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Raman Scattering by Hydrogenic Systems*

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We have calculated the cross section for Raman scattering of light from a hydrogenic atom, for a wide range of photon energies. The calculation assumes the photon encounters the atom in its ground state and excites it to the 2s state. Since various contributions to the matrix element may be isolated in the computation, the calculation allows one to obtain a notion of the relative importance of various classes of intermediate states in a given frequency range. We also point out that the Raman efficiency S may be expressed in terms of the derivative of the electronic polarizability tensor with respect to a parameter that measures the degree of excitation of the atom. Thus, the formal expression for S assumes an appearance identical to the expression encountered in the phenomenological theory of the first-order Raman effect in solids.

I. INTRODUCTION

THERE is currently a strong experimental and theoretical interest in the inelastic scattering of light from matter. Since the change in frequency of the light occurs because the incident photon has excited the scattering medium, the study of inelastic scattering of light provides detailed information about the nature of the excited states of the material under study. In solid-state physics, the development of laser sources has been of great value, since the high intensity of the incident beam makes processes with small cross sections experimentally accessible, and polarization studies may be carried out with precision.

While there has been a large amount of activity in this field, it has proved difficult both to measure and to compute the frequency dependence and the absolute value of the scattering cross sections. It is clear that a strong effort will be made to compute and to measure the frequency dependence and absolute magnitude of the scattering cross sections from various processes.

In this paper, we would like to present a detailed study of the cross section for Raman scattering of light from the simplest possible system, a one-electron hydrogenlike atom in which a $1s \rightarrow 2s$ transition is induced by the incoming photon. We note that Rapoport and Zon[1] have examined this problem and have expressed the cross section in closed form in terms of hypergeometric functions. While their work is elegant, these authors have presented no quantitative information concerning the magnitude of the cross section and its dependence on incident photon energy. It is precisely these questions we wish to examine in the present work. Furthermore, we shall find it of interest to separate out from the total Raman matrix element particular contributions, such as that from the bound states, from the continuum states, its imaginary part, etc. Thus, we choose to evaluate the Raman matrix element directly, rather than employ the result derived in Ref. 1. It is hoped that by examining the various pieces of the Raman matrix element for the simple hydrogenic atom, we can illustrate the features that will be important in more sophisticated theoretical studies of systems currently under experimental investigation.[2]

A detailed, quantitative study of Raman scattering from a hydrogenic atom may be carried out because analytical forms for the bound state and continuum wave functions are well known. This allows exact numerical evaluation of the sum over intermediate states that occurs in the expression for the Raman-scattering matrix element. By isolating various contributions to this sum, one may get a good feeling for their relative importance. For example, when the frequency of the exciting light is near the energy of an allowed transition between discrete states, the matrix element is often approximated by retaining only the term in the sum over intermediate states which exhibits the enhancement.[3] For the case we consider, one may examine the range of validity of such an approximation.

Also, the behavior of the matrix element for incident photon frequencies greater than the ionization energy is of interest. This frequency region is important, since many solid-state experiments are carried out under conditions in which the incident photon frequency lies in a continuum of allowed interband transitions. In this frequency region, the matrix element acquires an imaginary part, since the photon energy is sufficiently great for an energy allowed ground-state free-electron transition to be induced. We find that for incident photon frequencies $\hbar\omega_I$ in the region $|E_{1s}| < \hbar\omega_I < 10|E_{1s}|$, the imaginary part of the matrix element is in fact con-

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[1] L. P. Rapoport and B. A. Zon, Phys. Letters **26A**, 564 (1968).

[2] Shallow impurity states in semiconductors often have hydrogenlike energy spectra. Raman scattering from such centers has recently been reported by A. Mooradian and G. B. Wright, Phys. Rev. Letters **18**, 608 (1967). While the energy spectrum of the impurity center may be hydrogenlike, the wave functions differ greatly from simple atomic states, since the hydrogenlike envelope function is multiplied by a Bloch function. See W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5. The presence of the Bloch function part will strongly affect the matrix elements of the electronic momentum operator.

[3] D. G. Thomas and J. J. Hopfield, Phys. Rev. **175**, 1021 (1968).

siderably *larger* than the real part. At sufficiently high photon energies, the real part dominates the imaginary part, and the matrix element falls off to zero like $(\hbar\omega_I)^{-2}$. Another interesting feature of the computation is that the matrix element exhibits a frequency dependence quite close to this asymptotic frequency dependence for frequencies far below the range in which the true asymptotic behavior is found. That is to say, the matrix element M varies as $[f(\omega_I)/\omega_I^2]$, where the function $f(\omega_I)$ varies extremely slowly with ω_I. As $\omega_I \to \infty$, $f(\omega_I)$ approaches a constant asymptotic value, but far below the region where f assumes its asymptotic value; the slow variation of f with ω_I gives a matrix element that appears to vary like ω_I^{-2}, even though one is far from the true asymptotic region.

II. RAMAN-SCATTERING MATRIX ELEMENT

Our Hamiltonian in the presence of an electromagnetic field is

$$\mathcal{H} = (1/2m)[\mathbf{p} - (e/c)\mathbf{A}]^2 - e\phi(\mathrm{r}). \tag{2.1}$$

The potential $\phi(\mathbf{r})$ is given by

$$\phi(\mathbf{r}) = e/r. \tag{2.2}$$

Within the framework of second-order perturbation theory and assuming the vector potential $\mathbf{A}$ to vary slowly in space (i.e., the field is uniform over atomic dimensions), Sakurai[4] gives the following expression for the Raman matrix element between the two states $|a\rangle$ and $|b\rangle$:

$$\mathfrak{M} = e_\mu M_{\mu\nu} e_\nu', \tag{2.3}$$

where

$$M_{\mu\nu} = -\frac{1}{m}\sum_i \frac{\langle b|p_\nu|i\rangle\langle i|p_\mu|a\rangle}{E_i - E_a - \hbar\omega_I + i\epsilon} - \frac{1}{m}\sum_i \frac{\langle b|p_\mu|i\rangle\langle i|p_\nu|a\rangle}{E_i - E_b + \hbar\omega_I}. \tag{2.4}$$

In this expression, $\hat{e}$ and $\hat{e}'$ are the initial and final unit polarization vectors, respectively, $\mathbf{p}$ is the momentum operator of the electron, m is the electron mass, E_a, E_b, and E_i are the energies of the initial (1*s*), final (2*s*), and intermediate states, $\hbar\omega_I$ is the incident photon energy, and ϵ is a positive infinitesimal of importance for photon energies in the continuum.

The electric dipole approximation employed in Eq. (2.4) is valid when $kr_{\text{atom}} \ll 1$, where k is the photon wave vector. We may take r_{atom} as the Bohr radius $a_0 = \hbar^2/me^2$. Then $ka_0 \ll 1$ implies $[\hbar\omega_I/(e^2/2a_0)] \ll 2\hbar c/e^2$. Since $\hbar c/e^2 \approx 137$, this means that the incident photon energy should be much less than 275 times the ionization energy of the hydrogenic atom for this approximation to be valid.

Since the Raman-scattering efficiency S is the quantity usually referred to in describing solid-state Raman-scattering processes, it is desirable to relate S to the scattering cross section and Raman matrix element. The scattering efficiency S into a solid angle $d\hat{\Omega}$ is the ratio of the number of outgoing photons per unit time (having direction $d\hat{\Omega}$) to the number of incoming photons per unit time. For incoherent scattering from an array of impurities, S is the product of the number of scatterers per unit area (normal to the incoming beam of photons) with the scattering cross section per scatterer. With A the relevant area and L the length of the crystal perpendicular to A, we have for S

$$S(\hat{\Omega}) = \frac{N}{A}\frac{d\sigma}{d\Omega} = \left(\frac{N}{V}\right)L\frac{d\sigma}{d\Omega}, \tag{2.5}$$

where (N/V) is the impurity concentration, and[4]

$$d\sigma/d\Omega = r_0^2(\omega_S/\omega_I)|\mathfrak{M}|^2 \tag{2.6}$$

is the cross section for scattering by a single center. We define $r_0 = (e^2/mc^2)$, ω_S is the scattered photon frequency, and ω_I is the incident photon frequency.

Before computing the scattering efficiency S explicitly, it will be useful to bring out the analogy between Eq. (2.5) and expressions for the Raman efficiency derived elsewhere.[5,6]

In the theory of scattering of light by phonons, one relates the Raman efficiency S to derivatives of the electronic polarizability of a phonon normal coordinate. Crudely speaking, the phonon normal mode amplitude is a parameter that describes the degree of internal excitation present in the system. We show that in the present case, one may introduce such a parameter and write S in a form that involves the derivative of the appropriate dielectric function with respect to this parameter.

To begin, let us suppose at times near $t = -\infty$, the atom is in some state $|\psi_0(t)\rangle$, which we do not specify in detail at this time. Consider some operator O and suppose $|\psi_0(t)\rangle$ has the property that

$$\langle\psi_0|O|\psi_0\rangle = 0.$$

Now, we perturb the system with a perturbation of the form

$$V(t) = V_{(+)}e^{i\omega t}e^{\eta t} + V_{(-)}e^{-i\omega t}e^{\eta t},$$

with $V_{(+)} = (V_{(-)})^*$. We shall compute the expectation value $\langle O\rangle$ at time t to first order in V. If $|\varphi_m\rangle$ denotes a time-independent eigenfunction of the unperturbed Hamiltonian H_0, then from first-order perturbation theory, the change $|\delta\psi\rangle$ in the wave function $|\psi_0\rangle$ may

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[4] J. J. Sakurai, *Advanced Quantum Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1967), p. 49.

[5] R. Loudon, Proc. Roy. Soc. (London) **A275**, 218 (1963).

[6] E. Burstein, in *Dynamical Processes in Solid State Optics*, edited by R. Kubo and H. Kamimura (W. A. Benjamin, Inc., New York, 1967), p. 34.

be written, with $\hbar=1$,

$$|\delta\psi(t)\rangle=e^{i\omega t}\int_{-\infty}^{0}d\tau\, e^{\eta\tau}e^{i(E_m+\omega)\tau}\langle\varphi_m|V_{(+)}|\psi_0(t+\tau)\rangle$$

$$+e^{-i\omega t}\int_{-\infty}^{0}d\tau\, e^{\eta\tau}e^{i(E_m-\omega)\tau}\langle\varphi_m|V_{(-)}|\psi_0(t+\tau)\rangle.$$

To first order in V, one has

$$\langle O\rangle=\langle\psi_0(t)|O|\delta\psi(t)\rangle+\langle\delta\psi(t)|O|\psi_0(t)\rangle. \tag{2.7}$$

Before we write out Eq. (2.7) in detail, let us choose a specific form for $|\psi_0(t)\rangle$. We take $|\psi_0\rangle=|a\rangle e^{-iE_at}$, then add to this function a small amount of the state $|b\rangle$, which was the final state in the discussion of the Raman scattering, i.e., we write

$$|\psi_0(t)\rangle=|a\rangle e^{-iE_at}+\eta_{ab}|b\rangle e^{-iE_bt}, \tag{2.8}$$

where $|\eta_{ab}|\ll 1$. This function is normalized, so long as $|\eta_{ab}|\ll 1$ and terms of order (η_{ab}^2) may be ignored.

The parameter η_{ab} may be regarded as a measure of the amount of excitation present in the atomic system, if the state $|a\rangle$ is the ground-state wave function. Thus, there is a formal analogy between η_{ab} and the phonon coordinate in the theory of lattice vibrations. For $\langle O\rangle$, insertion of Eq. (2.8) into Eq. (2.7) gives

$$\langle O\rangle=e^{-i\omega t}\left(\sum_m\frac{\langle a|O|m\rangle\langle m|V_{(-)}|a\rangle}{E_{am}+\omega}+\frac{\langle a|V_{(-)}|m\rangle\langle m|O|a\rangle}{E_{am}-\omega}\right)$$
$$+\eta_{ab}{}^*e^{-i\omega_S{}^{(-)}t}\left(\sum_m\frac{\langle b|O|m\rangle\langle m|V_{(-)}|a\rangle}{E_{bm}+\omega_S{}^{(-)}}+\frac{\langle b|V_{(-)}|m\rangle\langle m|O|a\rangle}{E_{am}-\omega_S{}^{(-)}}\right)$$
$$+\eta_{ab}e^{-i\omega_S{}^{(+)}t}\left(\sum_m\frac{\langle a|O|m\rangle\langle m|V_{(-)}|b\rangle}{E_{am}+\omega_S{}^{(+)}}+\sum_m\frac{\langle a|V_{(-)}|m\rangle\langle m|O|b\rangle}{E_{bm}-\omega_S{}^{(+)}}\right)+\text{c. c.} \tag{2.9}$$

We have defined $\omega_S{}^{(\pm)}=\omega\pm(E_b-E_a)$, and $E_{mn}=E_m-E_n$. We shall next employ this result to compute currents induced by the external electromagnetic field by taking for the operator O the current component $j_\nu=-(e/m)p_\nu$, and $V=-(e/mc)\mathbf{A}\cdot\mathbf{p}$. One sees from the result above that driving the system with a field of frequency ω induces currents at frequencies $\omega'\neq\omega$, when the mixing parameter $\eta_{ab}\neq 0$. Indeed, the induced currents appear at the frequencies of the Stokes- and anti-Stokes-Raman radiation, in addition to the drive frequency ω.

Quite generally, if one begins with an initial state at $t=-\infty$ that is an admixture of eigenstates of H_0, then perturbs the system with some harmonic perturbation V, to first order in V the linear response of the system will contain frequencies other than the driving frequency ω. In Eq. (2.9), we have exhibited the response of the system for the special case in which one "mixing parameter" η_{ab} has a small, nonzero value. We introduce a generalized dielectric function that relates the current at frequency ω' to the electric field amplitude at frequency ω. In general, this function will depend on the admixture coefficients $\{\eta\}$. We write

$$\langle j_\mu(\omega')\rangle=i(\omega'/4\pi)\epsilon_{\mu\nu}(\omega',\omega;\{\eta\})E_\nu(\omega). \tag{2.10}$$

This equation defines the function $\epsilon_{\mu\nu}$. For $\omega=\omega'$ and all the η's$=0$, it reduces to the usual definition of the frequency-dependent dielectric function. When $\omega'\neq\omega$, $\epsilon_{\mu\nu}$ vanishes for $\{\eta\}=0$. Thus, for the case in which a single parameter $\eta_{ab}\neq 0$, and $|\eta_{ab}|\ll 1$, we make a Taylor-series expansion

$$\epsilon_{\mu\nu}(\omega',\omega;\{\eta\})=\eta_{ab}(\partial\epsilon_{\mu\nu}/\partial\eta_{ab})(\omega')+\cdots. \tag{2.11}$$

If we compute the current density from Eq. (2.9) and employ Eqs. (2.11) and (2.10), we obtain the following expression for $(\partial_{\mu\nu}/\partial\eta_{ab})$:

$$\frac{\partial\epsilon_{\mu\nu}}{\partial\eta_{ab}}(\omega_S{}^{(\pm)})=-\frac{4\pi}{\omega_S{}^2}\left(\frac{e^2}{m}\right)M_{\mu\nu}(\omega_S{}^{(\pm)}), \tag{2.12}$$

where for given driving frequency ω_I, ω_S assumes the two values $\omega_I\pm(E_b-E_a)$. Equation (2.12) is the analog for the present problem of Loudon's relation[5] between the Raman tensor and the elasto-optic coefficient in the theory of the first-order Raman effect in crystals. It is convenient to introduce the susceptibility derivative $(\partial\chi_{\mu\nu}/\partial\eta_{ab})$:

$$\frac{\partial\chi_{\mu\nu}}{\partial\eta_{ab}}=\frac{1}{4\pi}\frac{\partial\epsilon_{\mu\nu}}{\partial\eta_{ab}}.$$

The expression for the Raman efficiency/unit solid angle then assumes the familiar form

$$S=L\left(\frac{N}{V}\right)\left(\frac{\omega_S}{\omega_I}\right)\left(\frac{\omega_S}{c}\right)^4\left|\hat{e}'\cdot\frac{\partial\chi(\omega_S)}{\partial\eta_{ab}}\cdot\hat{e}\right|^2. \tag{2.13}$$

It should be noted that the result of Eq. (2.13) is quite general, since we have made no specific assumptions about the nature of the states involved in the calculation. Thus, it applies to complex impurity centers with wave functions that differ greatly from the hydrogenic states employed in the remainder of the paper. In the theory of phonon-induced scattering of light by crystals, it is useful to describe the scattering by imagining that the excitation of lattice vibrations modulates the dielectric function of the crystal in time. From Eq. (2.13), one sees that for impurity scattering, one may describe the scattering heuristically by supposing that internal excitation of the impurity center modulates the susceptibility $\chi_{\mu\nu}$. The modulated susceptibility then "beats" with the incident radiation to produce light at the Stokes- and anti-Stokes-Raman frequencies.

We next turn to a detailed calculation of the matrix element $M_{\mu\nu}$ for an atom of hydrogenic character.

III. EXPLICIT EVALUATION OF RAMAN MATRIX ELEMENT

Because we consider the initial and final states to be s states, and because of the degeneracy of states differing only in the magnetic quantum number, we may rewrite Eq. (2.3) as

$$\mathfrak{M}=-\frac{1}{3m}\hat{e}\cdot\hat{e}'\sum_i \langle b|\mathbf{p}|i\rangle\cdot\langle i|\mathbf{p}|a\rangle \times\left(\frac{1}{E_i-E_a-\hbar\omega_I+i\epsilon}+\frac{1}{E_i-E_b+\hbar\omega_I}\right). \quad (3.1)$$

We note that only p states will contribute to the sum. In fact, if we write the orthogonal p states so that they transform as x, y, and z, it is clear that

$$\mathfrak{M}=-\frac{1}{m}\hat{e}\cdot\hat{e}'\sum_j \langle b|p_z|jz\rangle\langle jz|p_z|a\rangle \times\left(\frac{1}{E_j-E_a-\hbar\omega_I+i\epsilon}+\frac{1}{E_j-E_b+\hbar\omega_I}\right). \quad (3.2)$$

The index j labels the radial quantum number denoted by n for bound states, and we add a prime and write n' for continuum states. The labels j and z are sufficient to identify the contributing intermediate states $|jz\rangle$.

To obtain the quantities $\langle b|p_z|jz\rangle$ and $\langle jz|p_z|a\rangle$, we evaluate $\langle b|z|jz\rangle$ and $\langle jz|z|a\rangle$, and then use the relation

$$\langle A|p_z|B\rangle=-(im/\hbar)(E_A-E_B)\langle A|z|B\rangle, \quad (3.3)$$

which is valid when either A or B is a bound state. Condon and Shortley[7] give expressions for some of the relevant matrix elements. For $j=n$ (i.e., the state j is a bound state),

$$\langle nz|z|a\rangle=(2^4a_0/\sqrt{3})n^{7/2}(n-1)^{n-5/2}(n+1)^{-n-5/2}, \quad (3.4)$$

$$\langle b|z|nz\rangle=3a_0 \quad \text{for} \quad n=2,$$

and

$$\langle b|z|nz\rangle=(2^{17/2}a_0/\sqrt{3})n^{7/2}(n^2-1)^{1/2}(n-2)^{n-3} \times(n+2)^{-n-3} \quad \text{for} \quad n>2. \quad (3.5)$$

To obtain the matrix elements to the continuum states, we first specify the quantity n'. In the bound-state region, the energy is given in atomic units $(e=\hbar=m=1)$ by

$$E_n=-1/2n^2. \quad (3.6)$$

For the continuum, we introduce the quantity n', which is related to the energy by[8]

$$E_{n'}=1/2(n')^2. \quad (3.7)$$

Since $E_k=\hbar^2k^2/2m=k^2/2$, we see that $n'=1/k$.

The continuum wave functions are usually normalized by the requirement

$$\int_0^\infty R_{k_1l}^*(r)R_{k_2l}(r)r^2dr=\delta(k_1-k_2). \quad (3.8)$$

We wish to employ the normalization convention

$$\int_0^\infty R_{n_1'l}^*(r)R_{n_2'l}(r)r^2dr=\delta(n_1'-n_2'). \quad (3.9)$$

The two normalizations can be related by using the identity

$$\delta(k_1-k_2)=|dn_2'/dk_2|\,\delta(n_1'-n_2') =(n')^2\delta(n_1'-n_2'). \quad (3.10)$$

Thus, the wave functions are related by

$$R_{kl}(r)=n'R_{n'l}(r). \quad (3.11)$$

In order to examine the behavior of the matrix element when the photon energy is near the ionization energy, it will be useful to show that the quantities $n^{3/2}R_{nl}(r)$ and $n'^{3/2}R_{n'l}(r)$ approach the same limit as n and n' become infinite. This means, as we shall see, that the bound-state contribution to the matrix element combines with the continuum contribution to produce a result that varies smoothly with ω_I.

From Landau and Lifshitz,[9] we have for bound states

$$R_{nl}(r)=\frac{2}{n^{l+2}(2l+1)}\left(\frac{(n+l)!}{(n-l-1)!}\right)^{1/2}(2r)^l e^{-r/n} \times F(-n+l+1,2l+2,2r/n), \quad (3.12)$$

and, after converting from k to n' normalization via Eq. (3.2), we have for continuum states

$$R_{n'l}(r)=\frac{2(n')^{1/2}}{[1-\exp(-2\pi n')]^{1/2}}\frac{1}{(2l+1)!}\prod_{s=1}^{l}\left(1+\frac{s^2}{(n')^2}\right)^{1/2} \times(2r)^l e^{-ir/n'}F(in'+l+1,2l+2,2ir/n'). \quad (3.13)$$

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[7] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1951), 2nd ed., p. 133.

[8] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic Press Inc., New York, 1967).

[9] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Pergamon Publishing Corp., New York, 1958), pp. 121–127.

$F(\alpha,\gamma,z)$ is the confluent hypergeometric function

$$F(\alpha,\gamma,z)=1+\frac{\alpha}{\gamma}\frac{z}{1!}+\frac{\alpha(\alpha+1)}{\gamma(\gamma+1)}\frac{z^2}{2!}+\cdots. \tag{3.14}$$

As $n\rightarrow\infty$, we may expand $R_{nl}(r)$ in inverse powers of n. The leading term is

$$n^{3/2}R_{nl}(r)\rightarrow (1/r)J_{2l+1}(\sqrt{(8r)}). \tag{3.15}$$

As $n'\rightarrow\infty$, we may similarly expand $R_{n'l}(r)$ in inverse powers of n'. The leading term is

$$(n')^{3/2}R_{n'l}(r)\rightarrow (1/r)J_{2l+1}(\sqrt{(8r)}). \tag{3.16}$$

In both expansions, we have employed the relation[9]

$$\begin{aligned}
&\lim_{|s|\rightarrow\infty} F(-s+l+1,2l+2,2r/s)\\
&=\lim_{|s|\rightarrow\infty}\left(1+\frac{-1+(l+1)/s}{(2l+2)}\frac{(2r)}{1!}\right.\\
&\left.+\frac{[-1+(l+1)/s][-1+(l+2)/s]}{(2l+2)(2l+3)}\frac{(2r)^2}{2!}+\cdots\right)\\
&=1-\frac{2r}{(2l+2)}+\frac{(2r)^2}{(2l+2)(2l+3)2!}+\cdots\\
&=(2l+1)!(2r)^{-l-1/2}J_{2l+1}(\sqrt{(8r)}).
\end{aligned} \tag{3.17}$$

J_{2l+1} is the Bessel function of order $2l+1$.

Hence, we have

$$\lim_{n\rightarrow\infty} n^{3/2}R_{nl}(r)=\lim_{n'\rightarrow\infty}(n')^{3/2}R_{n'l}(r). \tag{3.18}$$

This result implies that for the hydrogenlike systems the Raman matrix element is a continuous function of ω_I, as ω_I passes from the bound state to the continuum region. This is so because in performing the sum over intermediate bound states of very high quantum number, the sum over n may be replaced by an integration when the level spacing becomes small compared to the level width. One encounters this contribution from the bound states of large quantum numbers combined with the integration over the continuum. If both contributions are written as integrals over the energies $E=-\frac{1}{2}(n)^{-2}$ and $E=\frac{1}{2}(n')^{-2}$ in the two regions, the sum over intermediate states involves

$$\int^0 dE''\left|\frac{dn}{dE''}\right|\frac{R_{nl}^*(r)R_{nl}(r')}{E''-\hbar\omega_I}+\int_0 dE''\left|\frac{dn'}{dE''}\right|\frac{R_{n'l}^*(r)R_{n'l}(r')}{E''-\hbar\omega_I}.$$

The equality of Eq. (3.18) clearly implies that as E approaches zero from below, the integrand in the first (bound-state) term becomes equal to the integrand in the second (continuum) contribution, and so the Raman matrix element is a smooth function of ω_I in the vicinity of the continuum edge. In fact, while the above result is derived within the context of the present specific calculation, the proof is clearly quite general and may be applied to other processes such as the frequency dependence of the electronic polarizability, computed in the framework of perturbation theory.

This general property is seen quite nicely in Mahan's work[10] on two-photon absorption by solids. In this work, the absorption coefficients are calculated for transitions into the bound-state region and the continuum region, caused by the absorption of two photons. Mahan notes that the absorption coefficients are continuous as one goes from transition into the bound-state region to transitions into the continuum region.

Bethe and Salpeter[8] evaluate one of the needed matrix elements involving the continuum states; in n' normalization, it is given by

$$\langle n'z|z|a\rangle=\frac{2^4a_0(n')^{7/2}}{\sqrt{3}[1+(n')^2]^{5/2}}\frac{\exp[-2n'\tan^{-1}(1/n')]}{[1-\exp(-2\pi n')]^{1/2}}. \tag{3.19}$$

In the Appendix, we calculate $\langle b|z|n'z\rangle$ using the same method that Bethe and Salpeter use to calculate $\langle n'z|z|a\rangle$. The result is that

$$\langle b|z|n'z\rangle=\frac{2^{17/2}a_0(n')^{7/2}[1+(n')^2]^{1/2}\exp[-2n'\tan^{-1}(2/n')]}{\sqrt{3}[(n')^2+4]^3[1-\exp(-2\pi n')]^{1/2}}. \tag{3.20}$$

A bit of thought will convince one that Eqs. (3.4) and (3.19) have the same form as $n\rightarrow\infty$ and $n'\rightarrow\infty$. Similarly, for Eqs. (3.5) and (2.30).

Applying (3.3) to (3.4), (3.5), (3.19), and (3.20) gives (in atomic units with $a_0=1$)

$$\langle nz|p_z|a\rangle=i(8/\sqrt{3})n^{3/2}(n-1)^{n-3/2}(n+1)^{-n-3/2}, \tag{3.21}$$

$$\begin{aligned}
\langle b|p_z|nz\rangle&=0,\quad\text{for}\quad n=2\\
&=-i(32\sqrt{2}/\sqrt{3})n^{3/2}(n^2-1)^{1/2}(n-2)^{n-2}\\
&\quad\times(n+2)^{-n-2},\quad\text{for}\quad n>2
\end{aligned} \tag{3.22}$$

$$\langle n'z|p_z|a\rangle=i\frac{8}{\sqrt{3}}\frac{(n')^{3/2}}{[1+(n')^2]^{3/2}}\frac{\exp[-2n'\tan^{-1}(1/n')]}{[1-\exp(-2\pi n')]^{1/2}}, \tag{3.23}$$

$$\langle b|p_z|n'z\rangle=-i\frac{32\sqrt{2}}{\sqrt{3}}\frac{(n')^{3/2}[1+(n')^2]^{1/2}}{[(n')^2+4]^2}\times\frac{\exp[-2n'\tan^{-1}(2/n')]}{[1-\exp(-2\pi n')]^{1/2}}. \tag{3.24}$$

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[10] G. D. Mahan, Phys. Rev. **170**, 825 (1968).

Using the relationship

$$(n-s)/(n+s)=\exp[-2\tanh^{-1}(s/n)] \quad (s,n \text{ real}), \tag{3.25}$$

which is obtained by analytic continuation of the more familiar relation

$$(n-is)/(n+is)=\exp[-2i\tan^{-1}(s/n)] \quad (s,n \text{ real}), \tag{3.26}$$

we rewrite (3.21) and (3.22) as

$$\langle nz|p_z|a\rangle=i\frac{8}{\sqrt{3}}\frac{n^{3/2}}{(n^2-1)^{3/2}}\exp[-2n\tanh^{-1}(1/n)] \tag{3.27}$$

and

$$\langle b|p_z|nz\rangle=-i\frac{32\sqrt{2}}{\sqrt{3}}\frac{n^{3/2}(n^2-1)^{1/2}}{(n^2-4)^2}\times\exp[-2n\tanh^{-1}(2/n)]. \tag{3.28}$$

We introduce the parameter $r=\hbar\omega_I/|E_{1s}|$, and substitute the relevant matrix elements into (3.2) to obtain

$$\mathcal{M}=\mathcal{M}^{(b)}+\mathcal{M}^{(c)}, \tag{3.29}$$

where $\mathcal{M}^{(b)}$ gives the contribution from the bound states, and $\mathcal{M}^{(c)}$ gives the contribution from the intermediate states in the continuum. We have

$$\mathcal{M}^{(b)}=\frac{512\sqrt{2}}{3}\hat{e}\cdot\hat{e}'\times\sum_{n=3}^{\infty}\frac{n^3\exp[-2n\tanh^{-1}(1/n)-2n\tanh^{-1}(2/n)]}{(n^2-1)(n^2-4)^2}\times\left(\frac{1}{1-(1/n^2)-r}+\frac{1}{\frac{1}{4}-(1/n^2)+r}\right) \tag{3.30}$$

and

$$\operatorname{Re}\{\mathcal{M}^{(c)}\}=-\frac{512\sqrt{2}}{3}\hat{e}\cdot\hat{e}'\int_0^\infty dn'\frac{(n')^3\exp[-2n'\tan^{-1}(1/n')-2n'\tan^{-1}(2/n')]}{[(n')^2+1][(n')^2+4][1-\exp(-2\pi n')]}\times\left(\frac{1}{1+[1/(n')^2]-r}+\frac{1}{\frac{1}{4}+[1/(n')^2]+r}\right), \tag{3.31}$$

$$\begin{aligned}\operatorname{Im}\{\mathcal{M}^{(c)}\}&=0 \quad \text{for} \quad r<1, \quad r\neq 1-\frac{1}{n^2}, \quad \text{where} \quad n=1,2,3\\ &=\frac{512\sqrt{2}}{\sqrt{3}}\frac{\pi(n')^6\exp[-2n'\tan^{-1}(1/n')-2n'\tan^{-1}(2/n')]}{[(n')^2+1][(n')^2+4]^2[1-\exp(-2\pi n')]}\\ &\qquad \text{for} \quad r>1, \quad \text{with} \quad n'=[2(r-1)]^{-1/2}.\end{aligned} \tag{3.32}$$

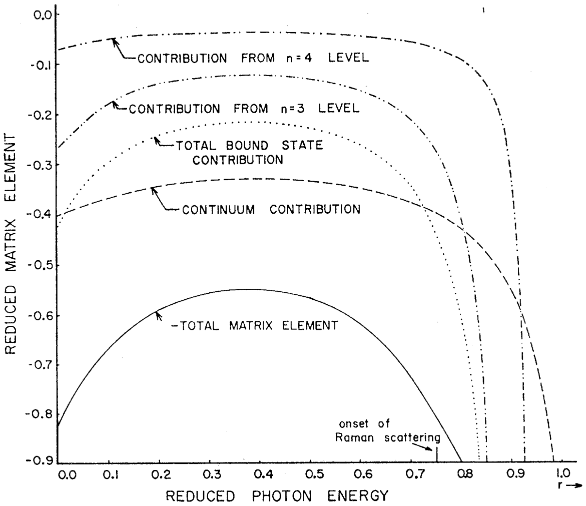

FIG. 1. Reduced Raman matrix element for photon energies below the ionization level. The solid line gives the value of the reduced matrix element M, and the remaining lines give various contributions to M. The following graphical notation is employed: – – –, the contribution from the continuum; · · ·, the contribution from the bound states; · ·–, the contribution from the $n=3$ level only; · – –, the contribution from the $n=4$ level.

Actually, for large n with $r<1$, the quantity $\operatorname{Im}\{\mathcal{M}^{(c)}\}$ is an envelope of δ functions, one for each bound state. Thus, $\operatorname{Im}\{\mathcal{M}^{(c)}\}$ is not really discontinuous, as Eq. (3.32) implies. In fact, level broadening effects cause each δ function to be replaced by an envelope function approximately Lorentzian in form, with a width equal to the intrinsic width of the level.

For large n, where the level breadth is large compared to the level splitting, one may average over the envelope functions to find

$$\operatorname{Im}\{\mathcal{M}^{(c)}\}=\frac{512\sqrt{2}}{\sqrt{3}}\times\frac{\pi n^6\exp[-2n\tanh^{-1}(1/n)-2n\tanh^{-1}(2/n)]}{(n^2-1)(n^2-4)}. \tag{3.33}$$

The quantity n is considered a continuous variable related to r by $n=1/[2(1-r)]^{1/2}$.

We note that the $n=2$ bound state does not contribute, because $\langle b|p_z|nz\rangle$ is zero for $n=2$. We also remark that for r_1 and r_2 related by $r_1+r_2=0.75$, the Raman matrix elements are identical. Thus the Raman matrix element, as a function of r, is symmetrical about

$r=0.375$. The cross section, however, does not have this symmetry.

From Eq. (3.32), we see that for large incoming photon energies (i.e., large r) $\mathrm{Im}\{\mathfrak{M}^{(c)}\}$ varies as $r^{-5/2}$. From Eqs. (3.30) and (3.31), we see that for large r, $\mathfrak{M}^{(b)}$ and $\mathrm{Re}\{\mathfrak{M}^{(c)}\}$ vary as r^{-2}. Thus, $\mathrm{Re}\{\mathfrak{M}\}$ will dominate $|\mathfrak{M}|^2$ for large r. We can derive the coefficient of r^{-2} in the expansion of $\mathrm{Re}\{\mathfrak{M}\}$ in powers of r^{-1}. We can do this by beginning with Eq. (3.1) and taking the limit as $\omega_I \to \infty$. One has

$$\mathrm{Re}\{\mathfrak{M}\} = -\frac{\hat{e}\cdot\hat{e}'}{3m}\sum_i \langle b|\mathbf{p}|i\rangle\cdot\langle i|\mathbf{p}|a\rangle \times\left[\frac{(E_i-E_a)+(E_i-E_b)}{(E_i-E_a-\hbar\omega_I)(E_i-E_b+\hbar\omega_I)}\right]. \quad (3.34)$$

Then after a short calculation, one finds

$$\lim_{\hbar\omega_I\to\infty} \mathrm{Re}\{\mathfrak{M}\} = \frac{\hbar^2 e(\hat{e}\cdot\hat{e}')}{3m(\hbar\omega_I)^2}\left\langle b\left|\nabla^2\left(\frac{e}{r}\right)\right|a\right\rangle \quad (3.35)$$

$$= \frac{4\pi\hbar^2 e^2}{3m(\hbar\omega_I)^2}(\hat{e}\cdot\hat{e}')\psi_b^*(0)\psi_a(0) \quad (3.36)$$

$$= \frac{4\sqrt{2}\hat{e}\cdot\hat{e}'}{3}\frac{(e^2/2a_0)^2}{(\hbar\omega_I)^2} = \frac{4\sqrt{2}}{3}\frac{\hat{e}\cdot\hat{e}'}{r^2}. \quad (3.37)$$

The last result follows upon taking for our problem

$$\psi_b(0) = \psi_{2s}(0) = (8\pi a_0^3)^{-1/2}$$

and

$$\psi_a(0) = \psi_{1s}(0) = (\pi a_0^3)^{-1/2}.$$

In Sec. IV, we write $\mathrm{Re}\{\mathfrak{M}\}$ in a form suitable for numerical computation. The result of Eq. (3.38) will serve as a useful means of checking the computation, since the numerical result should tend to this limit as $r\to\infty$.

Having analyzed $\mathfrak{M}$, the Raman matrix element, we now summarize our results for $d\sigma/d\Omega$, the Raman-scattering cross section. In terms of the quantity r, the Raman-scattering cross section is, from Eq. (2.6),

$$d\sigma/d\Omega = r_0^2[1-(0.75/r)]|\mathfrak{M}|^2. \quad (3.38)$$

For large r, we see that

$$\lim_{r\to\infty} (d\sigma/d\Omega) = r_0^2|\mathfrak{M}|^2. \quad (3.39)$$

For r near the threshold of 0.75 (photons with r below 0.75 do not have enough energy to Raman-scatter the ground state to the first excited state), the Raman cross section is linear in $r-0.75$. This follows because the absence of a contribution of $2p$ state to $\mathfrak{M}$ assures that $\mathfrak{M}$ varies smoothly near $r=0.75$, while the volume of phase space available for the final photon shrinks to zero. One has for $r\approx 0.75$,

$$d\sigma/d\Omega \cong \tfrac{4}{3} r_0^2 (r-0.75)|\mathfrak{M}(0.75)|^2.$$

IV. COMPUTATION AND DISCUSSION

In order to obtain numerical results for $\mathfrak{M}$, we must approximate the summation over the bound states and the integration over continuum states. For the bound states, we explicitly compute the sum from $n=3$ to $n=s$, where s is some large number. We then expand the summand in inverse powers of n and analytically com-

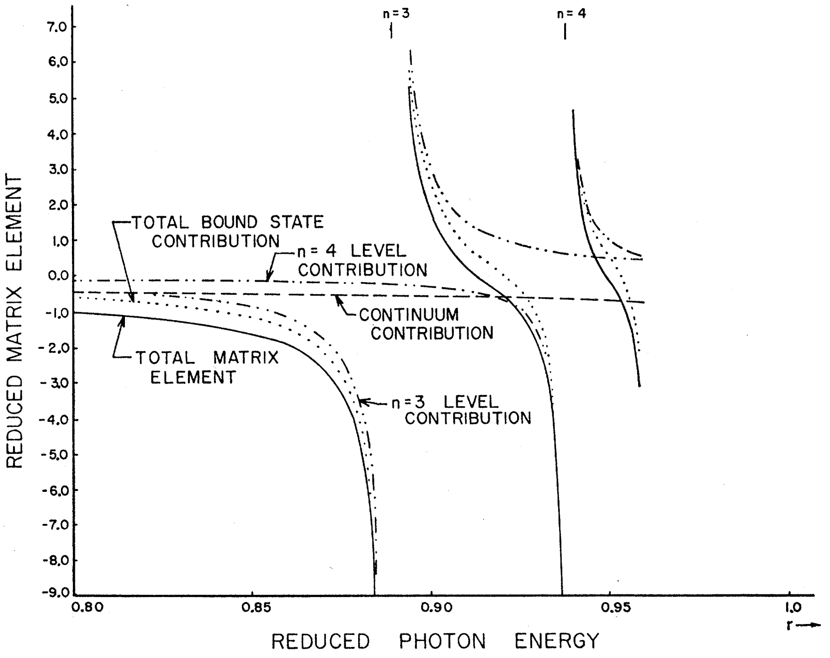

FIG. 2. Reduced Raman matrix element M for photon energies near the $n=3$ and $n=4$ bound levels. The convention is the same as that employed in Fig. 1.

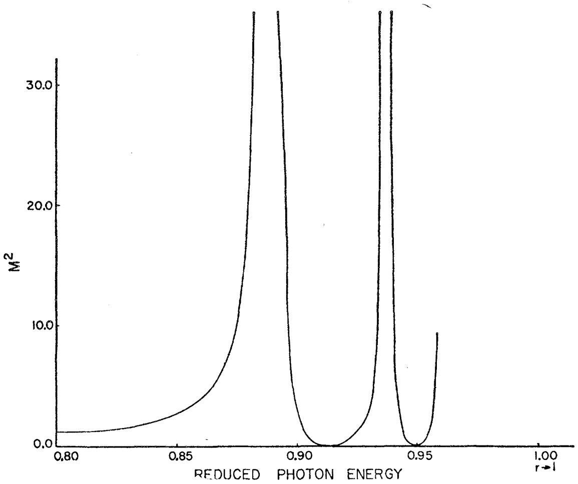

FIG. 3. Square of the reduced Raman matrix element for photon energies near the $n=3$ and $n=4$ bound levels.

pute the first few sums in the expansion. This is done by converting from a sum to an integral via the Euler-Maclaurin formula[11] and then integrating:

$$\sum_{n=s}^{\infty} f(n)=\int_{s}^{\infty} dn\, f(n)+R(s), \tag{4.1}$$

where

$$R(s)=\tfrac{1}{2}f(s)-\tfrac{1}{12}f'(s)+(1/720)f'''(s)+\cdots. \tag{4.2}$$

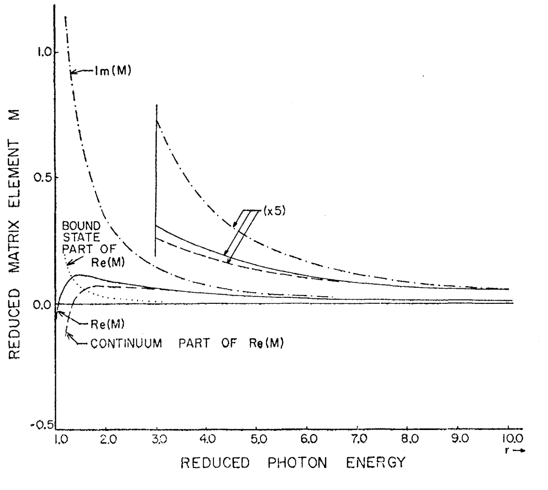

FIG. 4. Reduced matrix element M for photon energies in the vicinity of the continuum edge. The full line is the real part of M, while the dashed line shows the contribution of the continuum states to the real part and the dotted line the contribution of the bound states to the real part. The "dot-dash" line is the imaginary part of M.

The derivatives are computed numerically. The summation is thus computed as

$$\sum_{n=3}^{\infty} f(n)\cong\sum_{n=3}^{s-1} f(n)+R(s)+\int_{s}^{\infty} dn\, \tilde{f}(n), \tag{4.3}$$

where $\tilde{f}(n)$ denotes the first few terms in the expansion of $f(n)$ in inverse powers of n.

Similarly, the integration over bound states is performed as

$$\int_{0}^{\infty} dn'\, g(n')\cong\int_{0}^{t} dn'\, g(n')+\int_{t}^{\infty} dn\, \tilde{g}(n'). \tag{4.4}$$

This procedure hinges upon our ability to integrate the terms in the expansions $\tilde{f}(n)$ and $\tilde{g}(n')$. Fortunately, this presents us with no problems. Since the details of the algebra are tedious but straightforward, we refer the reader elsewhere[12] for details.

In Figs. 1–8, we present our results in graphical form. The figures contain plots for a number of frequency regions of the reduced matrix element M, where $\mathfrak{M}=\hat{e}\cdot\hat{e}'M$.

In Fig. 1, we plot M as a function of frequency for photon energies below the $n=3$ bound-state level. The solid line gives the value of M, and the remaining lines are particular contributions to M that have been isolated in order to give a feeling for their relative importance. In the frequency region illustrated in Fig. 1, the matrix element is very poorly approximated by only the $n=3$ contribution. Notice that a large contribution comes from the continuum states.

In Fig. 2, we present plots of M on a fine frequency scale near the $n=3$ and $n=4$ resonances, along with the various contributions considered in Fig. 1. One can see that the parameter r must be within about 0.02 units from the bound state before the matrix element is dominated by a single term in the sum over intermediate states.

The resonance region around the $n=4$ bound level is considerably narrower than the resonance region around the $n=3$ level. This is because the matrix element connecting the $n=4$ level to the initial ($1s$) and final ($2s$) state is considerably smaller than the matrix element of the $n=3$ level to these states. As n grows larger, the matrix elements get smaller, so the resonance regions become progressively narrower. This point is illustrated more clearly in Fig. 3, where we plot the square of the total reduced matrix element $|M|^2$ for photon energies in the vicinity of the $n=3$ and $n=4$ bound levels.

In Fig. 4, we give a plot of M for photon frequencies between the ionization threshold and 10 times the ionization energy. The real part of M is exhibited as the solid line and the imaginary part as the "dot-dash" line. The bound state and continuum contributions are given separately. As the variable $r\to 1$ from above,

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[11] See *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, D. C., 1964), p. 806.

[12] W. M. Saslow, thesis, University of California, 1968 (unpublished).

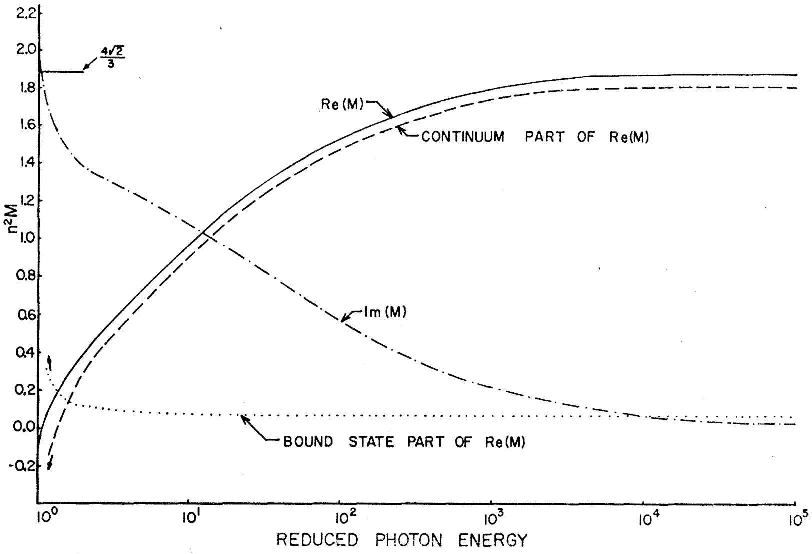

FIG. 5. Plot of r^2M as a function of r for large exciting frequencies. The same convention is employed here as in Fig. 4.

the imaginary part approaches a finite limit near 2 in value. The real part is also finite, although the bound state and continuum contributions each diverge. The reason for the cancellation of the divergencies in the real part was discussed above. It is interesting to note that in the region $1<r<10$, the imaginary part of the matrix element is larger than the real part. This is particularly true for r near 1, where the imaginary part of r is in fact much larger than the real part.

In the limit as $r\rightarrow\infty$, the discussion above shows that $\mathrm{Im}(M)\rightarrow 0$ faster than $\mathrm{Re}(M)$, so eventually the real part of M must dominate. That this is so is evident from Fig. 5, where we plot $r^2\mathrm{Re}(M)$ and $r^2\mathrm{Im}(M)$ for large values of r. One sees that for $r\gg 10$, $\mathrm{Im}(M)\ll\mathrm{Re}(M)$.

Actually, in Sec. II it was remarked that the electric dipole approximation breaks down in the region $r>275$. Thus, the values of M exhibited in Fig. 6 for r greater than this value cannot be applied to give an accurate estimate of the cross section. However, the curves are still of interest, because the approach to the asymptotic region of large r of the mathematical form M may then be studied.

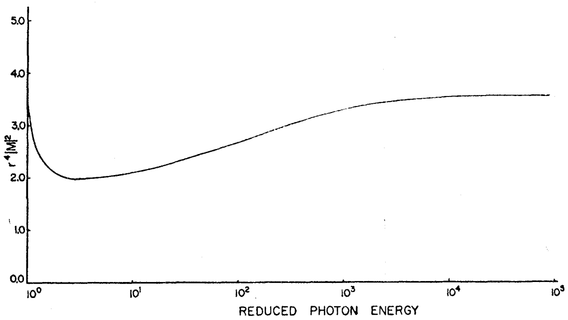

FIG. 6. Quantity $r^4|M|^2$ plotted as a function of the reduced photon energy r for large values of r.

Finally, in Fig. 6, we plot the quantity $r^4|M|^2$ for a wide range of values of $r>1$. Recall from the discussion above that one expects that $r^4|M|^2$ will approach the constant $(32/9)=3.55$ as $r\rightarrow\infty$. From Fig. 6, one sees that $r^4|M|^2=A(r)$ is a slowly varying function of frequency, since for all r, $A(r)$ lies between 2.0 and 3.6. Thus, the matrix element $|M|^2$ varies roughly as r^{-4} for all $r>5$ or so. However, the true asymptotic region, where $\mathrm{Im}(\mathfrak{M})\ll\mathrm{Re}(M)\approx 4\sqrt{2}/3r^2$, is not attained until r is in the range 10^3–10^4 (where, in fact, the electric dipole approximation breaks down).

V. CONCLUSIONS

We have carried out a detailed investigation of the frequency dependence and magnitude of the cross section of the Raman scattering of light by one of the simplest quantum-mechanical systems, the one-electron hydrogenlike atom. There are two features of the calculation we feel are of general interest. First, when the energy of the exciting light is near a resonance associated with a bound-state–bound-state transition, the Raman matrix element is given accurately by the single intermediate-state approximation when the photon frequency is quite close to the resonance. Second, when the photon frequency lies in the range of a continuum of allowed transitions, the matrix element acquires an imaginary part. We find that for an important range of photon energies, the imaginary part of the matrix element is in fact large compared to the real part. While this may not be true in general, it is clear from this work that one must not ignore the imaginary part of the Raman-scattering matrix element.

ACKNOWLEDGMENT

We have enjoyed discussions with Professor E. Burstein about several aspects of this work.

APPENDIX

Bethe and Salpeter calculate the quantity $\langle E_{n'}z|z|a\rangle$, where $E_{n'}=\frac{1}{2}(n')^2$. After the angular integration is done, $\langle E_{n'}z|z|a\rangle$ takes the form

$$\langle E_{n'}z|z|a\rangle=\frac{1}{\sqrt{3}}\int_0^\infty [R_{E_{n'},l=1}(r)]^*\times 2e^{-r}r^3dr. \quad \text{(A1)}$$

On using the integral representation,

$$R_{E_{n'},l=1}=\frac{2[1+(n')^2]^{1/2}}{[1-\exp(-2\pi n')]^{1/2}}(n')^2\left(\frac{1}{2r}\right)^2 \times\frac{1}{2\pi}\int e^{-2ir\xi/n'}(\xi+\tfrac{1}{2})^{-in'-2}(\xi-\tfrac{1}{2})^{in'-2}d\xi, \quad \text{(A2)}$$

where the integration contour is defined in Fig. 7, Eq. (A1) becomes

$$\langle E_{n'}z|z|a\rangle=\frac{(n')^2[1+(n')^2]^{1/2}}{4\pi\sqrt{3}[1-\exp(-2\pi n')]^{1/2}}\int_0^\infty dr\, r2e^{-r} \times\int e^{-2ir\xi/n'}(\xi+\tfrac{1}{2})^{-in'-2}(\xi-\tfrac{1}{2})^{in'-2}d\xi. \quad \text{(A3)}$$

Interchanging the order of integration, we have

$$\langle E_{n'}z|z|a\rangle=\frac{(n')^2[1+(n')^2]^{1/2}}{4\pi\sqrt{3}[1-\exp(-2\pi n')]^{1/2}}\int (\xi+\tfrac{1}{2})^{-in'-2} \times(\xi-\tfrac{1}{2})^{in'-2}d\xi\int_0^\infty dr\, re^{-2ir\xi/n'}2e^{-r}. \quad \text{(A4)}$$

The r integration can be done explicitly, giving an expression which exhibits a pole. By deforming the contour of integration to surround this pole (see Fig. 8) and using the method of residues, $\langle E_{n'}z|z|a\rangle$ may be obtained explicitly. The relation

$$\langle n'z|z|a\rangle=\sqrt{2}(n')^{3/2}\langle E_{n'}z|z|a\rangle$$

enables us to put the result in a more useful form.

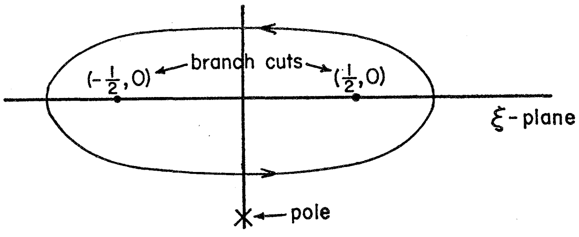

FIG. 7. Integration contour for Eq. (A2).

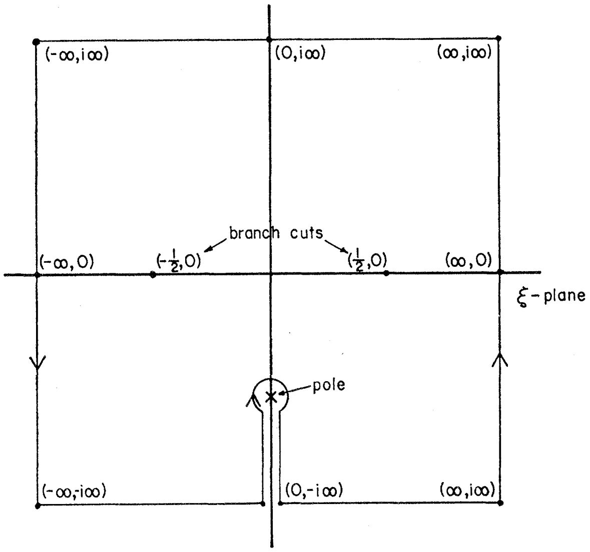

FIG. 8. Integration contour for Eq. (A4).

To obtain $\langle b|z|E_{n'}z\rangle$, we need only to modify the above procedure by replacing the $1s$ radial eigenfunction $2e^{-r}$ by the $2s$ radial eigenfunction $(1/\sqrt{2})(1-\frac{1}{2}r)e^{-r/2}$. Then

$$\langle b|z|n'z\rangle=\sqrt{2}(n')^{3/2}\langle b|z|E_{n'}z\rangle =\frac{\sqrt{2}(n')^{7/2}[1+(n')^2]^{1/2}}{4\pi\sqrt{3}[1-\exp(-2\pi n')]^{1/2}} \times\int (\xi+\tfrac{1}{2})^{-in'-2}(\xi-\tfrac{1}{2})^{in'-2}d\xi \times\int_0^\infty dr\, re^{-2ir\xi/n'}\frac{1}{2\sqrt{2}}\left(1-\frac{r}{2}\right)e^{-r/2}. \quad \text{(A5)}$$

Performing the r integration, we obtain

$$\langle b|z|n'z\rangle=\frac{(n')^{7/2}[1+(n')^2]^{1/2}}{8\pi\sqrt{3}[1-\exp(-2\pi n')]^{1/2}} \times\int (\xi+\tfrac{1}{2})^{-in'-2}(\xi-\tfrac{1}{2})^{in'-2}\left(\frac{1}{\lambda^2}-\frac{1}{\lambda^3}\right)d\xi, \quad \text{(A6)}$$

where $\lambda=\frac{1}{2}+2i\xi/n'$. On applying the method of residues, the term in $1/\lambda^2$ gives no contribution, but the term in $1/\lambda^3$ does contribute, in the amount given by Eq. (3.20).