

Moments of semiclassical and classical absorption and emission band shapes of impurities in solids

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General expressions for all moments are calculated for both semiclassical and classical approximations to absorption and emission band shapes due to impurities whose vibrational interactions with the surrounding lattice of a solid contain both linear and quadratic terms. The first five moments are presented and compared to the exact quantum-mechanical results. The semiclassical approximation is found to be most accurate for vibrational interactions having either linear or linear plus quadratic terms with strong coupling and/or high temperature. The semiclassical approximation is rarely, if ever, appropriate if only quadratic terms occur. The classical approximation is a valid representation of the semiclassical approximation at high temperatures. These conclusions are shown to be consistent with the correspondence principle.

I. INTRODUCTION

The method of moments is a useful tool for obtaining theoretical parameters from experimental optical-absorption and -emission band shapes originating from defects in solids. The method was originally developed by Lax,¹ and extended and applied by others.²⁻⁶ If an absorption band shape involves a single mode of vibration, then just five unknown parameters (see Sec. II) are needed to completely specify that band shape. These five unknowns could, in principle, be determined from the first five moments of the band shape; however, unambiguously determined moments of high order are often difficult to find from experimental data.^{7,8} The lowest three moments have been used in the interpretation of the band shapes of some impurities in solids.⁹⁻¹¹ Lax gave general expressions for the first five quantum-mechanical moments without introducing explicit expressions for the vibrational-interaction terms. A method for generating all quantum-mechanical moments is available,² but only the lowest five have been calculated.¹² To date there has been no derivation reported of all the moments for the general vibrational interaction.

We examine here the semiclassical approximation to the exact quantum-mechanical treatment. This approximation (developed by Williams¹³ and independently by Lax^{1,14}) considerably simplifies the mathematics. It treats the initial state of the electronic transition quantum mechanically and

the final state classically. We develop general expressions for semiclassical and classical (where both initial and final states are treated classically) absorption- and emission-band-shape moments. We then compare these moments to the exact quantum-mechanical results.

II. GENERAL FORMULATION

The absorption band shape I as a function of energy E for electric dipole transitions from the ground state (of energy $E_{a\alpha}$) to the excited state (of energy $E_{b\beta}$) of the defect is

$$I(E) = \sum_{\beta} \text{Av}_{\alpha} |\langle \Psi_{a\alpha} | A | \Psi_{b\beta} \rangle|^2 \delta(E - E_{b\beta} + E_{a\alpha}), \quad (1)$$

where the electronic-ground-state quantum number is a , and α is the vibrational-ground-state quantum number. Similarly, b and β refer to the excited-state quantum numbers. Also, Av_{α} designates a thermal average over the ground-state vibrational levels of the product of (i) the square of the matrix element of the electric dipole operator A and (ii) the δ function that locates the energy of the $a\alpha \rightarrow b\beta$ transitions (at this point, α and β are merely symbolic of the quantum numbers). The δ function may be rewritten in the form

$$\delta(E) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt e^{-iEt/\hbar},$$

so that Eq. (1) becomes

$$I(E) = (2\pi\hbar)^{-1} \text{Av}_{\alpha} \int_{-\infty}^{\infty} dt \sum_{\beta} \langle \Psi_{a\alpha} | A^* | \Psi_{b\beta} \rangle \langle \Psi_{b\beta} | A | \Psi_{a\alpha} \rangle \exp\{i[(E_{b\beta} - E_{a\alpha})/\hbar - \nu]t\}. \quad (2)$$

The energies $E_{b\beta}$ and $E_{a\alpha}$ can be replaced by the corresponding Hamiltonian operators if Eq. (2) is rewritten

$$I(E) = (2\pi\hbar)^{-1} \text{Av}_{\alpha} \int_{-\infty}^{\infty} dt \sum_{\beta} \langle \Psi_{a\alpha} | A^* | \Psi_{b\beta} \rangle \langle \Psi_{b\beta} | e^{iH_b t/\hbar} A e^{-iH_a t/\hbar} | \Psi_{a\alpha} \rangle e^{-i\nu t}. \quad (3)$$

Two approximations are commonly made at this point. The first (the adiabatic approximation) is that the total wave function Ψ may be written as the product of the electronic wave function ϕ and function χ (Ref. 15); the second (the Condon approximation) is that the electric dipole operator A is constant with respect to the nuclear coordinates. Then Eq. (3) becomes

$$I(E) = (2\pi\hbar)^{-1} f_{ab} A v_{\alpha} \int_{-\infty}^{\infty} dt \sum_{\beta} \langle \chi_{\alpha} | \chi_{\beta} \rangle \langle \chi_{\beta} | e^{i(H_b - H_a)t/\hbar} | \chi_{\alpha} \rangle e^{-iEt}, \quad (4)$$

where $f_{ab} = |\langle \phi_a | A | \phi_b \rangle|^2$. In the semiclassical approximation H_b is independent of β , and the closure relation $\sum_{\beta} |\chi_{\beta}\rangle \langle \chi_{\beta}| = 1$ can be used to obtain

$$I(E) = \int_{-\infty}^{\infty} dt (2\pi\hbar)^{-1} f_{ab} A v_{\alpha} e^{-iEt} \times \langle \chi_{\alpha} | e^{i(H_b - H_a)t/\hbar} | \chi_{\alpha} \rangle. \quad (5)$$

Equation (5) will be recognized as a Fourier transform, whose inverse is

$$f_{ab} A v_{\alpha} \langle \chi_{\alpha} | e^{i(H_b - H_a)t/\hbar} | \chi_{\alpha} \rangle = \hbar \int_{-\infty}^{\infty} d\nu I(E) e^{i\nu t} = \int_{-\infty}^{\infty} dE I(E) e^{iEt/\hbar}. \quad (6)$$

Taking the n th partial derivative with respect to it/\hbar and evaluating the result at $t=0$, the right-hand side of Eq. (6) becomes $\int dE I(E) E^n$, which is just the definition of the n th moment, M_n , of the absorption band shape. Thus, the semiclassical moments are

$$M_n = f_{ab} A v_{\alpha} \langle \chi_{\alpha} | (E_b - E_a)^n | \chi_{\alpha} \rangle. \quad (7)$$

Equation (7) may also be found by noting that the semiclassical band shape is the product of the probability of the electronic transition and the probability that the ground state is populated:

$$I(E) = f_{ab} A v_{\alpha} \chi_{\alpha}^2 \frac{dq}{dE}, \quad (8)$$

where dq/dE accounts for changing variables from q to E .¹⁶ The moments are

$$M_n = \int dE (E_b - E_a)^n I(E) = f_{ab} \int dq A v_{\alpha} \chi_{\alpha}^2 (E_b - E_a)^n. \quad (9)$$

III. EXPLICIT EXPRESSIONS FOR THE MOMENTS

To calculate the n th moment of the semiclassical band shape, we make the usual identification that the ground-state and excited-state potentials represent harmonic oscillators. Meyer⁴ originally considered the vibrational interaction between the impurity and the lattice to be linear in the normal coordinate that describes the interaction. This linear interaction requires that the ratio R (the

quadratic-interaction parameter) of the vibrational frequency of the excited state to that of the ground state be unity. The strength of the linear interaction is characterized by the Huang-Rhys factor $S = \omega q_0^2 / 2\hbar$ that measures the separation q_0 of the coordinates of the minima of the potential energy curves of the ground and excited states in the normal coordinate space. The vibrational frequency of the ground state is ω . At the normal coordinate value of $q=0$, the minimum of the electronic ground state, the curves are separated in energy by E_0 that is related to the purely electronic transition (refer to Fig. 1). The quadratic interaction¹⁷ occurs for $R \neq 1$ and $S=0$, and the more general interaction occurs for $R \neq 1$ and $S \neq 0$. In terms of the nuclear coordinate, and for the general vibrational interaction,

$$E_a = \frac{1}{2} \omega^2 q^2, \quad (10a)$$

$$E_{\alpha} = (\alpha + \frac{1}{2}) \hbar \omega, \quad (10b)$$

$$E_b = E_0 - SR\hbar\omega + [(\frac{1}{2}R^2\omega^2)^{1/2}q + (SR\hbar\omega)^{1/2}]^2, \quad (10c)$$

$$E_{\beta} = E_0 - SR\hbar\omega + R(\beta + \frac{1}{2})\hbar\omega, \quad (10d)$$

The ground-state wave function corresponding to E_a is¹⁷

$$\chi_{\alpha} = [(\omega/\pi\hbar)^{1/2} / 2^{\alpha} \alpha!]^{1/2} \times e^{-\omega q^2 / 2\hbar} H_{\alpha}((\omega/\hbar)^{1/2} q). \quad (11)$$

The thermal-averaging operator is

$$A v_{\alpha} [\xi] = 2 \sinh(\theta/2T) \sum_{\alpha=0}^{\infty} [\xi] e^{-(\alpha+1/2)\theta/T}, \quad (12)$$

where $\theta = \hbar\omega/k$. The zeroth moment is

$$M_0 = f_{ab} A v_{\alpha} \int \chi_{\alpha}^2 dq = f_{ab} \quad (13)$$

and the n th absorption moment takes the form

$$\frac{M_n}{M_0} = 2 \sinh\left(\frac{\theta}{2T}\right) \sum_{\alpha=0}^{\infty} \frac{(\omega/\pi\hbar)^{1/2}}{2^{\alpha} \alpha!} e^{-(\alpha+1/2)\theta/T} \times \int_{-\infty}^{\infty} dq e^{-\omega q^2 / \hbar} \left[H_{\alpha} \left(\left(\frac{\omega}{\hbar} \right)^{1/2} q \right) \right]^2 \times [(2SR^3\hbar\omega^3)^{1/2}q + \frac{1}{2}(R^2 - 1)\omega^2q^2]^n. \quad (14)$$

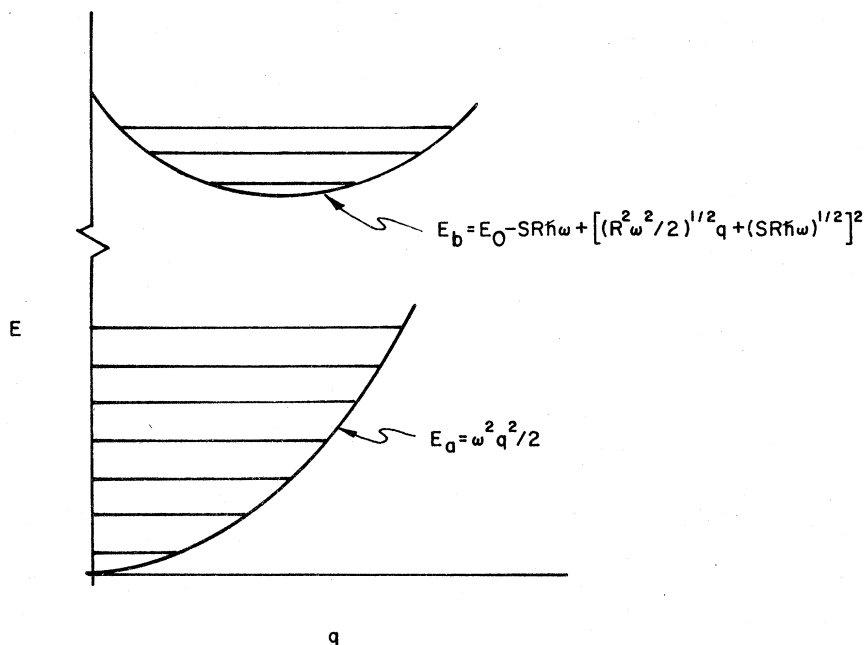


FIG. 1. Configuration-coordinate diagram representing the electronic ground and excited states and their associated vibrational levels: $E_a = (\alpha + \frac{1}{2})\hbar\omega$; $E_b = E_0 - SR\hbar\omega + R(\beta + \frac{1}{2})\hbar\omega$.

For mathematical convenience, we calculate the moments about E_0 . The Slater sum²

$$\sum_{j=0}^{\infty} \frac{e^{-(j+1/2)z}}{\sqrt{\pi} 2^j j!} H_j(x) H_j(y) \exp[-\frac{1}{2}(x^2 + y^2)] \\ = (2\pi \sinh z)^{-1/2} \exp\{-\frac{1}{4}[(x+y)^2 \tanh(\frac{1}{2}z) \\ + (x-y)^2 \coth(\frac{1}{2}z)]\} \quad (15)$$

is used to remove the Hermite polynomials in the integrand to give an integration that can be easily performed using the binomial expansion. The result is

$$\frac{M_n}{M_0(\hbar\omega)^n} = n! \sum_{i=0}^n \left(\frac{SR^3}{2}\right)^i \left(\frac{R^2-1}{8}\right)^{n-2i} \\ \times \frac{(2n-2i)! \coth^{n-i}(\theta/2T)}{(2i)!(n-2i)!(n-i)!} \quad (16)$$

The first five absorption moments are listed below. Unlike Eq. (14), Eq. (17b) shows M_1 taken about $E=0$. Higher moments are taken about M_1 , and are thus the central moments, m_n .

$$M_0 = |\langle \phi_a | A | \phi_b \rangle|^2, \quad (17a)$$

$$M_1/M_0(\hbar\omega) = E_0/\hbar\omega + \frac{1}{4}(R^2-1) \coth(\theta/2T), \quad (17b)$$

$$m_2/M_0(\hbar\omega)^2 = SR^3 \coth(\theta/2T) \\ + \frac{1}{8}(R^2-1)^2 \coth^2(\theta/2T), \quad (17c)$$

$$m_3/M_0(\hbar\omega)^3 = \frac{3}{2}(R^2-1)SR^3 \coth^2(\theta/2T) \\ + \frac{1}{8}(R^2-1)^3 \coth^3(\theta/2T), \quad (17d)$$

$$m_4/M_0(\hbar\omega)^4 = 3S^2R^6 \coth^2(\theta/2T) \\ + \frac{15}{4}(R^2-1)^2SR^3 \coth^3(\theta/2T) \\ + \frac{15}{64}(R^2-1)^4 \coth^4(\theta/2T). \quad (17e)$$

For emission, the relation corresponding to Eq. (7) is

$$M_{en} = f_{ba} \text{Av}_{\beta} \langle \chi_{\beta} | (E_b - E_a)^n | \chi_{\beta} \rangle, \quad (18)$$

where the vibrational wave functions for the excited state are¹⁸

$$\chi_{\beta} = [(R\omega/\pi\hbar)^{1/2}/2^{\beta}\beta!]^{1/2} \\ \times \exp\{-\frac{1}{2}[(R\omega/\hbar)^{1/2}q + (2S)^{1/2}]^2\} \\ \times H_{\beta}[(R\omega/\hbar)^{1/2}q + (2S)^{1/2}]. \quad (19)$$

The thermal-averaging operator is

$$\text{Av}_{\beta}[\xi] = 2 \sinh(R\theta/2T) \sum_{\beta=0}^{\infty} [\xi] e^{-(\beta+1/2)R\theta/T} \quad (20)$$

and $M_{e0} = f_{ba}$. The integration for emission that corresponds to Eq. (14) for absorption can be carried out to give the moments about E_0 :

$$\frac{M_{en}}{M_{e0}(\hbar\omega R^{-1})^n} = n! \sum_{i=0}^n \frac{(2i+2j)! [\frac{1}{8}(R^2-1) \coth(R\theta/2T)]^i}{i!(2j)!(i+j)!(n-i-2j)!} \left[\frac{1}{2}S \coth\left(\frac{R\theta}{2T}\right)\right]^j [-S(R^2+1)]^{n-i-2j}. \quad (21)$$

The first five moments for emission are listed below. M_{e1} is taken about $E=0$, but higher moments are taken about M_{e1} , and thus are central moments.

$$M_{e0} = |\langle \phi_b | A | \phi_a \rangle|^2, \quad (22a)$$

$$M_{e1}/M_{e0}(\hbar\omega R^{-1}) = RE_0/\hbar\omega - (1+R^2)S + \frac{1}{4}(R^2-1)\coth(R\theta/2T), \quad (22b)$$

$$m_{e2}/M_{e0}(\hbar\omega R^{-1})^2 = S\coth(R\theta/2T) + \frac{1}{8}(R^2-1)^2\coth^2(R\theta/2T), \quad (22c)$$

$$m_{e3}/M_{e0}(\hbar\omega R^{-1})^3 = \frac{3}{2}(R^2-1)S\coth^2(R\theta/2T) + \frac{1}{8}(R^2-1)^3\coth^3(R\theta/2T), \quad (22d)$$

$$m_{e4}/M_{e0}(\hbar\omega R^{-1})^4 = 3S^2\coth^2(R\theta/2T) + \frac{15}{4}(R^2-1)^2 \times S\coth^3(R\theta/2T) + \frac{15}{64}(R^2-1)^4\coth^4(R\theta/2T). \quad (22e)$$

In the case of the linear interaction (and also of the quadratic interaction), the moments can be calculated directly from the band shapes. Using the Slater sum to simplify $\text{Av}_\alpha\chi_\alpha^2$ and

$$\frac{dq}{dE} = [2\omega^2(R^2-1)(E-E_0) + 2SR^3\hbar\omega^3]^{-1/2}, \quad (23)$$

with $R=1$, one can compute the moments using Eq. (8). The central moments for absorption and emission are identical:

$$\frac{m_{2n}}{M_0} = \frac{m_{e(2n)}}{M_{e0}} = \frac{(2n)!}{n!} (2c_2)^{-2n}, \quad (24a)$$

$$m_{2n+1}/M_0 = m_{e(2n+1)}/M_{e0} = 0, \quad (24b)$$

where

$$c_2 = \hbar\omega [2S\coth(\theta/2T)]^{-1/2}.$$

Equation (24b) vanishes because in symmetric distributions (here I and I_e are Gaussians), every central moment of odd order is equal to zero.

The quadratic-interaction moments reduce to

$$m_n/M_0 = n! \left[-\frac{1}{4}\hbar\omega(R^2-1)\coth(\theta/2T) \right]^n \times \sum_{i=0}^n \frac{(2i)!(-\frac{1}{2})^i}{(i!)^2(n-i)!}. \quad (25)$$

To obtain the corresponding emission moments, replace ω and θ with $R^{-1}\omega$ and $R\theta$, respectively.

The classical band shape results when the final and initial states are both treated classically, thus permitting use of the completeness relations for both states. Then for absorption, Eq. (7) becomes

$$M_n = f_{ab} \left(\int_{-\infty}^{\infty} dq e^{-E_a/kT} \right)^{-1} \int_{-\infty}^{\infty} dq (E_b - E_a)^n e^{-E_a/kT}, \quad (26)$$

and similarly for emission. Performing the indicated integrations, one obtains just the semiclassical result in its high-temperature limit, where $\coth(\theta/2T)$ is replaced by $2T/\theta$. For emission, the same occurs but with $\coth(R\theta/2T)$ replaced by $2T/R\theta$.

IV. COMPARISON TO THE QUANTUM-MECHANICAL MOMENTS

The validity of the semiclassical approximation ultimately rests with the extent to which the resulting band shapes accurately reproduce the quantum-mechanical band shapes. If the semiclassical moments closely approximate the corresponding quantum-mechanical moments, then the semiclassical band shapes accurately reproduce the quantum-mechanical band shapes. Examination of the first few moments should reveal the extent of the accuracy of the semiclassical approximation. Only the five lowest quantum-mechanical moments have been calculated for the general interaction,¹² but all the quantum-mechanical moments for the linear interaction have been determined.¹⁹

It has been noted¹ that the semiclassical moments (Sec. II) and the quantum-mechanical moments (Ref. 13) agree exactly up through $n=2$. The difference between the third quantum-mechanical moment and the third semiclassical moment, Eq. (17d), is

$$(m_{3(QM)} - m_{3(SC)})/M_0(\hbar\omega)^3 = SR^3 + \frac{1}{4}(R^2-1)^2\coth(\theta/2T) \quad (27)$$

for absorption, while for the fourth absorption moments

$$(m_{4(QM)} - m_{4(SC)})/M_0(\hbar\omega)^4 = \frac{1}{4}(R^2-1)^2 + SR^3(4R^2-3)\coth(\theta/2T) + \frac{1}{4}(R^2-1)^2(2R^2-1)\coth^2(\theta/2T). \quad (28)$$

These differences, by themselves, provide one measure of validity of the semiclassical approximation, but a more meaningful assessment can be made by examining how these moments are related to the band shape.

The complex band shape that results from the general vibrational interaction can be described by the series expansion²⁰

$$I(E) = m_2^{-1/2} \left(\phi - \frac{\gamma_1}{3!} \phi^{(3)} + \frac{\gamma_2}{4!} \phi^{(4)} + \frac{10}{6!} \gamma_1^2 \phi^{(6)} - \frac{\gamma_3}{5!} \phi^{(5)} - \frac{35}{7!} \gamma_1 \gamma_2 \phi^{(7)} - \frac{280}{9!} \gamma_1^3 \phi^{(9)} + \dots \right) \quad (29)$$

about a Gaussian shape,

$$\phi = (2\pi)^{-1/2} \exp(-\frac{1}{2}x^2),$$

where $x = (E - M_1)m_2^{-1/2}$. Here $\phi^{(n)}$ represents the n th derivative of ϕ with respect to x . The coefficients of skewness and excess (kurtosis) are

$$\gamma_1 = m_3 m_2^{-3/2}, \quad (30)$$

$$\gamma_2 = m_4 m_2^{-2} - 3. \quad (31)$$

The coefficient of excess is a measure of the flattening near the band centroid; positive γ_2 means a taller and slimmer shape than the $\gamma_2 = 0$ Gaussian shape. These dimensionless coefficients show how the various moments affect the shape of the band. Thus, a measure of the accuracies of the semi-

classical and classical approximations are given by the accuracies of γ_1 and γ_2 . Errors in γ_1 and γ_2 directly contribute, via Eq. (29), to an inaccurate portrayal of the band shape.

Considering the absorption band shape, we define

$$\Delta\gamma_1 = (m_{3(\text{QM})} - m_{3(\text{SC})})m_2^{-3/2} \quad (32)$$

$$= \frac{4SR^3 + (R^2 - 1)^2 \coth(\theta/2T)}{4[SR^3 \coth(\theta/2T) + \frac{1}{8}(R^2 - 1)^2 \coth^2(\theta/2T)]^{3/2}} \quad (33)$$

and

$$\Delta\gamma_2 = (m_{4(\text{QM})} - m_{4(\text{SC})})m_2^{-2} \quad (34)$$

$$= \frac{(R^2 - 1)^2 + 4SR^3(4R^2 - 3) \coth(\theta/2T) + (R^2 - 1)^2(2R^2 - 1) \coth^2(\theta/2T)}{4[SR^3 \coth(\theta/2T) + \frac{1}{8}(R^2 - 1)^2 \coth^2(\theta/2T)]^2} \quad (35)$$

Comparison of higher coefficients is precluded because for the general interaction, quantum-mechanical moments higher than the fourth have not been determined. We note from Eqs. (33) and (35) that $\Delta\gamma_1$ and $\Delta\gamma_2$ both decrease (that is, the quantum-mechanical band shape approaches the semiclassical band shape) with increases in R , S , and/or T . These trends are depicted in Fig. 2. For typical values of R and S , $\Delta\gamma_1$ and $\Delta\gamma_2$ are well approximated by the linear-interaction results:

$$\Delta\gamma_1 = [S \coth^3(\theta/2T)]^{-1/2}, \quad (36)$$

$$\Delta\gamma_2 = [S \coth(\theta/2T)]^{-1}. \quad (37)$$

Both $\Delta\gamma_1$ and $\Delta\gamma_2$ become sufficiently small (for values of S and/or T that are not unreasonably large) that the semiclassical approximation is

often appropriate to the linear interaction and to the general interaction. For the quadratic interaction, however, small values of $\Delta\gamma_1$ and $\Delta\gamma_2$ occur only for unreasonably large values of R and/or T , and the semiclassical approximation is rarely appropriate. This observation is consistent with the strong dissimilarity between the shapes of the semiclassical and the quantum-mechanical bands presented by Keil.¹⁷ At high temperatures, $\coth(\theta/2T) \approx 2T/\theta$, which is equivalent to invoking the classical approximation.

V. DISCUSSION AND CONCLUSIONS

The n th semiclassical and classical moments are calculated for absorption and emission. Explicit expressions for the first five moments are

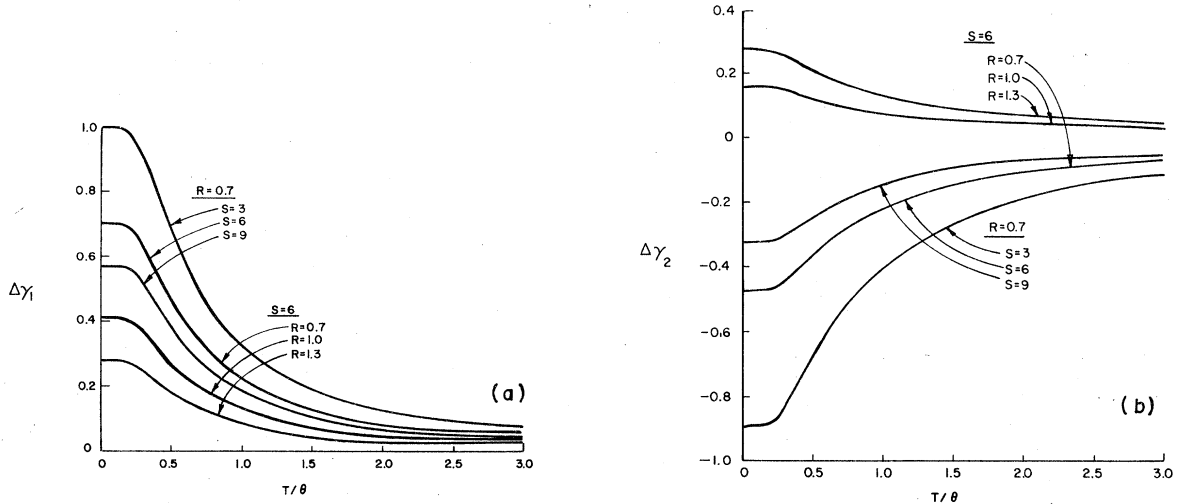


FIG. 2. Parametric dependence on T , S , and R of the changes introduced by the semiclassical approximation in (a) γ_1 , the coefficient of skewness; (b) γ_2 , the coefficient of excess.

presented. Errors in band skewness and kurtosis that are introduced by the semiclassical approximation are used as a measure of the validity of the approximation. For both the linear interaction and the general interaction, it is found that the semiclassical approximation is often valid, especially for high temperature and/or strong coupling. The classical approximation is valid for high temperatures. The regions of validity of these approximations are consistent with the correspondence principle that quantum-mechanical results reduce to classical results for large values of the quantum numbers. These approximations are rarely appropriate for the quadratic interaction.

For the linear interaction one can show that the major contribution to the n th absorption moment occurs at the energies

$$E_0 \pm 1.4k\theta [nS \coth(\theta/2T)]^{1/2}.$$

For emission, replace E_0 by $E_0 - 2S\hbar\omega$. For the lower moments the major contribution occurs in the vicinity of the half-width points. However,

the location of the major contributions to the moments becomes increasingly separated from the band centroid as n increases. Thus, if higher moments are to be computed from experiment, much care should be taken to ensure that the band intensity is accurate to energies well beyond the half-width points.

At high temperatures and/or strong coupling (for the linear and general vibrational interactions, but not for the quadratic), the semiclassical and classical moments accurately portray the quantum-mechanical moments. For these regimes, the expressions for the semiclassical and classical moments are more useful for extracting theoretical parameters from experimental data than are the expressions for the quantum-mechanical moments. Once these semiclassical and classical values of the theoretical parameters have been extracted, they could then be inserted as first-order estimates in the more exact quantum-mechanical expressions in an iterative procedure to determine the quantum-mechanical values of the parameters.

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