PHYSICAL REVIEW A VOLUME 5, NUMBER 3 MARCH 1972

Inclusion of Nuclear Motion in Calculations of Optical Properties of Diatomic Molecules[*]

Jerome M. Schulman[†] and Robert Detrano
Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

and

Jeremy I. Musher
Belfer Graduate School of Science, Yeshiva University, New York, New York 10033

(Received 14 June 1971)

An explicit expression is derived which permits the exact inclusion of nuclear motion in calculations of second-order optical and magnetic molecular properties within the Born-Oppenheimer approximation. Explicit calculations are carried out on the model problem of the hydrogen molecular ion for the exact *zz* component of the Rayleigh and vibrational Raman scattering tensors and for several approximations to these tensors. The result is somewhat sensitive to the approximate expression employed but the semiclassical approximation is accurate to within a percent in both cases.

I. INTRODUCTION

Optical and magnetic second-order properties of molecules are generally calculated either by taking the value determined at precisely the equilibrium internuclear separation, or, at best, by determining the static value at a number of internuclear separations and integrating the curve obtained over the appropriate vibrational wave functions. Such calculations, obviously, do not include the motion of the nuclei in any rigorous manner, although the second procedure is the exact semiclassical equivalent of the classical oscillating system.

The present paper describes a simple, but rigorous, procedure for including the effect of nuclear motion in such calculations within the Born-Oppenheimer (BO) approximation. This procedure is compared with several expansion procedures which we have discussed previously[1] in their historical context for the Raman-intensity problem, and the relative convergence of the expansions are estimated. Calculations are carried out for the *zz* component of the electric polarizability and the vibrational Raman-intensity tensors for the model problem of the H_2^+-molecular ion with the electric field along the internuclear axis. These results are compared with those obtained from truncating the various expansion procedures. The leading term of what we call[1] the BO *expansion*, without the Herzberg-Teller-like Taylor's-series expansion, which is the semiclassical result, gives values within 1% of the exact in accord with the theoretical expectation.

II. THEORY

The intensity of light scattered from the ground state $\Psi_0^0(r,\ R)$ of a homonuclear diatomic molecule can be obtained from the tensor

$$\overleftrightarrow{\alpha}_{ma}(\omega)=\sum_{n,k}\left[(W_n{}^k-W_0{}^0+\omega)^{-1}+(W_n{}^k-W_m{}^a-\omega)^{-1}\right]\times\langle m,a|\vec{\mathrm{r}}|n,k\rangle\langle n,k|\vec{\mathrm{r}}|0,0\rangle\ , \tag{1}$$

where $\Psi_m^a(r,\ R)$ is the final state of the molecule, the two indices referring to the electron and nuclear parts of the wave function which are introduced for convenience here but which are only given explicit meaning below. The $W_n{}^k$ are the eigenvalues of the total Hamiltonian H in a molecule-fixed coordinate system, corresponding to eigenfunctions $\Psi_n^k(r,\ R)$, and $\vec{\mathrm{r}}$ symbolizes $\sum\vec{\mathrm{r}}_i$ measured from the center of the molecule. When $m=0$ and $a=0,\ 1$, respectively, Eq. (1) determines the Rayleigh and vibrational Raman scattering intensities, respectively, which we will consider, for convenience, in the limit of $\omega=0$.

While this expansion could, in principle, be used in calculations, it is not within the range of present computational techniques to do so. It is therefore a practical necessity to introduce immediately the BO approximation not only for the ground state but for *all* the vibronic $\Psi_n^k(r,\ R)$, i.e., we write

$$\Psi_n^k(r,\ R)\approx\varphi_n(r,\ R)\chi_n^k(R)\ , \tag{2}$$

where the $\varphi_n(r,\ R)$ are eigenfunctions of

$$H_{\mathrm{el}}(r,\ R)\equiv H(r,\ R)-T_R\ , \tag{3}$$

with eigenvalues $E_n(R)$, parametric in R, where T_R is the kinetic-energy operator of the relative motion of the nuclei and the small terms[2] which couple the BO states, and which couple the vibrational motion to the rotational motion are neglected. (The necessity for introducing the BO approximation for all states, and not just for the ground state, is shown in a different way in Appendix A.) The vibrational function $\chi_n^k(R)$ is the kth eigenfunction satisfying

$$[T_R+E_n(R)-W_n{}^k]\chi_n^k(R)=0\ , \tag{4}$$

where W_n^k is now the *approximate* eigenvalue of H corresponding to the approximation (2) for the Ψ_n^k, and where the two small "adiabatic" or "diagonal" terms[3] are neglected.

The tensors $\overleftrightarrow{\alpha}_{0a} \equiv \overleftrightarrow{\alpha}_{0a}(0)$, from which the static polarizability and the zero-frequency Raman intensity are obtained for the appropriate values of a, can now be written as *double* integrals over a "polarizability kernel" $\overleftrightarrow{\alpha}(R, R')$ as

$$\begin{aligned}\overleftrightarrow{\alpha}_{0a} &= \int\int \chi_0^a(R)\overleftrightarrow{\alpha}(R, R')\chi_0^0(R')\,dR\,dR' \\ &= \sum_n \int\int \chi_0^a(R) f_n(R) \sum_k [(W_n^k - W_0^0)^{-1} + (W_n{}^k - W_0{}^a)^{-1}] \\ &\qquad \times \chi_n^k(R)\chi_n^k(R') f_n(R')\chi_0^0(R')\,dR\,dR' , \qquad (5)\end{aligned}$$

where the (vector) electric dipole matrix element $f_n(R)$ is defined by

$$f_n(R) \equiv \langle \varphi_0(r, R) | \vec{\mathrm{r}} | \varphi_n(r, R)\rangle_r , \qquad (6)$$

the integration being taken over the electron coordinates only, and $f_n(R)$ is for convenience assumed to be real with the appropriate linear combination of any degenerate functions assumed to have been taken.

The principal difficulty in dealing with (5) lies in the sum over the vibrational states k which requires that the nuclear motion must be treated explicitly during the excitation process, even in the BO approximation, which thus prevents $\overleftrightarrow{\alpha}_{0a}$ from being written as a single integral over an effective R-dependent polarizability $\overleftrightarrow{\alpha}(R)$. Equivalently, the k dependence of the energy denominators prevents the use of the closure identity

$$\sum_k \chi_n^k(R)\chi_n^k(R') = \delta(R - R') \qquad (7)$$

to eliminate the sum over k. The sum can, however, be eliminated by substituting for the $W_n{}^k$ using (4) to give the expression[1]

$$\begin{aligned}\overleftrightarrow{\alpha}_{0a} = \sum_n \langle \chi_0^a(R) | f_n(R) \{ [T_R + E_n(R) - W_0{}^0]^{-1} \\ + [T_R + E_n(R) - W_0{}^a]^{-1} \} f_n(R) | \chi_0^0(R) \rangle . \qquad (8)\end{aligned}$$

This result is just the usual perturbation-theory expression for the *nuclear* part of the perturbation-theory problem within the BO approximation as derived in Appendix A where the closure (7) is not necessary as the complete set of vibrational functions with index k is never introduced. This can be solved by inverting the operator (analogous to the sum-rule technique of Dalgarno and Lewis[4] for electronic problems) and solving for the vector functions $G_n{}^a(R)$ defined by

$$[T_R + E_n(R) - W_0^a] G_n^a(R) = f_n(R)\chi_0^a(R) , \qquad (9)$$

there being no solution to the homogeneous equation. The tensors $\overleftrightarrow{\alpha}_{0a}$ can thus be written as

$$\begin{aligned}\overleftrightarrow{\alpha}_{0a} = \sum_n [\langle \chi_0^a(R) | f_n(R) | G_n^0(R) \rangle \\ + \langle G_n^a(R) | f_n(R) | \chi_0^0(R) \rangle] , \qquad (10)\end{aligned}$$

which is the desired result.

III. APPROXIMATE EXPRESSIONS

It will be of interest to compare the exact result (within the BO approximation) of (10) with two approximate procedures which, for convenience, are described here only for Rayleigh scattering, with the subscripts 0, 0 dropped.

The Franck-Condon principle would suggest that the expansion

$$\begin{aligned}(W_n{}^k - W_0{}^0)^{-1} = [E_n(R_0) - W_0{}^0]^{-1} \\ \times \left(1 + \frac{E_n(R_0) - W_n{}^k}{E_n(R_0) - W_0{}^0} + \cdots\right) \qquad (11)\end{aligned}$$

with R_0 the minimum of $E_0(R)$ should converge rapidly for the set of states k which give sizable contributions to (5) although it is not convergent for all k. Such an expansion about a physically derived effective "average energy" was probably first used by Van Vleck,[5] who chose the minima of the respective potential energy curves, i.e., $\min[E_n(R)]$, for calculating Raman intensities. Similar expressions have proven convenient for calculating van der Waals energies[6] where the divergent behavior has been shown explicitly, and for showing the near equal magnitudes of "second-order" Coulomb and exchange interactions between two hydrogen atoms.[7] This expansion has also been used with an arbitrary average energy to give a formal expression for the Raman intensity by Tang and Albrecht[8] in their "ground-state approach" whose leading term is generally referred to as the Unsöld approximation. In their calculations these authors choose the average energy to correspond with that obtained from a particular variational procedure.

When (11) is substituted into (5) the tensor $\overleftrightarrow{\alpha}$ can be written as the series

$$\begin{aligned}\overleftrightarrow{\alpha} &= 2\sum_n \langle \chi_0^0 | f_n(R) [E_n(R_0) - W_0{}^0]^{-1} \\ &\qquad \times [1 + X_n(R) + \cdots] f_n(R) | \chi_0^0 \rangle \\ &\equiv \overleftrightarrow{\alpha}{}^0_{\mathrm{FC}} + \overleftrightarrow{\alpha}{}^1_{\mathrm{FC}} + \cdots , \qquad (12)\end{aligned}$$

where $X_n(R)$ is the operator

$$X_n(R) = [E_n(R_0) - E_n(R) - T_R]/[E_n(R_0) - W_0{}^0] \qquad (13)$$

and where the device of Van Vleck[5] and Musher[6] is used to transform the k-dependent terms in the numerator ($W_n{}^k \chi_n{}^k$) into operator terms so that the summation over k can be eliminated using (7).[4]

A second expansion which turns out to be most useful is

$$\begin{aligned}(W_n{}^k - W_0{}^0)^{-1} = [E_n(R) - E_0(R)]^{-1} \\ \times \left(1 + \frac{E_n(R) - W_n{}^k + W_0{}^0 - E_0(R)}{E_n(R) - E_0(R)} + \cdots\right) . \qquad (14)\end{aligned}$$

This at first seems rather unusual as it is an expansion of a *number* in a series each of whose terms is a *function* of R; although, in fact, the sum over k itself implicitly introduces an R dependence, the most simple example being the closure relation (7). The convergence of this series depends not only on k but also on R, but it should be reasonably rapid for the dominant set of states k and the dominant region of R.

When (14) is substituted into (5), the tensor $\overleftrightarrow{\alpha}$ can be written as the series

$$\overleftrightarrow{\alpha} = 2\sum_n \langle\chi_0^0|\, f_n(R)\,[E_n(R) - E_0(R)]^{-1} \times [1 + Y_n(R) + \cdots\,]\, f_n(R)\,|\chi_0^0\rangle$$

$$\equiv \overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}} + \overleftrightarrow{\alpha}{}^{1}_{\mathrm{BO}} + \cdots\ , \qquad (15)$$

where $Y_n(R)$ is the operator

$$Y_n(R) = [W_0{}^0 - E_n(R) - T_R]/[E_n(R) - E_0(R)]\ , \qquad (16)$$

and the higher terms $[Y_n(R)]^j$ for $j > 1$ in (15) are defined with T_R *not* operating on the denominators of the successive $Y_n(R)$'s. Since the leading term of this series gives the BO polarizability, i.e., the polarizability calculated at each value of R,

$$\overleftrightarrow{\alpha}_{\mathrm{BO}}(R) = 2\sum_n [E_n(R) - E_0(R)]^{-1}\,|\langle\varphi_0|\, z\,|\varphi_n\rangle(R)|^2, \qquad (17)$$

averaged over the vibrational function

$$\overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}} = \int \chi_0^0(R)\,\overleftrightarrow{\alpha}_{\mathrm{BO}}(R)\,\chi_0^0(R)\,dR\ , \qquad (18)$$

it is called the BO expansion, and is not to be confused with the BO approximation (2) itself. This leading term, $\overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}}$, which can be considered as the semiclassical result, has been used in the most sophisticated molecular calculations to date, such as that of Kołos and Wolniewicz,[9] although it has not been generally recognized to be only an approximate result, rather than an exact (BO) one. For Raman intensities the semiclassical argument was first developed by Placzek[10] and was interpreted further by Shorygin[11] and Wolkenstein.[12]

In order to calculate the first-order terms, which are the first difficult terms of the series (12) and (15), it is convenient to use the identities

$$[E_n(R_0) - W_0{}^0]\,X_n f_n \chi_0^0 = [E_n(R_0) - E_n(R) + E_0(R) - W_0{}^0] \times f_n\chi_0^0 + (2M)^{-1} f_n{}''\chi_0^0 + M^{-1} f_n{}' \frac{\partial}{\partial R}\chi_0^0 \qquad (19)$$

and

$$[E_n(R) - E_0(R)]\,Y_n f_n \chi_0^0 = (2M)^{-1} f_n{}''\chi_0^0 + M^{-1} f_n{}' \frac{\partial}{\partial R}\chi_0^0\ , \qquad (20)$$

which are readily derived[1] from (4), where primes indicate derivatives with respect to R and the reduced mass M appears due to $T_R = -(2M)^{-1}(\partial^2/\partial R^2)$ up to the neglected rotational-mixing terms. The term in $f_n{}'$ can be seen to be approximately $\omega/[E_n(R_0) - W_0{}^0]$ smaller that the first term on the right-hand side of (19), where ω is the effective vibrational energy, and since $f_n(R)$ is usually a smoothly varying function of R, both of these terms can be neglected in an approximate calculation, so that the first-order terms of (12) and (15) become

$$\overleftrightarrow{\alpha}{}^{1}_{\mathrm{FC}} \approx 2\sum_n \langle\chi_0^0|\, f_n{}^2(R)\,[E_n(R_0) - W_0{}^0]^{-2} \times [E_n(R_0) - E_n(R) + E_0(R) - W_0{}^0]\,|\chi_0^0\rangle \qquad (21a)$$

and

$$\overleftrightarrow{\alpha}{}^{1}_{\mathrm{BO}} \approx 0\ . \qquad (21b)$$

By repeated application of the operators X_n and Y_n the higher orders of the respective series are generated. Since the same type of terms appear in all powers of $X_n{}^j f_n\chi_0^0$ and $Y_n{}^j f_n\chi_0^0$ as in the $j = 1$ term just discussed, we find the remarkable result that other than terms which are small relative to $\overleftrightarrow{\alpha}{}^{1}_{\mathrm{FC}}$, all the $\overleftrightarrow{\alpha}{}^{j}_{\mathrm{BO}}$ are zero (for $j > 0$). Thus

$$\overleftrightarrow{\alpha} = \overleftrightarrow{\alpha}{}^{0}_{\mathrm{FC}} + \overleftrightarrow{\alpha}{}^{1}_{\mathrm{FC}} + \cdots \approx \overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}}\ , \qquad (22)$$

a theoretical result which will be confirmed quantitatively in the example given below.[13] The error is not entirely negligible *circa* 1% in the example, so that the exact result should be used wherever possible, although it appears to be of the magnitude that one would estimate for the error in the BO expresion [Eq. (2)] itself. It is interesting to note that not only is the semiclassical result $\overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}}$, highly accurate, but that *a fortiori* this result is independent of whether the vector potential or scalar potential is used in the Hamiltonian, as the appropriate approximate formulas using the dipole-velocity and dipole-length matrix elements are exactly equal to each other.

It has long been assumed that the matrix elements $f_n(R)$ are sufficiently smoothly varying functions of R and that nuclear oscillations are over such short distances that Taylor's-series expansion of the $f_n(R)$ with the subsequent assumption of harmonic behavior for the vibrational functions should be rapidly convergent. Such an expansion, usually referred to as a Herzberg-Teller expansion[14] has, to our knowledge, never been investigated quantitatively, so it will be of some interest to consider those terms of (12) and (15) which possess such expansions and their rates of convergence.

The $\overleftrightarrow{\alpha}(R, R')$ of (5) can be written as

$$\overleftrightarrow{\alpha}(R,\ R') = \overleftrightarrow{\alpha}{}^{0}(R)\,\delta(R - R') + \overleftrightarrow{\alpha}{}'(R,\ R') + \cdots$$

for both the FC and BO expansions, so that both $\overleftrightarrow{\alpha}{}^{0}_{\mathrm{FC}}$ and $\overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}}$ can be expanded as

$$\overleftrightarrow{\alpha}{}^{0}_{\mathrm{FC}} = \overleftrightarrow{\alpha}{}^{0,0}_{\mathrm{FC}} + \overleftrightarrow{\alpha}{}^{0,1}_{\mathrm{FC}} + \cdots \qquad (23)$$

and

$$\overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}} = \overleftrightarrow{\alpha}{}^{0,0}_{\mathrm{BO}} + \overleftrightarrow{\alpha}{}^{0,1}_{\mathrm{BO}} + \cdots \qquad (24)$$

by taking the Taylor's series of the appropriate $\overleftrightarrow{\alpha}^{0}(R)$ and where the explicit expressions for the expansion terms are given in Appendix B. As a result of the T_R dependence of $X_n(R)$ and $Y_n(R)$, there is *no* single Taylor's-series expansion for the integrands of $\overleftrightarrow{\alpha}^{1}_{\mathrm{FC}}$, $\overleftrightarrow{\alpha}^{1}_{\mathrm{BO}}$, etc., but if the small vibrationlike terms are neglected, as in the discussion following (19) and (20) above, then $\overleftrightarrow{\alpha}^{1}_{\mathrm{FC}}$ can be expanded approximately as

$$\overleftrightarrow{\alpha}^{1}_{\mathrm{FC}} \approx \overleftrightarrow{\alpha}^{1,0}_{\mathrm{FC}} + \overleftrightarrow{\alpha}^{1,1}_{\mathrm{FC}} + \cdots , \tag{25}$$

with again the explicit expressions given in Appendix B.

IV. EXAMPLE

Calculations were carried out for the zz component of the polarizability tensor $\overleftrightarrow{\alpha}_{00}$ and the vibrational Raman tensor $\overleftrightarrow{\alpha}_{01}$ for the one-electron problem of the hydrogen molecular ion H_2^+ with the field direction along the internuclear axis. A set of 16 σ_g and 16 σ_u orbitals were generated at appropriate values of R from a basis set of 10 s- and 5 p-Gaussian-type functions on each center. Such a basis has been previously shown to be essentially complete[15] and thus gives a highly accurate finite approximation to the electronic continuum. Initial calculations[1] using the approximate expressions for $\overleftrightarrow{\alpha}^{0}_{\mathrm{FC}}$ and $\overleftrightarrow{\alpha}^{0}_{\mathrm{BO}}$ showed that the $1\sigma_u$ state, i.e., the lowest-lying excited state of odd symmetry, contributes over 98% of the quantity

$$\sum_n |\langle 1\sigma_g | z | n\sigma_u\rangle|^2 (\epsilon_{n\sigma u} - \epsilon_{1\sigma g})^{-1}$$

over the entire range of $R = 1.5 - 2.5 a_0$ where a_0 is the Bohr radius for which χ_0^0 is significant (the classical turning points are $1.7a_0$ and $2.3a_0$) for the denominators both R dependent and evaluated at $R = R_0 = 2.00a_0$. Since absolute errors of the order of a few percent were of no concern in what is, after all, only a model problem, the entire calculation was simplified to the extent that only this one excited state was included, and the summations over n in the various expansions were dropped.

The exact polarizability and Raman contributions were obtained from

$$\alpha = 2\langle \chi_0^0 | f_1 | G_1{}^0 \rangle \tag{26a}$$

and

$$\alpha = \langle \chi_0^1 | f_1 | G_1{}^0 \rangle + \langle G_1{}^1 | f_1 | \chi_0^0 \rangle , \tag{26b}$$

respectively, where

$$\left(- (2M)^{-1} \frac{d^2}{dR^2} + \epsilon_{1\sigma u}(R) - W_0{}^a \right) G_1{}^a(R) = f_1(R) \chi_0^a(R) ,$$
$$a = 0,\ 1, \quad G_1{}^a(0) = G_1{}^a(\infty) = 0 , \tag{27}$$

and $M = 918.048$. Values of $f_1(R)$, $\epsilon_{1\sigma g}(R)$, and $\epsilon_{1\sigma u}(R)$ on a grid were generated by performing the molecular orbital calculations at 30 points between $1a_0$ and $3a_0$ as well as several points further out. The resulting values of f_1 and the ϵ's were then fit with a linear combination of Slater functions of the form

$$S_n = R^n e^{-nR/R_0} ,$$

with n a positive integer, according to the method of Lee.[16] From these analytic expressions, values of the functions were generated on a grid of $0.005a_0$ from 0 to $15a_0$ on which the differential equations were solved and the integrals for α evaluated.

The vibrational functions χ_0^0 and χ_0^1 were obtained as the solutions to

$$\left[- (2M)^{-1} \frac{d^2}{dR^2} + \epsilon_{1\sigma g}(R) \right] \chi_0^a = W_0{}^a \chi_0{}^a , \quad a = 0,\ 1 \tag{28}$$

according to the method of Cooley[17] and the values of $W_0{}^0$ and $W_0{}^1$ obtained were 0.005 25 and 0.015 26 a.u., respectively, referred to the bottom of the potential well, in good agreement with the values of Beckel *et al.*,[18] of 0.005 26 and 0.015 23 a.u.

To obtain $G_1{}^0$ and $G_1{}^1$ the inhomogeneous equations were converted to algebraic band matrix equations using a three-point finite difference approximation and solved by successive forward and backward substitution. The boundary condition forcing each G to vanish at $15a_0$ was used rather than a continuum asymptote and the solution was shown to be insensitive to the exact location of the boundary. All required integrals were obtained using Simpson's rules and the final values are believed good to within 1%.

The exact values for the electric polarizability (Rayleigh scattering intensity) and the vibrational-Raman-intensity tensor components, both at zero frequency, are presented in Tables I and II along with their approximate values determined from the FC and BO expansions, and the further Herzberg-Teller expansions. The explicit expressions for all these approximations are taken from Appendix B where the sum over states n is reduced to the single $n = 1$ term as indicated above.

The following observations can be made:

(i) The α^{0}_{BO} are indeed very close to the exact values, the error being 0.2% for the two examples.

(ii) The FC expansion converges reasonably well, the first two terms leaving errors of 4 and 9% for the polarizability and Raman intensity, respectively.

TABLE I. Exact and approximate values of $\alpha_{zz}^{\mathrm{Rayleigh}}$ for H_2^+ (in a_0^3).

		$\alpha^{n,0}$	$\alpha^{n,1}$	$\alpha^{n,0}+\alpha^{n,1}$	α^{n}	α_{exact}
α_{FC}	$n=0$	5.078	0.222	5.300	5.372	5.781
	$n=1$	0.062	0.213	0.275	0.241	
	$(n=0)+(n=1)$	5.140	0.435	5.575	5.613	
α_{BO}	$n=0$	5.071	0.448	5.519	5.791	

TABLE II. Exact and approximate values of $\alpha_{zz}^{\text{Raman}}$ for H_2^+ (in a_0^3).

		$\alpha^{n,1}$	α^{n}	α_{exact}
	$n=0$	0.832	0.870	1.980
α_{FC}	$n=1$	0.891	0.926	
	$(n=0)+(n=1)$	1.723	1.796	
α_{BO}	$n=0$	1.661	1.984	
	$n=0$	0.411	0.430	0.974
$\alpha_{\text{FC}}(W_0^0)$ [a]	$n=1$	0.430	0.457	
	$(n=0)+(n=1)$	0.841	0.887	

[a] From Eq. (8) $\alpha_{\text{FC}}^{\text{Raman}}$ can be written as $\alpha_{\text{FC}}^{\text{Raman}}(W_0{}^0)+\alpha_{\text{FC}}^{\text{Raman}}(W_0{}^1)$ whereas $\alpha_{\text{BO}}^{\text{Raman}}$ is the sum of two equal terms.

(iii) The Herzberg-Teller expansions for the α_{FC}^0's are rapidly convergent, the error in taking the first nonvanishing term alone is 5–6%. The Herzberg-Teller expansions for the α_{FC}^1's are also reasonably convergent being better for the Raman whose error through $\alpha_{\text{FC}}^{1,1}$ is only 4% whereas the corresponding error for the polarizability is 14%. The $\alpha_{\text{FC}}^{1,0}$ does not vanish identically for the polarizability as $R_{00}\neq 0$ although had R_e been used rather than R_0 in the expansion, this term would have vanished.

(iv) The leading Herzberg-Teller terms $\alpha_{\text{FC}}^{0,0}$ and $\alpha_{\text{FC}}^{1,1}$ for the Raman expansion are almost equal (or equivalently α_{FC}^0 and α_{FC}^1 are almost equal). This is a manifestation of the sum rule

$$\textstyle\sum_n f_n{}^2(R)[E_n(R)-E_0(R)]=\frac{1}{2}\ , \tag{29}$$

valid at all R which is easily derived from the identity

$$\langle\varphi_0|z[H_{\text{el}}-E_0(R)]z|\varphi_0\rangle=\tfrac{1}{2}\ . \tag{30}$$

When the derivative of (29) is taken with respect to R we obtain

$$\textstyle\sum_n\{2f_n'[E_n(R)-E_0(R)+f_n(R)E_n'(R)\}=0\ , \tag{31}$$

which provides the equality

$$2f_1'=(E_0-E_1)^{-1}E_1'f_1 \tag{32}$$

if the one-state approximation is assumed to be as valid for (31) as it is for the α's. We thus have, from (B11) and (B13), that

$$\alpha_{\text{FC}}^{0,1}=\alpha_{\text{FC}}^{1,1}\ , \tag{33}$$

where the vibrational terms (-0.005 and -0.015 for $W_0{}^0$ and $W_0{}^1$, respectively) of (B13) are neglected. Notice that this is not an exact relation but only holds in a one-state (or effective one-state problem). In the present example, the left-hand side of (29) is 0.47, in error by 6% in the one-state approximation, which led to the corresponding "error" in (33) of 4%. A similar argument has been given previously by Tang and Albrecht[8(a)] (see their Appendix A) and is used in their calculations.

(v) The Herzberg-Teller expansions for the α_{BO}^0's are not as rapidly convergent with the leading term being in error by 14 and 20% for the polarizability and Raman intensity, respectively. This implies that even the most accurate calculation for the polarizability derivative can give the components of $\overleftrightarrow{\alpha}$ off by as much as 20% with more drastic consequences for the anisotropies which govern the depolarization ratios. The evaluation of the polarizability at only R_0 (or R_e) can also be relatively inaccurate. The significance of these results have been emphasized previously by Kołos and Wolniewicz.[9]

(vi) The Bell and Long calculation[18] for $\alpha_{\text{BO}}^{0,0}$ gave $1.55a_0^3$ and the Tang and Albrecht calculation[8(a)] gave $1.59a_0^3$ (converted using our value of $R_{01}=0.2289a_0$) both of which are quite close to the accurate value of $1.66a_0^3$ even though they are far from α_{BO}^0 itself. This can be attributed to the validity of the one-state approximation and the accuracy to which this state can be approximated by the simple function $z\varphi_0(r,\ R)$. It should be noted that there is no reason to assume a dominant one-state behavior for more complex systems merely by analogy with the present example of H_2^+ in a finite basis. Thus the use of single-term trial functions, just as the equality of (33), cannot *a priori* be expected to give accurate approximations in the general case.

(vii) The fact that a single excited state, in the present discrete approximation to the (electronic) continuum, gives 98% of the contribution to the α's does not, of course, imply that such will be the case in general.

(viii) While the present discussion has been limited to problems involving the ground vibrational state, similar analyses can be carried out for the higher vibrational states where it is expected that the approximate expressions are less accurate.

ACKNOWLEDGMENTS

The authors are grateful to Dr. J. K. Percus for his continued interest in this problem and to the New York University A. E. C. Computing Center at the Courant Institute for a generous grant of computing time. J. I. M. is grateful to Professor B. Pullman for the hospitality of the Institut de Biologie Physico-Chimique, Fondation Edmond de Rothschild, Paris, where this manuscript was drafted.

APPENDIX A

The fact that the BO approximation must be introduced for the excited states as well as the ground state can be seen from the following argument. Taking the BO approximation for the ground state, the static polarizability can be written as

$$\overleftrightarrow{\alpha} = 2\langle \chi_0^0\varphi_0 | \vec{r}(H - W_0{}^0)^{-1}\vec{r} | \varphi_0\, \chi_0^0\rangle , \qquad \text{(A1)}$$

which equals

$$2\langle \chi_0^0\varphi_0 | \vec{r} | Q\rangle \qquad \text{(A2)}$$

for $Q(r,\ R)$ the solution to

$$(H - W_0{}^0)Q(r,\ R) = \vec{r}\varphi_0(r,\ R)\chi_0^0(R) . \qquad \text{(A3)}$$

If $Q(r,\ R)$ is expanded in a complete set of functions of r with coefficients arbitrary functions of R, i.e.,

$$Q(r,\ R) = \textstyle\sum_n G_n(R)\varphi_n(r,\ R) , \qquad \text{(A4)}$$

with $\varphi_n(r,\ R)$ eigenfunctions of (3), then (A3) reduces to

$$\textstyle\sum_n [T_R + E_n(R) - W_0{}^0]G_n(R)\varphi_n(r,\ R) = \vec{r}\varphi_0(r,\ R)\chi_0^0(R) . \qquad \text{(A5)}$$

The usual procedure which would give differential equations for each of the $G_n(R)$ independently, i.e., by multiplying on the left by $\varphi_m^*(r,\ R)$ and integrating over r, cannot be applied directly because of the R dependence of these functions. Thus the BO approximation which neglects the mixing due to this R dependence must be introduced in order that the equations decouple and reduce to the set of equations (9).

APPENDIX B

For the polarizability the explicit expressions for the expansion terms are

$$\overleftrightarrow{\alpha}{}^{0}_{\mathrm{FC}} = 2\textstyle\sum_n [E_n(R_0) - W_0^0]^{-1}\langle\chi_0^0 | f_n{}^2 | \chi_0^0\rangle , \qquad \text{(B1)}$$

$$\overleftrightarrow{\alpha}{}^{0,0}_{\mathrm{FC}} = 2\textstyle\sum_n (E_n - W_0{}^0)^{-1} f_n{}^2 , \qquad \text{(B2)}$$

$$\overleftrightarrow{\alpha}{}^{0,1}_{\mathrm{FC}} = 4R_{00}\textstyle\sum_n (E_n - W_0{}^0)^{-1} f_n f_n' , \qquad \text{(B3)}$$

$$\overleftrightarrow{\alpha}{}^{1}_{\mathrm{FC}} = 2\textstyle\sum_n [E_n(R_0) - W_0{}^0]^{-2}$$
$$\times\langle\chi_0^0 | [E_1(R_0) - E_1 + E_0 - W_0{}^0] f_n{}^2 | \chi_0^0\rangle , \qquad \text{(B4)}$$

$$\overleftrightarrow{\alpha}{}^{1,0}_{\mathrm{FC}} = 2(E_0 - W_0{}^0)\textstyle\sum_n (E_n - W_0{}^0)^{-2} f_n{}^2 , \qquad \text{(B5)}$$

$$\overleftrightarrow{\alpha}{}^{1,1}_{\mathrm{FC}} = -2R_{00}\textstyle\sum_n (E_n - W_0{}^0)^{-2}$$
$$\times [f_n{}^2 E_1' - 2(E_0 - W_0{}^0) f_n f_n'] , \qquad \text{(B6)}$$

$$\overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}} = 2\textstyle\sum_n \langle\chi_0^0 | (E_n - E_0)^{-1} f_n{}^2 | \chi_0^0\rangle , \qquad \text{(B7)}$$

$$\overleftrightarrow{\alpha}{}^{0,0}_{\mathrm{BO}} = 2\textstyle\sum_n (E_n - E_0)^{-1} f_n{}^2 , \qquad \text{(B8)}$$

$$\overleftrightarrow{\alpha}{}^{0,1}_{\mathrm{BO}} = 2R_{00}\textstyle\sum_n (E_n - E_0)^{-1}$$
$$\times [2 f_n f_n' - (E_n - E_0)^{-1} f_n{}^2 E_n'] , \qquad \text{(B9)}$$

where the functions E_0, E_n, f_n, and the derivatives E_n' and f_n' are evaluated at R_0 in the Herzberg-Teller expansions, but are functions of R in the nonexpanded expressions, except as indicated otherwise in (B1) and (B4), and where $R_{00} = \langle\chi_0^0 | R - R_0 | \chi_0^0\rangle = 0.06215$. The second term on the right-hand side (B6) is a vibration-type term which is included explicitly in the calculation as is consistent with keeping the entire expression $\overleftrightarrow{\alpha}{}^{1,0}_{\mathrm{FC}}$.

For the Raman intensity the explicit expressions for the expansion terms are

$$\overleftrightarrow{\alpha}{}^{0}_{\mathrm{FC}} = (1 + P_{01})\textstyle\sum_n [E_n(R_0) - W_0{}^0]^{-1}$$
$$\times\langle\chi_0^1 | f_n{}^2 | \chi_0^0\rangle , \qquad \text{(B10)}$$

$$\overleftrightarrow{\alpha}{}^{0,1}_{\mathrm{FC}} = 2R_{01}(1 + P_{01})\textstyle\sum_n (E_n - W_0{}^0)^{-1} f_n f_n' , \qquad \text{(B11)}$$

$$\overleftrightarrow{\alpha}{}^{1}_{\mathrm{FC}} = (1 + P_{01})\textstyle\sum_n [E_n(R_0) - W_0^0]^{-2}$$
$$\langle\chi_0^1 | [E_n(R_0) - E_n + E_0 - W_0^0] f_n^2 | \chi_0^0\rangle , \qquad \text{(B12)}$$

$$\overleftrightarrow{\alpha}{}^{1,1}_{\mathrm{FC}} = -R_{01}(1 + P_{01})\textstyle\sum_n (E_n - W_0^0)^{-2}$$
$$\times [f_n^2 E_1' - 2(E_0 - W_0^0) f_n f_n'] , \qquad \text{(B13)}$$

$$\overleftrightarrow{\alpha}{}^{0}_{\mathrm{BO}} = 2\textstyle\sum_n \langle\chi_0^1 | (E_n - E_0)^{-1} f_n{}^2 | \chi_0^0\rangle , \qquad \text{(B14)}$$

$$\overleftrightarrow{\alpha}{}^{0,1}_{\mathrm{BO}} = 2R_{01}\textstyle\sum_n (E_n - E_0)^{-1}$$
$$\times [2 f_n f_n' - (E_n - E_0)^{-1} f_n{}^2 E_n'] , \qquad \text{(B15)}$$

with

$$\overleftrightarrow{\alpha}{}^{0,0}_{\mathrm{FC}} = \overleftrightarrow{\alpha}{}^{1,0}_{\mathrm{FC}} = \overleftrightarrow{\alpha}{}^{0,0}_{\mathrm{BO}} = 0 \qquad \text{(B16)}$$

due to $\langle\chi_0^1 | \chi_0^0\rangle = 0$, where $R_{01} = \langle\chi_0^1 | R - R_0 | \chi_0^0\rangle = 0.2289$ and where P_{01} operates on the vibrational index of W_0^0 such that $P_{01}W_0^0 = W_0^1$.

Various approximate relations between the expansion terms are easily noted. Thus, for example,

$$\overleftrightarrow{\alpha}{}^{0,1}_{\mathrm{BO}} \approx \overleftrightarrow{\alpha}{}^{0,1}_{\mathrm{FC}} + \overleftrightarrow{\alpha}{}^{1,1}_{\mathrm{FC}} , \qquad \text{(B17)}$$

which is the semiclassical result for the Raman intensity interpreted by Shorygin[11] and Wolgenstein[12] and discussed in Ref. 1.

All equations are written, for simplicity, as if only diagonal components of the $\overleftrightarrow{\alpha}$'s are to be calculated. For off-diagonal components, the proper dyadic form must be taken, e.g., in (B3), $2f_n f_n'$ is replaced by $f_n f_n' + f_n' f_n$. Also, to avoid confusion it should be noted that relation (33) is obviously only valid for the diagonal component discussed in that section. It is also valid for the polarizability.

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*Research supported in part by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. PRF-3547-A5), by the National Science Foundation (Grant No. GP-26430), and by the Research Corporation.

†Alfred P. Sloan Fellow 1971–3.

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$$\overleftrightarrow{\alpha}_{oa}^{\text{eff}}(R)=\sum f_n(R)\{G_n^0(R)[\chi_0^0(R)]^{-1}+G_n{}^a(R)[\chi_0{}^a(R)]^{-1}\}.$$

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PHYSICAL REVIEW A VOLUME 5, NUMBER 3 MARCH 1972

Čerenkov Radiation near a Dielectric Boundary

R. B. Thomas, Jr.
Lockheed Research Laboratory, Palo Alto, California 94304

(Received 20 August 1970; revised manuscript received 6 August 1971)

The influence of Čerenkov-radiation loss on the emission spectrum and motion of an electron passing near the surface of a semi-infinite plane dielectric is treated on the basis of several simplifying assumptions. Equations of motion are obtained and solved for electron velocities just above radiation threshold in a region of anomalous dispersion. Expressions are found for the spatial and temporal dependence of the emission spectrum. A determination is made of the electron's total angular deflection which may exceed 10^{-2} deg; this result is shown to be in reasonable agreement with an estimate based on measured emission levels. Possible corrections resulting from induced bremsstrahlung and inelastic interactions with the dielectric are discussed.

I. INTRODUCTION

After Frank and Tamm's original investigation of Čerenkov radiation in an infinite dielectric medium,[1] it was some time before there appeared a treatment of a related problem involving a bounded medium; this was the work of Ginsburg and Frank in which they studied the radiation generated by an electron moving in the proximity of a dielectric medium.[2] This work was motivated by an earlier proposal of Ginsburg to generate microwave radiation by means of the Čerenkov effect.[3] To eliminate the dominant ionization energy loss, which always occurs when an energetic charged particle traverses matter, Ginsburg and Frank considered the radiation emitted by electrons traveling within a hollow cylindrical channel contained in an infinite dielectric. Later the problem of radiation from electrons moving uniformly parallel to the surface of a semi-infinite plane dielectric was treated by several authors.[4–8] In all of these investigations it was assumed that the radiating electron moved with constant velocity and remained unaffected by the loss of energy and momentum resulting from