crossing may be calculated by perturbation theory to be $\Delta\nu = W_a - W_b = 0.701 H_{\mathrm{rf}}$ Mc/G for H_{rf} small. The uncertainty in the measured rf field is then $\delta H_{\mathrm{rf}} = 1.43\delta(\Delta\nu)$ G/(Mc/sec). One can determine the center of our K^{39} lines to about 1 kc/sec or $\delta(\Delta\nu)$ to about 2 kc/sec which would give an uncertainty in measured rf field of about 0.003 G. For comparison, optimum power for a one quantum transition is ~ 0.02 G.

Measurements of rf magnetic fields are sometimes made relative to optimum power for some transition. However, determination of the actual rf magnetic field in gauss which corresponds to optimum power requires a knowledge of the velocity distribution of the atoms. The method outlined above is independent of the velocity distribution of the atoms and may in fact be used in conjunction with a measurement of optimum power to determine the velocity of the atoms in an almost monochromatic beam. The shape of the rf envelopes should be taken into account in any calculations of rf magnetic-field strengths.

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Two-Photon Processes in Complex Atoms*

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The off-diagonal matrix elements of the polarizability operator when operating within an l^N configuration of a complex atom can be approximately written in simple tensor-operator form. The resulting expressions are discussed in terms of two-photon absorption and the recently observed electronic Raman scattering in the trivalent rare-earth ions.

I. INTRODUCTION

The extremely intense light fluxes available from optical maser sources have revived interest in interactions in which atomic matter and two or more quanta of electromagnetic energy are involved.[1] The most easily observable two-photon effects, Rayleigh and Raman scattering, were given modern quantum-mechanical treatment by Dirac.[2] Two-photon absorption and emission, also predicted by second-order perturbation theory, were first discussed by Goeppert-Mayer.[3]

Of the recently investigated two photon effects at optical frequencies, several have occurred in systems which to a good approximation can be described as free atoms. Thus, two-photon absorption has been observed by Kaiser and Garrett[4] in Eu^{2+} in a matrix of CaF_2, and in atomic Cd vapor by Abella.[5] The first observed atomic Raman transitions were reported recently by Hougen and Singh.[6] Sorokin and Braslau[7] have recently suggested the possibility of producing stimulated two-photon emission at optical frequencies by triggering with intense light at the subharmonic frequency. In view of the possible importance of such processes, the purpose of the present paper is to examine the second-order perturbation expansions which determine two-photon interaction in complex atoms in the hope of developing approximate expressions more amenable to both qualitative and quantitative evaluation. The development is similar in spirit to the polarizability approximation introduced by Placzek[8] and others for treating vibrational and rotational Raman transitions.

II. FORMULAS AND APPROXIMATIONS

Consider an atomic system in an eigenstate β but with other allowed eigenstates β', β'', etc., upon which monochromatic light of frequency ω_1 is incident. The result of the second-order electric-dipole-interaction perturbation[2] can be summarized by attributing to the atomic system induced-oscillator dipole moments with (complex) amplitudes of the form

$$(\beta'|\mathbf{P}(\omega_2)|\beta) = (\beta'|\boldsymbol{\alpha}|\beta)\cdot\boldsymbol{\mathcal{E}}(\omega_1),$$

where $\boldsymbol{\mathcal{E}}(\omega_1)$ is the electric field associated with the incident radiation and the oscillator frequencies ω_1 and ω_2

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[1] See, for example, J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

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[3] M. Goeppert-Mayer, Anw. Physik **9**, 273 (1931).

[4] W. Kaiser and C. G. B. Garrett, Phys. Rev. Letters **7**, 229 (1961).

[5] I. D. Abella, Phys. Rev. Letters **9**, 453 (1962).

[6] J. T. Hougen and S. Singh, Phys. Rev. Letters **10**, 406 (1963).

[7] P. P. Sorokin and N. Braslau, IBM J. Res. Develop. **8**, 177 (1964).

[8] G. Placzek, *Handbuch der Radiologie* (Akademische Verlagsges, Leipzig, 1934), Vol. 6, Part 2, p. 205.

are related by

$$E(\beta')-E(\beta)=\hbar\omega(\beta')=\hbar[\omega_1+\omega_2].$$

The induced moment $\mathbf{P}(\omega_2)$ interacts with a radiation field at ω_2 (or in the case of spontaneous emission with its zero-point fluctuations) in a manner calculable with regard to both rate and radiation pattern by familiar classical dipolar-radiation theory. Thus, for example, the toal radiated power at frequency ω_2 is given by

$$\hbar\omega_2\cdot A(\beta'\rightarrow\beta)=[\omega_2{}^4/3c^3]\,|(\beta'|\mathbf{P}(\omega_2)|\beta)|^2.$$

The appearance (or disappearance) of a photon at ω_2 is accompanied by simultaneous appearance (disappearance) of a photon at ω_1 in such a manner as to conserve energy. The components of the second-order tensor $(\beta'|\boldsymbol{\alpha}|\beta)$ are given by

$$(\beta'|\alpha_{ij}|\beta)=\sum_{\beta''}\frac{(\beta'|M_i|\beta'')(\beta''|M_j|\beta)}{E(\beta'')-E(\beta)-\hbar\omega_1}+\frac{(\beta'|M_j|\beta'')(\beta''|M_i|\beta)}{E(\beta'')-E(\beta)-\hbar\omega_2}, \qquad (1)$$

where M_i, M_j are the components of the dipole operator $e\sum\mathbf{r}$ along i, $j=x$, y, z coordinate axes. *Note that the expressions above pertain to both two-photon absorption and scattering with the stipulation of assigning a positive frequency to a photon absorbed from the radiation field and a negative frequency to an emitted photon.*[9]

In even modestly complex atoms the sum over the excited intermediate states β'' in Eq. (1) in a straightforward manner is not a practical course of action, and some manner of simplication must be accomplished to proceed further. The form of the expression suggests the use of the closure operation $\sum_{\beta''}M_i|\beta'')(\beta''|M_j=M_iM_j$ providing the energy denominators do not cause the expression to become a rapidly changing function of β''. In fact both Judd[10] and Ofelt[11] have recently developed essentially similar procedures for performing such closure operations piecewise over small subgroups of degenerate or nearly degenerate intermediate states. These writers were interested in application of their results to the problem of crystal-field-induced dipole transitions; however, the expressions have a general validity for second-order perturbation expansions. Referring the reader to the original papers for derivations and additional discussion, the result of the application of this treatment to the problem at hand can be immediately given.

If the dipole moment operator is written in linearly and circularly polarized components

$$M_0=eD_0{}^{(1)}=e\sum z,$$
$$M_{\pm1}=eD_{\pm1}{}^{(1)}=\mp e\sum(x\pm iy)/\sqrt{2},$$

then providing that the eigenstates are expanded in a ψJM representation, immediate use can be made of equations such as (7) or (9) of Ref. 10. As Judd[10] points out, the resulting simplification is not great until the subgroup of degenerate states is expanded to include all the states of a given excited configuration. When this assumption has been made Ref. 10, Eq. (9), gives contributions to $\alpha_{\rho\mu}$ of the form

$$\begin{aligned}\sum_{\psi'',J'',M''}&(l^N\psi JM|D_\rho{}^{(1)}|l^{N-1}(n'l')\psi''J''M'')\\&\times(l^{N-1}(n'l')\psi''J''M''|D_\mu{}^{(1)}|l^N\psi'J'M')\\=\sum_{\lambda=0,1,2}&(-1)^{\rho+\mu+1}(2\lambda+1)\begin{pmatrix}1&\lambda&1\\\rho&-(\rho+\mu)&\mu\end{pmatrix}\\&\times\begin{Bmatrix}1&\lambda&1\\l&l'&l\end{Bmatrix}(l\|\mathbf{C}^{(1)}\|l')^2\\&\times(nl|r|n'l')^2(l^N\psi JM|U_{\rho+\mu}{}^{(\lambda)}|l^N\psi'J'M').\end{aligned}$$

Upon rearrangement and substitution of explicit expressions for the various $n-j$ symbols, it is found that the components of $\boldsymbol{\alpha}$ when expressed in spherical coordinates[12] and acting within states of an l^N manifold can be generated by the operator

$$\alpha_{\text{eff}}=\begin{array}{c}\begin{array}{ccc}(+1)&(0)&(-1)\end{array}\\\left[\begin{array}{ccc}\alpha_2{}^{(2)}&2^{-1/2}(-\alpha_1{}^{(1)}+\alpha_1{}^{(2)})&6^{-1/2}(\sqrt{2}\alpha_0{}^{(0)}-\sqrt{3}\alpha_0{}^{(1)}+\alpha_0{}^{(2)})\\2^{-1/2}(\alpha_1{}^{(1)}+\alpha_1{}^{(2)})&3^{-1/2}(-\alpha_0{}^{(0)}+\sqrt{2}\alpha_0{}^{(2)})&2^{-1/2}(-\alpha_{-1}{}^{(1)}+\alpha_{-1}{}^{(2)})\\6^{-1/2}(\sqrt{2}\alpha_0{}^{(0)}+\sqrt{3}\alpha_0{}^{(1)}+\alpha_0{}^{(2)})&2^{-1/2}(\alpha_{-1}{}^{(1)}+\alpha_{-1}{}^{(2)})&\alpha_{-2}{}^{(2)}\end{array}\right]\end{array}\begin{array}{c}\\(+1)\\(0)\\(-1)\end{array} \qquad (2)$$

where the $\alpha_\kappa{}^{(\lambda)}$ are themselves spherical tensor operators of rank λ, i.e.,

$$(l^N\psi JM|\alpha_\kappa{}^{(\lambda)}|l^N\psi'J'M')=(-1)^{J-M}\begin{pmatrix}J&\lambda&J'\\-M&\kappa&M'\end{pmatrix}(l^N\psi J\|\boldsymbol{\alpha}^{(\lambda)}\|l^N\psi'J'), \qquad (3)$$

and the reduced matrix elements are given by

$$(l^N\psi J\|\boldsymbol{\alpha}^{(\lambda)}\|l^N\psi'J')=\alpha_\lambda'(l^N\psi J\|\mathbf{U}^{(\lambda)}\|l^N\psi'J'), \qquad (4)$$

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[9] Second-order perturbation theory also admits the transition $\beta'\rightarrow\beta$ accompanied by spontaneous emission of two photons. The probability per unit time of emission of one photon in the frequency interval about $\omega_1 d\omega_1$ with a second photon in the complementary interval is [see J. Shapiro and G. Breit, Phys. Rev. **113**, 179 (1959)]

$$dA=(8\omega_1{}^3\omega_2{}^3/\pi c^6)\langle|(\beta|\alpha_{ij}|\beta')|^2\rangle_{Av}d\omega_1$$

by using the sign convention given above and noting that $E(\beta)$ and $E(\beta')$ are also to be interchanged in Eq. (1). The average is taken over the polarization directions i, j of the emitted photons.

[10] B. R. Judd, Phys. Rev. **127**, 750 (1962).

[11] G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).

[12] Some care is necessary in the manipulation of spherical vector components. In particular the defining relation for a vector in terms of unit spherical basis vectors $\mathbf{e}_q$ is $\mathbf{F}=\Sigma_q(-1)^qF_{-q}\mathbf{e}_q$. The form of the expression for the induced polarization consistent with this and the above definition of $\boldsymbol{\alpha}$ is $\mathbf{P}_q=\Sigma_{q'}(-1)^{q'}\alpha_{q'q}\mathcal{E}_{-q}$. Consult Ref. 10 for the undefined quantities in the preceding expression.

and

$$\alpha_0{}'=\frac{e^2}{\hbar}\sum_{n',l\pm1}-\frac{(l+l'+1)}{[3(2l+1)]^{1/2}}(nl|r|n'l')^2\times\frac{[\omega(n'l')-\frac{1}{2}(\omega_1+\omega_2)]}{[\omega(n'l')-\omega_1][\omega(n'l')-\omega_2]},\qquad(5a)$$

$$\alpha_1{}'=\frac{e^2}{\hbar}\sum_{n',l\pm1}(-1)^{(l-l'-1)/2}\left[\frac{(l+l'+1)(3l-l'+1)}{2(2l+1)}\right]^{1/2}\times(nl|r|n'l')^2\frac{\frac{1}{2}(\omega_1-\omega_2)}{[\omega(n'l')-\omega_1][\omega(n'l')-\omega_2]},\qquad(5b)$$

$$\alpha_2{}'=\frac{e^2}{\hbar}\sum_{n',l\pm1}-\left[\frac{(l+l'+1)(3l-l'+1)(4l-2l'+1)}{2\times3(l+l')(l+l'+2)}\right]^{1/2}\times(nl|r|n'l')^2\frac{[\omega(n'l')-\frac{1}{2}(\omega_1+\omega_2)]}{[\omega(n'l')-\omega_1][\omega(n'l')-\omega_2]}.\qquad(5c)$$

Several points must be mentioned with respect to Eqs. (3)–(5). The mean or effective energy of the $n'l'$ configuration with respect to the initial state is $\Delta E(n'l')=E(n'l')-E(\beta)=\hbar\omega(n'l')$. The $n'l'$ excited configurations must include not only configurations $l^{N-1}(n',l\pm1)$ for all excited n', but also those configurations $(n''l'')^{4l''+1}l^{N+1}$ which arise from removing a single electron from a closed $n''l''$ shell, providing again that $l''=l\pm1$. $\mathbf{U}^{(\lambda)}$ is the sum over all electrons of the single-electron tensor operators $\mathbf{u}^{(\lambda)}$ normalized by the condition $(l\|\mathbf{u}^{(\lambda)}\|l)=1$ and

$$(nl|r|n'l')=\int_0^\infty \mathcal{R}(nl)r\mathcal{R}(n'l')dr,$$

where $\mathcal{R}(nl)/r$ is the radial wave function appropriate to the (nl) configuration. From the result

$$(l^N\beta|U_0{}^{(0)}|l^N\beta')=N\delta(\beta,\beta')/(2l+1)^{1/2},$$

one sees that $\boldsymbol{\alpha}^{(0)}$ contributes only to Rayleigh scattering. The frequency factors appearing in Eqs. (5) for $\alpha_1{}'$ and $\alpha_2{}'$ are in the approximate ratio $(\omega_1-\omega_2)/2\omega(n'l')$ if ω_1, $\omega_2<\omega(n'l')$. Thus although the term in $\boldsymbol{\alpha}^{(1)}$ has been included for generality, for the case in which the radiation frequencies are far from resonant (which is the case for which the above expansions will be most valid), the contribution to two photon processes of $\boldsymbol{\alpha}^{(1)}$ are probably small enough in comparison to $\boldsymbol{\alpha}^{(2)}$ to be ignored. (Note that in the physically interesting case of two-photon absorption from the same source ω_1 equals ω_2 and the term in $\boldsymbol{\alpha}^{(1)}$ vanishes exactly.)

In order to apply Eqs. (2)–(5) in an actual case the eigenfunctions $|\beta)$, $|\beta')$ must be specified and in order to evaluate the quantities $\alpha_\lambda{}'$ values for the various $\omega(n'l')$ and $(nl|r|n'l')$ must be given also. Since the latter are rarely known with any degree of accuracy it will often be convenient and useful to consider the quantities $\alpha_\lambda{}'$ as numerical parameters. Simple relations concerning the *relative* strengths of various possible transitions often result. This is illustrated in the following section.

Although Eqs. (2)–(5) essentially constitute the desired result of this paper it is possible to calculate explicitly the angular dependence once and for all if spherical symmetry is preserved (as in free atoms or ions), or if by suitable averaging the spherical symmetry is effectively preserved.[13] Making use of the simplifying relation

$$\sum_{MM'}(\gamma JM|U_q{}^{(k)}|\gamma'J'M')(\gamma JM|U_{q'}{}^{(k')}|\gamma'J'M')^\dagger=(\gamma J\|\mathbf{U}^{(k)}\|\gamma'J')^2\delta(k,k')\delta(q,q')/(2k+1),$$

the level strengths

$$S_\rho(\gamma J,\gamma'J')=\sum_{MM'}|(\gamma JM|\mathbf{P}_\rho|\gamma'J'M')|^2$$

are found to be

$$\begin{aligned}S_{\pm1}(\gamma J,\gamma'J')&=\tfrac{1}{3}|\mathcal{E}_{\pm1}|^2(\gamma J\|\boldsymbol{\alpha}^{(0)}\|\gamma'J')^2+\tfrac{1}{6}[|\mathcal{E}_{\pm1}|^2+|\mathcal{E}_0|^2]\\&\quad\times(\gamma J\|\boldsymbol{\alpha}^{(1)}\|\gamma'J')^2+(1/30)\\&\quad\times[|\mathcal{E}_{\pm1}|^2+3|\mathcal{E}_0|^2+6|\mathcal{E}_{\mp1}|^2](\gamma J\|\boldsymbol{\alpha}^{(2)}\|\gamma'J')^2,\end{aligned}\qquad(6a)$$

$$\begin{aligned}S_0(\gamma J,\gamma'J')&=\tfrac{1}{3}|\mathcal{E}_0|^2(\gamma J\|\boldsymbol{\alpha}^{(0)}\|\gamma'J')^2+\tfrac{1}{6}[|\mathcal{E}_{+1}|^2+|\mathcal{E}_{-1}|^2]\\&\quad\times(\gamma J\|\boldsymbol{\alpha}^{(1)}\|\gamma'J')^2+(1/30)\\&\quad\times[3|\mathcal{E}_{+1}|^2+4|\mathcal{E}_0|^2+3|\mathcal{E}_{-1}|^2](\gamma J\|\boldsymbol{\alpha}^{(2)}\|\gamma'J')^2,\end{aligned}\qquad(6b)$$

and

$$\sum_\rho S_\rho(\gamma J,\gamma'J')=\tfrac{1}{3}\sum_\lambda(\gamma J\|\boldsymbol{\alpha}^{(\lambda)}\|\gamma'J')^2|\boldsymbol{\varepsilon}|^2.\qquad(7)$$

The angular dependence of scattering processes are commonly described by a depolarization ratio ρ which is the ratio of the intensity of light polarized along the propagation axis of the incident light to that polarized in a plane perpendicular to this axis, the observation made at right angles to the incident beam. For the spherically symmetric atomic case considered above for linearly polarized incident light

$$\rho_l=\frac{5(\gamma J\|\boldsymbol{\alpha}^{(1)}\|\gamma'J')^2+3(\gamma J\|\boldsymbol{\alpha}^{(2)}\|\gamma'J')^2}{4(\gamma J\|\boldsymbol{\alpha}^{(2)}\|\gamma'J')^2},\qquad(8a)$$

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[13] To a good approximation, the interaction of rare-earth ions with neighboring atoms in a solid results only in the (partial) removal of the $(2J+1)$-fold degeneracy of the free-ion levels. If the additional splitting of the ground states is small enough that they can be considered to be equally occupied, the principle of spectroscopic stability requires the sum of the transition strengths between two split J manifolds to be independent of the splitting, that is the same as for the unsplit free-ion manifold. It is in this sense that effective spherical symmetry is used above.

and for unpolarized (natural) excitation

$$\rho_n=\frac{10(\gamma J\|\boldsymbol{\alpha}^{(1)}\|\gamma'J')^2+6(\gamma J\|\boldsymbol{\alpha}^{(2)}\|\gamma'J')^2}{5(\gamma J\|\boldsymbol{\alpha}^{(1)}\|\gamma'J')^2+7(\gamma J\|\boldsymbol{\alpha}^{(2)}\|\gamma'J')^2}, \tag{8b}$$

which under conditions where

$$(\gamma J\|\boldsymbol{\alpha}^{(1)}\|\gamma'J')^2\ll(\gamma J\|\boldsymbol{\alpha}^{(2)}\|\gamma'J')^2$$

reduces to $\rho_l=\frac{3}{4}$, $\rho_n=6/7$ which characterizes the anisotropic form for the polarizability tensor $\boldsymbol{\alpha}^{(2)}$. [That $\boldsymbol{\alpha}^{(2)}$ is indeed of anisotropic form is quickly verified by writing Eq. (2) in terms of Cartesian basis vectors.]

III. AN EXAMPLE

The experimental conditions under which Hougen and Singh[6] observed electronic Raman effect in PrCl_3 correspond only moderately well to optimum conditions for application of the above approximations. In particular, the wavelength of the exciting radiation (Hg 2537 Å) is short enough that the resonance denominators in Eqs. (5) become unpleasantly small for the lowest lying $4f5d$ levels.[14] Nevertheless, if the assumption $\boldsymbol{\alpha}^{(1)}\ll\boldsymbol{\alpha}^{(2)}$ is made, the relative intensities of the Raman transitions are proportional to the quantities $(\gamma J\|\mathbf{U}^{(2)}\|\gamma'J')^2$ for the levels involved. These quantities are compared in Table I with the qualitative scattering intensities reported in Ref. 6. All of the levels of the f^2 configuration for which $\mathbf{U}^{(2)}$ does not vanish in the Russell-Saunders approximation are listed. The matrix elements are evaluated also in the Russell-Saunders limit, an oversimplification which does not appreciably affect the quantities of interest. The selection rules on the operator $\mathbf{U}^{(2)}\Delta S=0$; ΔL, $\Delta J\leqslant 2$ do obtain quite generally for electronic two-photon processes but can be deduced more simply. What is significant and not intuitively obvious is the widely differing magnitude of the allowed values of $\mathbf{U}^{(2)}$ and its correlation with observed transition intensity. Since more precise experimental measurements are not available at the present time, a more extensive calculation taking crystal-field effects into account seems unwarranted.[15]

TABLE I. Comparison of observed raman intensity with $(\gamma J\|\mathbf{U}^{(2)}\|\gamma'J')^2$.

$S'L'J'$	Approximate energy (cm^{-1})	$(S'L'J'\|\mathbf{U}^{(2)}\|{}^3H_4)^2$	Observed intensity (Ref. 6)
${}^3F_4$	6800	0.0027	not obs.
${}^3F_3$	6200	0.070	not obs.
${}^3F_2$	4900	0.50	medium
${}^3H_6$	4200	0.0019	not obs.
${}^3H_5$	2200	0.11	weakest
${}^3H_4$	~100	0.82	strongest

Turning finally to a consideration of the absolute magnitude of two-photon effects, suppose Pr^{3+} as a representative trivalent rare-earth ion. By again supposing that ω_1, $\omega_2\ll\omega(n'l')$, Eq. (5c) becomes

$$\alpha_2'=-e^2\sum_{n'}\left[\left(\frac{2^3\times 9}{5\times 7}\right)^{1/2}\frac{(4f|r|n'd)^2}{\hbar\omega(n'd)}+\left(\frac{2^3\times 5}{7\times 9}\right)^{1/2}\frac{(4f|r|n'g)^2}{\hbar\omega(n'g)}\right]\approx-1.0\times 10^{-24}\ \text{cm}^3.$$

Following Judd,[10] the d-electron contribution is assumed entirely due to $5d$ orbitals at $\hbar\omega(5d)=50\,000$ cm^{-1}, whereas the $n'g$ orbitals which contribute about 25% to the value of α_2' are all assumed to lie at an effective ionization limit which is taken to be $\hbar\omega(n'g)=160\,000$ cm^{-1}. The latter approximation allows $\sum_{n'}(4f|r|n'g)^2$ to be replaced by $(4f|r^2|4f)=1.46$ a.u. This value, as well as $(4f|r|5d)^2=0.81$ a.u. are calculated by Rajnak.[16] This leads to a cross section of 4.5×10^{-28} cm^2 for total Raman scattering of 5000-Å radiation within the ${}^3H_4$ manifold, for which the matrix elements of $\mathbf{U}^{(2)}$ are most favorable. This figure taken as a measure of a strongly allowed Raman transition is less by factors of roughly 10^3 and 10, respectively, from the most optimistic and conservative estimates of Kleinman.[17] Estimates for the cross sections for other two-photon processes are similarly reduced in the same ratio.

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[14] G. H. Dieke, H. M. Crosswhite, and B. Dunn, J. Opt. Soc. Am. **51**, 820 (1961).

[15] *Note added in proof.* In a more recent and detailed account of their work [Proc. Roy. Soc. **A277**, 193 (1963)] Hougen and Singh make essentially the comparison given in Table I above, along with a less formal and detailed justification for neglecting the contribution of the $\boldsymbol{\alpha}^{(0)}$ and $\boldsymbol{\alpha}^{(1)}$ terms.

[16] K. Rajnak, J. Chem. Phys. **37**, 2440 (1962).

[17] D. A. Kleinman, Phys. Rev. **125**, 87 (1962).