# Relation between Classical and Quantum Formulations of the Franck–Condon Principle: The Generalized r-Centroid Approximation

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The classical transition point $r^*_{v'v''}$ for the $(v', v'')$ band is introduced as the point where the kinetic energy does not change during the transition (classical statement of the Franck–Condon principle). It is shown that when the r-centroid approximation is valid, it implies that the r centroid $\bar{r}_{v'v''}$ equals $r^*_{v'v''}$, allowing a new connection to be made between the classical and quantum statements of the Franck–Condon principle. The r-centroid approximation fails for some classically allowed bands having large Franck–Condon factors. This occurs when the $(v', v'')$ band has more than one classical transition point. A generalization of the r-centroid approximation permits such bands to be used in determining the variation of the electronic transition moment with internuclear distance.

## I. INTRODUCTION

It is well known that the relative intensities of electronic transitions in a diatomic molecule are governed by the product of two factors, the rotational line strength $S_{J'J''}$ and the vibrational band strength $p_{v'v''}$ (*1–3*). The former can be calculated by diagonalizing the full rotational Hamiltonian to obtain the required rotational wavefunctions. The latter is given by the expression

$$p_{v'v''} = \left| \int_0^\infty \psi_{v'}(r) R_e(r) \psi_{v''}(r) dr \right|^2$$

$$\equiv |\langle v' | R_e(r) | v'' \rangle|^2, \tag{1}$$

where $\psi_v(r)$ is the vibrational wavefunction and

$$R_e(r) = \int \psi_e^* M_e \psi_{e'} d\tau_e \tag{2}$$

is the electronic transition moment. In Eq. (2), $\psi_e$ is the electronic wavefunction and $M_e$ is the electronic dipole moment operator. By assuming that the electronic transition moment is constant (the Condon approximation) (*4–6*), Eq. (1) may be rewritten as

$$p_{v'v''} = R_e^2 q_{v'v''}, \tag{3}$$

where

$$q_{v'v''} = |\langle v' | v'' \rangle|^2 \tag{4}$$

is the square of the vibrational overlap integral, i.e., the Franck–Condon factor, and $R_e^2$ is the square of the electronic transition moment. Equations (3) and (4) may be

regarded as the quantum description of the Franck–Condon principle. Actually, the first statement of the principle was classical, involving the concept that the positions and velocities of the nuclei were essentially unchanged during the transition (4, 5). Only later was a quantum formulation stated (6). Because of the oscillatory nature of the vibrational wavefunctions, $q_{v'v''}$ varies over many orders of magnitude and the weak dependence of the electronic transition moment on internuclear distance is often obscured. However, with increasingly accurate intensity measurements, improvements on the Condon approximation become necessary.

Fraser (7) introduced the $r$-centroid approximation which states that

$$p_{v'v''} = R_e^2(\bar{r}_{v'v''})|\langle v'|v''\rangle|^2$$

$$\equiv R_e^2(\bar{r}_{v'v''})q_{v'v''} , \tag{5}$$

where

$$\bar{r}_{v'v''} = \frac{\langle v'|r|v''\rangle}{\langle v'|v''\rangle} \tag{6}$$

is called the $r$ centroid. Hereafter, we sometimes omit the subscripts $v'v''$ when no confusion results. The reasoning behind Eq. (5) is as follows. Suppose $R_e(r)$ can be represented by a limited power series in $r$

$$R_e(r) = R_e(1 + a_1r + a_2r^2 + a_3r^3 + \cdots). \tag{7}$$

If only the first term in Eq. (7) is retained, then Eq. (5) becomes identical to Eq. (3), i.e., the Condon approximation results. If the first two terms in Eq. (7) are kept, then Eq. (5) is exact. If higher terms are retained, then it is necessary that

$$\bar{r}^n = \overline{r^n}$$

$$\equiv \frac{\langle v'|r^n|v''\rangle}{\langle v'|v''\rangle} \tag{8}$$

holds for Eq. (5) to be satisfied. Thus the $r$-centroid approximation consists in replacing an arbitrary function $f(r)$ by

$$f(\bar{r}) = \frac{\langle v'|f(r)|v''\rangle}{\langle v'|v''\rangle} . \tag{9}$$

The method for determining the variation of the electronic transition moment with internuclear distance has the following steps: (1) band strengths $p_{v'v''}$ are determined experimentally for different $(v', v'')$ bands; (2) the corresponding Franck–Condon factors $q_{v'v''}$ and $r$-centroids $\bar{r}_{v'v''}$ are calculated numerically from a knowledge of the upper- and lower-state potential curves; and (3) the transition moment variation is found by calculating

$$R_e(\bar{r}_{v'v''}) = \left[\frac{p_{v'v''}}{q_{v'v''}}\right]^{1/2} \tag{10}$$

and interpolation is made between various $R_e(\bar{r})$ values as a function of $\bar{r}$.

The $r$-centroid approximation has been widely used (see, for example (8)) to determine the variation of the electronic transition moment $R_e(r)$, although the

"power series approach" is known to be superior (see Appendix). The validity of the r-centroid approximation has been a topic of much controversy ever since Fraser presented empirical criteria for its validity in his original paper (7). James (9) has criticized the approximation, based on its inability to find a unique value of $R_e(\bar{r})$ for some bands of the $N_2$ $B^3\Pi_g-A^3\Sigma_u^+$ system. He concluded that "the r-centroid approximation will be an unsatisfactory method of treating experimental data in many cases." Halevi (10) also criticized the approximation and introduced an alternative formula, which has limited practical use because it contains more parameters. Smith (11) employed semiclassical wavefunctions to analyze quantitatively the validity of the r-centroid approximation, but so many additional approximations are required that the results of his analysis are not straightforward. Despite these efforts, a survey of the literature shows that it has remained a puzzle why the r-centroid approximation works so well for some bands and so poorly for others.

The emphasis of this paper is not on the most reliable way of determining the variation of the electronic transition moment with internuclear distance (which is discussed in the Appendix) but instead on the nature of classical and quantum formulations of the Franck–Condon principle and their connection through the r-centroid approximation. From an examination of this problem, new criteria were found for judging the validity of the r-centroid approximation. Bands can be divided into two classes, those that are classically allowed and those that are forbidden. The r-centroid approximation fails to hold for some types of classically allowed bands as well as the classically forbidden bands. The former exceptions, however, can be satisfactorily treated by extending Fraser's method. We call this extension the "generalized r-centroid approximation" and we illustrate its use by applying it to the well-known $Na_2$ $A^1\Sigma_u^+-X^1\Sigma_g^+$ and LiH $A^1\Sigma^+-X^1\Sigma^+$ band systems.

## II. RELATION BETWEEN THE r CENTROID AND THE CLASSICAL TRANSITION POINT

The classical statement of the Franck–Condon principle is "the electron jump in a molecule takes place so rapidly in comparison to the vibrational motion that immediately afterwards the nuclei still have very nearly the same relative position and velocity before the jump" (p. 194 of Ref. (1)). It should be remembered that the conservation of the relative velocity is equivalent to the conservation of the kinetic energy of the nuclei. Schwartz (12) pointed out that this classical statement violates the uncertainty principle and therefore the Franck–Condon principle is only correctly described by its quantum expression. However, as was shown by Mulliken (13), a semiclassical treatment yields results comparable to the quantum results. Moreover, it is shown below that the classical description is correct in terms of the weighted average values of internuclear distance and kinetic energy of the nuclei.

The role of kinetic energy in the Franck–Condon principle was reexamined in 1971 by Mulliken (13), who considered the intensity structure (fluctuation bands) in bound–free transitions. His discussion is easily extended to bound–bound transitions. Here it is useful to introduce once again the Mulliken difference potential (13), which is defined as

$$U_M(r) = U''(r) + E_{v'} - U'(r), \tag{11}$$

where $U(r)$ is the potential energy function and $E_{v'}$ is the upper-state vibrational
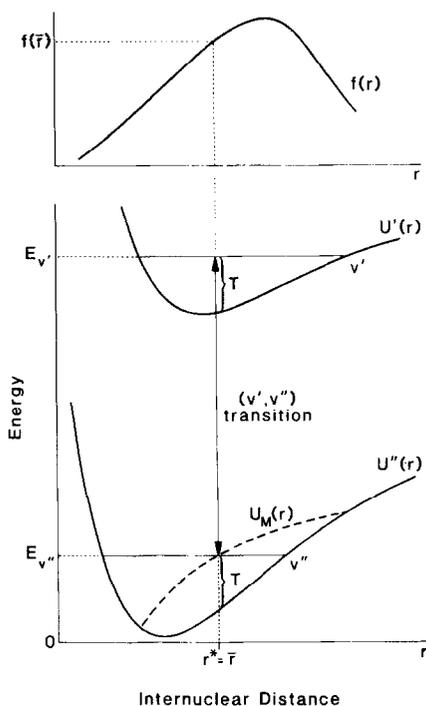
FIG. 1. Radial dependence of the upper- and lower-state potential energy functions showing the classical transition point, $r^*$, at which point the kinetic energy of the nuclei, $T$, is conserved during the $(v', v'')$ transition. Also indicated is the Mulliken difference potential $U_M(r) = U''(r) + E_{v'} - U'(r)$. When the *r*-centroid approximation is valid, $\bar{r} = r^*$ and the dependence of an arbitrary function $f(r)$ on internuclear distance is represented by $f(\bar{r})$.

energy (see Fig. 1). We define the point $r^*$ by the condition that the Mulliken difference potential equals the lower-state vibrational energy, i.e.,

$$E_{v''} = U_M(r^*)$$

$$= U''(r^*) + E_{v'} - U'(r^*). \tag{12}$$

From Eq. (12) it follows that

$$E_{v''} - U''(r^*) = E_{v'} - U'(r^*). \tag{13}$$

Equation (13) shows that the kinetic energy, $E_v - U(r)$, is the same for the upper and lower states at $r = r^*$ (see Fig. 1). Consequently, if the transition is considered classically, it occurs *only* at $r = r^*$. Hence we call $r^*$ the "classical transition point," which is seen to be the point where the vertical transition occurs. Figure 1 also shows that $r^*$ is the point where the Mulliken difference potential $U_M(r)$ crosses $E_{v''}$.

Because the $r$ centroid, $\bar{r}$, is calculated as the weighted average value of internuclear distance during the transition, this suggests that we associate $\bar{r}$ with the classical transition point $r^*$. To do this, let us consider the matrix element of the vibrational difference Hamiltonian $H' - H''$ for the upper and lower states:

$$\langle v'|H' - H''|v''\rangle = (E_{v'} - E_{v''})\langle v'|v''\rangle. \tag{14}$$

Because $H = T + U(r)$, Eq. (14) may be rewritten as

$$\langle v'|H' - H''|v''\rangle = \langle v'|T' + U'(r) - T'' - U''(r)|v''\rangle$$

$$= \langle v'|U'(r) - U''(r)|v''\rangle \tag{15}$$

where we use the fact that $T' = T''$ since the kinetic energy operator is the same for both states. By making the $r$-centroid approximation [see Eq. (9)], we have

$$\langle v'|U'(r) - U''(r)|v''\rangle = [U'(\bar{r}) - U''(\bar{r})]\langle v'|v''\rangle. \tag{16}$$

From Eqs. (14)–(16), we obtain

$$E_{v'} - E_{v''} = U'(\bar{r}) - U''(\bar{r}), \tag{17}$$

which is recognized as being equivalent to Eq. (13) if

$$r^* = \bar{r}. \tag{18}$$

Therefore, the classical transition point $r^*$ equals the $r$ centroid $\bar{r}$ when the $r$-centroid approximation is valid. Equation (18) was tested numerically for transitions between Morse potentials by Nicholls (14) but a general algebraic proof appears not to have been given previously.

In a similar manner, the "kinetic-energy-centroid" $\bar{T}_{v'v''}$ can be evaluated:

$$\bar{T}_{v'v''} \equiv \langle v'|T|v''\rangle/\langle v'|v''\rangle$$

$$= \langle v'|H' - U'(r)|v''\rangle/\langle v'|v''\rangle$$

$$= E_{v'} - \langle v'|U'(r)|v''\rangle/\langle v'|v''\rangle$$

$$= E_{v'} - U'(\bar{r})$$

$$= E_{v''} - U''(\bar{r}). \tag{19}$$

Hence in the classical limit where $\bar{r}$ may be equated to $r^*$, the quantity $E_{v'} - U'(r^*)$ $= E_{v''} - U''(r^*)$ is equal to the kinetic energy to be conserved during the transition. Thus the classical description of the Franck–Condon principle can be connected with the quantum mechanical formulation through use of the $r$-centroid approximation.

The $r$ centroid for the $(v', v'')$ band may be written as

$$\bar{r} = \int_0^\infty r w(r) dr, \tag{20}$$

where the weighting function

$$w(r) dr = \frac{\psi_{v'}(r)\psi_{v''}(r) dr}{\int_0^\infty \psi_{v'}(r)\psi_{v''}(r) dr} \tag{21}$$

gives the normalized probability of the $(v', v'')$ transition occurring between $r$ and

$r + dr$. The spread in the $r$ centroid is conveniently described in terms of the variance

$$(\Delta \bar{r})^2 = \overline{r^2} - \bar{r}^2$$

$$= \int_0^\infty r^2 w(r)dr - \left[ \int_0^\infty rw(r)dr \right]^2. \tag{22}$$

If the *r*-centroid approximation, Eq. (8), is exact, then $\Delta \bar{r}$ is equal to zero and the transition takes place only at $\bar{r} = r^*$. Thus the variance $(\Delta r)^2$ becomes smaller as the transition approaches the classical limit for which quantum effects may be neglected and the uncertainty becomes zero. Hence the more classical the transition, the more accurate is the *r*-centroid approximation. Conversely, the application of the *r*-centroid approximation is restricted only to the classically allowed transitions.

As a result, we understand the general rules often stated for the validity of the *r*-centroid approximation: the approximation works better (i) for heavier molecules (more classical molecules), (ii) for transitions between higher vibrational levels (larger kinetic energy), and (iii) for transitions in which quantum effects are smaller. The breakdown of the *r*-centroid approximation often observed for hydrides can be understood by rule (i). When the Franck–Condon factor is very small for a transition that is nevertheless classically allowed, the *r*-centroid approximation may not hold well according to rule (iii), because the very small Franck–Condon factor is a result of a large quantum effect (destructive internal diffraction).

Figure 1 also shows schematically the physical meaning of the *r*-centroid approximation. The $(v', v'')$ transition will occur at $r = r^*$, which is equal to $\bar{r}$, when the *r*-centroid approximation is valid. Consequently, any functional dependence of $f(r)$ is replaced by its value at $r = r^* = \bar{r}$, which is the substance of Eq. (9). As shown in Fig. 1, $r^*$ may not be always located at a classical turning point, i.e., vertical transitions do not occur exclusively from the classical turning points (*13*) (which is often incorrectly stated as the classical Franck–Condon principle).

### III. GENERALIZED *r*-CENTROID APPROXIMATION

When the Mulliken difference potential crosses the vibrational energy level twice (Fig. 2), there exist two classical transition points, $r_<^*$ and $r_>^*$. Because the $r$ centroid is single-valued, it cannot represent $r^*$ in this case, and the *r*-centroid approximation fails. Since the classical transition points still retain their physical meaning as the internuclear distance where the vertical transition occurs, it is possible to introduce "generalized $r$ centroids," $\bar{r}_<$ and $\bar{r}_>$ as

$$\bar{r}_< = \frac{\displaystyle\int_0^a \psi_{v'}(r) r \psi_{v''}(r) dr}{\displaystyle\int_0^a \psi_{v'}(r) \psi_{v''}(r) dr}$$

and

$$\bar{r}_> = \frac{\displaystyle\int_a^\infty \psi_{v'}(r) r \psi_{v''}(r) dr}{\displaystyle\int_a^\infty \psi_{v'}(r) \psi_{v''}(r) dr} \tag{23}$$
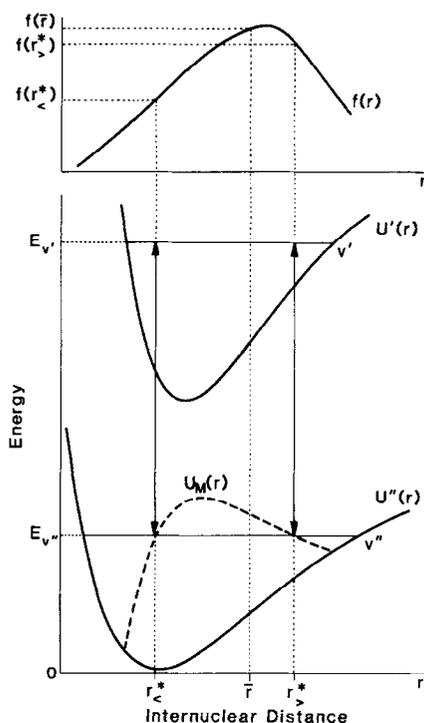
FIG. 2. Radial dependence of the upper- and lower-state potential energy functions and the Mulliken difference potential, showing a $(v', v'')$ transition having two classical transition points, $r^*_<$ and $r^*_>$. Here $\bar{r}$ does not represent the location of the classical transition and the $r$-centroid approximation fails.

so that each can be related to the corresponding transition point. The constant $a$ in the integrals is chosen between the transition points so that each integral can be carried out about the corresponding classical transition point. Choice of the constant $a$ normally will not affect the results seriously, since the transition probability density $\psi_{v'}(r)\psi_{v''}(r)dr$ is only sizable around $r = r^*$. An exception may occur when $r^*_<$ and $r^*_>$ approach one another.

In analogy to Eq. (9), the generalized $r$-centroid approximation is given by

$$f(\bar{r}_<) = \frac{\displaystyle\int_0^a \psi_{v'}(r)f(r)\psi_{v''}(r)dr}{\displaystyle\int_0^a \psi_{v'}(r)\psi_{v''}(r)dr}$$

and

$$f(\bar{r}_>) = \frac{\displaystyle\int_a^\infty \psi_{v'}(r)f(r)\psi_{v''}(r)dr}{\displaystyle\int_a^\infty \psi_{v'}(r)\psi_{v''}(r)dr} . \qquad (24)$$

When there exist $n$ transition points, Eqs. (23) and (24) should be modified in the appropriate obvious manner:

$$\bar{r}_k = \frac{\int_{a_{k-1}}^{a_k} \psi_{v'}(r) r \psi_{v''}(r) dr}{\int_{a_{k-1}}^{a_k} \psi_{v'}(r) \psi_{v''}(r) dr} \tag{25}$$

and

$$f(\bar{r}_k) = \frac{\int_{a_{k-1}}^{a_k} \psi_{v'}(r) f(r) \psi_{v''}(r) dr}{\int_{a_{k-1}}^{a_k} \psi_{v'}(r) \psi_{v''}(r) dr}, \tag{26}$$

where $a_{k-1} < r_k^* < a_k$, $a_0 = 0$, $a_n = \infty$, and $r_k^*$ is the $k$th classical transition point.

Actually, the use of the generalized *r*-centroid approximation is not totally straight-forward because it is not possible to determine several $R_e(\bar{r}_k)$ values from one $(v', v'')$ band strength measurement. Let us restrict ourselves to the case of only two classical transition points. From Eq. (1) we may write the identity

$$\int_a^\infty \psi_{v'}(r) R_e(r) \psi_{v''}(r) dr = p_{v'v''}^{1/2} - \int_0^a \psi_{v'}(r) R_e(r) \psi_{v''}(r) dr. \tag{27}$$

Thus, provided we know $R_e(\bar{r}_<)$ or $R_e(\bar{r}_>)$ from additional $(v', v'')$ band strength data, then we may find the other. Specifically,

$$R_e(\bar{r}_>) = \frac{p_{v'v''}^{1/2} - R_e(\bar{r}_<) \int_0^a \psi_{v'}(r) \psi_{v''}(r) dr}{\int_a^\infty \psi_{v'}(r) \psi_{v''}(r) dr} \tag{28a}$$

or

$$R_e(\bar{r}_<) = \frac{p_{v'v''}^{1/2} - R_e(\bar{r}_>) \int_a^\infty \psi_{v'}(r) \psi_{v''}(r) dr}{\int_0^a \psi_{v'}(r) \psi_{v''}(r) dr}. \tag{28b}$$

Hence the generalized *r*-centroid approximation relies on having band strengths for a sufficient number of different bands that either $R_e(\bar{r}_<)$ or $R_e(\bar{r}_>)$ can be determined from the *r*-centroid approximation. It is only for bands with multiple classical transition points that the generalized *r*-centroid approximation needs to be applied. We stress that the validity of Eq. (28) assumes that the two vertical transitions at $r_<^*$ and $r_>^*$ occur independently; however, when $r_<^*$ and $r_>^*$ draw close together quantum interference effects are expected to make Eq. (28) a poorer approximation. Nevertheless, because the overlap of the vibrational wavefunction tend to be peaked about $r_<^*$ and $r_>^*$, and $r_<^*$ and $r_>^*$ are usually well separated, it is anticipated that Eq. (28) will have general validity.

In the foregoing, we have concentrated our attention on bound–bound transitions, but the same considerations also apply to transitions in which one or both states are free.
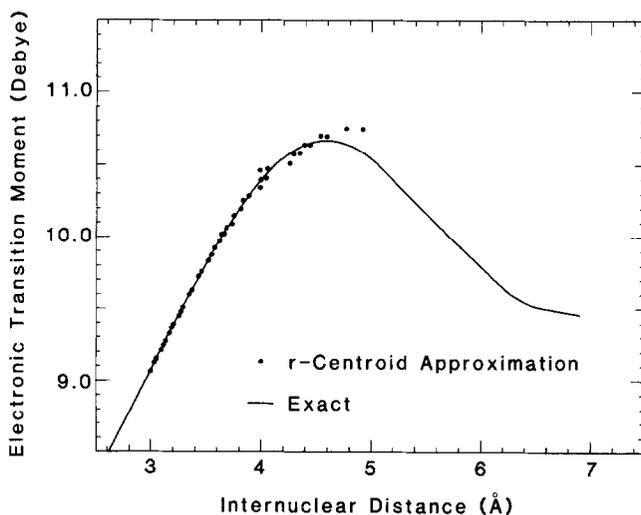
FIG. 3. Comparison of exact and calculated values of $R_e(r)$ versus $r$ for the Na$_2$ $A^1\Sigma_u^+$-$X^1\Sigma_g^+$ band system. The $r$-centroid approximation faithfully reproduces the *ab initio* values for the transitions connecting $v' = 10$ and $12$ to $v'' = 0$-$30$ with Franck–Condon factors greater than 0.01. Each $(v', v'')$ band has one classical transition point.

## IV. TEST OF THE GENERALIZED $r$-CENTROID APPROXIMATION

A convenient test of the generalized $r$-centroid approximation was accomplished by calculating the electronic transition moment $R_e(r)$ from synthesized band strength data for the Na$_2$ $A^1\Sigma_u^+$-$X^1\Sigma_g^+$ and LiH $A^1\Sigma^+$-$X^1\Sigma^+$ band systems. In both cases RKR potential curves were calculated (3) from molecular constants, using the data of Kusch and Hessel (15) for the Na$_2$ $X^1\Sigma_g^+$ state, Kaminsky (16) for the Na$_2$ $A^1\Sigma_u^+$ state, Orth and Stwalley (17) for the LiH $X^1\Sigma^+$ state, and Li and Stwalley (18) for the LiH $A^1\Sigma^+$ state. Bound (3) and continuum (19) vibrational wavefunctions were calculated numerically by solving the appropriate radial Schrödinger equation. Then vibrational band strengths $p_{v'v''}$ were found from Eq. (1), where we took for the electronic transition moment $R_e(r)$ the *ab initio* values given by Stevens *et al.* (20) for the Na$_2$ $A$-$X$ system and by Docken and Hinze (21) for the LiH $A$-$X$ system. These $p_{v'v''}$ values were treated as "idealized" experimental data having no scatter.

### 1. Na$_2$ A–X System

Figure 3 shows the results of the $r$-centroid approximation for the electronic transition moment of the Na$_2$ $A$-$X$ system determined from transitions connecting $v' = 10$ and $v' = 12$ to $v'' = 0$-$30$. For each of these bands there exists one classical transition point. Only bands with Franck–Condon factors greater than 0.01 were used. For such bands, the $r$-centroid approximation works fairly well. In Fig. 4, wavefunctions for $v' = 12$ and $v'' = 20$, their product $\psi_{v'}(r)\psi_{v''}(r)$, and the smoothed product $S(r)$ are shown. The smoothed product $S(r)$ is calculated by
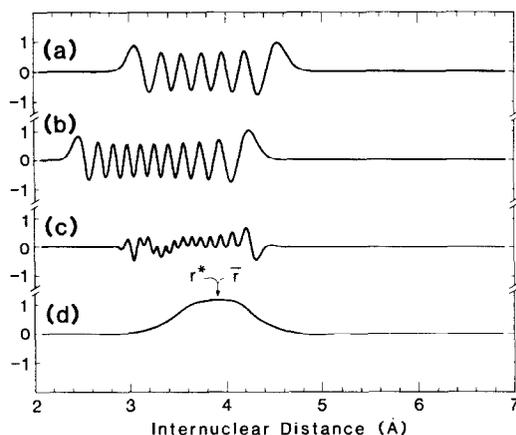
FIG. 4. Vibrational wavefunctions and their overlap for a $(v', v'')$ band having one classical transition point: (a) $\psi_{v'=12}$ of the Na$_2$ $A^1\Sigma_u^+$ state; (b) $\psi_{v''=20}$ of the Na$_2$ $X^1\Sigma_g^+$ state; (c) the product of the wavefunctions in (a) and (b); and (d) the smoothed product (see text). The locations of the $r$ centroid, $\bar{r}$, and the classical transition point, $r^*$, coincide to three significant figures, as shown. The ordinate scales are arbitrary but are chosen to be the same as in Figs. 8 and 9. The value of $q_{12,20}$ is 0.0481.

$$S(r_0) = \int_{r_0-a}^{r_0+a} \psi_{v'}(r)\psi_{v''}(r)t(r - r_0)dr, \qquad (29)$$

where

$$t(x) = x/a + 1 \qquad (x \le 0)$$

$$= -x/a + 1 \qquad (x > 0). \qquad (30)$$
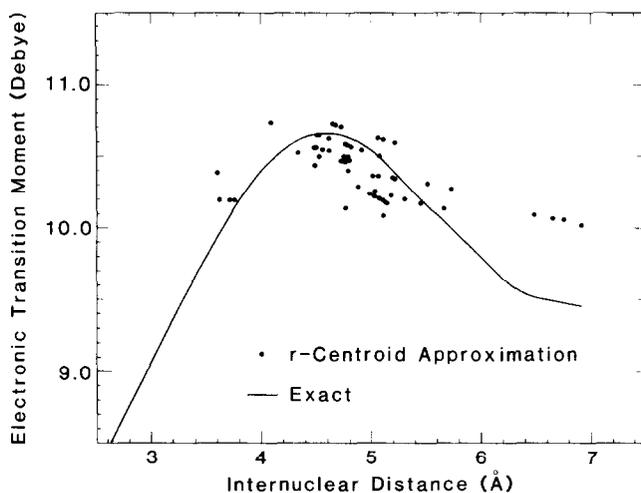


FIG. 5. Plot of $R_e(r)$ versus $r$ for the Na$_2$ $A^1\Sigma_u^+$–$X^1\Sigma_g^+$ band system comparing the values of $R_e(\bar{r})$ calculated using the $r$-centroid approximation to the exact values of $R_e(r)$. Shown are the transitions connecting $v' = 30$–35 and $v'' = 38$–53 with Franck–Condon factors greater than 0.01. Each $(v', v'')$ band has two classical transition points.
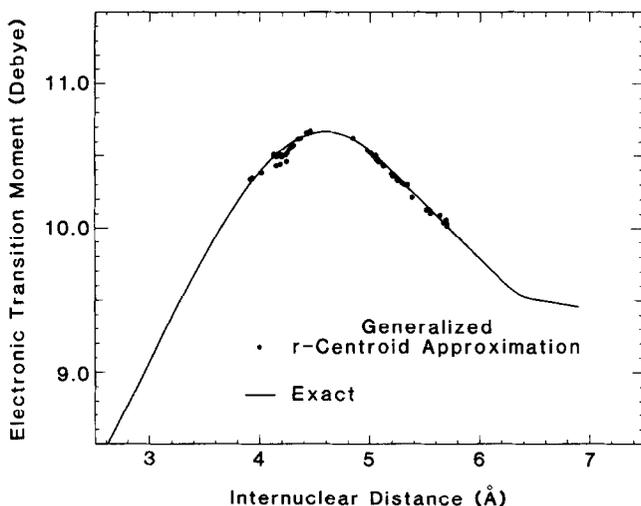
FIG. 6. Comparison of exact and calculated values of $R_e(r)$ versus $r$ using Eq. (24) for the same bands shown in Fig. 5.

Here $t(x)$ is a triangle-shaped weighting function and $a = 1.5$ Å. As clearly shown by the smoothed product, the overlap of $\psi_{v'}(r)$ and $\psi_{v''}(r)$ shows constructive interference around $r = r^*$, but destructive interference otherwise. Hence, the contribution of $\psi_{v'}(r)\psi_{v''}(r)$ to the vibrational overlap integral is largest at $r = r^*$, where the $r$ centroid $\bar{r}$ is located.

For the transitions connecting $v' = 30$–$35$ to $v'' = 38$–$53$, there exist two classical transition points for each band. For such transitions, the $r$-centroid approximation does not hold, as shown in Fig. 5. Again only bands with Franck–Condon factors greater than 0.01 were used. Next $R_e(\bar{r}_<)$ and $R_e(\bar{r}_>)$ were individually calculated by carrying out the integrations indicated in Eq. (24). Here data with the square of the partial overlap integral [denominators in Eq. (24)] less than 0.01 were discarded. In sharp contrast to Fig. 5, the results yield fairly good agreement with $R_e(r)$, as shown in Fig. 6. Of course, this procedure [the individual calculation of $R_e(\bar{r}_<)$ and $R_e(\bar{r}_>)$] is not practical in general and requires the prior knowledge of $R_e(r)$. However, Fig. 6 does show the validity of the generalized $r$-centroid method.

In Fig. 7, plots of $R_e(\bar{r}_>)$ evaluated from Eq. (28a) are shown for three different choices of the integration limit, $a = 4.50$ Å, $a = 4.68$ Å, where $dU_M(r)/dr = 0$, and $a = 4.80$ Å. These three results are almost identical from which it is clear that the choice of the integration limit does not affect the validity of the method. Figure 7 simulates the analysis of actual experimental intensity data using the generalized $r$-centroid method.

We present in Fig. 8 the wavefunctions for $v' = 34$ and $v'' = 46$ their product, and the smoothed product. Corresponding to the two classical transition points, $r_<^*$ and $r_>^*$, the smoothed product has two maxima at which the largest contributions to the vibrational overlap integral arise. It should be noted that the generalized $r$ centroids, $\bar{r}_<$ and $\bar{r}_>$, well represent the two maxima, while the $r$ centroid, $\bar{r}$, does not. A closer examination shows that $\bar{r}_<$ and $\bar{r}_>$ differ slightly from $r_<^*$ and $r_>^*$. Most
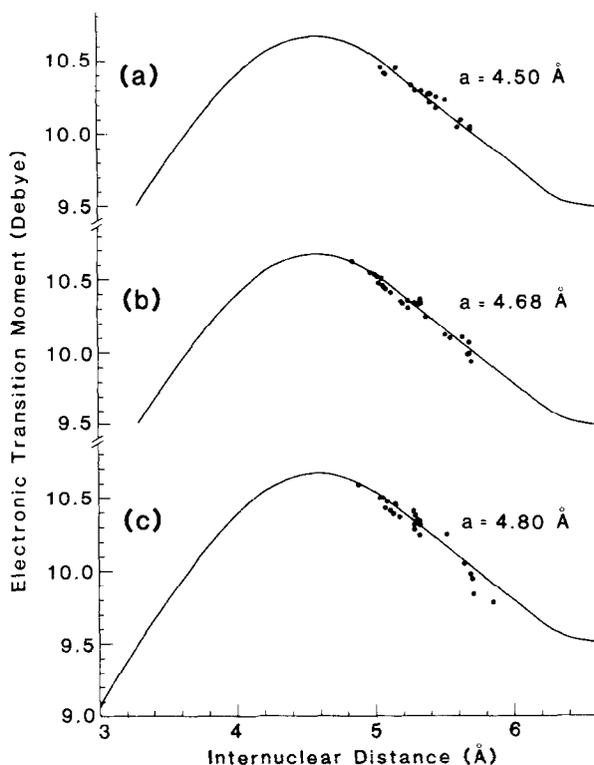
FIG. 7. Comparison of exact and calculated values of $R_e(r)$ versus $r$ using the generalized $r$-centroid approximation [Eq. (28a)] with different choices of the integration limit, $a$, for the same bands shown in Fig. 5.
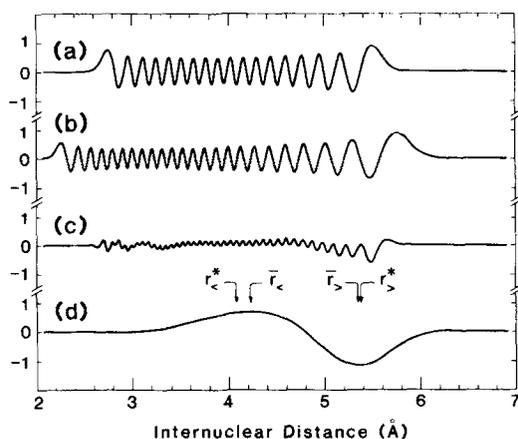


FIG. 8. Vibrational wavefunctions and their overlap for a $(v', v'')$ band having two classical transition points: (a) $\psi_{v'=34}$ of the $Na_2 A^1\Sigma_u^+$ state; (b) $\psi_{v''=46}$ of the $Na_2 X^1\Sigma_g^+$ state; (c) the product of the wavefunctions in (a) and (b); and (d) the smoothed product (see text). The locations of $r_<^*$, $r_>^*$, $\bar{r}_<$, and $\bar{r}_>$ are indicated (the location of $\bar{r} = 9.86$ Å is off scale). The ordinate scales are arbitrary but are chosen to be the same as in Figs. 4 and 9. The value of $q_{34,46}$ is 0.00149 while the overlap integrals from 0 to $a = 4.68$ Å and from $a$ to $\infty$ are 0.158 and $-0.196$, respectively.
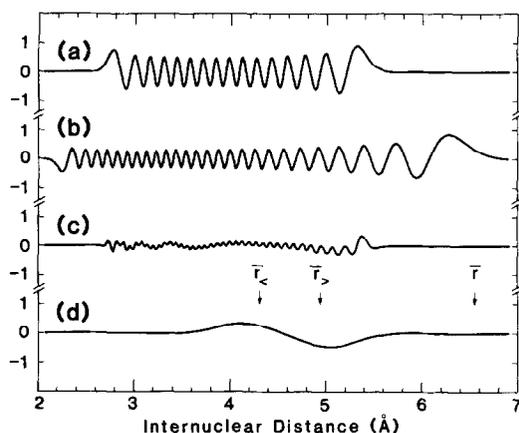
FIG. 9. Vibrational wavefunctions and overlap integrals for a forbidden $(v', v'')$ band having no classical transition point: (a) $\psi_{v'=30}$ of the $Na_2$ $A^1\Sigma_u^+$ state; (b) $\psi_{v''=51}$ of the $Na_2$ $X^1\Sigma_g^+$ state; (c) the product of the wavefunctions in (a) and (b); and (d) the smoothed product (see text). The locations of $\bar{r}_<$, $\bar{r}_>$, and $\bar{r}$ are indicated. The ordinate scales are arbitrary but are chosen to be the same as in Figs. 4 and 8. The value of $q_{30,51}$ is 0.000590 while the overlap integrals from 0 to $a$ = 4.68 Å and from $a$ to $\infty$ are 0.0599 and −0.0842, respectively.

of this discrepancy can be attributed to the quantum interference caused by contribution from both classical transition points. For comparison, a similar figure for the transition with no classical transition point, i.e., a classically forbidden transition, is shown in Fig. 9. Overlap of wavefunctions is always destructive and, as a result, the smoothed product is uniformly small and the Franck–Condon factor is small. As expected, the $r$-centroid approximation poorly describes the average value of $r$ during such a transition. It is for this reason that the $r$-centroid approximation cannot be applied with success to the analysis of the variation of the electronic transition moment with internuclear distance for classically forbidden bands.

## 2. LiH A–X System

Similar calculations have been carried out for the LiH $A^1\Sigma^+$–$X^1\Sigma^+$ system but in this case bound–free as well as bound–bound transitions are analyzed. Note that LiH is an extremely light molecule so that quantum effects are accentuated here. Figure 10 shows the $X$ and $A$ state RKR potential curves along with the Mulliken difference potentials for transitions involving several selected upper-state vibrational levels. Figure 11 shows the results of the $r$ centroid approximation for $R_e(r)$. The closed circles refer to transitions that connect $v'$ = 3–5 and $v''$ = 0–18 for which there is one classical transition point. Good agreement is seen with the $ab$ $initio$ values of $R_e(r)$. The open circles refer to transitions that connect $v'$ = 15 to the continuum levels of the $X$ state between 20 700 and 22 700 $cm^{-1}$ (which is the highest energy for which a transition is classically allowed). These continuum transitions have two classical transition points (see Fig. 10) and the $r$-centroid approximation fails to track $R_e(r)$. Figure 11 is similar to Fig. 1 of Docken (22), who concluded that "deviations from the theoretical calculated curve start to appear in the region of the maximum where $R_e(r)$ is nonlinear." As will be seen below, these
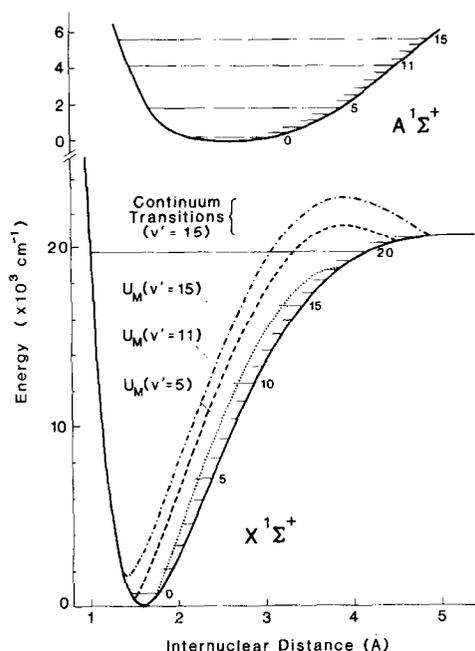
FIG. 10. RKR potential curves of the LiH $X^1\Sigma^+$ and $A^1\Sigma^+$ states. Also shown are selected vibrational energy levels and the Mulliken difference potentials for the transitions involving $v' = 5$, 11, and 15. Bound-free transitions connecting the $v' = 15$ level of the upper-state and the continuum levels between $E'' = 20\ 700$ and $22\ 700\ \mathrm{cm}^{-1}$ of the ground state are classically allowed.
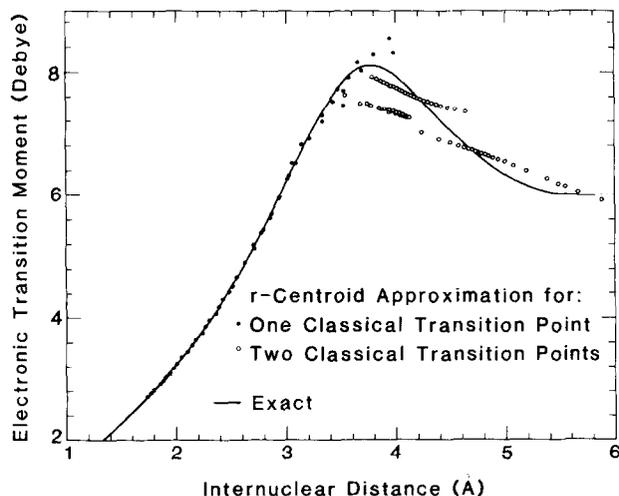


FIG. 11. Comparison of exact and calculated values of $R_e(r)$ versus $r$ for the LiH $A^1\Sigma^+-X^1\Sigma^+$ band system using the *r*-centroid approximation. The closed circles show the results obtained from the transitions connecting $v' = 3$–5 and $v'' = 0$–18, each of which has one classical transition point. The open circles show the results obtained from the continuum transitions connecting $v' = 15$ and $E'' = 20\ 700$– $22\ 700\ \mathrm{cm}^{-1}$, each of which has two classical transition points. Discrete transitions with Franck–Condon factors less than 0.01 are omitted.
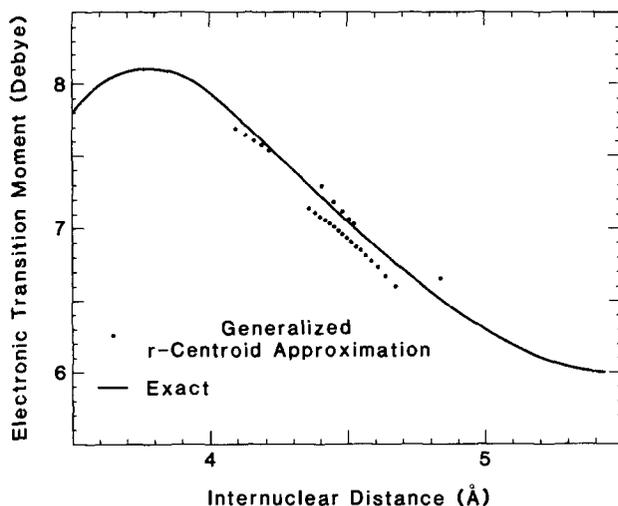
FIG. 12. Comparison of exact and calculated values of $R_e(r)$ versus $r$ using the generalized $r$-centroid approximation for the same continuum transitions as in Fig. 11.

deviations can be understood as resulting from the existence of two classical transition points rather than the shape of the electronic transition moment.

As seen in Fig. 11 some values of $R_e(\bar{r})$ obtained from the continuum transitions are virtually coincident with the exact values. An examination of the partial overlap integrals for each continuum transition shows that this agreement is obtained only when either of the partial overlap integrals is very small. Moreover, the deviation is the largest when the partial overlap integrals are of the same order of magnitude.
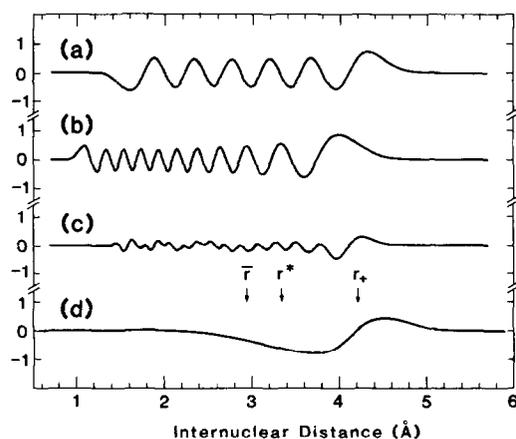


FIG. 13. Vibrational wavefunctions and their overlap for the (11, 20) band of the LiH $A$–$X$ system: (a) $\psi_{v'=11}$ of the $A^1\Sigma^+$ state; (b) $\psi_{v''=20}$ of the $X^1\Sigma^+$ state; (c) the product of the wavefunctions in (a) and (b); and (d) the smoothed product (see text). The locations of the $r$ centroid, $\bar{r}$, the classical transition point, $r^*$, and the outer turning point of the $v'' = 20$ level, $r_+$, are indicated. The ordinate scales are arbitrarily chosen.

Again this analysis supports the conclusion that the *r*-centroid approximation fails when two or more classical transitions contribute.

The results of the generalized *r*-centroid approximation for the electronic transition moment are pictured in Fig. 12. Here the same continuum transitions as shown in Fig. 11 were used in conjunction with Eq. (28a). The integration limit was chosen to be $a = 3.91$ Å, where the Mulliken difference potential for $v' = 15$ has a maximum. The agreement is satisfactory suggesting that the generalized *r*-centroid approximation may be applied to both bound–bound and bound–free vibrational transitions.

The above agreement is all the more remarkable because the LiH molecule is expected to show large quantum effects. Indeed, we wish to point out an exceptional situation. Consider the transition between $v' = 11$ and $v'' = 20$ (see Fig. 10) for which only one classical transition point exists. However, since the vibrational wavefunction for $v'' = 20$ has a very large amplitude at its outer classical turning point, $r_+$, some contribution to the vibrational overlap integral arises in the vicinity of $r_+$ (see Fig. 13) even though the kinetic energy of the transition is not conserved. As a consequence, the *r*-centroid approximation fails. However, if the generalized *r*-centroid approximation is used in which the integration was carried out about both $r^*$ and $r_+$, then agreement is found once more.

Finally, we remark in closing that the generalized *r*-centroid approximation has not been introduced so much as a method for determining $R_e(r)$ but as a means of understanding the meaning of the Franck–Condon principle.

## APPENDIX

It has been recommended by Zare (footnote 38 of Ref. (*3*)), James (*9*), and Klemsdal (*23*) to expand the electronic transition moment $R_e(r)$ in a power series, e.g., Eq. (7), and to determine the coefficients from accurate intensity measurements by a least-squares fit in which the various $\overline{r^n}$ are evaluated numerically. This power series approach has several advantages over the *r*-centroid approximation: (i) it is always exact within the accuracy of the expansion; (ii) it is almost as straightforward as the *r*-centroid approximation; (iii) the error involved can be estimated more easily than that of the *r*-centroid approximation, and (iv) all the intensity data can be used while the *r*-centroid approximation is restricted to classically allowed bands. Therefore the power series approach rather than the *r*-centroid approximation is preferred for accurate work. Recently, Coxon and Foster (*24*) elegantly applied the power series approach to the determination of the spin–orbit operator in the $X^2\Pi$ state of OH.

## REFERENCES

*1.* G. HERZBERG, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," Van Nostrand-Reinhold, New York, 1950.
*2.* J. B. TATUM, *Astrophys. J. Suppl. Ser.* **16**, 21–56 (1967).
*3.* R. N. ZARE, *J. Chem. Phys.* **40**, 1934–1944 (1964).
*4.* J. FRANCK, *Trans. Faraday Soc.* **21**, 536–542 (1925).
*5.* E. U. CONDON, *Phys. Rev.* **28**, 1182–1201 (1926).
*6.* E. U. CONDON, *Phys. Rev.* **32**, 858–872 (1928); *Amer. J. Phys.* **15**, 365–374 (1947).
*7.* P. A. FRASER, *Canad. J. Phys.* **32**, 515–521 (1954).
*8.* G. ENNEN, B. FIELDER, AND CH. OTTINGER, *J. Chem. Phys.* **75**, 59–67 (1981).
*9.* T. C. JAMES, *J. Mol. Spectrosc.* **20**, 77–87 (1966).
*10.* P. HALEVI, *Proc. Phys. Soc.* **86**, 1051–1054 (1965).
*11.* A. L. SMITH, *J. Mol. Spectrosc.* **28**, 269–271 (1968).
*12.* S. E. SCHWARTZ, *J. Chem. Ed.* **50**, 608–610 (1973).
*13.* R. S. MULLIKEN, *J. Chem. Phys.* **55**, 309–314 (1971).
*14.* R. W. NICHOLLS, *Proc. Phys. Soc.* **89**, 181–183 (1966).
*15.* P. KUSCH AND M. M. HESSEL, *J. Chem. Phys.* **68**, 2591–2606 (1978).
*16.* M. E. KAMINSKY, *J. Chem. Phys.* **66**, 4951–4953 (1977).
*17.* F. B. ORTH AND W. C. STWALLEY, *J. Mol. Spectrosc.* **76**, 17–38 (1979).
*18.* K. C. LI AND W. C. STWALLEY, *J. Mol. Spectrosc.* **69**, 294–318 (1978).
*19.* H. KATÔ AND C. NODA, *J. Chem. Phys.* **73**, 4940–4945 (1980).
*20.* W. J. STEVENS, M. M. HESSEL, P. J. BERTONCINI, AND A. C. WAHL, *J. Chem. Phys.* **66**, 1477–1482 (1977).
*21.* K. K. DOCKEN AND J. HINZE, *J. Chem. Phys.* **57**, 4928–4936, 4936–4952 (1972).
*22.* K. K. DOCKEN, *Chem. Phys. Lett.* **30**, 334–336 (1975).
*23.* H. KLEMSDAL, *Phys. Norv.* **5**, 123–133 (1971).
*24.* J. A. COXON AND S. C. FOSTER, *J. Mol. Spectrosc.* **91**, 243–254 (1982).