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Rapid Method to Construct "True" Potential Curves of Diatomic Molecules

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A rapid method to evaluate the classical turning points of vibrational levels for the electronic states of diatomic molecules whose energy terms can be represented adequately by a quadratic in $(v+\frac{1}{2})$ is discussed. The method is based on the fact that the internuclear distance " r " corresponding to energy " U " can be represented by an equation of the form $y(r) = mx(U) + c$, the equation of a straight line. The method is also extended to electronic states whose $\omega_e x_e$ is not very large. To check the validity of these procedures potential energy curves are constructed for $X^2\Sigma^+$, $A^2\Pi_{3/2}$, and $A^2\Pi_{1/2}$ states of CN; $X^1\Sigma_g^+$ and $A^2\Sigma_u^+$ states of N_2 ; and $^3\Pi_{0,+}$ state of $^{79}\text{Br}^{81}\text{Br}$. All these values are compared with those obtained by RKR method. In all cases the agreement is found to be satisfactory, with a deviation of less than 0.1% to RKR values. Further, a method to check the validity of a Morse function for a particular electronic state is discussed, and a method to adjust the Morse function to represent the true curve is illustrated by considering the $A^2\Pi_{3/2}$ state of CN.

I. INTRODUCTION

The construction of the true potential energy curves, based on the WKB approximation, is developed by Rees¹ by giving analytical expressions for " f " and " g " involved in the calculation of r values. Vanderslice *et al.*² modified this method so as to apply it for any electronic state irrespective of its vibrational term representations (e.g., quadratic, cubic, etc). However, the evaluation of r values is quite laborious. Hence, a rapid method which gives sufficiently accurate results is desirable, and it can be achieved if one can find an empirical relation connecting r and U .

II. THEORETICAL: AN EMPIRICAL RELATION CONNECTING r AND U

A. $E(v, K)$ a Quadratic in $(v+\frac{1}{2})$

For rotationless state ($J=0$) the general expression representing the energy of an electronic state is

$$E_v = \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + \omega_e y_e(v+\frac{1}{2})^3 - \omega_e z_e(v+\frac{1}{2})^4 + \dots \quad (1)$$

But for most electronic states E_v can be represented fairly accurately by the first two terms of Eq. (1) by a least-square fitting to the constants ω_e and $\omega_e x_e$. To derive an empirical relation connecting r and U one can use Morse function,

$$U(r) = D\{1 - \exp[-\alpha(r-r_e)]\}^2 \quad (2)$$

since it satisfies Schrodinger's equation for energy states which can be represented by a quadratic in $(v+\frac{1}{2})$. From Eq. (2),

$$-\alpha(r-r_e) = \ln\{1 \pm [U(r)/D]^{1/2}\}$$

since $D = \omega_e^2/4\omega_e x_e$, and α and αr_e are constants, one can write the above expression as

$$\log\{[\omega_e \pm (4\omega_e x_e U)^{1/2}]/\omega_e\} = -\alpha' r + \alpha' r_e \quad (3)$$

where $\alpha' = 2.3026\alpha$, i.e.,

$$\log[\omega_e \pm (4\omega_e x_e U)^{1/2}] = -\alpha' r + \alpha' r_e + \log \omega_e.$$

If we replace $-\alpha'$ by " m " and $(\alpha' r_e + \log \omega_e)$ by " c ,"

$$\log[\omega_e \pm (4\omega_e x_e U)^{1/2}] = m r + c. \quad (4)$$

Thus, for r_{\max} and r_{\min} sides one can write expressions as

$$r > r_e, \quad \log[\omega_e - (4\omega_e x_e U)^{1/2}] = m_+ r_{\max} + c_+, \quad (5)$$

$$r < r_e, \quad \log[\omega_e + (4\omega_e x_e U)^{1/2}] = m_- r_{\min} + c_-, \quad (6)$$

or, vice versa. Now the half-width,

$$\frac{1}{2}(r_{\max} - r_{\min}) = (2\alpha)^{-1} \log \frac{\omega_e + (4\omega_e x_e U)^{1/2}}{\omega_e - (4\omega_e x_e U)^{1/2}}. \quad (7)$$

Equation (7) is identical with expression for f in Ree's quadratic method. Thus by using Expressions (5) and (6) one can find r values corresponding to any energy value U , provided m and c are known. These constants can be determined with a knowledge of r values evaluated by using RKR method corresponding to two energy states. Thus, after knowing m and c the evaluation of r values for the remaining vibrational levels of that electronic state is simple and rapid.

B. $E(v, K)$, a Cubic in $(v+\frac{1}{2})$

For certain electronic states it is not possible to represent the whole vibrational term system by a single quadratic equation in $(v+\frac{1}{2})$. But for states whose $\omega_e y_e$ is not appreciably large it can be divided into segments, each segment consisting of a few vibrational levels can be represented fairly accurately by suitable choices of ω and ωx . After such an adjustment the method outlined in the preceding section can be employed. But in this case, if there are " n " segments ($n+1$) r values must be known. However, in practice for such states two segments are found to be enough to represent the whole system; only very seldom are three necessary. Hence, in this case also, this method is of particular importance due to its rapidity.

III. EXAMPLES

A. P.E. Curves of CN and N₂

As an illustration, as well as a check to this new procedure, we calculated r values for $X^2\Sigma^+$ state of CN which can be represented adequately by a quadratic in $(v+\frac{1}{2})$ after a least-square fitting. The constants ω and ωx after least-square fitting are given in Table I. The r values calculated by this method are tabulated in Table II together with RKR values.³ The agreement is found to be remarkably good. Further, we constructed P.E. curves for the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ states of CN. They are given in Tables III and IV, respectively. RKR values are also given in these tables for comparison.

As a further check, r values are evaluated for $X^1\Sigma^+$ and $A^3\Sigma_u^+$ states of N₂ and are compared with RKR values^{4,5} (Table V). The agreement is found to be good and the deviation is within 0.1% or less.

B. P.E. Curve of ⁷⁹Br⁸¹Br

To illustrate the procedure outlined in II.B. we considered $^3\Pi_{0u}^+$ state of ⁷⁹Br⁸¹Br. The whole system consisting of 21 vibrational levels can be represented adequately by two quadratic equations in $(v+\frac{1}{2})$, one for $v=0$ to 14 and the other for $v=14$ to 21. The constants ω and ωx are evaluated by the method of least squares, and the values thus obtained are given in Table I. The r values thus evaluated for a few vibrational levels are given in Table VI, and there is a close agreement with RKR values.⁴

IV. A STUDY OF MORSE FUNCTION

Due to its simplicity, the Morse function is of particular importance for various problems connected with diatomic molecules. Since the Morse function leads to an exact solution of the one-dimensional Schrodinger's equation, and describes the energy levels E_v as a quadratic in $(v+\frac{1}{2})$, it must represent such states fairly accurately. The agreement will however, depend on the choice of constants α and r_e .

From Relations (4) and (5) one can arrive at the following requirements for the Morse function to be a good approximation to a particular electronic state:

$$(i) \quad m_+ = m_- \quad \text{and} \quad (ii) \quad c_+ = c_-, \quad (8)$$

where $+$ and $-$ denotes the constants for $r > r_e$ and $r < r_e$, respectively.

These conditions can be tested for a particular state by drawing a graph with $\log[\omega_e \pm (4\omega_e x_e U)^{1/2}]$ vs r . If it is a straight line, the two conditions are satisfied and a Morse function is a good approximation to that state. But if $m_+ \neq m_-$, the plot will deviate from a straight line, and this would represent a deviation of the Morse curve from the true curve. For the molecular states ($^2\Sigma^+$, $^2\Pi$ of CN and $^1\Sigma^+$, $^3\Sigma^+$ of N₂) studied here, al-

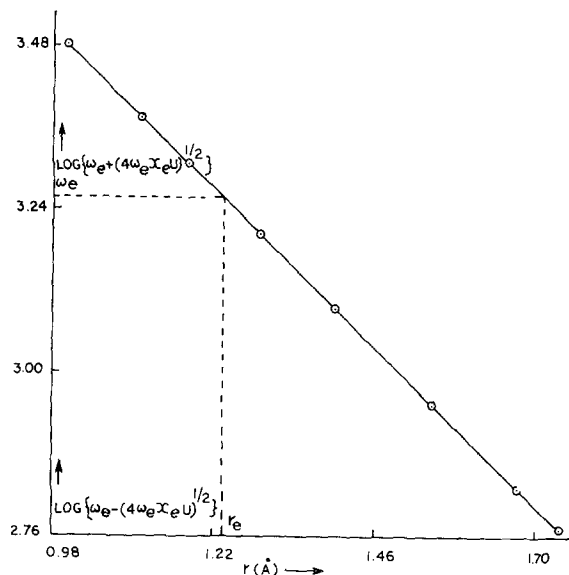


FIG. 1. A plot of $\log [\omega_e \pm (4\omega_e x_e U)^{1/2}]$ vs r for the $A^2\Pi_{3/2}$ state of CN to test the validity of Morse function.

though in general m_+ and m_- are found to be slightly different, the plot of $\log[\omega_e \pm (4\omega_e x_e U)^{1/2}]$ vs r can be reasonably well represented by a single straight line, thereby indicating that the Morse function is a good approximation for them. Figure 1 shows such a plot for the $^2\Pi_{3/2}$ state of CN.

A. Adjustment of Morse Function to Represent the True Curve

As already mentioned, Morse function can be adjusted so as to represent the true curve by choosing proper constants α and r_e . From the graph {i.e., $\log[\omega_e \pm (4\omega_e x_e U)^{1/2}]$ vs r } one can find the slope m and it is related to α by

$$\alpha = 2.3026m, \quad (9)$$

as is obvious from Eq. (3).

At the equilibrium distance r_e , $U=0$, Relation (4) shows that r_e can be determined from the graph as the r value corresponding to $\log\omega_e$.

B. Adjusted Morse Function for $A^2\Pi_{3/2}$ State of CN

Using the constants α and r_e obtained from the graph (Fig. 1), we calculated r values for a few vibrational states of $A^2\Pi_{3/2}$ state of CN, which are given in Table II. It is evident that the adjusted Morse function represents that electronic state fairly well. The maximum deviation from RKR data is only 0.2%. However, it can be seen that the r values obtained from the new procedure (rapid method) are in better agreement with the RKR values than those from the adjusted Morse function. This is due to the fact that the graphical m value used for the determination of the Morse con-

TABLE I. Constants ω and ωx after least-square fitting.

Molecule	Electronic state	v		ω	ωx
		From	To		
CN	$X \ ^2\Sigma^+$	0	18	2069.2202	13.25942
	$A \ ^2\Pi_{1/2}$	0	18	1813.7369	12.8722
CN	$A \ ^2\Pi_{3/2}$	0	15	2358.6004	14.38766
N ₂	$X \ ^1\Sigma_g^+$	0	9	1460.6913	13.9247
N ₂	$A \ ^3\Sigma_u^+$	0	14	165.6759	1.71608
⁷⁹ Br ⁸¹ Br	$B \ ^3\Pi_{0u}^+$	14	21	168.3185	1.89825

TABLE II. P.E. curve for $X \ ^2\Sigma^+$ state of CN.

v	U (cm ⁻¹)	r_{\min} (Å)	r_{\max} (Å)	RKR method	
				r_{\min} (Å)	r_{\max} (Å)
0	1 031.2	1.1237 ^a	1.2244 ^a	1.1237	1.2244
1	3 073.6	1.0924	1.2677	1.0923	1.2676
2	5 089.7	1.0723	1.3001	1.0722	1.2997
3	7 079.5	1.0568	1.3275	1.0566	1.3274
4	9 042.8	1.0439	1.3526	1.0438	1.3525
5	10 980	1.0328	1.3760	1.0327	1.3760
6	12 890	1.0231	1.3983	1.0230	1.3984
7	14 775	1.0144	1.4198	1.0143	1.4198
8	16 632	1.0064	1.4406	1.0063	1.4406
9	18 463	0.9991	1.4609	0.9991	1.4610
10	20 267	0.9923	1.4809	0.9924	1.4809
11	22 045	0.9861	1.5005	0.9861	1.5005
12	23 797	0.9802	1.5199	0.9803	1.5200
13	25 520	0.9748	1.5392	0.9749	1.5393
14	27 217	0.9696	1.5583	0.9696	1.5583
15	28 887	0.9648	1.5774	0.9648	1.5774
16	30 530	0.9602 ^a	1.5964 ^a	0.9602	1.5964
17	32 146	0.9559	1.6154	0.9558	1.6153
18	33 734	0.9517	1.6344	0.9516	1.6343

^a Values used for evaluating m and c and in this case they are $m_- = -0.9887761$, $m_+ = -0.9742839$, $c_- = 4.4733975$, $c_+ = 4.4566335$.

TABLE III. P.E. curve for $A \ ^2\Pi_{1/2}$ state of CN.

$$T_e = 1.14959 \text{ eV}, J = 1/2$$

v	$U(r)$ (cm ⁻¹)	r_{\min} (Å)	r_{\max} (Å)	RKR method	
				r_{\min} (Å)	r_{\max} (Å)
0	903.99	1.1816	1.2891	1.1816	1.2891
3	6 189.4	1.1111	1.4009	1.1109	1.4006
6	11 245	1.0762	1.4785	1.0759	1.4783
9	16 070	1.0514	1.5476	1.0512	1.5475
12	20 663	1.0320	1.6133	1.0319	1.6133
15	25 031	1.0162	1.6777	1.0161	1.6778
18	29 142	1.0029	1.7422	1.0028	1.7423

TABLE IV. P.E. curve for $A \ ^2\Pi_{3/2}$ state of CN.
(Comparison with adjusted Morse function)
 $T_e = 1.14332, J = 3/2$

v	$U(r)$ (cm ⁻¹)	r_{\min} (Å)	r_{\max} (Å)	RKR method		Adjusted Morse function ^a	
				r_{\min} (Å)	r_{\max} (Å)	r_{\min} (Å)	r_{\max} (Å)
0	903.99	1.1827	1.2900	1.1827	1.2900	1.1826	1.2900
3	6 189.4	1.1107	1.4006	1.1105	1.4001	1.1114	1.4005
6	11 245	1.0747	1.4775	1.0749	1.4773	1.0758	1.4773
9	16 070	1.0492	1.5459	1.0497	1.5459	1.0506	1.5456
12	20 663	1.0293	1.6109	1.0298	1.6111	1.0310	1.6106
15	25 021	1.0131	1.6748	1.0134	1.6750	1.0149	1.6744
18	29 142	0.9995	1.7386	0.9994	1.7388	1.0014	1.7382

^a $\alpha = 2.2275, r_e = 1.2331$.

TABLE V. P.E. curves of N₂.

v	$U(r)$ (cm ⁻¹)	r_{\min} (Å)	r_{\max} (Å)	RKR method	
				r_{\min} (Å)	r_{\max} (Å)
$X \ ^1\Sigma_g^+$ state					
0	1 175.5	1.0548	1.1454	1.0548	1.1454
3	8 078.9	0.9941	1.2378	0.9941	1.2376
6	14 725.9	0.9633	1.3011	0.9635	1.3006
9	21 111.1	0.9415	1.3568	0.9419	1.3564
12	27 235.0	0.9242	1.4082	0.9244	1.4082
15	33 095.5	0.9100	1.4591	0.9100	1.4589
$A \ ^3\Sigma_u^+$ state					
0	726.7	1.2328	1.3481	1.2328	1.3481
1	2 159.6	1.1979	1.3992	1.1980	1.3992
2	3 564.9	1.1758	1.4379	1.1759	1.4378
3	4 942.3	1.1590	1.4716	1.1589	1.4715
4	6 291.9	1.1451	1.5027	1.1450	1.5025
5	7 613.7	1.1333	1.5320	1.1332	1.5319
6	8 907.2	1.1230	1.5603	1.1230	1.5602
7	10 172.4	1.1138	1.5878	1.1137	1.5877
8	11 409.1	1.1056	1.6148	1.1055	1.6148
9	12 616.8	1.0981	1.6414	1.0981	1.6418

TABLE VI. P.E. curve for $B \ ^3\Pi_{0u}^+$ state of ⁷⁹Br⁸¹Br.

v	$U(r)$ (cm ⁻¹)	r_{\min} (Å)	r_{\max} (Å)	RKR method	
				r_{\min} (Å)	r_{\max} (Å)
0	82.3	2.596	2.740	2.597	2.740
5	860.5	2.479	2.976	2.479	2.976
10	1552.7	2.430	3.153	2.430	3.153
15	2152.3	2.393	3.330	2.394	3.329
20	2652.9	2.359	3.524	2.360	3.523

stant α is only an average value while actually m_+ and m_- corresponding to the r_{\max} and r_{\min} sides are slightly different.

V. Conclusion

Thus, this method gives a means to calculate r values with sufficient accuracy and at the same time quite rapidly. The success of this method mainly depends upon the accurate determination of the constants m and c , which in turn depend on the accuracy of r values

used as standards. Hence, one must evaluate r values using RKR method as accurate as possible, at least up to the fourth decimal place.

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Configuration-Interaction Calculations for Small Pi Systems. II. The Benzyl and Linear Heptatriene Radicals

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The results of full CI calculation for the pi orbitals of benzyl and the linear polyene C_7H_9 are reported. The spin density on each carbon atom is calculated and compared with data available from other approximations. For benzyl the best agreement is with the empirical variant of the unrestricted Hartree-Fock method, while for the linear polyene our results show a definite trend of increasing positive spin densities towards the center of the polyene in agreement with valence bond calculations.

INTRODUCTION

We report a series of complete configuration-interaction calculations for the ground state of two pi-electron radicals, benzyl and the linear polyene C_7H_9 . This note is, in fact, an application of the procedure described in a recent publication by Amos and Woodward.¹ Thus we take as Hamiltonian the pi-electron model Hamiltonian which has nonzero matrix elements only with respect to a finite basis set, and therefore, the exact eigenfunctions and eigenvalues of this model system can be expressed as a linear sum of antisymmetrized products of the basis functions. Previously results were given for systems with at most five spatial functions in the basis, but we extend it to seven functions so as to treat benzyl and linear heptatriene. There are separate reasons for wanting the exact results, within the pi-electron approximation, for these two radicals. For benzyl we wish to have the exact spin densities in order to compare with the large number of approximate computations² which have been made. For the linear polyene we hope to resolve the contradiction between valence bond and molecular orbital theory which predict qualitatively different spin distributions in the linear polyene radicals.^{3,4}

METHOD OF CALCULATION

The theory is exactly as described in Paper I. Since the radicals considered contained seven electrons and

the ground state is a doublet, it can be written as

$$\Psi = \sum C[i_1, i_2, i_3, i_4 | j_1, j_2, j_3] \times |\omega_{i_1}\alpha \omega_{i_2}\alpha \omega_{i_3}\alpha \omega_{i_4}\alpha \omega_{j_1}\beta \omega_{j_2}\beta \omega_{j_3}\beta|, \quad (1)$$

where the sum is over all the set of ordered integers,

$$1 \leq i_1 < i_2 < i_3 < i_4 \leq 7,$$

$$1 \leq j_1 < j_2 < j_3 \leq 7,$$

and the notation is that of Paper I. Here the seven spatial functions are pi orbitals, one centered on each carbon atom. The coefficients in (1) could be found from the lowest eigenvector of the Hamiltonian matrix as was done in Paper I. In this case, however, such a procedure would involve diagonalizing a 1225×1225 matrix, which is out of the question on the computer available to us. Therefore we have resorted to a simple, and standard, iteration procedure⁵ where the $(i+1)$ st order approximation was taken as

$$\Psi_{i+1} = H\Psi_i / (\langle H\Psi_i | H\Psi_i \rangle)^{1/2}. \quad (2)$$

The function $H\Psi_i$ is easily found using the matrix elements of H given in Paper I. The zero-order approximation was taken as

$$\begin{aligned} \Psi^0 &= |\phi_1\alpha \phi_2\alpha \phi_3\alpha \phi_4\alpha \phi_1\beta \phi_2\beta \phi_3\beta| \\ &= \sum C_0[i_1, i_2, i_3, i_4 | j_1, j_2, j_3] \\ &\quad \times |i_1, i_2, i_3, i_4, j_1, j_2, j_3|, \quad (3) \end{aligned}$$