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Expansion approach to photodissociation dynamics. II.
Correction formula for linewidth and numerical examples for HCN

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A correction formula for energy disposal and linewidth of photodissociation dynamics is proposed. This formula was derived from an identity similar to the Kato identity of the scattering theory. Thanks to the correction formula the resultant linewidth turns out to be more accurate and stable even when a relatively poor basis set is used. Numerical examples for assumed direct dissociation of HCN, DCN, and TCN and for the predissociation of HCN and DCN are presented.

I. INTRODUCTION

In the preceding paper (paper I), a new method was proposed in which an expansion technique of the scattering theory can be applied to photodissociation (and other dissociation phenomena), and some merits of the theory were emphasized. Letting $i$ and $f$ denote electronic states and $a$ and $m$ nuclear states, the partial linewidth due to the transition from state $(i, a)$ to state $(f, m)$ may be written as $\Gamma_{if}^e$. In the derivation of this quantity it was assumed that exact eigenfunctions of the Schrödinger equation that describes the collision process on a repulsive surface are known. However, no exact eigenfunction is available in general; thus some approximate functions that are based on a truncated basis set must be used to calculate $\Gamma_{if}^e$. The resulting “primitive” value of $\Gamma_{if}^e$ may be inaccurate and may also be unstable to changes of basis set. Thus, a correction formula, which yields reliable values even when a relatively poor (truncated) basis set is used, is highly desirable.

The approach to be taken here has an analogy in the variational method of quantum scattering theory. As is well known, one of the greatest merits of the variational scattering theory is that the variational functional itself is a correction formula for the reactance ($K$) or scattering ($S$) matrix. The zeroth order $K$ matrix that is calculated by solving an algebraic equation derived from a variational theory is very often inaccurate. However, the “corrected value” from the variational functional becomes dramatically more accurate and is expected to be close to the exact value even for a relatively poor basis set.

In this paper, the existence of such a correction formula for photodissociation will be shown by presenting its mathematical form explicitly. Further, it will be seen that the corrected energy disposal has the same accuracy as the transition probability of the $V-T$ energy transfer process, if the transition probability is estimated by the corrected $K$-matrix.

Another objective of this paper is to present some numerical examples of the theory we have proposed. Through the computation of assumed direct dissociation of HCN, DCN, and TCN some characteristics of the theory will be illustrated. Subsequently, we will present the results of HCN and DCN predissociation, some data for which were obtained in the recent experiment of MacPherson and Simons. All the geometries are assumed to be linear in our computational scheme.

II. CORRECTION FORMULA FOR $\Gamma_{if}^e$

In this section, a correction formula for $\Gamma_{if}^e$ is presented. To begin with, a brief outline of the MBD (minimum basis dependence) method for a variational scattering theory is presented, since the theoretical basis of the correction formula for $\Gamma_{if}^e$ is the same as that for the $K$ matrix given by the scattering theory. Also, we will adopt the MBD method as a tool to obtain an approximate scattering wave function, through which both the transition probabilities of the $V-T$ process and the $K$-matrix are calculated.

A. Outline of the MBD method

The MBD method is composed of a set of simple linear equations which are easily programmed. It is anomaly free and reliable. In addition, it provides a measure by which one can judge the reliability of the wave function.

Using long-range functions $S_a$ and $C_m$ ($m = 1, 2, \ldots$) as well as short-range ($L^1$) functions $g_b$ (the definitions of the symbols of this paper are basically the same as those cited in paper I (Ref. 1)), the column vector composed of the wave functions can be expanded as

$$\lambda = S + CK + gD,$$  \hspace{1cm} (2.1)

where the component $\lambda_m$ is an approximation to the exact function $\lambda^e_m$

$$(E - H_f)|\lambda^e_m\rangle = 0 \quad (m = 1, 2, \ldots, N_e).$$  \hspace{1cm} (2.2)

(The bar on any symbol in this section will be taken to indicate the exact value.) Equation (2.2) is the Schrödinger equation on a dissociative surface. If we define the basis transformation

$$\eta = g + SP^d + CP^e,$$  \hspace{1cm} (2.3)

then Eq. (2.1) can be rewritten as

$$\lambda = ST^d + CT^e + \eta D,$$  \hspace{1cm} (2.4a)

where

$$T^d = I - P^d,$$  \hspace{1cm} (2.4b)

$$T^e = K - P^d.$$  \hspace{1cm} (2.4c)

The functions $\eta_b$ are chosen to satisfy...
The mth element of the vector \( \vec{W} \) is
\[
\vec{W}_m = \langle \chi_m | X_m | \psi_n^\dagger \rangle .
\]
(2.11)

Equations (2.10) were derived essentially on the basis of Eq. (2.2). Therefore, Eq. (2.10) must be corrected when exact \( \chi_m \) are replaced by approximate \( \lambda_m \). 23-26

The following identity holds even when \( \lambda_m \) is not an exact wave function:
\[
\langle \chi_m | (E - H_f) | \psi_n^\dagger \rangle = \langle \chi_m | X_m | \psi_n^\dagger \rangle
\]
(2.12)

where \( \chi_m \) is the exact solution of
\[
(E - H_f) \chi_m = X_m | \psi_n^\dagger \rangle
\]
(2.13)

with an asymptotic form:
\[
\chi_m \approx \sum_{n} (A_n C_n - B_n S_n) ,
\]
(2.14)

\[\begin{aligned}
\langle S_m | (E - H_f) | \eta_h \rangle &= 0 \\
\langle C_m | (E - H_f) | \eta_h \rangle &= 0 \quad (2.5a) \\
\langle A_m | (E - H_f) | \eta_h \rangle &= 0 \quad (2.5b)
\end{aligned}\]

for all \( m \) and \( h \). The scattering wave functions \( \lambda_m (m = 1, 2, \ldots , N_c) \) of the MBD method are determined subject to:
\[
\langle g_m | (E - H_f) | \lambda_h \rangle = 0 \quad (2.6a)
\]

and the minimization of a norm:
\[
I_{MBD} = \text{Tr} \left( (T^m)^\dagger (T^m) + (T^r)^\dagger (T^r) \right) .
\]
(2.6b)

The correction of \( \Gamma_{im} \) is corrected as
\[
\Gamma_{im}^{\text{new}} - \frac{1}{2} \left( \Gamma_{im}^{\text{old}} + \delta_{im} \right)
\]
(2.7)

with this correction, the error is second order in \( \delta_{im} \) and \( \lambda_m - \lambda_h \). However, because this deviation gives an \( S \) matrix that is not unitary, \( \Gamma_{im}^{\text{new}} \) should be symmetrized:
\[
[K] = \frac{1}{2} \left( [K'] + [K']^\dagger \right). \quad (2.8)
\]

In general, \([K] \) is much closer to \( \overline{K} \) than \( K \) is, since \([K] \) includes only the second order error in \( \lambda_m - \lambda_h \).

**B. Correction of \( \Gamma_{im}^{\text{new}} \)**

As shown in paper I, the flux (on channel \( m \)), which is calculated based on the exact solution of an inhomogeneous Schrödinger equation [see Eq. (2.7b) of I], is given by
\[
\Gamma_{im}^{\text{new}} = A_m^2 + B_m^2 ,
\]
(2.9)

where
\[
A_n = -2 (I + K')^{-1} \vec{W} ,
\]
(2.10a)

and
\[
B_n = -2 \vec{K} (I + K')^{-1} \vec{W} .
\]
(2.10b)

The flux \( \Gamma_{im}^{\text{new}} \) was derived essentially on the basis of Eq. (2.2). Therefore, Eq. (2.10) must be corrected when exact \( \chi_m \) are replaced by approximate \( \lambda_m \). 23-26

Equation (2.12) corresponds to the Kato identity \(^8\) of the scattering theory. For the exact \( \chi_m \), the second term in Eq. (2.12) would be zero [see Eq. (2.2)]; however, for approximate \( \lambda_m \) the term \( \langle \chi_m | (E - H_f) | \lambda_m \rangle \) must be estimated. \( \chi_m \) can be expanded in terms of a complete set of basis functions as
\[
\chi_m = \sum_{n} (A_n C_n - B_n S_n) + \sum_{n} C_n | \psi_n^\dagger \rangle + \sum_{n} S_n | \psi_n^\dagger \rangle .
\]
(2.16)

In this equation the short-range functions of the complete set are separated into two sets, \( G_1 \) and \( G_2 \). The functions contained in \( G_1 \) are those used to construct the approximate scattering function \( \lambda_m \) [see Eq. (2.1)] and are defined by the condition Eq. (2.6a). \( G_2 \) is the complementary set of \( G_1 \). If the set \( G_1 \) is physically sufficient, we will have
\[
\langle \chi_m | (E - H_f) | \lambda_m \rangle \approx \sum_{n} (A_n C_n - B_n S_n) + \sum_{n} C_n | \psi_n^\dagger \rangle + \sum_{n} S_n | \psi_n^\dagger \rangle .
\]
(2.17)

to a good approximation due to Eq. (2.6a) and since the contribution from \( G_2 \) should be very small. Then Eq. (2.12) turns out to be
\[
\begin{aligned}
\sum_{n} (- \frac{1}{2} \delta_{mn} + \langle C_n | (E - H_f) | \lambda_m \rangle) A_n \\
- \frac{1}{2} K_{mn} + \langle S_m | (E - H_f) | \lambda_m \rangle) B_n \approx \langle \lambda_m | X_m | \psi_n^\dagger \rangle
\end{aligned}
\]
(2.18)
or in matrix notation
\[
(\Lambda^e - \frac{1}{2} I) A - (\Lambda^e + \frac{1}{2} K^e) B \approx W ,
\]
(2.19)

where \( \Lambda^e = \langle C_n | (E - H_f) | \lambda_m \rangle \) and \( \Lambda^e = \langle S_m | (E - H_f) | \lambda_m \rangle \). Using the relation Eq. (2.15), we get
\[
\vec{A} \approx [(\Lambda^e - \frac{1}{2} I) - (\Lambda^e + \frac{1}{2} K^e)]^{-1} \vec{W} ,
\]
(2.20a)

\[
\vec{B} \approx (\Lambda^e - \frac{1}{2} I) - (\Lambda^e + \frac{1}{2} K^e)]^{-1} \vec{W} .
\]
(2.20b)

Again \( \vec{K} \) is not available. Instead, we can replace \( \vec{K} \) by the accurate \([K] \) of Eq. (2.8). Therefore, the corrected values of \([A] \) and \([B] \) will be
\[
[A] = [(\Lambda^e - \frac{1}{2} I) - (\Lambda^e + \frac{1}{2} K^e)]^{-1} W
\]
(2.21a)

and
\[
[B] = [K] [(\Lambda^e - \frac{1}{2} I) - (\Lambda^e + \frac{1}{2} K^e)]^{-1} W .
\]
(2.21b)

Apparently, it is \( \Lambda^e \) and \( \Lambda^e \) that were introduced into Eq. (2.10) as a correction. Thus \( \Gamma_{im}^{\text{new}} \) is corrected as
\[
\Gamma_{im}^{\text{new}} = [A_m^2] + [B_m^2] .
\]
(2.22)

The essential approximation made to obtain Eq. (2.21) was
\[
\langle g_f | (E - H_f) | \lambda_m \rangle = 0 \quad (g_f \in G_2) .
\]
(2.23)

This approximation was also adopted in order to derive \([K] \) of Eq. (2.7). 5 Thus the order of the accuracy of \([A] \) and \([B] \) is similar to that of \([K] \). When \( G_1 \) is nearly complete, \( I_{MBD} \) should be quite small. Then \([K] \) becomes a very good approximation, and subsequently so do \([A] \), \([B] \), and \( \Gamma_{im}^{\text{new}} \). So, \( I_{MBD} \) may also be considered as a measure of accuracy for \( \Gamma_{im}^{\text{new}} \).

Finally, we will describe \([A]\) and \([B]\) of Eq. (2.21) in
terms of the language of the MBD method. Define matrices $a$ and $b$ by

$$a = M^{a}T^{a} + M^{c}T^{c}$$  

(2.24a)

and

$$b = M^{a}T^{e} + M^{c}T^{c}$$  

(2.24b)

where $M^{a} = (C_{a} \odot (E - H_{f}))(S_{a})$ and so on. After some manipulation we have

$$[A] = -2(I + K[K] + 2b[K] - 2a)^{-1}W,$$  

(2.25a)


(2.25b)

The matrices in parentheses in Eqs. (2.25) are all needed needed for the computation of $\lambda$, therefore little extra time is necessary for the correction.

III. COMPUTATIONAL DETAIL FOR TRIATOMIC MOLECULES

A. Hamiltonian

Consider the dissociation of a linear molecule,  

$$A - B - C \rightarrow A + B + C,$$  

where the masses and coordinates of each atom are denoted by $m_{A}$, $m_{B}$, and $m_{C}$ and $x_{A}$, $x_{B}$, and $x_{C}$, respectively. As is well known, a transformed set of coordinates, where

$$x = -x_{A} + x_{B},$$  

(3.1)

$$R = x_{A} - \frac{m_{B}}{m_{A} + m_{B}} x_{B} - R_{0},$$  

(3.2)

with $x_{B} = 0$ gives a Hamiltonian of the form

$$H = -\frac{1}{2\mu_{ab}} \frac{g^{2}}{\partial r^{2}} - \frac{1}{2\mu} \frac{g^{2}}{\partial R^{2}} + V(r, R),$$  

(3.3)

where

$$\frac{1}{\mu_{ab}} = \frac{1}{m_{A}} + \frac{1}{m_{B}}, \quad \frac{1}{\mu} = \frac{1}{m_{A} + m_{B}} + \frac{1}{m_{C}}.$$  

(3.4)

In Eqs. (3.1) and (3.2), $x_{0}$ and $R_{0}$ are constants arbitrarily determined. The potential function $V$ is defined as follows: for the bound state

$$V_{C} = \frac{1}{2}K_{1}(x_{A} - x_{C})^{2} + \frac{1}{2}K_{2}(x_{A} - x_{C})^{2} + K_{1}(x_{A} - x_{C})(x_{A} - x_{C}) + \Delta E_{e},$$  

(3.5)

and for the repulsive surface

$$V_{G} = \frac{1}{2}K_{3}(x_{A} - x_{C})^{2} + D \exp(-x_{A}) + \Delta E_{e}. $$  

(3.6)

$x_{A}$ and $x_{C}$ are the equilibrium positions of atoms A and C on the bound state surface, and $x_{A}$ is the equilibrium position of atom A in the A-B molecule after the dissociation. Hereafter we set $x_{A} = x_{A}$. Further, $\Delta E_{e}$ and $\Delta E_{e}$ are the energetic origins of the bound and repulsive surfaces. Although the repulsive part of Eq. (3.6) is described as a single term, a more general form

$$\sum_{i} D_{i} \exp(-\alpha_{i} x_{e})$$  

(3.7)

may be necessary to describe \textit{ab initio} potential surfaces and/or to incorporate an attractive part into $V_{G}$.  

B. Basis functions

The short-range functions are taken to be the Hermitean functions. The ground state wave functions $\psi_{i}^{R}$ are expanded as

$$\psi_{i}^{R} = \sum_{\mu} \sum_{\nu} C_{i}^{\mu} \xi_{i}^{\nu}(r - x_{i}) \xi_{j}^{\nu}(R - R_{i}),$$  

(3.8)

where $x_{i}$ and $R_{i}$ are the equilibrium positions of atoms in the $(r, R)$ representation. If desired, anharmonicity may be taken into account in $V_{C}$. For this reason, normal coordinates have not been used for $\psi_{i}^{R}$

The long-range functions are taken to be

$$S_{m} = \{(\mu/k_{m})^{1/2} \xi_{m}(r/R) \sin(k_{m} R)$$  

(3.9a)

$$C_{m} = \{(\mu/k_{m})^{1/2} \xi_{m}(r/R) \cos(k_{m} R)$$  

(3.9b)

In the above equations, $\xi_{m}(r/R)$ is the eigenfunction for the resultant oscillator $A - B$ [see Eq. (3.6)]. The parameters $k_{m}$ (for all $m$) were fixed at a value of 5 in our later calculations since this seemed to give the best results. The smooth functions $S_{m}$ and $C_{m}$ ($m = 0, 1, \ldots, N_{c} - 1$) satisfy the necessary boundary conditions where $N_{c}$ is the number of open channels.

The short-range functions $(g_{i}^{s})$, which are used to expand $\zeta_{m}$, are the product of the Hermitian functions $g_{i}(r, R) = \xi_{i}^{s}(r/R) \xi_{j}^{s}(R/B)$.

$$d = 0, 1, \ldots, N_{c} - 1$$  

(3.10)

$$e = 0, 1, \ldots, N_{c} - 1$$  

The nonlinear parameter $\zeta_{i}$ is to be selected, as well as $R_{0}$, so as to give good results.

Almost all the necessary integrals (the overlap integrals and the matrix element of $E - H_{f}$) are generated by recursion formulae that allow efficient and highly accurate computations. As an example, the recursion formula for the Franck-Condon overlap integral is shown in the Appendix.

IV. RESULTS FOR HCN

In this section some results are presented using the formalism developed in this and the preceding papers. Because of the wealth of experimental and theoretical information available, HCN, DCN, and TCN have been chosen to test the method. The reaction of interest is

$$\operatorname{HCN}(X^{1}S^{-}) \rightarrow \operatorname{HCN}(C^{1}A^{-}) + \operatorname{CN}(B^{2}S^{+}) + \operatorname{CN}(B^{2}S^{+}).$$  

(4.1)

Many dynamical theories have been tested by using this reaction as a direct dissociation. Very recently, however, Simons and his co-workers have confirmed experimentally that HCN dissociates via a predissociative path, viz.

$$\operatorname{HCN}(X^{1}S^{-}) \rightarrow \operatorname{HCN}(C^{1}A^{-}) + \operatorname{CN}(B^{2}S^{+}) + \operatorname{CN}(B^{2}S^{+}).$$  

(4.2)

Our sample calculations were carried out for both the assumed direct dissociation and the predissociation. In all cases the reaction is assumed to take place within
TABLE I. Molecular parameters.a

A. Direct dissociation [HCN(X 2\Sigma^+)]

\[ \beta_1 = 2.011 \]
\[ \beta_2 = 2.174 \]
\[ K_1 = 0.373 \quad (\omega_1 = 3311.5 \text{ cm}^{-1}) \]
\[ K_2 = 1.150 \quad (\omega_2 = 2096.7 \text{ cm}^{-1}) \]
\[ K_3 = 0.0 \]
\[ \Delta E_g - \Delta E_e = 0.3175 \text{ (8.64 eV)} \]
\[ \alpha = 3.535 \text{ bohr}^{-1} \text{ (6.630 Å)} \]

B. Predissociation [HCN(\tilde{C}^1\Pi), \text{DCN}(\tilde{C}^1\Pi)]

\[ \beta_{\text{DCN}} = 2.066 \]
\[ \beta_{\text{HCN}} = 2.386 \]
\[ K_1 (\text{HCN}) = 0.171 \quad (\omega_1 = 2273 \text{ cm}^{-1}) \]
\[ K_1 (\text{DCN}) = 0.165 \quad (\omega_1 = 1454 \text{ cm}^{-1}) \]
\[ K_2 (\text{HCN}) = 0.629 \quad (\omega_2 = 1655 \text{ cm}^{-1}) \]
\[ K_2 (\text{DCN}) = 0.492 \]

C. CN(\tilde{A}^2\Pi)

\[ \beta_{\text{CN}} = 2.174 \]
\[ K_1 = 1.145 \quad (\omega = 2164.1 \text{ cm}^{-1}) \]

aIn atomic units. Length is in bohrs, energy in hartrees, and force constant in hartree/bohr (Ref. 2).

Reference 15.

Reference 4.

collinear geometries.

The molecular parameters necessary for the computation are listed in Table I. The exponential factor \( \alpha = 3.535 \text{ bohr}^{-1} \) of the purely repulsive surface is the same as that used by Band and Freed, 12 Atabek et al., 13 and Shapiro et al. 14 The preexponential factor \( D \) in Eq. (3.6) is varied in order to investigate its effect on the results. The bond lengths for \( \tilde{C}^1\Pi(3^1\Pi) \) in theoretical notation 15 were taken from the theoretical results of Schaefer et al. 16 The difference in the energy origins of the ground and excited states, that is \( \Delta E_g - \Delta E_e \), was estimated to be 0.3175 a.u. (8.64 eV) on the basis of the dissociation energy of HCN given by Davis and Okabe 14 and spectroscopic data. 15 The threshold energy for dissociation of HCN has been reported as 8.8 \pm 1.0 \text{ eV} based on electron impact experiments. 16 All other parameters, except for those given by the experiment of McPherson and Simons, 4 were obtained from Herzberg. 17

As stated in Sec. II, the MBD method has been used to solve the full collision problem \( V-T \) energy transfer process on the repulsive surface). To make sure that the program coded for the MBD method works correctly, a part of the data given by Clark and Dickinson 19 was successfully reproduced.

A. Effect of the correction formula \([\Gamma_{\text{mbd}}^m]\)

Calculations have been performed for the assumed direct dissociation, with wavelength \( \lambda = 1350 \text{ Å} \), to investigate the behavior of \( \Gamma_{\text{mbd}}^m \) and \( \Gamma_{\text{mp}}^m \). In this section and Sec. IV B the ground state basis set \( (N_x', N_y') \) is taken to be \((7,7), \) with \( \beta_1 = 5.148, 5.959, \) and 6.537 for HCN, DCN, and TCN, respectively, and \( \alpha_1 = 10.771 \) for all three species.

In Tables II and III are shown the fluxes relative to \( \Gamma_{\text{mbd}}^m \) or \( \Gamma_{\text{mp}}^m \) \( \chi_{ij}^m \) is set to unity throughout this paper. Also listed in the tables are \( \Gamma_{\text{mbd}}^m \), some elements of the \( K \)-matrix and its correction \( [K] \), and the corresponding transition probabilities for the \( V-T \) process. The latter is defined by

\[ P_{ij} = |[S_{ij}]|^2, \]

where \( |S_{ij}| \) is the \((i,j)\) element of the \( S \)-matrix calculated from \([K]\).

The dependence of \([\Gamma_{\text{mbd}}^m]\) on basis set size is shown in Table II. Clearly, \([\Gamma_{\text{mbd}}^m]\) and \([\Gamma_{\text{mp}}^m]\) converge considerably

TABLE II. Basis size dependence of the branching ratio, \( K \)-matrix, and transition probability for an assumed direct dissociation of HCN at \( \lambda = 1350 \text{ Å}, \)

\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\((N_x', N_y')\) & \( I_{\text{mbd}} \) & \( \Gamma_{\text{mbd}}^1 \) & \( \Gamma_{\text{mbd}}^2 \) & \( K_{\text{mbd}} \) & \( P_{\text{mbd}} \) & \( P_{\text{mp}} \) \\
\hline
\((5, 5)\) & 0.635 (0) & 0.316 (2) & 0.516 (0) & 0.647 (0) & 0.761 (0) & 0.161 (0) \\
& 0.211 (0) & 0.514 (2) & 0.902 (1) & 0.894 (0) & & \\
\((5, 10)\) & 0.979 (0) & 0.269 (0) & 0.502 (2) & 0.108 (1) & 0.137 (0) & 0.286 (0) \\
& 0.131 (0) & 0.210 (2) & 0.105 (1) & 0.103 (0) & & \\
\((5, 15)\) & 0.508 (0) & 0.131 (0) & 0.208 (2) & 0.976 (0) & 0.138 (0) & 0.287 (0) \\
& 0.129 (0) & 0.205 (2) & 0.103 (1) & 0.101 (0) & & \\
\((5, 20)\) & 0.310 (0) & 0.138 (0) & 0.223 (2) & 0.104 (1) & 0.138 (0) & 0.285 (0) \\
& 0.128 (0) & 0.202 (2) & 0.102 (1) & 0.100 (0) & & \\
\((5, 25)\) & 0.401 (0) & 0.114 (0) & 0.162 (2) & 0.101 (1) & 0.138 (0) & 0.285 (2) \\
& 0.128 (0) & 0.201 (2) & 0.102 (1) & 0.100 (0) & & \\
\((5, 30)\) & 0.435 (0) & 0.128 (0) & 0.196 (2) & 0.103 (1) & 0.138 (0) & 0.285 (2) \\
& 0.128 (0) & 0.201 (2) & 0.102 (1) & 0.100 (0) & & \\
\((5, 35)\) & 0.311 (0) & 0.138 (0) & 0.216 (2) & 0.103 (1) & 0.138 (0) & 0.285 (2) \\
& 0.128 (0) & 0.201 (2) & 0.102 (1) & 0.100 (0) & & \\
\((7, 20)\) & 0.310 (0) & 0.138 (0) & 0.223 (2) & 0.104 (1) & 0.138 (0) & 0.285 (2) \\
& 0.128 (0) & 0.202 (2) & 0.102 (1) & 0.100 (0) & & \\
\hline
\end{tabular}

aComputational results with \( \beta_0 = 4.25, \beta_1 = 3.18, \) and \( N_x = 3; \) \( \Gamma_{\text{mp}}^m \) is abbreviated \( \Gamma_{\text{mp}}^1. \)

bNumbers in parentheses indicate multiplicative power of 10.

faster than \( r_1 \) almost the same for \( \alpha_r \) and \( (5, 30) \). This curious behavior suggests that Hermi­
open channels \( \Gamma_\text{open} \) given the exact value and even \( (5, 15) \) produces good
Eq. (3.10)) to the third open channel is not negligible, \( P_{02} \):
that the contribution from the closed channels
\( \Gamma_\text{closed} \) respectively, for the \( (5, 20) \) basis. This discrepancy means
Truncation of the basis set size to \( N_r = 3 \) (the number of
open channels \( N_r = 3 \)) has a negative effect on
\( \Gamma_\text{open} \) for the same system.\( \Gamma_\text{open} \) for the \( (5, 20) \) basis. This discrepancy means
As is expected, the extent of convergence of \( \Gamma_\text{open} \) is almost the same for \( \Gamma_\text{closed} \), in spite of a considerably larger \( \Gamma_\text{MBD} \).
Note that any results having \( \Gamma_\text{MBD} \) larger than \( 0.5 \times 10^3 \) were discarded. Fur­
ther, the \( \Gamma_\text{MBD} \) for \( (5, 20) \) is smaller than those of \( (5, 25) \) and \( (5, 30) \). This curious behavior suggests that Hermi­
tian functions may not necessarily be good basis func­
tions for describing a simple repulsive surface.

Another important point arising from Table II concerns the effect of the closed channels on \( \Gamma_\text{open} \) and \( P_{02} \). Truncation of the basis set size to \( N_r = 3 \) (the number of open channels \( N_r = 3 \)) has a negative effect on \( \Gamma_\text{open} \) and \( P_{02} \).\( \Gamma_\text{open} \): \( \Gamma_\text{open} \) = 0.196 \times 10^{10} \text{ and } P_{02} = 0.269 \times 10^{-7}, \text{ for the (3, 20) basis, while 0.202 \times 10^{-7} \text{ and 0.285 \times 10^{-2}, respectively, for the (5, 20) basis. This discrepancy means that the contribution from the closed channels [\( d = 4 \) for Eq. (3.10)] to the third open channel is not negligible. Therefore, one must be careful about the high channels when a small \( N_r \) basis set is used. Fortunately, the values for high channels, for example \( \Gamma_\text{open} \) and \( P_{02} \), are generally so small that the total values, such as \( \Gamma_\text{open} \) or the total cross section, will not be appreciably in­
fluenced by including the closed channel contributions.

Table III shows the dependence on the nonlinear par­

ter \( \beta \) [Eq. (3.10)] for the same system. Since \( \beta \) is not optimized in the process of the MBD method, \( \Gamma_\text{open} \) should depend on \( \beta \). As can be seen from the table \( \Gamma_\text{open} \) is much more stable than \( \Gamma_\text{open} \). It is some­
what surprising that \( \Gamma_\text{open} \) remains quite good even when \( \Gamma_\text{MBD} \) becomes large. However, this is not a general
phenomenon, since we have found many examples in which \( \Gamma_\text{open} \) is poor when \( \Gamma_\text{MBD} \) is large.

The accuracy and stability of \( \Gamma_\text{open} \), which are expected theoretically, have been demonstrated. In the remainder of this paper, we will use the symbols \( \Gamma_\text{open} \) and \( \Gamma_\text{open} \) for the values that have already been corrected, since the
uncorrected (zeroth order) values will not henceforth be of interest. The basis set used for excited states in the
remainder of the paper is \( (5, 30) \).

### B. Isotope effect

In order to reproduce the experimental results ob­
tained by Mele and Okabe\(^2\) for HCN photodissociation,
Band and Freed (BF)\(^1\) determined the potential func­
tion parameters as \( \alpha = 3.535 \text{ bohrs}^{-1} \text{ and } D = 3.57 \times 10^3 \text{ hartrees} \), while Atabek, Jortner, and co-workers (AJ)\(^3\)
use \( \alpha = 3.535 \text{ bohrs}^{-1} \text{ and } D = 12.86 \text{ hartrees} \). Thus, the repulsive surface of BF is located 1.59 bohr farther from the carbon atom than that of AJ. Naturally, the isotope effect estimated by these two groups should dif­
fer: \( \Gamma_{00} \) (DCN)/\( \Gamma_{00} \) (HCN) \( \sim 10^{-4} \) for BF and \( \Gamma_{00} \) (DCN)/
\( \Gamma_{00} \) (HCN) \( \sim 0.2 \) for AJ at \( \lambda = 1295 \AA \). Since these computa­tions are based on the assumed direct dissociation, the result may not necessarily have physical meaning. Nonetheless, we have also investigated some general properties of the HCN isotope effect at \( \lambda = 1295 \AA \), since the problem has theoretical importance.

Band and Freed\(^1\) have proposed the following relationship for isotope effects:
\[
\Gamma_{00} \propto \exp \left(- L_1 \mu \right),
\]
where \( L_1 \) is some constant. To test this equation, \( \ln \Gamma_{00} \) is plotted as a function of \( \mu \) for a range of \( D \) values in Fig. 1. In spite of the fact that Eq. (4.4) was derived as a rough estimate of the isotope effect, our full quantum mechanical calculation has shown that Eq. (4.4) holds almost exactly in the tunneling region (large \( D \) region). Only below \( D \sim 50 \text{ hartree do serious deviations from Eq. (4.4)} \) appear. As suggested by AJ the constant \( L_1 \) of Eq. (4.4) depends on \( D \). To see this, \( \ln \Gamma_{00} \) (of HCN, DCN, and TCN), and \( \ln \Gamma_{00} \) (of HCN and DCN) vs \( D \) are depicted in Fig. 2. Qualitatively, \( \Gamma_{00} \) in the tunneling region (\( D \approx 190 \)) are proportional to \( D \); furthermore, their linearity coefficients are proportion­
al to \( \mu \), that is
\[
\ln \Gamma_{00} \propto L_2 D \mu \mu \text{,} \text{ (4.5)}
\]
where \( L_2 \) is a constant. Physically, we have \( D \propto \exp (\alpha R_\text{ex}) \) [see Eqs. (3.2) and (3.6)], where \( R_\text{ex} \) is the distance be­tween the repulsive surface and the harmonic potential on the \( R \) coordinate (see Fig. 3). Thus we have
\[
\ln \Gamma_{00} \propto L_2 D \mu \mu \text{ exp}(\alpha R_\text{ex}) \text{, (4.6)}
\]
Although Eq. (4.6) is merely an empirical expression, this suggests a strong dependence of the isotope effect on the repulsive surface.

In contrast to \( \Gamma_{00} \), the branching ratio \( \Gamma_{02} \) is not as sensitive to \( D \) in the tunneling region (Fig. 2). Therefore we cannot expect large changes of \( \Gamma_{02} \) with the var­i­
at of \( D \) in the tunneling region.

---

**TABLE III. Effect of nonlinear parameter \( \beta \) on the branching ratio and transition probability of HCN direct dissociation at \( \lambda = 1350 \AA \),**

<table>
<thead>
<tr>
<th>( \beta )</th>
<th>( \Gamma_{00} )</th>
<th>( \Gamma_{01} )</th>
<th>( \Gamma_{02} )</th>
<th>( P_{01} )</th>
<th>( P_{02} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.85</td>
<td>0.144 (1)</td>
<td>0.131 (0)</td>
<td>0.209 (2)</td>
<td>0.203 (2)</td>
<td>0.138 (0)</td>
</tr>
<tr>
<td>4.00</td>
<td>0.194 (2)</td>
<td>0.128 (0)</td>
<td>0.215 (2)</td>
<td>0.203 (2)</td>
<td>0.138 (0)</td>
</tr>
<tr>
<td>4.15</td>
<td>0.233 (4)</td>
<td>0.128 (0)</td>
<td>0.229 (2)</td>
<td>0.202 (2)</td>
<td>0.138 (0)</td>
</tr>
<tr>
<td>4.30</td>
<td>0.355 (4)</td>
<td>0.138 (0)</td>
<td>0.225 (2)</td>
<td>0.202 (2)</td>
<td>0.138 (0)</td>
</tr>
<tr>
<td>4.60</td>
<td>0.743 (3)</td>
<td>0.128 (0)</td>
<td>0.234 (2)</td>
<td>0.201 (2)</td>
<td>0.138 (0)</td>
</tr>
<tr>
<td>4.90</td>
<td>0.253 (3)</td>
<td>0.123 (0)</td>
<td>0.190 (2)</td>
<td>0.201 (2)</td>
<td>0.138 (0)</td>
</tr>
<tr>
<td>5.20</td>
<td>0.164 (2)</td>
<td>0.131 (0)</td>
<td>0.207 (2)</td>
<td>0.201 (2)</td>
<td>0.138 (0)</td>
</tr>
<tr>
<td>5.50</td>
<td>0.377 (2)</td>
<td>0.146 (0)</td>
<td>0.245 (2)</td>
<td>0.201 (2)</td>
<td>0.138 (0)</td>
</tr>
</tbody>
</table>

*Comparative results with basis set \( N_r = 5 \) and \( \beta = 3.535 \times 10^3 \text{ bohrs}^{-1} \). \( \Gamma_{02} \) abbreviates \( \Gamma_{02} \).

*Numbers in parentheses indicate multiplicative power of 10.
FIG. 1. Isotope effect of HCN (DCN, TCN) system for assumed direct dissociation at λ=1295 Å.

FIG. 2. D dependence of isotope effect of HCN (DCN, TCN) for assumed direct dissociation at λ=1295 Å. Broken lines show logarithm of partial linewidth vs D.

In Table IV, \( \Gamma_m^f \) (\( m = 0-3 \)), which were calculated with \( D = 12.86, 50, \) and 190, are shown. Higher values of \( D \) need not be investigated since for \( D > 190 \) hartrees, \( \Gamma_m^f \) is nearly independent of \( D \). It should be clear that the best fit values of \( D \) to reproduce the results of Mele-Okabe will be found in the range of \( 12.86 < D < 50 \). We did not attempt to look for the best \( D \) value, since the assumed direct dissociation may not have physical meaning. Now, the isotope ratio for the line widths is \( \Gamma_m^f(DCN)/\Gamma_m^f(HCN) \sim 0.80, 1.17, \) and 0.313 for \( D \).

TABLE IV. D dependence of branching ratio for HCN, DCN, and TCN. Direct dissociation at \( \lambda = 1295 \) Å.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>( D = 12.86 )</th>
<th>( D = 50 )</th>
<th>( D = 190 )</th>
<th>Mele-Okabe(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>0.79 (0)(^a)</td>
<td>0.126 (0)</td>
<td>0.978 (−1)</td>
<td>0.455 (0)</td>
</tr>
<tr>
<td>DCN</td>
<td>0.140 (0)</td>
<td>0.180 (0)</td>
<td>0.114 (0)</td>
<td></td>
</tr>
<tr>
<td>TCN</td>
<td>0.499 (0)</td>
<td>0.263 (0)</td>
<td>0.108 (0)</td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>0.115 (0)</td>
<td>0.432 (−2)</td>
<td>0.261 (−2)</td>
<td>0.682 (−1)</td>
</tr>
<tr>
<td>DCN</td>
<td>0.200 (−1)</td>
<td>0.713 (−2)</td>
<td>0.286 (−2)</td>
<td></td>
</tr>
<tr>
<td>TCN</td>
<td>0.260 (−1)</td>
<td>0.772 (−2)</td>
<td>0.215 (−2)</td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>0.360 (−2)</td>
<td>0.362 (−4)</td>
<td>0.171 (−4)</td>
<td>0.909 (−2)</td>
</tr>
<tr>
<td>DCN</td>
<td>0.189 (−2)</td>
<td>0.421 (−4)</td>
<td>0.107 (−4)</td>
<td></td>
</tr>
<tr>
<td>TCN</td>
<td>0.101 (−2)</td>
<td>0.289 (−4)</td>
<td>0.439 (−5)</td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>0.448 (−5)</td>
<td>0.148 (−7)</td>
<td>0.562 (−8)</td>
<td>&lt;0.909 (−2)</td>
</tr>
<tr>
<td>DCN</td>
<td>0.842 (−7)</td>
<td>0.274 (−9)</td>
<td>0.437 (−10)</td>
<td></td>
</tr>
</tbody>
</table>

\( \Gamma_m^f(DCN)/\Gamma_m^f(HCN) \) \sim 0.80, 1.17, \) and 0.313 for \( D \).

\( a \)Numbers in parentheses indicate multiplicative power of 10.

\( b \)Reference 21.

\( \Gamma_m^f(DCN)/\Gamma_m^f(HCN) \) \sim 0.80, 1.17, \) and 0.313 for \( D \).

\( \Gamma_m^f(DCN)/\Gamma_m^f(HCN) \) \sim 0.80, 1.17, \) and 0.313 for \( D \).

\( \Gamma_m^f(DCN)/\Gamma_m^f(HCN) \) \sim 0.80, 1.17, \) and 0.313 for \( D \).

\( \Gamma_m^f(DCN)/\Gamma_m^f(HCN) \) \sim 0.80, 1.17, \) and 0.313 for \( D \).

\( \Gamma_m^f(DCN)/\Gamma_m^f(HCN) \) \sim 0.80, 1.17, \) and 0.313 for \( D \).
In these calculations a (8, 8) basis set was used for the
transition of paper I, a subscript
bound, excited state in the predissociation process. )
been determined experimentally. (Following the nota­
tion of (1, 9, 11) and (0, 0, 0) of C\(^{1}A\)' HCN for D=12.86, 50, and 190 hartrees. All of the \(\Gamma_{sa}\) for (1, \(v'_{0}\)) \((v'_{0}= 9, 10, 11) can be much larger than the others only when \(D=190\). Therefore, the
experimental fact cannot be accounted for by \(D=12.86\) and
50 (non tunneling mechanism).

The situation is illustrated in Fig. 3 (after Simons\(^{4}\)),
where the potential function for the \(x_{p}\) coordinate is plotted.
Classical turning points of the \(S_{0}\) wave [see Eqs. (3.9a) and (2.1)] for the
given energies of some entrance channels (sa) are also depicted. For the bound
state, the \(x_{p}\) potential is taken to be harmonic, while
the repulsive curve is modeled by \(D(\exp(-\alpha_{p}x))\). For
\(D=190\) hartrees, the classical turning points of the
channels (1, \(v'_{0}\), 0) \((v'_{0}= 9, 10, 11) of HCN which were con­
cidered in Table V are inside of the C–H Franck–Condon
region having \(v'_{1}=1\), whereas the turning points of other
channels of HCN are located outside the range of the C–H
Franck–Condon region with \(v'_{1}=0\) (small Franck–Condon
overlap). In clear contrast to the case of \(D=190\), the
potentials with \(D=12.86\) and 50 do not have such a
characteristic. On the other hand, even (2, \(v'_{0}\), 0) \((v'_{0}
= 7, 8, 9) of DCN have the turning points outside of the
Franck–Condon region of \(v'_{1}\) (CD). (However, the turn­
ing point of (2, 9, 0) of DCN is too close to that of the vibra­tional level of \(v'_{1}\) (CD)=2. Thus, there remains
some probability of \(D>190\).)

In addition to the above geometrical inspection, we
have carried out more extensive calculations on the
(0, 9, 0) and (1, 9, 0) bands to determine the \(D\) dependence
in HCN. The ratio of the total width of (0, 9, 0) to that of
(1, 9, 0) varies as

\[
D=190 \quad 271 \quad 385 \quad 549
\]

\[
\Gamma(1,9,0)/\Gamma(0,9,0) = 21.5 \quad 31.9 \quad 47.3 \quad 62.5.
\]

This shows that the linewidth of (1, 9, 0) is much larger than
that of (0, 9, 0) even when (1, 9, 0) is also located in the
tunneling region (outside the Franck–Condon region).
Therefore, the geometrical consideration gives only a
necessary condition for missing the (1, \(v'_{0}\), 0)–(0, 0, 0)
band. Note also that once again the branching ratio was not
sensitive to \(D\) in the tunneling region.

Finally, the branching ratio of both HCN and DCN is shown
in Tables VI and VII, respectively, for \(D=190\). Since,
as discussed above, there is a significant possibly for \(D>190\) in considering the DCN case, the \(\Gamma_{sa}\)
corresponding to \(D=271\) is also shown in Table VIII. It is
likely that the real \(D\) is closer to 271 than to 190. (The
branching ratios of HCN do not change significantly even if \(D=271\) is used.) From Tables VII and VIII, population
inversion is predicted to occur in some channels of
DCN. Among them, channels (2, 7, 0), (2, 8, 0), and
(2, 9, 0) overlap energetically with (0, 9, 1), (10, 10) and
(0, 11, 1), respectively. Since the (0, \(v'_{2}\), 1) channels
\((v'_{2}=9,10,11) have much larger \(\Gamma_{sa}\) if one takes account
of this overlap, the population inversion will be resolved
macroscopically. However, the channels (1, 11, 0),

<table>
<thead>
<tr>
<th>Channel</th>
<th>(D=12.86)</th>
<th>(D=50.0)</th>
<th>(D=190.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0, 9, 0)</td>
<td>0.108 (3)</td>
<td>0.261 (2)</td>
<td>0.571 (0)</td>
</tr>
<tr>
<td>(0, 10, 0)</td>
<td>0.139 (3)</td>
<td>0.348 (2)</td>
<td>0.906 (0)</td>
</tr>
<tr>
<td>(0, 11, 0)</td>
<td>0.117 (3)</td>
<td>0.375 (2)</td>
<td>0.241 (1)</td>
</tr>
<tr>
<td>(0, 7, 1)</td>
<td>0.997 (2)</td>
<td>0.232 (2)</td>
<td>0.254 (0)</td>
</tr>
<tr>
<td>(0, 8, 1)</td>
<td>0.714 (2)</td>
<td>0.287 (2)</td>
<td>0.410 (0)</td>
</tr>
<tr>
<td>(0, 9, 1)</td>
<td>0.664 (3)</td>
<td>0.334 (2)</td>
<td>0.654 (0)</td>
</tr>
<tr>
<td>(0, 6, 2)</td>
<td>0.815 (2)</td>
<td>0.217 (2)</td>
<td>0.160 (0)</td>
</tr>
<tr>
<td>(0, 7, 2)</td>
<td>0.899 (2)</td>
<td>0.273 (2)</td>
<td>0.277 (0)</td>
</tr>
<tr>
<td>(1, 9, 0)</td>
<td>0.788 (2)</td>
<td>0.752 (2)</td>
<td>0.123 (2)</td>
</tr>
<tr>
<td>(1, 10, 0)</td>
<td>0.744 (2)</td>
<td>0.730 (2)</td>
<td>0.158 (2)</td>
</tr>
<tr>
<td>(1, 11, 0)</td>
<td>0.543 (2)</td>
<td>0.666 (2)</td>
<td>0.199 (2)</td>
</tr>
</tbody>
</table>

\(\text{Numbers in parentheses indicate multiplicative power of } 10. \) Units of \(D\) are hartrees.
TABLE VI. Partial linewidth of HCN predissociation. \(D = 190\).

<table>
<thead>
<tr>
<th>Channel</th>
<th>(r_{\text{I}}^*)</th>
<th>(r_{\text{II}}^*)</th>
<th>(r_{\text{III}}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0, 9, 0)</td>
<td>0.657 (0)(^a)</td>
<td>0.235 (−1)</td>
<td>⋮</td>
</tr>
<tr>
<td>(0, 10, 0)</td>
<td>0.872 (0)</td>
<td>0.106 (0)</td>
<td>⋮</td>
</tr>
<tr>
<td>(0, 11, 0)</td>
<td>1.089 (0)</td>
<td>0.260 (0)</td>
<td>0.160 (−3)</td>
</tr>
<tr>
<td>(0, 7, 1)</td>
<td>0.213 (−1)</td>
<td>0.396 (−1)</td>
<td>⋮</td>
</tr>
<tr>
<td>(0, 8, 1)</td>
<td>0.302 (−1)</td>
<td>0.935 (−1)</td>
<td>⋮</td>
</tr>
<tr>
<td>(0, 3, 1)</td>
<td>0.332 (−1)</td>
<td>0.141 (0)</td>
<td>0.209 (−2)</td>
</tr>
<tr>
<td>(0, 6, 2)</td>
<td>0.607 (0)</td>
<td>0.442 (−1)</td>
<td>⋮</td>
</tr>
<tr>
<td>(0, 7, 2)</td>
<td>0.491 (0)</td>
<td>0.124 (0)</td>
<td>0.667 (−2)</td>
</tr>
</tbody>
</table>

\(^a\)A dash indicates that the corresponding channel is closed.

\(^b\)Numbers in parentheses indicate multiplicative power of 10.

(1, 8, 1), and (1, 9, 1) do not overlap with other channels. We cannot determine, at this stage, whether or not this population inversion is real,\(^2\) since this population inversion will disappear if a very large \(D\) is used and since the rotational motion and its coupling with the bending mode were completely neglected within our computation.

V. CONCLUDING REMARKS

We have proposed a correction formula for \(r_{\text{I}}^*\). As shown both theoretically and numerically the corrected value of \(r_{\text{III}}^2\), that is, \([r_{\text{I}}^*]^2\), converges quite rapidly and is stable with respect to the variation of basis set. Therefore, this correction formula is strongly recommended even when other variational scattering functions, such as that of the Kohn method,\(^2\) the minimum norm method,\(^2\) the optimized anomaly free method,\(^2\) and so on,\(^1\) are used.

Some general properties of the photodissociation of HCN were considered. In particular, our calculation demonstrated that the equation of Band and Freed for isotope effects, Eq. (4.4), holds for the tunneling mechanism. Further, a theoretical prediction of the general behavior of HCN and DCN predissociation was presented. An attempt to search for the potential parameters of the repulsive surface was not made, since the aim of this paper has been to prepare a tractable and accurate method that can predict \(r_{\text{III}}^*\) or other observables. The use of \textit{ab initio} methods to search for the potential surface parameters will be the subject of later papers.

ACKNOWLEDGMENTS

We thank Mr. James W. Caldwell for his support of our computations and for critically reading the manuscript. The North Dakota State University Computer Center is also acknowledged for the computation time made available to us. This work was supported by the National Science Foundation Grant No. CHE 78-18070.

APPENDIX: FRANCK-CONDON OVERLAP INTEGRAL

Although there have been several methods\(^2\) to calculate the Franck-Condon factor, we will show a recursion formula that is easily understood. The Franck-Condon integral is defined by

\[
F_{mn} = \int_{-\infty}^{\infty} \xi_m(a_1|\vec{r} - \vec{r}_1|) \xi_n(a_2|\vec{r}_2|) d\vec{r}_1 ,
\]

(A1)

where \(\xi_m(a_1|\vec{r} - \vec{r}_1|)\) and \(\xi_n(a_2|\vec{r}|)\) are the Hermitian functions with exponents \(a_1\) and \(a_2\), respectively. Reflecting the difference in potential minima on the upper and lower surfaces, a coordinate displacement \(\vec{r}_1\) is included. Let us consider the following integral

\[
G_{mn} = \int_{-\infty}^{\infty} \xi_m(a_1|\vec{r} - \vec{r}_1|) \xi_n(a_2|\vec{r}_2|) \exp(pr) d\vec{r}_1 .
\]

(A2)

Of course we have,
\[ F_{m} = G_{m1} |_{\theta = 0}. \] (A3)

Using the relation for the Hermitian function\(^{27}\)
\[ r \xi_{m}(r)^{2} = 2^{-1/2} \left\{ (m + 1)^{1/2} \xi_{m+1}(r) + m^{1/2} \xi_{m-1}(r) \right\}, \]
one gets
\[ \alpha_{f} \frac{\partial G_{m}}{\partial \theta} = 2^{-1/2} \left\{ (m + \frac{1}{2}) G_{m+1} + n^{1/2} G_{m-n} \right\} \] (A4)
and
\[ \alpha_{f} \left( \frac{\partial}{\partial \theta} - \frac{\partial}{\partial \theta} \right) G_{m} \]
\[ = 2^{-1/2} \left\{ (m + \frac{1}{2}) G_{m+1,n} + n^{1/2} G_{m-n,n} \right\}. \] (A5)

Elimination of \( \partial G_{m}/\partial \theta \) from (A5) and (A6) will give
\[ G_{m+1,n} = (m + 1)^{1/2} \left\{ \alpha_{f} (m + \frac{1}{2}) G_{m+1,n} - 2^{1/2} \alpha_{f} \right\} G_{m,n} \]
\[ + \alpha_{f} n^{1/2} G_{m,n+1} - m^{1/2} G_{m-1,n}. \] (A7)

This equation shows that the sequence of \( m+1 \)th row \((n = 0, 1, \ldots)\) of the \( G \) matrix can be calculated if the sequence of \( m \)th row \((m = 1, 2, \ldots)\) are known.

In order to initialize the recursion formula (A7), we must determine \( G_{0,n}(n = 1, 2, \ldots) \). This is also simple as shown below. From Eq. (A5), we have
\[ G_{0,m} = (m + 1)^{1/2} \left\{ 2^{1/2} \alpha_{f} \frac{\partial G_{m}}{\partial \theta} - n^{1/2} G_{m,n} \right\}. \] (A8)

Further, the definition of the Hermite function and
\[ G_{0,0} = \frac{2 \alpha_{f} \alpha_{f}}{(\alpha_{f}^{2} + \alpha_{f}^{2})^{1/2}} \exp\left[ -\frac{1}{2} (\alpha \bar{r})^{2} \right] \exp\left[ \frac{\left( \theta + \alpha \bar{r} \alpha_{f} \right)}{2 (\alpha_{f}^{2})} \right] \] (A9)

suggests that \( G_{0,0} \) may be written as
\[ G_{0,0} = \xi_{0} \xi_{0}, \] (A10)
where \( \xi_{0} \) is a polynomial of \( \rho \) of order, at highest, \( n \).
Again we can obtain a recursion formula for \( \xi_{0} \) by putting Eq. (A10) in Eq. (A8).
\[ \xi_{m} = (m + 1)^{1/2} \left\{ 2^{1/2} \alpha_{f} \alpha_{f}^{2} (\alpha_{f}^{2} + \alpha_{f}^{2})^{1/2} (\rho + \alpha_{f} \alpha_{f} \bar{r}) \xi_{0} + 2^{1/2} \alpha_{f} \alpha_{f}^{2} n^{1/2} G_{m-1,n} \right\}. \] (A11)

Since \( \xi_{m} \) is a simple polynomial, it is quite easy to accomplish the computation of Eq. (A11).

We would like to point out that similar recursion equations hold for multidimensional harmonic functions in which the Dushinsky matrix is nondiagonal.\(^{28}\) Finally, the computational technique used in (A2) is applied to estimate other integrals in which the Hermitian functions are involved.


\(^{6}\)Note that most of the variational functions satisfy this condition. See Ref. 2.

\(^{7}\)Recently, Nesbet has developed a method to ensure the symmetry of the \( G \)-matrix. R. K. Nesbet, Phys. Rev. A 18, 955 (1978).


\(^{9}\)Except for the time to compute the Franck-Condon overlap integrals, computational time to get \([A]\) is almost the same as that to solve \( V-T \) process.

\(^{10}\)For reviews, (a) W. A. Gelbart, Annu. Rev. Phys. Chem. 36, 323 (1977); (b) J. P. Simons, *Gas Kinetics and Energy Transfer*, Special Periodical Report (Chemical Society, London, 1977), p. 59; (c) See also references cited in Ref. 4.


\(^{19}\)For a discussion of the basis set, see Refs. 2c and 2d.


\(^{21}\)At \( \lambda < 1363, 1295, \) and 1304 Å, no population inversion for both HCN and DCN was found by the experiment of Simons *et al.* (Ref. 16e). On the other hand, the wavelength of the experiment for DCN cited in Table VII (VIII) is in 1326 < \( \lambda < 1355 \) Å.


\(^{26}\)For example, see the appendix of A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1969).