[2] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, New York, 1965).

[3] The selection rules for the other quantum numbers which determine the electron state of the molecule may also be mentioned. If both the terms are Σ terms ($\Lambda=0$) the component d_ξ has nonzero matrix elements only for the transitions $\Sigma^+\to\Sigma^+$ and $\Sigma^-\to\Sigma^-$. If the molecule consists of similar atoms, the matrix elements are nonzero only for transitions between states of different parity.

[4] See Ref. 2, Eqs. (87.4) and (87.1).

[5] H. Buchholz, *The Confluent Hypergeometric Function* (Springer, Berlin, 1969).

[6] As in the case of the Morse potential, the boundary conditions are defined in the singular points of the potential (18), i.e., for $y=0$ and $y=\infty$, corresponding to $r=\infty$ and $r=-\infty$. This approximation does not give rise to any substantial errors, since the functions $rR(r)$ will be extremely small at $r=0$.

[7] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Vol. 1, p. 524.

[8] See Ref. 5, p. 86, Eq. (5c) and make the change of variables $s=(\cosh v-1)/(\cosh v+1)$. By an analytic continuation argument, we find that the integral representation for the product of the two functions $M_{t\beta,\zeta}(y)$ and $W_{t\beta,\zeta}(y)$ holds without the restriction $\mathrm{Re}(\zeta-t\beta+\frac{1}{2})>0$ [L. Hostler, J. Math. Phys. 5, 591 (1964)]. By going over from the real to the contour integral (which begins at $s=1$, circles the point $s=0$ in the positive sense and then returns to $s=1$) we must introduce on the right-hand side in Eq. (26) the factor $\exp[\pi i(t\beta-\zeta+\frac{1}{2})]/2i\sin[\pi(\zeta-t\beta-\frac{1}{2}]$.

[9] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Tables of Integral Transform* (McGraw-Hill, New York, 1954), Vol. 1.

[10] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 1.

[11] To integrate we made use of Eq. (16) given in Ref. 9, p. 216 and assume that $\beta-v+x>\frac{1}{2}$.

[12] See Ref. 10, p. 47, Eq. (4).

[13] G. H. Dunn, Phys. Rev. **172**, 1 (1968).

[14] D. R. Bates, J. Chem. Phys. **19**, 1122 (1951).

[15] We use in (14) Eqs. (35) and (22) for the radial wave functions of the initial and final states, respectively, and Eq. (26) for the Green's function of the intermediate term. For integration over y_1 see Ref. 9, p. 197, Eq. (20). We assume that $\beta-v+\zeta+x_i>\frac{1}{2}$.

[16] See Ref. 9, p. 216, Eq. (14). We assume that $t'\beta-v'+\zeta+x_j>\frac{1}{2}$ and $t'\beta-v'+\beta-v+x_i+x_j>1$.

[17] Equation (45) has been used to calculate the two-photon excitation of H_2^+. See M. Trahin and I. I. Tugov (unpublished).

[18] G. Mainfray, C. Manus, and I. Tugov, Zh. Eksp. Teor. Fiz. Pis'ma v Redaktsiyu 16, 19 (1972). [JETP Lett. 16, 12 (1972)].

[19] N. K. Berejetskaya, G. S. Voronov, G. A. Delone, N. B. Delone, and G. K. Piskova, Zh. Eksp. Teor. Fiz. **58**, 753 (1970) [Sov. Phys.-JETP 31, 403 (1970)].

[20] M. Lu Van, G. Mainfray, C. Manus, and I. Tugov, Phys. Rev. A 7, 91 (1973).

PHYSICAL REVIEW A VOLUME 8, NUMBER 2 AUGUST 1973

Perturbation Theory in Closed Form for Heteronuclear Diatomic Molecules

I. I. Tugov*

Service de Physique Atomique, Centre d'Etudes Nucléaires de Saclay, B. P. n°2, 91, Gif-sur-Yvette, France

(Received 25 August 1972; revised manuscript received 30 March 1973)

Within the framework of the Born–Oppenheimer approximation questions are considered involving application of time-dependent perturbation theory to diatomic heteronuclear molecules. A potential-energy model of the form $V_i(r)=A_i/(r-r_i)^2-B_i/(r-r_i)+Q_i$ is proposed which gives a good representation of the true curves of the ground and excited states of a molecule. The relation $\omega_e x_e=6D^2/m=3\omega_e^{4/3}/2m^{1/3}$ has been obtained between the dissociation energies into free ions D, vibrational frequencies ω_e, and vibrational anharmonicity parameters $\omega_e x_e$ of the ground state of polar molecules. Analytical expressions are derived for vibration-rotation spectra, wave functions, and radial matrix elements considered in the first-order perturbation theory. An explicit expression obtained for the Green's function of the model enables a closed form to be given for matrix elements appearing in the higher-order perturbation theory involved in calculation of multiphoton molecular transitions.

I. INTRODUCTION

Perturbation theory is one of the most promising approaches to molecular quantum mechanics and particularly to multiphoton processes in nonlinear optical phenomena. Application of time-dependent perturbation theory ordinarily leads to multiple infinite summations of matrix elements over discrete energy states and to integration over continuum spectrum of the unperturbed Hamiltonian. Unfortunately, in most molecular problems, it is difficult to construct a satisfactory unperturbed Hamiltonian for which the complete set of eigenfunctions and eigenvalues is known. Using, as a first-order approximation, the usual separability of the wave functions (Born–Oppenheimer), the application of the perturbation theory to molecular problems may be considerably simplified.

After the selection rules for rotational and electronic quantum numbers have been established, the treatment of N-photon molecular transitions within the framework of the N-order time-dependent perturbation theory reduces essentially to calculating $(N-1)$ sums over vibrational structure of intermediate transitions. Each of these sums is extended over complete sets of vibrational states of all electronic states allowed by the selection rules and for all allowed values of rotational quantum numbers.[1] The procedure used to evaluate the sums over vibrational states is proposed. This procedure is based on the use of the explicit expression of the Green's functions for the internuclear potentials of intermediate electronic states.

It is evident that the construction of the potential-energy-curve model for a number of electronic states of a molecule plays the most important part in these considerations. Such a model must give a good representation of the true curves of the ground and excited electronic states. At the same time it must be simple enough to enable us to write analytic expressions for vibrational eigenenergies, eigenfunctions, and Green's functions of all electron terms.

In the present paper, a model of potential-energy curves for diatomic heteronuclear molecules is proposed. This model gives a good representation of true curves and analytic expressions for vibrational and electronic transitions induced by radiation acting on a molecule are able to be obtained. The presence of closed-form expressions for the Green's functions of the model gives the possibility to calculate radial matrix elements which appear in treatment of multiphoton molecular transitions. General expressions for cross sections of multiphoton transitions in a molecule are given in Ref. 1 as well as the Morse-type potential-energy model for homopolar diatomics.

In their lowest electronic states, the diatomic heterpolar molecules behave essentially like pairs of oppositely charged ions. The most successful model for predicting ground-state properties of the heteropolar diatomics if the classical ionic model proposed by Rittner[2]:

$$V(r)=Ae^{-r/\rho}-C/r^6-e^2/r -e^2(\alpha_+ +\alpha_-)/2r^4-2e^2\alpha_+\alpha_-/r^7\,, \tag{1}$$

where A and ρ are repulsion constants, α_+ and α_- are the polarizabilities of the ions, and C is the constant of van der Waals interaction. Equation (1) gives a good representation of the true curve for large internuclear distance r; however it does not give a particularly good representation of the internuclear potential in the region close to the equilibrium separation. Indeed, a correct picture of the interatomic forces in this region evidently plays an important part in the description of molecular properties for the lowest vibrational quantum numbers. The calculation within the Rittner model of vibrational frequencies of alkali halide molecules (which represent the most clearly defined cases of what is called heteropolar binding) does not, however, give results in good agreement with experimental data.[3] It should also be noted that there are no analytic expressions for eigenenergies and eigenfunctions in the Rittner model and the numerical solution of Schrödinger equation with potential (1) are to be undertaken in any specific case.

In the present paper the following potential is proposed as the ground-state potential energy for the heteronuclear diatomic molecule:

$$V(r)=\frac{A}{(r-r_c)^2}-\frac{Z^2e^2}{r-r_c} \tag{2}$$

in the region $r>r_c$, and $V(r)=\infty$ in the region $r\le r_c$ (see Fig. 1). Note that $V(r)$ behaves as $-Z^2e^2/r$ as $r\to\infty$. The Schrödinger equation with potential (2) allows analytic solutions.

In Sec. II explicit formulas are obtained for vibrational-rotational spectrum, wave functions, and Green's function of the model (2).

An interesting feature of the potential (2) lies in the fact that any two of three parameters D, ω_e, $\omega_e x_e$, which determine the vibrational spectrum of

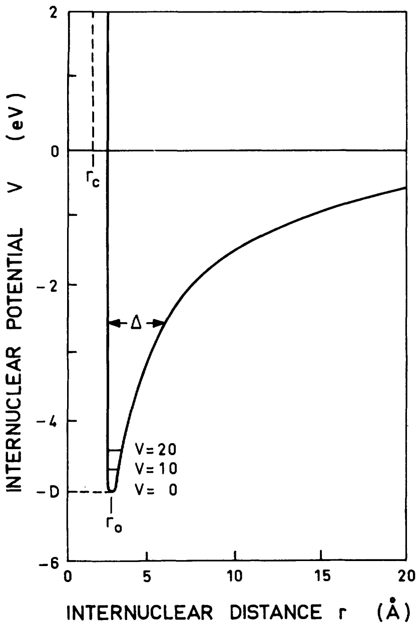

FIG. 1. Ground-state potential curve for NaI calculated from Eq. (2) ($D=5.09$ eV, $r_c=1.30$ Å).

the problem

$$E_v = -D + \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 \ldots$$

are mutually connected with each other by means of simple relations. This gives the possibility to compare theoretical values with experimental ones. As an illustration, ground-state dissociation energies to free ions (D) and vibration-anharmonicity parameters ($\omega_e x_e$) have been calculated (using the experimental data for vibrational frequencies ω_e) for all alkali halide molecules. The results are presented in Table I. The mean value

In Secs. III and IV the analytic expressions are derived for matrix elements of one-photon vibrational and electronic transitions within the framework of the developed model. Thus the construction of the first-order perturbation theory for heteronuclear diatomics is achieved. One further remark may be inserted about the part which the potentials (3) play in the higher orders of time-dependent perturbation theory involved in the calculation of multiphoton molecular transitions.[1] The cross section of the N-photon molecular transition contains the $(N-1)$ infinite summations over intermediate states. Each of these sums is extended over a complete set of molecular states; each term of the multiple sum involves the product of N of the first-order matrix elements. It is clear that without explicit expressions for the Green's functions of all intermediate electron terms involved in multiphoton transition it should be practically impossible to calculate the multiphoton-transition cross sections in molecules.

of the quantity $|D/D^{\text{expt}} - 1|$ for 16 alkali halides (excluding that of Li) is about 2%, and the mean value of $|(\omega_e x_e/\omega_e x_e^{\text{expt}}) - 1|$ is 12%. It should be noted that the monoparametric model (2) (the vibrational structure of the spectrum does not depend, evidently, on r_c) ensures better agreement with the experimental data than the Rittner potential (1).[4]

TABLE I. Comparison of theoretical and experimental results for dissociation energy into free ions (D) and vibrational anharmonicity ($\omega_e x_e$) of alkali halides. The theoretical values were calculated from $D=\frac{1}{2}(m\omega_e^2)^{1/3}$ and $\omega_e x_e = \frac{3}{2}(\omega_e^4/m)^{1/3}$ using experimental data for vibrational frequencies ω_e.

Salt	m^b	ω_e^{expt} (cm^{-1})	D^{theor} (eV)	$D^{\text{expt a}}$ (eV)	$(\omega_e x_e)^{\text{theor}}$ (cm^{-1})	$(\omega_e x_e)^{\text{expt}}$ (cm^{-1})
LiF	5.125	910^c	7.39	7.82	10.4	7.9^c
NaF	10.41	536^d	6.58	6.55	4.06	3.83 ± 0.14^d
KF	12.79	426^d	6.05	5.90	2.79	2.43^d
RbF	15.59	373^d	5.92	5.68	2.19	2.18 ± 0.03^d
CsF	16.63	352^d	5.82	5.55	1.98	1.62^d
LiCl	5.806	661^e	6.23	6.51	6.52	...
NaCl	13.95	366 ± 4^f	5.63	5.63	2.21	2.05^f
KCl	18.60	281 ± 6^f	5.19	4.98	1.41	1.30^f
RbCl	25.07	228 ± 6^f	4.99	4.77	0.96	0.92^f
CsCl	28.00	209 ± 6^f	4.89	4.77	0.83	0.75^f
LiBr	6.455	563.5^g	5.80	6.24 $(6.05)^e$	6.09	3.88^g
NaBr	17.86	302 ± 4^f	5.38	5.38	1.58	1.50^f
KBr	26.26	213 ± 6^f	4.84	4.77	0.87	0.80^f
RbBr	40.91	169.5^g	4.82	4.58	0.554	0.463^g
CsBr	49.53	149.5^g	4.72	4.59	0.44	0.36^g
LiI	6.582	501^f	5.38	5.85 $(5.57)^e$	4.34	3.1^g
NaI	19.47	258 ± 6^f	5.00	5.09	1.25	1.08^f
KI	29.82	186.5^g	4.52	4.51	0.70	0.574^g
RbI	50.89	138.5^g	4.53	4.31	0.394	0.335^g
CsI	64.94	101^f $(119)^g$	4.00 4.45	4.29	0.238 0.297	0.254^g

[a] L. Brewer and E. Brackett, Chem. Rev. 61, 425 (1961).

[b] From G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, 2nd ed. (Van Nostrand, Princeton, N.J., 1950). The values of mass are given in the units of $\frac{1}{16}$ of the mass of O^{16}.

[c] G. L. Vidale, J. Phys. Chem. 64, 314 (1960).

[d] S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965).

[e] R. S. Berry and W. Klemperer, J. Chem. Phys. 26, 724 (1957).

[f] S. A. Rice and W. Klemperer, J. Chem. Phys. 27, 573 (1957).

[g] J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962).

The rotational structure of the spectrum is determined (for the small vibrational quantum numbers) by the internuclear equilibrium distance r_0. (The rotational constant, which corresponds to equilibrium separation r_0, is $B_e = \hbar^2/2mr_0$.) For a given value of D (or for a given value of ω_e or $\omega_e x_e$) the difference $(r_0 - r_c)$ has a definite value $r_0 - r_c = Z^2e^2/2D$. Using r_0 from the rotational structure of spectrum, r_c can be obtained.

The true potential-energy curves of excited electron terms $|i\rangle$ may be described by the following generalization of Eq. (2):

$$V_i(r) = \frac{A_i}{(r-r_c)^2} - \frac{B_i}{r-r_c} + Q_i \tag{3}$$

in the region $r > r_c$, and $V_i = \infty$ in the region $r \leq r_c$; $B_i > 0$ for the attractive curves and $B_i < 0$ for the repulsive potentials (see Fig. 2).

In Secs. III and IV the analytic expressions are derived for matrix elements of one-photon vibrational and electronic transitions within the framework of the developed model. Thus the construction of the first-order perturbation theory for heteronuclear diatomics is achieved. One further remark may be inserted about the part which the potentials (3) play in the higher orders of time-dependent perturbation theory involved in the calculation of multiphoton molecular transitions.[1] The cross section of the N-photon molecular transition contains the $(N-1)$ infinite summations over intermediate states. Each of these sums is extended over a complete set of molecular states; each term of the multiple sum involves the product of N of the first-order matrix elements. It is clear that without explicit expressions for the Green's functions of all intermediate electron terms in-

volved in multiphoton transition it should be practically impossible to calculate the multiphoton-transition cross sections in molecules.

II. EIGENENERGIES, WAVE FUNCTIONS, AND GREEN'S FUNCTIONS

Within the Born-Oppenheimer approximation, the molecular wave function can be expressed as a product of electronic (ψ) and nuclear (ξ) wave functions, $\Psi=\psi\xi$. The radial part of ξ, $R(r)$, satisfies the equation

$$\left[\frac{d^2}{d^2r}+\frac{2m}{\hbar^2}\left(E-\frac{\hbar^2}{2m}\frac{K(K+1)}{r^2}-V(r)\right)\right]rR(r)=0\ , \tag{4}$$

where

$$V(r)=\frac{A}{(r-r_c)^2}-\frac{B}{r-r_c}+Q$$

is the internuclear potential of the attractive ($B>0$) or repulsive ($B<0$) electron term, $|n\Lambda\rangle$ for $r>r_c$; in the region $r\leq r_c$, $V(r)=\infty$. E_{vK} is the energy eigenvalue of the state with vibrational and rotational quantum numbers, v and K, respectively. The condition of the continuity of $R(r)$ at $r=r_c$ gives $R(r_c)=0$ [in the region $r<r_c$, evidently $R(r)=0$].

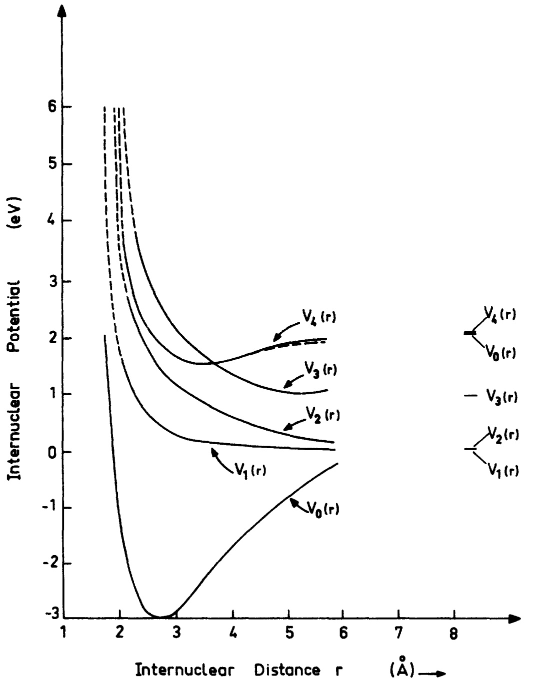

FIG. 2. Potential curves for the lower excited electronic states of NaI. The solid curves show the experimental potential energies taken from Ref. 5. The dashed curves are calculated from Eq. (3) using the following sets of parameters: $V_1(r)$: $r_c=1.30$ Å; $A_1=0.83$ eV (Å)^2; $B_1=-0.018$ eV Å; $Q_1=-2.04$ eV. $V_2(r)$: $r_c=1.30$ Å; $A_2=1.51$ eV (Å)^2; $B_2=-0.96$ eV Å; $Q_2=-2.04$ eV. $V_3(r)$: $r_c=1.30$ Å; $A_3=3.08$ eV (Å)^2; $B_3=-0.13$ eV Å; $Q_3=-1.1$ eV. $V_4(r)$: $r_c=1.80$ Å; $A_4=1.42$ eV (Å)^2; $B_4=1.85$ eV Å; $Q_4=0.1$ eV.

In what follows, the centrifugal repulsion term is treated in Eq. (4) approximately, using the effective potential

$$V_{\text{eff}}=\frac{A'}{(r-r_c)^2}-\frac{B}{r-r_c}+Q\ ,$$

where

$$A'=A+\frac{\hbar^2K(K+1)}{2m}\left(\frac{r_0-r_c}{r_0}\right)^2 .$$

V_{eff} satisfies the relation

$$V_{\text{eff}}(r_0)=V(r_0)+\hbar^2K(K+1)/2mr_0^2,$$

which enables a correct description to be given for the rotational energy of a molecule in the vicinity of the internuclear equilibrium distance r_0. Introducing the variables $r'=r-r_c$, $x=rR$, the following equation is obtained:

$$\frac{d^2x}{dr'^2}+\frac{2m}{\hbar^2}\left(E-Q-\frac{A'}{r'^2}+\frac{B}{r'}\right)x=0\ , \tag{5}$$

which reduces to Whittaker's form

$$x''+\{-\tfrac{1}{4}+n/\bar{r}+[\tfrac{1}{4}-(s+\tfrac{1}{2})^2]/\bar{r}^2\}x=0\ . \tag{5$'$}$$

Here $\bar{r}=2\zeta r'$, $\zeta=[-2m(E-Q)]^{1/2}/\hbar$, $n=mB/\hbar^2\zeta$, and s is the positive root of the equation $s(s+1)=2mA'/\hbar^2$. Equation (5′) has two linearly independent solutions. The Whittaker function $M_{n,s+1/2}(2\zeta r')$ is regular when $r'\rightarrow 0$,

$$M_{n,s+1/2}(2\zeta r')=e^{-\zeta r'}(2\zeta r')^{s+1}\Phi(1-n+s,2s+2,2\zeta r'), \tag{6}$$

where Φ is the confluent hypergeometric function. The Whittaker function $W_{n,s+1/2}(2\zeta r')$—another fundamental solution of Eq. (5′)—is regular for $r'\rightarrow\infty$. Using the fundamental solutions of Eq. (5′) and calculating the Wronskian[6] gives the Green's function of the radial Schrödinger equation (5),

$$g(r_1',r_2'|E)=-\frac{m}{\hbar^2\zeta}\frac{\Gamma(1+s-n)}{\Gamma(2s+2)}\times M_{n,s+1/2}(2\zeta r_<')W_{n,s+1/2}(2\zeta r_>'), \tag{7}$$

where $r_<'$ ($r_>'$) is the smaller (larger) of the quantities r_1' and r_2'. When $B>0$, the poles of the Γ function $\Gamma(1+s-n)$ at $1+s-n=-v$, $v=0, 1, 2, \ldots$, determine the infinite discrete spectrum of bound states,

$$E_{vK}=Q-\frac{B^2m}{2\hbar^2(s+1+v)^2}$$
$$=Q-D+\hbar\omega_e(v+\tfrac{1}{2})-\hbar\omega_e x_e(v+\tfrac{1}{2})^2$$
$$+B_e(K+\tfrac{1}{2})^2+\cdots\ . \qquad (8)$$

Here $v=0, 1, 2, \ldots$ is the vibrational quantum number $(n=s+1+v)$, $D=B^2/4A$ is the bond dissociation energy, $\omega_e=2D(2mA)^{-1/2}$ is the vibrational frequency at $v=0$, $\omega_e x_e=\frac{3}{2}(\hbar D/mA)$ is the vibrational anharmonicity parameter, $B_e=\hbar^2/2J$ is the rotational constant, $J=mr_0^2$ is the moment of inertia, and $m=m_1m_2(m_1+m_2)^{-1}$ is the reduced mass of the molecule. The expression (8) was obtained by expanding $B^2m/2\hbar^2(s+1+v)^2$ as a power series in the small parameter $\hbar(2mA)^{-1/2}$.

For the ground states $|0\rangle$ of the heteronuclear diatomics parameter, B is determined by the asymptotic form of the potential $V_0(r)$ for large r,

$$V(r)\approx -Z^2e^2/r+O(1/r^2),$$

$B=Z^2e^2$, where Z is charge of ions.

When $B>0$, the potential (3) has the minimum at $r_0=r_c+2A/B$, $V(r_0)=-D+Q$. The position of the minimum is connected with the half-width Δ of the potential curve $\Delta=2^{3/2}(r_0-r_c)$. At $B=Z^2e^2$ the vibrational spectrum of a molecule is determined by the parameter A which is connected with the dissociation energy into free ions, $D=Z^4e^4/4A$, as well as with vibrational constants ω_e and $\omega_e x_e$:

$$2mA/\hbar^2=Z^4(\mathcal{R}/D)\,(m/m_e)\,,$$
$$\hbar\omega_e=2DZ^{-2}[(m/m_e)(\mathcal{R}/D)]^{-1/2}, \qquad (9)$$
$$\hbar\omega_e x_e=(3D^2Z^{-4}/\mathcal{R})(m_e/m)\,.$$

Here m_e is the electron mass and $\mathcal{R}=m_e e^4/2\hbar^2=13.605$ eV. In atomic units,

$$D=\tfrac{1}{2}(m\,\omega_e^2 Z^4)^{1/3},$$
$$\omega_e x_e=6D^2/mZ^4=\tfrac{3}{2}(\omega_e^4/m Z^4)^{1/3}. \qquad (9')$$

Table I gives the dissociation energies into free ions (D) and vibrational anharmonicity parameters ($\omega_e x_e$) calculated from Eq. (9′) using the experimental data for vibrational frequencies ω_e.

The theoretical values are compared with the experimental ones for all alkali halides. Excluding the halides of Li, the mean deviation of $|D/D^{\mathrm{ext}}|$ from unity is about 2% and the mean value of $|1-(\omega_e x_e/\omega_e x_e^{\mathrm{ext}})|$ is about 12%. In many cases the errors are within the experimental ones.

The normalized wave functions of the discrete spectrum are determined as the residues in the poles of the Green's function (7),

$$x_{vK}(r')=\frac{[\Gamma(2s+2+v)]^{1/2}}{a^{1/2}(s+1+v)\Gamma(2s+2)(v!)^{1/2}}$$
$$\times M_{s+1+v,\,s+1/2}\left(\frac{2r'}{a(s+1+v)}\right), \qquad (10)$$

where $a=\hbar^2/Bm=a_0m_e/mZ^2$ is the Coulomb unit of length. According to Eq. (6),

$$x_{vK}(r')=\frac{[\Gamma(2s+2+v)]^{1/2}}{a^{1/2}(s+1+v)\,(v!)^{1/2}\Gamma(2s+2)}\left(\frac{2r'}{a(s+1+v)}\right)^{s+1}e^{-r'/a(s+1+v)}\,\Phi\left(-v,\,2s+2,\,\frac{2r}{a(s+1+v)}\right)\ . \qquad (10')$$

The wave functions (10) satisfy the boundary conditions and are normalized so that $\int_0^\infty x_{vK}^2(r')dr'=1$.

Continuum wave functions $(E-Q>0)$ in the attractive $(B>0)$ or repulsive fields $(B<0)$ have the form of Eq. (6) with

$$\zeta=[-2m(E-Q)]^{1/2}/\hbar=iq\ ,$$

where q is the wave number of particles:

$$x_{qK}(r')=\frac{e^{i\pi n/2}}{(2\pi)^{1/2}i^{s+1}}\,\frac{|\Gamma(s+1+n)|}{\Gamma(2s+2)}\,M_{n,s+1/2}(2iqr')$$
$$=\frac{e^{i\pi n/2}}{(2\pi)^{1/2}}\ \frac{|\Gamma(s+1+n)|}{\Gamma(2s+2)}\ e^{-iqr'}(2qr')^{s+1}$$
$$\times\Phi(1-n+s,\,2s+2,\,2iqr')\ . \qquad (11)$$

Here $n=mB/\hbar^2\zeta=-i(mB/\hbar^2q)$. The normalization coefficient in (11) corresponds to the asymptotic form of $x(r)$ for large r

$$x_{qK}(r)\approx(2/\pi)^{1/2}\sin[qr+in\ln 2q(r-r_c)$$
$$-\tfrac{1}{2}\pi s-qr_c+\delta_s] \qquad (12)$$

where $\delta_s=\arg\Gamma(s+1+n)$.

It is evident from Table I that the potential (2) at $B=e^2$, $A=e^4/4D$, gives results very close to the true values of the ground-state vibrational constants for most of the alkali halide molecules. The excited-state potential may be well fitted to empirical expressions (3) (see Fig. 2). For this reason the analytic calculations—within the framework of the proposed model—of the probabilities of arbitrary one-photon transitions in heteronuclear diatomics would be of interest so that comparison with various experimental data related to the spectra of salt vapors may be made.

III. ONE-PHOTON VIBRATIONAL TRANSITIONS

First consider one-photon transitions which take place without change in the electronic state of a molecule, that is, that occur between two vibrational states $|n\rangle$ and $|n'\rangle$ (of discrete or continuous spectrum) of the same electron term ($s=s'$):

$$I_{nn'}=\int_0^\infty R_n(r)R_{n'}(r)r^3dr$$
$$=\int_0^\infty x_n(r')x_{n'}(r')\,(r'+r_c)\,dr'$$
$$=\int_0^\infty x_n(r')x_{n'}(r')\,r'\,dr' \tag{13}$$

due to the orthogonality of eigenfunctions at $n'\neq n$; $r'=r-r_c$. Denoting the normalization coefficients for the initial and final states as N_n and $N_{n'}$, respectively, and integrating,[7]

$$I_{nn'}=\int_0^\infty N_nN_{n'}M_{n,s+1/2}\left(\frac{2r}{an}\right)M_{n',s+1/2}\left(\frac{2r}{an'}\right)r\,dr$$

$$=\frac{\hbar^4 2^{2s+2}}{B^2m^2}\,N_nN_{n'}\,\frac{\Gamma(2s+4)\,(nn')^{s+3}}{(n+n')^{2s+4}}\,F(\alpha+2)\;. \tag{14}$$

Here $a=\hbar^2/Bm$ ($B\gtrless 0$), $n=s+1+v$ for the discrete spectrum wave function ($B>0$), $n=-i(mB/\hbar^2q)$ for the continuum wave function ($B\lessgtr 0$), q is the wave number for the state of positive eigenenergy, s is the positive root of equation

$$s(s+1)=2mA/\hbar^2+K(K+1)\,(r_0-r_c)^2/r_0^2\;,$$

$F(\alpha+2)=F_2(\alpha+2;\; s+1-n,\; s+1-n';\; \alpha,\; \alpha;\; x,\; y)$ is the generalized hypergeometric series of two variables,[8] $\alpha=2s+2$, $x=2n'(n+n')^{-1}$, $y=2n(n+n')^{-1}$, and $x+y=2$. The function $F(\alpha+2)$ is calculated in the Appendix. Using Eq. (A5) and the normalization coefficients from Eqs. (10) and (11), then for the radial matrix elements of vibrational transitions there are the three following cases.

A. Bound-Bound Transitions

In this case

$$I_{vv'}=\frac{a_0m_e2^{2s+3}(-1)^{v+1}(v'-v)^{v+v'-2}\left[(s+1+v)\,(s+1+v')\right]^{s+2}\left[\Gamma(2s+2+v)\Gamma(2s+2+v')\right]^{1/2}}{m\,Z^2\Gamma(2s+2)\,(v!\,v'!)^{1/2}(2s+2+v+v')^{2s+2+v+v'}}$$
$$\times\left[\frac{2vv'+(s+1)(v+v')}{2s+2+v+v'}\;{}_2F_1\left(-v,\,-v';\,2s+2;\;-\frac{4(s+1+v)\,(s+1+v')}{(v'-v)^2}\right)\right.$$
$$\left.+\frac{2vv'(s+1+v)\,(s+1+v')}{(s+1)\,(v'-v)^2}\;{}_2F_1\left(-v+1,\,-v'+1;\,2s+3;\;-\frac{4(s+1+v)\,(s+1+v')}{(v-v')^2}\right)\right]\;. \tag{15}$$

For two hypergeometric functions, ${}_2F_1$ being the polynomial of degree v and $v+1$, respectively (assume $v<v'$), Eq. (15) is easily calculated for small values of v. For Γ functions which appear in (15), one uses the Stirling-series approximation. The latter ensures high precision for physical values of the parameters (for alkali halides, $130<s<600$). Thus, for example, for transitions from the $v=0$ vibrational level,

$$I_{0v'}=-\,(r_0-r_c)\,\frac{(v')^{v'-1}}{[v'!(2s+2)^{v'}]^{1/2}}\;\frac{(1+s+v')^{s+2}(1+s)^{s+1+v'}}{(s+1+\frac{1}{2}v')^{2s+3+v'}}\;. \tag{16}$$

For $v'\ll 2s+2$ the second fraction in Eq. (16) may be put equal to unity.

B. Bound-Free Transitions

In this case, $n=s+1+v$ and $n'=-imB/\hbar^2q$, $B>0$, where q is the wave number of dissociating particles, is put in Eq. (A5):

$$I_{vq}=-\frac{(2/\pi)^{1/2}a^{3/2}2^s[\Gamma(2s+2+v)]^{1/2}\,|\Gamma(s+1-i/aq)|}{(aq)^{s+3}\,(v!)^{1/2}\,\Gamma(2s+2)}\left(\frac{2s+2+2v}{1/a^2q^2+(s+1+v)^2}\right)^{s+2}$$
$$\times\exp\left(\frac{1}{aq}\,[\tfrac{3}{2}\pi+2\,\mathrm{ctn}^{-1}\,aq(s+1+v)]+i(2v-2)\,\mathrm{ctn}^{-1}\,aq(s+1+v)]\right)$$
$$\times\left[\left(\frac{2nn'}{n+n'}-s-1\right)\;{}_2F_1\left(-v,\,s+1-n';\,2s+2;\;\frac{-4nn'}{(n-n')^2}\right)\right.$$
$$\left.+\frac{2nn'(n-s-1)\,(n'-s-1)}{(s+1)\,(n'-n)^2}\;{}_2F_1\left(-v+1,\,s+2-n';\,2s+3;\;\frac{-4nn'}{(n-n')^2}\right)\right]\;; \tag{17}$$

recall that $a=\hbar^2/mB$, $n'=-i/aq$, $aq=[(E-Q)/D]^{1/2}s^{-1}$.

C. Free-Free Transitions

The radial matrix element for the scattering which takes place without change in the electron terms of the particles may be obtained by substituting Eq. (A5) in (14) and using continuum spectrum normalization from Eq. (11). The quantities n and n' are defined by the formulas $n=-imB/\hbar^2 q$, $n'=-imB/\hbar^2 q'$, $B \gtrless 0$, where q and q' are the wave numbers of relative motion of the particles before and after scattering.

IV. ONE-PHOTON ELECTRONIC TRANSITIONS

In Sec. III, the radial matrix elements which involve nuclear wave functions belonging to one and the same electron term were calculated. Now consider transitions between the ground $|0\rangle$ and excited $|1\rangle$ electron terms. The potential energies of combining terms $|0\rangle$ and $|1\rangle$ are described by Eq. (3) with the following sets of parameters: A, $B>0$, r_c, $Q=0$ and $A^{(1)}$, $B^{(1)} \gtrless 0$, $r_c^{(1)}$, $Q^{(1)}$, respectively. The bound-state function (10) for the ground term and the bound or continuum wave functions [Eqs. (10) and (11)] for the excited term shall be used as the eigenfunctions of initial (n) and final (n') vibrational states (which belong to different terms $|0\rangle$ and $|1\rangle$).

Since the true curves of repulsive states may be well approximated by Eq. (3) with $r_c^{(1)}=r_c^{(0)}$ (see Fig. 2), in this case

$$I_{n,n'}^{0,1}=\int_0^\infty R_n^{(0)}(r)R_{n'}^{(1)}(r)r^3\,dr$$

$$=\int_0^\infty x_n^{(0)}(r')x_{n'}^{(1)}(r')\,(r'+r_c)\,dr' \,, \tag{18}$$

where the new variable $r'=r-r_c$ has been introduced and the fact that the integrand in Eq. (18) vanishes in the region $r<r_c$ [the continuity of $x(r)$ at the point $r=r_c$] is used. The functions $x_n^{(0)}$ and $x_{n'}^{(1)}$ are defined as the functions of the argument $r'=r-r_c$ in Eqs. (10) and (11). Now take the ground-state wave function (10′) in the form

$$x_{vK}(r')=\frac{[v!]^{1/2}e^{-r'/a(s+1+v)}}{[a\Gamma(2s+2+v)]^{1/2}(s+1+v)}$$

$$\times\sum_{l=0}^{v} a_l^{(v)}\left(\frac{2r'}{a(s+1+v)}\right)^{s+l+1} \,, \tag{19}$$

where $a_l^{(v)}$ are the coefficients of the Laguerre polynomials of degree v,

$$L_v^{(2s+1)}\left[\frac{2r'}{a(s+1+v)}\right]$$

$$=\frac{\Gamma(2s+2+v)}{v!\,\Gamma(2s+2)}\,\Phi\left(-v,\,2s+2,\,\frac{2r'}{a(s+1+v)}\right)$$

$$=\sum_{l=0}^{v} a_l^{(v)}\left(\frac{2r'}{a(s+1+v)}\right)^{l} \,. \tag{20}$$

Thus, for $v=0$, $a_0^{(0)}=1$; for $v=1$, $a_0^{(1)}=2s+2$, $a_1^{(1)}=-1$. Then the radial matrix element for the electronic transition becomes

$$I_{vK,n'K'}^{0,1}=\frac{[v!]^{1/2}N_{n'}^{(1)}}{[a\Gamma(2s+2+v]^{1/2}(s+1+v)}\sum_{l=0}^{v} a_l^{(v)}\mathcal{T}_l \,, \tag{21}$$

where

$$\mathcal{T}_l=\int_0^\infty e^{-r'/a(s+1+v)}\left(\frac{2r'}{a(s+1+v)}\right)^{s+l+1}$$

$$\times(r'+r_c)M_{n',s'+1/2}\left(\frac{2r'}{a'n'}\right)dr' \,. \tag{22}$$

Here $a=\hbar^2/Bm>0$ is the Coulomb unit of length defined for the initial-state term potential $a'=\hbar^2/B^{(1)}m$, $B^{(1)}\gtrless 0$ is the parameter of potential (3) for the final electronic state. s must be taken as the positive root of equation

$$s(s+1)=\frac{2mA}{\hbar^2}+K(K+1)\left(\frac{r_0-r_e}{r_0}\right)^2 \;;$$

s' is the positive root of

$$s'(s'+1)=\frac{2mA^{(1)}}{\hbar^2}+K'(K'+1)\left(\frac{r_0-r_c}{r_0}\right)^2 \;;$$

$n=s+1+v$; $n'=s'+1+v'$ for the bound final state ($B^{(1)}>0$); and $n'=-imB^{(1)}/\hbar^2 q$ for continuum wave function ($B^{(1)}\gtrless 0$). The coefficient $N_{n'}^{(1)}$ is defined according to Eqs. (10) or (11). Integrating[9] in Eq. (22),

$$\int_0^\infty r^{s+l+1}e^{-r/an}M_{n',s'+1/2}\left(\frac{2r}{a'n'}\right)dr$$

$$=\frac{2^{s'+1}(an)^{s+s'+3+l}(a'n')^{s+2+l}\,\Gamma(s+s'+3+l)}{(an+a'n')^{s+s'+3+l}}$$

$$\times\,{}_2F_1\left(s+s'+3+l,\,s'-n'+1;\,2s'+2;\,\frac{2an}{an+a'n'}\right) \,. \tag{23}$$

Equations (21) and (23) give the final analytic expressions for radial matrix elements of arbitrary electronic transitions in a heteronuclear diatomic molecule. For the bound final state $n'=s'+1+v'$, Eq. (23) reduces to a polynomial of degree v'. The most important of all possible applications of Eqs. (21) and (23) seems to be the calculation of the photodissociation cross sections for the salt vapors.

APPENDIX: CALCULATION OF THE FUNCTION $F(\alpha+2)$

To calculate the function

$$F(\alpha+2)\equiv F_2(\alpha+2;\, s+1-n,\, s+1-n';\, \alpha,\, \alpha;\, x,\, y)\,, \tag{A1}$$

first note that[10]

$$\begin{aligned} F(\alpha) &\equiv F_2(\alpha;\, s+1-n,\, s+1-n';\, \alpha,\, \alpha;\, x,\, y) \\ &= (1-x)^{n-s-1}(1-y)^{n'-s-1} \\ &\quad \times {}_2F_1(s+1-n,\, s+1-n';\, \alpha;\, xy/(1-x)(1-y))\,. \end{aligned} \tag{A2}$$

Then use the recursion relation[11]

$$F(\alpha+1)=\frac{1}{\alpha}\left[x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}\right]F(\alpha)+F(\alpha) \tag{A3}$$

to calculate the function $F(\alpha+1)\equiv F_2(\alpha+1;\; s+1-n,\; s+1-n';\; \alpha,\, \alpha;\, x,\, y)$,

$$\begin{aligned} F(\alpha+1) = (1-x)^{n-s-2}(1-y)^{n'-s-2}\Bigg[&\left((1-x)(1-y)-\frac{n-s-1}{\alpha}\,x(1-y)-\frac{n'-s-1}{\alpha}\,y(1-x)\right) \\ &\times {}_2F_1\left(s+1-n,\, s+1-n';\, 2s+2;\, \frac{xy}{(1-x)(1-y)}\right)+\frac{(n-s-1)(n'-s-1)}{(2s+2)^2} \\ &\times xy\,\frac{2-x-y}{(1-x)(1-y)}\;{}_2F_1\left(s+2-n,\, s+2-n';\, 2s+3;\, \frac{xy}{(1-x)(1-y)}\right)\Bigg]\,. \end{aligned} \tag{A4}$$

It may be noted that for $x=2n'(n+n')^{-1}$, $y=2n(n+n')^{-1}$, and $n'\neq n$, then $F(\alpha+1)=0$ (the orthogonality of the wave functions). At $n=n'=s+1+v$ ($v=0,\, 1,\, 2,\, \ldots$), Eq. (A4) enables the normalization coefficient to be obtained for the discrete spectrum eigenfunctions given in Eq. (10).

Once more using Eqs. (A3) and (A4) and taking into account that after the calculation of the derivatives the function $F(\alpha+1)$ and the coefficients which stand before the functions ${}_2F_1$ in Eq. (A4) and equal to zero, then

$$\begin{aligned} F(\alpha+2)=\frac{(-1)^{n-s}}{(s+1)(2s+3)}\left(\frac{n'-n}{n'+n}\right)^{n'+n-2s-4}\Bigg[&\left(\frac{2nn'}{n+n'}-s-1\right)\,{}_2F_1\left(s+1-n,\, s+1-n';\, 2s+2;\, \frac{-4nn'}{(n-n')^2}\right) \\ &+\frac{2nn'(n-s-1)(n'-s-1)}{(s+1)(n'-n)^2}\,{}_2F_1\left(s+2-n,\, s+2-n';\, 2s+3;\, \frac{-4nn'}{(n-n')^2}\right)\Bigg]\,. \end{aligned} \tag{A5}$$

ACKNOWLEDGMENTS

The author is grateful to Professor F. V. Bunkin for a number of useful discussions and to Dr. C. Manus and Dr. G. Mainfray for their hospitality during his stay in Centre d'Etudes Nucléaires de Saclay.

---

*1971–1972 Visiting Fellow. Permanent address: P. N. Lebedev Physics Institute, USSR Academy of Sciences, Moscow, USSR.

[1] F. V. Bunkin and I. I. Tugov (unpublished).

[2] E. S. Rittner, J. Chem. Phys. **19**, 1030 (1951).

[3] C. Maltz, Chem. Phys. Lett. **3**, 707 (1969).

[4] The values D and $\omega_e x_e$ calculated in Ref. 3 from the Rittner potential for some alkali halides give rise to mean errors equal to 3 and 13%, respectively.

[5] J. Berkowitz and W. A. Chupka, J. Chem. Phys. **45**, 1287 (1966).

[6] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Vol. 1, p. 524. When $B>0$ Eq. (7) of the present paper corresponds to the expression for the Green's function of the Fues-Kratzer potential $V(r)=A/r^2-B/r$. See F. V. Bunkin and I. I. Tugov, Zh. Eksp. Teor. Fiz. 58, 1987 (1970) [Sov. Phys.-JETP 31, 1071 (1970)].

[7] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Tables of Integral Transform* (McGraw-Hill, New York, 1954), Vol. 1. p. 216, Eq. (14). Since the radial functions $x_n(r')$ vary very slowly with K we put $s(K)=s(K+1)$. Note that

Eqs. (16) and (17) may be obtained also using the recursion relations for Coulomb matrix elements [see W. Gordon, Ann. Physik 2, 1031 (1929)].

[8] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 1.

[9] See Ref. 7, p. 215, Eq.(11).

[10] See Ref. 8, p. 238, Eq.(3).

[11] P. Appell and Kampe de Feriet, Fonctions Hypergeométriques et Hypersphériques. (Polynômes d' Hermite, Paris, 1926) (unpublished).

PHYSICAL REVIEW A VOLUME 8, NUMBER 2 AUGUST 1973

Multiphoton Processes in Heteropolar Diatomic Molecules

F. V. Bunkin
P. N. Lebedev Physics Institute, USSR Academy of Sciences, Moscow, 117333, USSR

I. I. Tugov*
Service de Physique Atomique, Centre d'Etudes Nucléaires de Saclay, 91, Gif-sur-Yvette, France

(Received 25 August 1972; revised manuscript received 5 June 1973)

Within the framework of the Born–Oppenheimer approximation and the theory of multiphoton molecular transitions, a method is proposed for calculating matrix elements of multiphoton processes in a heteropolar diatomic molecule. The method is based on the application of the explicit expressions of the Green's functions of the internuclear potentials. Analytical expressions are derived for the two-photon transitions. Results for higher-order processes are presented in a form which is convenient for numerical computation.

I. INTRODUCTION

In a previous paper[1] general expressions have been derived for the cross sections of multiphoton processes induced by radiation acting on a diatomic molecule.

Within the framework of time-dependent perturbation theory and the Born–Oppenheimer approximation, a method has been proposed for evaluating the sums over intermediate states. The method is based on the application of the explicit expressions for the Green's functions of the internuclear potentials. The Morse-type model of potential-energy curves has been used which gives a good representation of true curves of the ground and excited electronic states of some homopolar diatomic molecules.

It is evident that the description of the interaction of intense electromagnetic radiation with a heteropolar molecule would also be of interest from the different points of view. In the most clearly defined cases of what is called heteropolar binding all the valency electrons pass over from their own atoms to other atoms, so that the heteropolar molecule unlike the homopolar one has appreciable dipole moment in the ground state.

This gives rise to rich rotation-vibration spectra in ordinary spectroscopy of such diatomics. In the treatment of multiphoton processes it becomes necessary to take into account the intermediate transitions which occur without change in electronic state. Theoretically, two-photon vibrational transitions in a heteronuclear diatomic molecule have been considered using the Morse potential[2] and the Kratzer potential[3] as internuclear potential energy.

The application of the Green's functions of these potentials obtained in closed forms permits analytic solution of the problem. However, the potentials used do not give a particularly good representation of true curves in the case of heteropolar binding. At the same time the experimental investigation of the interaction of heteropolar diatomics with the electromagnetic field has been the subject of a large number of works. Terenin first initiated the study of spectra of heteropolar diatomics.[4] Actually, such research plays an important part both for the theory of molecular structure in general and for nonlinear optical phenomena in particular.

It is clear that the possibilities of the theoretical treatment of the processes induced by radiation acting on a molecule depend on the presence of the potential-energy-curve model for the ground and excited molecular states. Such a model must well describe the true curves and at the same time be simple enough to enable us to write analytic expressions for wave functions and a Green's function of all electron terms involved in the transition.

In the present paper we shall use the following internuclear potentials proposed in the paper[5]:

$$V_j(r) = \frac{A_j}{(r-\rho_j)^2} - \frac{B_j}{r-\rho_j} + Q_j \qquad (1)$$