$  in bohrs.

Whereas the correct wavefunction satisfies

$$R'' = GR, \tag{A3}$$

it may be shown that the approximate functions

$$\begin{aligned} R_\infty &= e^{-\epsilon\rho}, \\ \bar{R}_\infty &= e^{-\epsilon\rho}[1 + \mu A_6/(5\epsilon\rho^5)], \end{aligned} \tag{A4}$$

satisfy, respectively,

$$\begin{aligned} R_\infty'' &= gR_\infty, \\ \bar{R}_\infty'' &= \bar{g}\bar{R}_\infty, \end{aligned} \tag{A5}$$

where

$$\begin{aligned} g &= G - 2\mu U, \\ \bar{g} &= G + 6\mu A_6/[\epsilon\rho^2 r(\rho)] - 2\mu^2 A_6^2/[5\epsilon\rho^{11} r(\rho)] - 2\mu A_8 \rho^{-8}, \end{aligned} \tag{A6}$$

and

$$r = e^{\epsilon\rho} \bar{R}_\infty. \tag{A7}$$

From the values of  $A_6$  and  $A_8$  and the reduced mass of  $\text{Ar}_2$ ,

$$\mu = 36420.2 \text{ a.u.}, \tag{A8}$$

it may be verified for  $\rho \geq 36$  bohrs and all eigenvalues of Table IV that

$$\bar{g} < G < g. \tag{A9}$$

This establishes the statement that while the asymptotic dependence  $R_\infty$  of (A4) is equivalent to neglecting  $U$  for large  $\rho$ ,  $\bar{R}_\infty$  is equivalent to using an attractive potential  $\bar{U}$  whose magnitude is larger than  $U$ .

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