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**Avco  
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**RESEARCH  
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a division of  
**AVCO CORPORATION**

**VIBRATIONAL WAVE FUNCTIONS AND  
OVERLAP INTEGRALS OF VARIOUS BAND SYSTEMS**

D. R. Childs

**RESEARCH REPORT 147**

**Contract No. DA-19-020-ORD-5476**

**January 1963**

prepared for  
**ADVANCED RESEARCH PROJECTS AGENCY**  
monitored by the  
**ARMY MISSILE COMMAND**  
**UNITED STATES ARMY**  
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**NO. OTS**

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## ABSTRACT

The vibrational wave functions of a diatomic molecule have been calculated for a Morse potential. A generating function for the polynomials has been obtained which enables one to derive recursion relationships among the polynomials. With the aid of these recursion relationships overlap integrals between the various vibrationally excited electronic states have been calculated for a Morse potential and a general expression has been obtained. Overlap integrals are exhibited for low vibrational quantum numbers for fifteen band systems.

## I. Introduction

In calculations of molecular radiation it is often assumed that the electronic transition probability is insensitive to small variations in internuclear separation so that the intensity is proportional to the square of the integral over the product of the vibrational eigenfunctions of the two states involved (i. e., the square of the overlap integral).<sup>1</sup> Early workers, who had to solve this problem, used harmonic oscillator approximations and adjusted the well parameters for each state. More recent investigators have solved the more reasonable Morse potential with approximate wave functions<sup>2</sup> and numerical integrations.<sup>3</sup> These are difficult and tedious methods. The present work indicates an analytic approach for obtaining overlap integrals for the Morse potential by providing a recursion relation solution to the problem. Because of the importance of small numerical differences which occur in application of this procedure a great many significant figures are required. The accuracy of the final results depend on the limitations of the Morse potential, however, the parameters of this potential can be made dependent on the vibration states of interest.

The well known Morse potential<sup>4</sup> approximation for the internuclear potential of a diatomic molecule has been used,

$$V(r) = D_e [ 1 - e^{-\beta(r-r_e)} ]^2, \quad (1)$$

where  $D_e$  is the depth of the well at the minimum

$r_e$  is the position of the minimum

$\beta$  is a well parameter.

A typical Morse curve is shown in Fig. 1.

As  $r \rightarrow \infty$ ,  $V(r)$  tends to  $D_e$  which is the dissociation energy of the molecule, and as  $r \rightarrow r_e$ ,  $V(r)$  is a minimum. A Taylor expansion about  $r = r_e$  shows that  $\beta^2 = m\omega^2/2D_e$ ,  $\omega$  being the frequency of a harmonic oscillator. As  $r \rightarrow 0$ ,  $V(r)$  departs from the correct potential, but it does become greater than  $D_e$  so long as  $\beta r_e > \ln 2$ . This requirement is true for nearly all diatomic molecules so that any vibrational wave functions calculated for bound states will be approximately correct. The potential curve to the left of the minimum rises more slowly than it would for the true potential but this effect does not show up until a high vibrational number is reached, so again the vibrational wave function will be nearly correct for bound states.

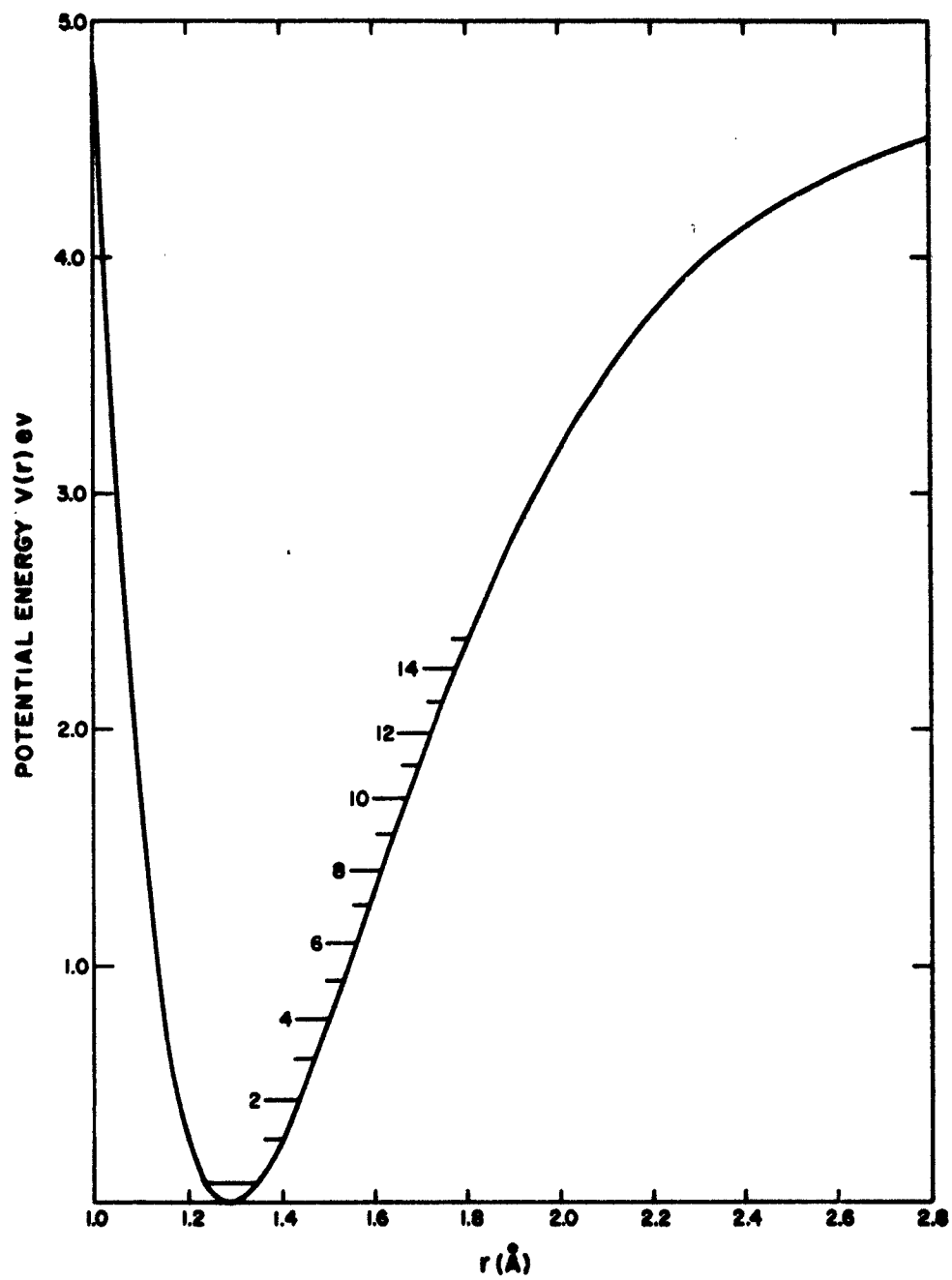


Fig. 1 Morse Curve of Diatomic Molecule ( $A^3\Sigma_u^+$  of  $N_2$ ).

## II. Vibrational Wave Functions

The vibrational wave equation for a Morse potential is written as

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + D_e [1 - e^{-\beta(r-r_e)}]^2 \psi = E\psi. \quad (2)$$

If we let  $\psi(\vec{r}) = 1/r \phi(\vec{r})$

$$-\frac{\hbar^2}{2m} \left( \frac{d^2 \phi}{dr^2} - \frac{l(l+1)}{r^2} \phi \right) + D_e [1 - e^{-\beta(r-r_e)}]^2 \phi = E\phi. \quad (2a)$$

This equation can be solved in closed form only for  $l = 0$  states. Fortunately it has been shown<sup>5</sup> that the overlap integrals calculated for  $l = 0$  states are valid for all  $l$ .

It is convenient to define a parameter  $\lambda = 2D/\hbar\omega$  and a variable  $\xi = \lambda e^{-\beta(r-r_e)}$ . Using these parameters we obtain the well known energy level formula.

$$E = (n + 1/2) \hbar\omega - (n + 1/2)^2 \frac{\hbar^2 \omega^2}{4D}. \quad (3)$$

The wave function is of the form

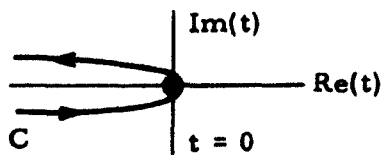
$$\psi = \frac{1}{r} e^{-\xi} \xi^{\lambda-n-1/2} \phi(-n; 2\lambda - 2n; 2\xi), \quad (4)$$

where  $\phi(a; b; x)$  is the confluent hypergeometric function. If  $a$  is equal to a negative integer and if  $(b-a)$  is a positive integer the confluent hypergeometric function reduces to a Laguerre polynomial. However, in our case  $b-a$  is not a positive integer since  $\lambda$  is not integral, so we have a function which behaves markedly differently from a Laguerre polynomial and have chosen to call it  $D_n^\lambda$ .

We define  $D_n^\lambda(x)$  by an integral representation of the following form:

$$D_n^\lambda(x) = e^x x^{2n+1-2\lambda} \frac{1}{2\pi i} \int_C e^{-(t+x)} \frac{(t+x)^{2\lambda-n-1}}{t^{n+1}} dt, \quad (5)$$

where the contour  $C$  is shown in Fig. 2.



From this, one can derive a generating function which enables one to derive certain recursion relationships among the polynomials. The generating function is

$$U_{\lambda}(x, s) = \sum_{n=0}^{\infty} D_n^{\lambda}(x) s^n = \frac{(1/2)^{2\lambda} e^{\frac{x}{2} - \frac{x}{2} \sqrt{1+4s}} [1 + \sqrt{1+4s}]^{2\lambda}}{\sqrt{1+4s}} \quad (6)$$

This immediately yields the following recursion relationships which are important in a discussion of overlap integrals:

$$D_n^{\lambda-1/2}(x) = D_n^{\lambda}(x) - D_{n-1}^{\lambda-1}(x) \quad (7a)$$

$$\frac{d D_n^{\lambda}(x)}{dx} = -D_{n-1}^{\lambda-1/2}(x) = -D_{n-1}^{\lambda}(x) + D_{n-2}^{\lambda-1}(x) \quad (7b)$$

$$x D_n^{\lambda+1/2}(x) = (2\lambda-n) D_n^{\lambda}(x) - (n+1) D_{n+1}^{\lambda+1}(x). \quad (7c)$$

The first few polynomials are

$$\begin{aligned} D_0^{\lambda}(x) &= 1 \\ D_1^{\lambda}(x) &= (2\lambda-2) - x \\ D_2^{\lambda}(x) &= (\lambda-2)(2\lambda-3) - (2\lambda-3)x + 1/2 x^2 \\ D_3^{\lambda}(x) &= 1/3 (2\lambda-4)(\lambda-3)(2\lambda-5) - (\lambda-2)(2\lambda-5)x + (\lambda-2)x^2 - 1/6 x^3 \end{aligned} \quad (8)$$

The polynomials satisfy the following orthonormality condition

$$N^2 = \int_0^{\infty} e^{-2x} x^{2\lambda-n-m-2} D_n^{\lambda}(2x) D_m^{\lambda}(2x) dx = \frac{(2\lambda-n-1)!}{(2\lambda-2n-1)!} \frac{1}{n!} \frac{1}{2^{2\lambda-2n-1}} \delta_{m,n} \quad (9)$$

The wave function for a Morse potential is, from Eqs. (4) and (9) of the form

$$\psi = \frac{1}{N} \cdot \frac{1}{r} e^{-\xi} \xi^{\lambda-n-1/2} D_n^{\lambda}(2\xi), \quad (10)$$

where

$$\xi = \lambda e^{-\beta(r-r_e)}.$$

### III. Overlap Integrals

The overlap integral between two vibrational states  $n_1$  and  $n_2$  of two different wells is defined to be

$$q_{n_1 n_2} = \left| \int_0^\infty \psi_{n_1}(\vec{r}) \psi_{n_2}(\vec{r}) d^3 r \right|^2, \quad (11)$$

where  $\psi_{n_1}(\vec{r})$  and  $\psi_{n_2}(\vec{r})$  are the vibrational wave functions of which Eq. (10) represents only the  $l = 0$  state. The closure property of eigenfunctions of Hermitian operators enables one to obtain the relation

$$\sum_{n_1} q_{n_1, n_2} = \sum_{n_2} q_{n_1, n_2} = 1; \quad (12)$$

$$\begin{aligned} \text{for } \sum_{n_1} q_{n_1, n_2} &= \sum_{n_1} \int_0^\infty \int_0^\infty \psi_{n_1}(\vec{r}) \psi_{n_2}(\vec{r}) \psi_{n_1}(\vec{\rho}) \psi_{n_2}(\vec{\rho}) dr d\rho \\ &= \int_0^\infty \int_0^\infty \psi_{n_2}(\vec{r}) \psi_{n_2}(\vec{\rho}) \delta(\vec{\rho} - \vec{r}) dr d\rho \\ &= \int_0^\infty \left| \psi_{n_2}(r) \right|^2 dr = 1. \end{aligned}$$

$$\text{We define } V_{n_1, n_2}^{\lambda_1, \lambda_2} = \int_0^\infty \psi_{n_1}^{\lambda_1}(r) \psi_{n_2}^{\lambda_2}(r) dr, \quad (13)$$

$$\text{so that } q_{n_1, n_2} = \left| V_{n_1, n_2}^{\lambda_1, \lambda_2} \right|^2.$$

$$\text{Then } V_{n_1, n_2}^{\lambda_1, \lambda_2} = \int_0^\infty \frac{e^{-\xi_1 - \xi_2} \xi_1^{\lambda_1 n_1 - 1/2} \xi_2^{\lambda_2 n_2 - 1/2} D_{n_1}^{\lambda_1(2\xi_1)} D_{n_2}^{\lambda_2(2\xi_2)} dr}{N_1 N_2} \quad (14)$$

Making use of the recursion relations (Eq. (7)), we find that

$$V_{n_1, n_2+1}^{\lambda_1, \lambda_2} = \sqrt{\frac{2\lambda_2 - n_2 - 2}{n_2 + 1}} V_{n_1, n_2}^{\lambda_1, \lambda_2 - 1} - \sqrt{\frac{2\lambda_2 - 2n_2 - 3}{n_2 + 1}} V_{n_1, n_2}^{\lambda_1, \lambda_2} + \sqrt{\frac{n_2(2\lambda_2 - 2n_2 - 3)}{(n_2 + 1)(2\lambda_2 - 2n_2 - 1)}} V_{n_1, n_2 - 1}^{\lambda_1, \lambda_2 - 1}$$

and (15)

$$V_{n_1+1, n_2}^{\lambda_1, \lambda_2} = \sqrt{\frac{2\lambda_1 - n_1 - 2}{n_1 + 1}} V_{n_1, n_2}^{\lambda_1 - 1, \lambda_2} - \sqrt{\frac{2\lambda_1 - 2n_1 - 3}{n_1 + 1}} V_{n_1, n_2}^{\lambda_1, \lambda_2} + \sqrt{\frac{n_1(2\lambda_1 - 2n_1 - 3)}{(n_1 + 1)(2\lambda_1 - 2n_1 - 1)}} V_{n_1 - 1, n_2}^{\lambda_1 - 1, \lambda_2}$$

From these recursion formulas one can obtain the  $V_{0,0}^{\lambda_1, \lambda_2}$  matrix element, the  $V_{0,0}^{\lambda_1, \lambda_2 - n_2}$  element, and the  $V_{0,0}^{\lambda_1 - n_1, \lambda_2}$  element and generate all elements  $V_{n_1, n_2}^{\lambda_1, \lambda_2}$  from relationship (15).

This method consists of calculating far more quantities than are required and can be quite tedious, especially since the  $V_{0,0}^{\lambda_1, \lambda_2}$  quantities cannot be integrated in closed form. However, this method is quite useful if one is interested in transitions connecting low vibrational quantum numbers. For higher quantum numbers Eqs. (15) present a formidable problem, but fortunately they can be solved for  $V_{n_1, n_2}^{\lambda_1, \lambda_2}$  in terms of  $V_{0,0}^{\lambda_1 - 1, \lambda_2 - n}$ . The solution is as follows:

$$V_{n_1, n_2}^{\lambda_1, \lambda_2} = \frac{1}{\sqrt{n_1 n_2}} \sum_{k_1=1}^{n_1} \sum_{k_2=1}^{n_2} (-1)^{k_1+k_2} \binom{n_1}{k_1} \binom{n_2}{k_2} \frac{(2\lambda_1 - n_1 - 1)!(2\lambda_2 - n_2 - 1)!}{(2\lambda_1 - 2n_1 - 1 + k_1)!(2\lambda_2 - 2n_2 - 1 + k_2)!} \quad (16)$$

$$\times \left[ \frac{(2\lambda_1 - 2n_1 + 2k_1 - 2)!(2\lambda_1 - 2n_1 - 1)(2\lambda_2 - 2n_2 + 2k_2 - 2)!(2\lambda_2 - 2n_2 - 1)}{(2\lambda_1 - n_1 - 1)!(2\lambda_2 - n_2 - 1)!} \right]^{1/2} V_{0,0}^{\lambda_1 - n_1 + k_1, \lambda_2 - n_2 + k_2}$$

where the  $V_{0,0}^{\lambda_1 - n_1 + k_1, \lambda_2 - n_2 + k_2}$  are the (0-0) transitions with the  $\lambda_1$  replaced by  $(\lambda_1 - n_1 + k_1)$ . These  $V_{0,0}$  have only one maximum and can be integrated easily by machine, but not in closed form. To facilitate these calculations, recursion relationships exist for these quantities:

$$V_{0,0}^{\lambda_1 - m_1, \lambda_2 - m_2} = \frac{\beta_1 \sqrt{(2\lambda_1 - 2m_1)(2\lambda_1 - 2m_1 - 1)} V_{0,0}^{\lambda_1 - m_1 + 1, \lambda_2 - m_2}}{\beta_1(2\lambda_1 - 2m_1 - 1) + \beta_2(2\lambda_2 - 2m_2 - 1)} +$$

$$\frac{\beta_2 \sqrt{(2\lambda_2 - 2m_2)(2\lambda_2 - 2m_2 - 1)} V_{0,0}^{\lambda_1 - m_1, \lambda_2 - m_2 + 1}}{\beta_1(2\lambda_1 - 2m_1 - 1) + \beta_2(2\lambda_2 - 2m_2 - 1)}$$

Thus one can calculate by machine  $V_{0,0}^{\lambda_1, \lambda_2 - n_2}$  and  $V_{0,0}^{\lambda_1 - n_1, \lambda_2}$  and then generate all  $V_{0,0}^{\lambda_1 - m_1, \lambda_2 - m_2}$  with  $0 < m_1 < n_1$  and  $0 < m_2 < n_2$ . With these quantities the  $V_{n_1, n_2}^{\lambda_1, \lambda_2}$  and thus  $q_{n_1, n_2} = \left| V_{n_1, n_2}^{\lambda_1, \lambda_2} \right|^2$  are found from Eq. (16).

#### IV. Numerical Calculations

Some overlap integrals were calculated for some 15 band systems;  $N_2(1+)$ ,  $N_2(2+)$ ,  $N_2^+$  (Meinel),  $N_2^+(1-)$ ,  $O_2$  (Schumann-Runge),  $NO(\beta)$ ,  $NO(\gamma)$   $NO$  (Ogawa),  $CN$  (violet),  $CN$  (red),  $CH$  (3900),  $CH$  (4300),  $CO^+$  (comet tail),  $C_2$  (Swan), and  $AlO(A \rightarrow X)$ . The first fourteen band systems are found most frequently in our shock tube work. Table 1 gives the parameters for the various molecules and Tables 2-16 give the vibrational overlap integrals for the various band systems.

The tables do not have a large number of entries since we were not prepared to do the calculations with the precision necessary to obtain them. The terms in Eq. (16) all represent large numbers, so that Eq. (16) is made up of terms which are alternately sums and differences of large numbers. In an  $n_1 \rightarrow n_2$  vibrational transition, there are  $(n_1 + 1)(n_2 + 1)$  terms in the series each of the order  $10^{(n_1 + n_2)}$  so that a large number of significant figures are required. These tables were done on an IBM 7090 computer with 16 figure accuracy. The  $V_{0,0}^{\lambda_1 - k_1, \lambda_2 - k_2}$  were calculated by the method of steepest descents and were limited by the precision of the machine.

Even though the high precision required is a definite drawback to this method, the method compensates for this by the speed at which the overlap integrals can be obtained. The first fourteen band systems were done in about 20 minutes or a little over a minute for a band system. This is a redeeming feature and the method is ideal for a computer with multiple precision.

Table 1 gives the well parameters of several molecules in which the band system takes place. Tables 2-16 give overlap integrals of various band systems.

The entries in each table are given as  $\left| \int_{-\infty}^{\infty} \psi_{n_1}(\vec{r}) \psi_{n_2}(\vec{r}) d^3 r \right|^2$  where  $n_1$  is the quantum level of the upper vibrational state and  $n_2$  is the quantum level of the lower vibrational state. The integral was taken from  $-\infty$  to  $\infty$  to facilitate the integration. This is a very good approximation since the wave function to the left of  $r = 0$  decays to zero almost instantaneously. To the right of each row is given the partial sum  $\sum_{n_1, n_2} q_{n_1, n_2}^2$  and at the bottom of each row is given the partial sum  $\sum_{n_2} q_{n_1, n_2}^2$ . These numbers give a measure of how complete are the entries. Only the  $\beta$  band system of  $NO$  fails to be complete along any row or column. Below each entry and in parentheses are given the results of Jarman and Nicholls, whenever they exist. The agreement is found to be excellent. At the bottom of each table, where previous calculations exist, the source of the entries will be given in parentheses.

#### V. Acknowledgment

The author would like to give special acknowledgment to Mr. J. Robert Cornelius of the Computing Group for his diligence in programming and calculating the overlap integrals.

TABLE 1

## Constants

	$\lambda$	$\beta \text{ \AA}^{-1}$	$r_1 (\text{ \AA}^0)$
$\text{N}_2\text{-A}^3\Sigma\text{u}^+$	52.5653	2.40221	1.293
$\text{N}_2\text{-B}^3\Pi\text{g}$	59.9208	2.45176	1.2123
$\text{N}_2\text{-C}^3\Pi\text{u}$	59.5755	2.66372	1.1482
$\text{N}_2^+\text{-X}^2\Sigma\text{g}^+$	68.3933	2.58904	1.116
$\text{N}_2^+\text{-A}^2\Pi$	63.8108	2.48874	1.177
$\text{N}_2^+\text{-B}^2\Sigma\text{u}^+$	52.1742	3.10378	1.075
$\text{O}_2\text{-X}^3\Sigma\bar{\text{g}}$	65.4502	2.39349	1.20739
$\text{O}_2\text{-B}^3\Sigma\bar{\text{u}}$	43.7615	1.94860	1.604
$\text{NO-X}^2\Pi$	68.1471	2.48773	1.1508
$\text{NO-A}^2\Sigma^+$	81.8819	2.53273	1.0637
$\text{NO-B}^2\Pi$	68.1941	1.83526	1.415
$\text{NO-a}^4\Pi$	39.8046	2.38127	1.36
$\text{NO-b}^4\Sigma^-$	43.9097	2.42734	1.26
$\text{CN-X}^2\Sigma^+$	78.6938	2.24493	1.1718
$\text{CN-A}^2\Pi$	70.4195	2.22253	1.2327
$\text{CN-B}^2\Sigma^+$	53.4353	2.78645	1.1506
$\text{CH-X}^2\Pi$	22.2519	.595568	1.1198
$\text{CH-A}^2\Delta$	16.1559	.706171	1.1026
$\text{CH-B}^2\Sigma^-$	34.0088	1.43597	1.1861
$\text{CO}^+\text{X}^2\Sigma^+$	73.0097	2.48366	1.1150
$\text{CO}^+\text{A}^2\Pi$	57.7257	2.34603	1.2436
$\text{C}_2\text{-X}^3\Pi\text{u}$	70.3235	2.03828	1.3117
$\text{C}_2\text{-A}^3\Pi\text{g}$	54.3862	2.41924	1.2660
$\text{AlO-X}^2\Sigma^+$	68.6938	2.05967	1.6176
$\text{AlO-A}^2\Sigma^+$	114.4737	1.50470	1.6667

TABLE 2

 $N_2(1+)$  Band System,  $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ 

$n_1/n_2$	0	1	2	3	4	5	6	7	8	Sum
0	.3385 (.3382)	.3253 (.3248)	.1904 (.1900)	.0889 (.0886)	.0366 (.0365)	.0141 (.0140)	.0051 (.0051)	.0019 (.0019)	.0007 (.0007)	1.0018
1	.4071 (.4065)	.0024 (.0023)	.1031 (.1032)	.1784 (.1782)	.1453 (.1450)	.0866 (.0865)	.0438 (.0437)	.0201 (.0200)	.0086 (.0086)	1.0014
2	.1975 (.1975)	.2118 (.2120)	.1134 (.1132)	.0011 (.0012)	.0700 (.0772)	.1026 (.1275)	.0022 (.1127)			.6986
3	.0502 (.0501)	.2983 (.2987)	.0385 (.0387)	.1755 (.1623)	.0156 (.0323)	.0010 (.0091)				.5791
4	.0072 (.0072)	.1326 (.1318)	.2559 (.2738)	.0381 (.0018)						.4338
5	.0006 (.0006)	.0295 (.0273)	.2991 (.2106)							.3292
6	.0000	.0323 (.0029)								.0323
Sum	1.0011	1.0322	1.0004	.4820	.2675	.2043	.0511	.0220	.0093	
$n_1/n_2$	9	10	11	12	13	14	15	16	17	
0	.0002 (.0002)	.0001 (.0001)	.0000	.0000	.0000	.0000	.0000	.0000	.0000	
1	.0036 (.0036)	.0015 (.0015)	.0006 (.0006)	.0002 (.0002)	.0001 (.0001)	.0000	.0000	.0000	.0000	
Sum	.0038	.0016	.0006	.0002	.0001					

(Entries compared with R. W. Nicholls, *Journal of Research of the National Bureau of Standards*, Vol. 65A, No. 5, Pg. 455, Sept. 1961)

TABLE 3  
 $N_2(2+)$  Band System ( $C^3\Pi_u - B^3\Pi_g$ )

$n_1/n_2$	0	1	2	3	4	5	6	Sum
0	.4492 (.4493)	.3289 (.3287)	.1471 (.1469)	.0523 (.0523)	.0164 (.0163)	.0048 (.0047)	.0018 (.0013)	1.0005
1	.3899 (.3899)	.0186 (.0187)	.2037 (.2038)	.2005 (.2003)	.1124 (.1124)	.0500 (.0484)		.9751
2	.1349 (.1349)	.3222 (.3223)	.0330 (.0330)	.0597 (.0596)	.1541 (.1614)	.1182 (.1427)		.8221
3	.0236 (.0236)	.2514 (.2515)	.1615 (.1630)	.1306 (.1181)	.0549 (.0018)			.6220
4	.0022 (.0022)	.0695 (.0696)	.3034 (.3034)	.0156 (.0475)				.3907
5	.0001	.0107	.0665					.0773
6	.0000	.0034						.0034
	.9999	1.0047	.9152	.4587	.3378	.1730	.0018	

(Entries compared with R. W. Nicholls, Journal of Research of the National Bureau of Standards, Vol. 65A, No. 5, pg. 454, Sept. 1961.)

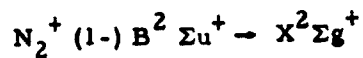
TABLE 4

 $N_2^+$  (Meinel) ( $A^2 \Pi_u - X^2 \Sigma_g^+$ )

$n_1/n_2$	0	1	2	3	4	5	6	Sum
0	.4514 (.4751)	.3873 (.3798)	.1342 (.1226)	.0241 (.0206)	.0024 (.0019)	.0002 (.0001)	.0000 (.0000)	.9996
1	.3288 (.3255)	.0191 (.0311)	.3193 (.3358)	.2504 (.2368)	.0706 (.0624)	.0107 (.0079)		.9989
2	.1458 (.1360)	.2058 (.2245)	.0338 (.0214)	.1584 (.1857)	.2906 (.2946)	.0549 (.1171)		.8893
3	.0515 (.0453)	.2012 (.1990)	.0606 (.0797)	.1001 (.1049)	.0977 (.0627)			.5111
4	.0160 (.0133)	.1122 (.1032)	.1830 (.1745)	.0002 (.0072)				.3114
5	.0046 (.0036)	.0483 (.0414)	.0002 (.1395)	.0352 (.1077)				.0883
6	.0019	.0587	.1914					.2520
Sum	1.0000	1.0326	.9225	.5684	.4613	.0548		

(Entries compared with R. W. Nicholls, *Journal of Research of the National Bureau of Standards*, Vol. 65A, No. 5, pg. 458, Sept. 1961)

TABLE 5



$n_1/n_2$	0	1	2	3	4	5	6	7	Sum
0	.6780 (.6509)	.2464 (.2588)	.0614 (.0702)	.0129 (.0160)	.0024 (.0033)	.0004 (.0006)	.0001 (.0001)	.0000 (.0000)	1.0016
1	.2836 (.3014)	.2633 (.2260)	.2878 (.2860)	.1204 (.1324)	.0355 (.0428)	.0086 (.0114)	.0019 (.0027)	.0004 (.0006)	1.0015
2	.0381 (.0454)	.3958 (.4060)	.0779 (.0506)	.2447 (.2290)	.1541 (.1654)	.0549 (.0711)			.9655
3	.0016 (.0022)	.0903 (.1056)	.4179 (.4137)	.0215 (.0121)	.2346 (.1557)				.7659
4	.0000 (.0000)	.0048 (.0069)	.1526 (.1660)	.1465 (.3792)					.3039
5	.0000 (.0000)	.0000 (.0000)	.0022 (.0134)						.0022
6	.0000 (.0000)	.0000 (.0000)							.0000
Sum	1.0013	1.0006	.9998	.5460	.4266	.0639	.0020	.0004	

(Entries compared with R. W. Nicholls, *Journal of Research of the National Bureau of Standards*, Vol. 65A, No. 5, Pgs. 458 and 459, Sept. 1961)

TABLE 6

O<sub>2</sub> (Schumann Runge) B<sup>3</sup> Σu<sup>-</sup> → X<sup>3</sup> Σg<sup>-</sup>

n <sub>1</sub> /n <sub>2</sub>	0	1	2	3	4	5	6	7	8	Sum	
0	.0000	.0000	.0000	.0000	.0000	.0003	.0014	.0046 (.0047)	.0122 (.0125)	.9869	
1	.0000	.0000	.0000	.0001	.0006	.0023	.0077	.0200 (.0205)	.0418 (.0426)	.8503	
2	.0000	.0000	.0001	.0005	.0022	.0079	.0215	.0433 (.0442)		.0755	
3	.0000	.0000	.0002	.0014	.0058	.0176	.0401	.0577		.1168	
4	.0000	.0001	.0006	.0033	.0120	.0298	.0560	.0450		.1468	
5	.0000	.0002	.0014	.0065	.0207	.0342	.1940			.2570	
6	.0000	.0004	.0027	.0111	.0312	.0277				.0731	
Sum	.0000	.0007	.0050	.0229	.0726	.1198	.3207	.1706	.0530		
n <sub>1</sub> /n <sub>2</sub>	9	10	11	12	13	14	15	16	17	18	19
0	.0273 (.0280)	.0521 (.0536)	.0852 (.0867)	.1198 (.121)	.1455 (.146)	.1528 (.153)	.1387 (.138)	.1089 (.107)	.0737 (.0721)	.0429 (.0416)	.0214 (.0205)
1	.0698 (.0708)	.0921 (.0927)	.0923 (.0920)	.0643 (.0629)	.0234 (.0218)	.0003 (.0001)	.0166 (.0183)	.0643 (.0670)	.1117 (.1140)	.1299 (.1300)	.1131 (.1120)
Sum	.0971	.1442	.1775	.1841	.1689	.1531	.1553	.1732	.1854	.1728	.1345

(Entries compared with G. R. Hébert and R. W. Nicholls, Proc. of the Phys. Soc., Vol. 78, Pg. 1030, 1961.)

TABLE 7  
NO ( $\beta$ )  $B^2\Pi \rightarrow X^2\Pi$

$n_1/n_2$	0	1	2	3	4	5	6	7	Sum
0	.0000 (.0001)	.0003 (.0003)	.0021 (.0020)	.0086 (.0086)	.0257 (.0256)	.0581 (.0580)	.1033 (.1033)	.1458 (.1480)	.3439
1	.0002 (.0001)	.0021 (.0021)	.0110 (.0109)	.0350 (.0349)	.0748 (.0746)	.1102 (.1103)	.1091 (.1097)	.0509 (.0643)	.3933
2	.0008 (.0008)	.0074 (.0073)	.0300 (.0297)	.0698 (.0696)	.0984 (.0984)	.0777 (.0778)	.0292 (.0228)	.0024 (.0014)	.3157
3	.0024 (.0024)	.0177 (.0175)	.0548 (.0545)	.0882 (.0882)	.0715 (.0701)	.0066 (.0148)	.1116 (.0604)		.3528
4	.0056 (.0055)	.0329 (.0325)	.0748 (.0745)	.0760 (.0757)	.0235 (.0219)	.0586 (.0033)			.2714
5	.0110 (.0108)	.0501 (.0496)	.0797 (.0798)	.0445 (.0418)	.0061 ( 0 )				.1914
6	.0186 (.0183)	.0645 (.0644)	.0697 (.0675)	.0081 (.0107)					.1609
Sum	.3860	.1750	.3221	.3302	.3000	.3112	.3532	.1991	

(Entries compared with R. W. Nicholls, The University of Western Ontario Scientific Report, Part XIX, Table 8, May 15, 1961.)

TABLE 8  
NO ( $\gamma$ )  $A^2\Sigma^+ - X^2\Pi$

$n_1/n_2$	0	1	2	3	4	5	6	7	Sum
0	.1653 (.1654)	.2636 (.2636)	.2377 (.2376)	.1606 (.1604)	.0908 (.0907)	.0456 (.0456)	.0211 (.0211)	.0092 (.0092)	1.0003
1	.3291 (.3291)	.1050 (.1049)	.0008 (.0008)	.0721 (.0721)	.1349 (.1349)	.1340 (.1339)	.0987 (.0986)	.0609 (.0608)	1.0004
2	.2906 (.2906)	.0146 (.0146)	.1545 (.1545)	.0753 (.0752)	.0006 (.0005)	.0342 (.0343)	.0884 (.0885)	.1057 (.1057)	.9984
3	.1504 (.1504)	.1904 (.1903)	.0500 (.0488)	.0309 (.0372)	.0295 (.1131)				.4512
4	.0508 (.0507)	.2370 (.2374)	.0366 (.0354)	.1526 (.1263)					.4770
5	.0116 (.0117)	.1588 (.1338)	.1077 (.1976)						.2781
6	.0032 (.0019)	.0352 (.0443)							.0384
Sum	1.0010	1.0046	.5873	.4915	.2558	.2138	.2082	.1758	
$n_1/n_2$	8	9	10	11	12	13	14	15	
0	.0039 (.0038)	.0016 (.0016)	.0006 (.0006)	.0002 (.0002)	.0001 (.0001)	.0000	.0000	.0000	
1	.0334 (.0333)	.0169 (.0169)	.0081 (.0081)	.0037 (.0037)	.0017 (.0016)	.0007 (.0007)	.0003 (.0003)	.0001 (.0001)	
2	.0900 (.0899)	.0630 (.0629)	.0388 (.0387)	.0218 (.0218)	.0115 (.0115)	.0058 (.0058)	.0027 (.0028)	.0009 (.0013)	
Sum	.1273	.0815	.0475	.0257	.0133	.0065	.0030	.0010	

(Entries compared with R. W. Nicholls, The University of Western Ontario Scientific Report, Part XIX, Table 9, May 15, 1961.)

TABLE 9  
 NO (Ogawa)  $b^4\Sigma^- \rightarrow a^4\Pi$

$n_1/n_2$	0	1	2	3	4	5	6	7	Sum
0	.2983	.2998	.1956	.1066	.0532	.0254	.0117	.0049	.9865
1	.4246	.0116	.0577	.1336	.1333	.0974	.0615	.0437	.9634
2	.2201	.1987	.1330	.0032	.0277	.0587	.0156		.6570
3	.0514	.3310	.0285	.1576	.0858	.2053			.8596
4	.0054	.1370	.3104	.0001	.3253				.7782
5	.0002	.0202	.2442	.0928	.0479				.4053
6	.0000	.0012	.0120						.0132
Sum	1.0000	.9995	.9814	.4939	.6732	.3868	.0888	.0486	

TABLE 10  
CN (Violet)  $B^2 \Sigma^+ - X^2 \Sigma^+$

$n_1/n_2$	0	1	2	3	4	5	6	Sum
0	.9201 (.920 )	.0743 (.074 )	.0054 (.005 )	.0003 ( 0 )	.0000	.0000	.0000	1.0001
1	.0788 (.079 )	.7863 (.787 )	.1207 (.121 )	.0133 (.014 )	.0008	.0000		.9999
2	.0011 (.001 )	.1369 (.137 )	.6915 (.691 )	.1480 (.147 )	.0198			.9973
3	.0000 (.000 )	.0025 (.002 )	.1784 (.180 )	.6475 (.625 )				.8284
4	.0000	.0000	.0049	.0198				.0247
5	.0000	.0000	.0413					.0413
6	.0000	.0000						.0000
Sum	1.0000	1.0000	1.0422	.8289	.0206	.0000	.0000	

(Entries compared with P. A. Fraser, W. R. Jarman and R. W. Nicholls, Transition Probabilities of Molecular Band Systems, Part VI, The University of Western Ontario Scientific Report No. 10, Pg. 5, July 1, 1953.)

TABLE 11

CN (Red)  $A^2 \Pi \rightarrow X^2 \Sigma^+$ 

$n_1/n_2$	0	1	2	3	4	5	6	Sum
0	.4995 (.499)	.3701 (.370)	.1110 (.111)	.0175 (.018)	.0016 (.002)	.0001 (.000)	.0000 (.000)	.9998
1	.3208 (.321)	.0463 (.046)	.3492 (.348)	.2218 (.223)	.0554 (.055)	.0030 (.007)		.9965
2	.1257 (.126)	.2425 (.242)	.0117 (.012)	.2152 (.209)	.2659 (.288)			.8610
3	.0394 (.040)	.1949 (.195)	.1029 (.100)	.0606 (.089)				.3978
4	.0109 (.011)	.0940 (.094)	.1747 (.184)					.2796
5	.0029 (.003)	.0462 (.036)						.0491
6	.0012 (.000)							.0012
Sum	1.0004	.9940	.7495	.5151	.3229	.0031	.0000	

(Entries compared with P. A. Fraser, W. R. Jarman and R. W. Nicholls, Transition Probabilities of Molecular Band System, Part VI, The University of Western Ontario Scientific Report No. 10, Pg. 4, July 1, 1953)

TABLE 12  
 CH (3900) B<sup>2</sup> Σ<sup>-</sup> → X<sup>2</sup> Π

$n_1/n_2$	0	1	2	3	4	5	6	7	Sum
0	.5937	.0006	.1691	.0525	.0080	.0557	.0331	.0017	.9144
1	.0013	.2176	.0167	.1116	.1397	.0068	.0457	.1127	.6521
2	.1845	.0166	.0004	.0162	.0018	.0453	.0244	.0006	.2898
3	.0000	.2174	.0012	.0745	.0087	.0092	.0428	.0791	.4329
4	.0811	.0165	.0576	.0142	.0389	.0049	.0039		.2171
5	.0007	.1610	.0215	.0010					.1842
6	.0383	.0102	.0813	.0513					.1811
Sum	.8996	.6399	.3478	.3213	.1971	.1219	.1499	.1941	

TABLE 13  
CH (4300) A<sup>2</sup> Δ - X<sup>2</sup> Π

$n_1/n_2$	0	1	2	3	4	5	6	7	Sum
0	.9996	.0002	.0000	.0000	.0000	.0000	.0000	.0000	.9998
1	.0002	.9986	.0001	.0000	.0001	.0000	.0000	.0000	.9990
2	.0000	.0001	.9947	.0028	.0000	.0000	.0000		.9976
3	.0000	.0000	.0032	.9819	.0131	.0016	.0001		.9999
4	.0000	.0000	.0000	.0146	.9253	.0421			.9820
5	.0000	.0000	.0000	.0000	.0496	.8862			.9358
6	.0000	.0000	.0001	.0023	.0128				.0152
Sum	.9998	.9989	.9981	1.0016	1.0009	.9299	.0001	.0000	

TABLE 14

CO<sup>+</sup> (Comet Tail) A<sup>2</sup> Π → X<sup>2</sup> Σ<sup>+</sup>

$n_1/n_2$	0	1	2	3	4	5	6	7	Sum
0	.0428 (.042)	.1520 (.149)	.2498 (.246)	.2514 (.249)	.1732 (.174)	.0860 (.089)	.0309 (.035)	.0045 (.011)	.9906
1	.1151 (.113)	.1932 (.191)	.0803 (.083)	.0006 (.000)	.0922 (.084)	.1940 (.183)	.1949 (.180)		.8703
2	.1698 (.166)	.0973 (.099)	.0033 (.002)	.1089 (.104)	.0791 (.089)	.0001 (.001)			.4585
3	.1825 (.180)	.0127 (.015)	.0751 (.071)	.0640 (.072)	.0000 (.002)				.3343
4	.1600 (.159)	.0058 (.004)	.0940 (.096)	.0015 (.001)					.2613
5	.1218 (.122)	.0452 (.041)	.0504 (.051)						.2174
6	.0832 (.085)	.0786 (.078)							.1618
Sum	.8752	.5848	.5529	.4264	.3445	.2801	.2258	.0045	

(Entries compared with W. R. Jarman, P. A. Fraser and R. W. Nicholls, *Astrophysics Journal* 122, 59 (1955))

TABLE 15

 $C_2$  (Swan)  $A^3\Pi_g \rightarrow X^3\Pi_u$ 

$n_1/n_2$	0	1	2	3	4	5	6	7	Sum
0	.7352 (.731)	.2132 (.211)	.0432 (.042)	.0074 (.007)	.0011 (.001)	.0001 (.000)	.0005 (.000)	.0000 (.000)	1.0007
1	.2396 (.237)	.3634 (.363)	.2786 (.280)	.0917 (.088)	.0223 (.020)	.0030 (.005)	.0030 (.000)		1.0016
2	.0245 (.024)	.3614 (.356)	.1617 (.162)	.2694 (.280)	.1334 (.124)	.1077 (.030)			1.0581
3	.0007 (.001)	.0598 (.060)	.4161 (.405)	.0675 (.057)	.2822 (.263)				.8263
4	.0000 (.000)	.0023 (.003)	.1142 (.097)	.1914 (.427)					.3079
5	.0000 (.000)	.0005 (.000)	.0198 (.006)						.0203
6	.0000 (.000)	.0000 (.000)							.0000
Sum	1.0000	1.0006	1.0336	.6274	.4390	.1108	.0035	.0000	

(Entries compared with P. A. Fraser, W. R. Jarman and R. W. Nicholls, Transition Probabilities of Molecular Band Systems, Part VI, The University of Ontario Scientific Report No. 10, Pg. 6, July 1, 1953.)

TABLE 16  
 $AlO(A-X) A^2 \Sigma^+ \rightarrow X^2 \Sigma^+$

$n_1/n_2$	0	1	2	3	4	5	6	Sum
0	.7298 (.7298)	.2377 (.2379)	.0307 (.0307)	.0016 (.0016)	.0000 ( 0 )	.0000 ( 0 )	.0000 ( 0 )	.9998
1	.2245 (.2244)	.3565 (.3565)	.3427 (.3429)	.0713 (.0715)	.0057 (.0047)	.0000 (.0007)		1.0001
2	.0402 (.0402)	.3007 (.3006)	.1604 (.1604)	.3894 (.3776)	.0531 (.1124)	.0156 (.0086)		.9594
3	.0050 (.0050)	.0881 (.0879)	.3012 (.3038)	.0748 (.0632)				.4691
4	.0004 (.0004)	.0166 (.0153)	.2053 (.1290)					.2223
5	.0000 ( 0 )	.0269 (.0017)						.0269
Sum	.9999	1.0265	1.0403	.5371	.0582	.0156	.0000	

(Entries compared with G. R. Hébert and R. W. Nicholls, Proc. of the Phys. Soc., Vol. 78, Pg. 1030, 1961.)

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<p>Aveo-Event Research Laboratory, Everett, Massachusetts  <b>VIBRATIONAL WAVE FUNCTIONS AND OVERLAP INTEGRALS OF VARIOUS BAND SYSTEMS</b>, by D. R. Childs. January 1963. 24 p. incl. illus. (Aveo-Event Research Report 147)  (Contract DA-19-020-ORD-5476)</p> <p>The vibrational wave functions of a diatomic molecule have been calculated for a Morse potential. A generating function for the polynomials has been obtained which enables one to derive recursion relationships among the polynomials. With the aid of these recursion relationships overlap integrals between the various vibrationally excited electronic states have been calculated for a Morse potential and a general expression has been obtained. Overlap integrals are exhibited for low vibrational quantum numbers for fifteen band systems.</p>	<p>Aveo-Event Research Laboratory, Everett, Massachusetts  <b>VIBRATIONAL WAVE FUNCTIONS AND OVERLAP INTEGRALS OF VARIOUS BAND SYSTEMS</b>, by D. R. Childs. January 1963. 24 p. incl. illus. (Aveo-Event Research Report 147)  (Contract DA-19-020-ORD-5476)</p> <p>The vibrational wave functions of a diatomic molecule have been calculated for a Morse potential. A generating function for the polynomials has been obtained which enables one to derive recursion relationships among the polynomials. With the aid of these recursion relationships overlap integrals between the various vibrationally excited electronic states have been calculated for a Morse potential and a general expression has been obtained. Overlap integrals are exhibited for low vibrational quantum numbers for fifteen band systems.</p>	<p>UNCLASSIFIED</p> <p>Molecules - Morse potential.  Radiation, molecular.  Morse potential.  Band systems - Overlap integrals.  I. Title.  II. Childs, D. R.  III. Aveo-Event Research Report 147.  IV. Contract DA-19-020-ORD-5476.</p>	<p>UNCLASSIFIED</p> <p>Molecules - Morse potential.  Radiation, molecular.  Morse potential.  Band systems - Overlap integrals.  I. Title.  II. Childs, D. R.  III. Aveo-Event Research Report 147.  IV. Contract DA-19-020-ORD-5476.</p>
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