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Collective Properties of Polyatomic Gases in a Magnetic Field: Effects on Light Scattering Spectrum

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The effect of magnetic fields on collective properties of polyatomic gases has been extended outside the hydrodynamic regime. The calculations are based on a linearized Waldmann–Snider equation. The Waldmann–Snider collision operator is truncated yielding a finite matrix equation. The resulting matrix equation is solved on a computer to yield the polarized and depolarized light scattering spectra. These spectra are calculated in the absence and presence of a magnetic field. For long wavelengths it is found that the magnetic effects are of the same order of magnitude as in the Senftleben–Beenakker effects. For shorter wavelengths the effects disappear due to Doppler effects.

KEY WORDS: Senftleben–Beenakker effects; hydrodynamics; light scattering; Waldmann–Snider equation; generalized hydrodynamics; projection operator techniques.

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1. INTRODUCTION

The first indication that collective properties of polyatomic gases are affected by a magnetic field was given by Senftleben(1) in 1930 when he observed that the thermal conductivity of oxygen was changed by a few per cent by the application of a field. The corresponding effect on the shear viscosity was seen by Engelhardt and Sack(2) in 1932. A similar effect was seen for nitric oxide but nothing at the time was observed for diamagnetic gases. However, in 1962 Beenakker *et al.*(3) demonstrated experimentally that the shear viscosity of carbon monoxide showed field effects similar to those of the paramagnetic gases. The corresponding thermal conduction effect was observed by Gorelik and Sinitsyn(4) in 1964.

The field effects on the transport coefficients are now well understood in terms of the coupling of the rotational magnetic moment of a polyatomic molecule to the magnetic field. Taking into account this coupling, McCourt and Snider(5) have calculated the transport coefficients in a static field for molecules having a constant g factor using the Waldmann–Snider(6) (WS) transport equation. Their analysis was extended to include collinear static and oscillatory magnetic fields by Fleming and Martin(7) and Roden *et al.*(8) Fleming and Martin have extended the analysis to include a distribution of molecular magnetic moments, which is important when discussing paramagnetic gases. A more extensive discussion of field effects on transport properties is contained in the excellent review by Beenakker and McCourt.(9)

If the transport coefficients of a polyatomic gas are affected by a magnetic field, then there will be a corresponding effect on the hydrodynamic(10) equations for the gas. In this work we have extended the theory of the collective behavior of polyatomic gases outside the hydrodynamic regime. We expect this extended theory to be useful in the analysis of neutron and light scattering experiments. Our calculation of the depolarized light scattering spectrum includes the rotational Raman lines as well as the Rayleigh line. This extends the calculations of Hess,(11) who treated only the Rayleigh line.

2. KINETIC THEORY

In order to calculate the collective properties of polyatomic gases we need a kinetic equation which includes internal degrees of freedom and can be extended to shorter than hydrodynamic wavelengths. An equation(12) is used which is an extension of the WS equation:

$$[z - (\mathbf{p} \cdot \mathbf{k}/m)]\, G(\mathbf{k}\mathbf{p}\mathbf{p}'z) - \int d\bar{\mathbf{p}}\, \Omega(\mathbf{p}\bar{\mathbf{p}})\, G(\mathbf{k}\bar{\mathbf{p}}\mathbf{p}'z) = \delta(\mathbf{p} - \mathbf{p}')\, 1_2 \qquad (1)$$

where $\mathbf{k}$ is the wave vector and z is a complex frequency such that $\operatorname{Im} z > 0$. Here G is an analytic function of z in the upper half-plane. In addition to the explicit dependence on the spatial variables, G is also a two-particle operator in the direct product space of internal variables. 1_2 is the corresponding unit operator in that space. If $f_{\lambda\lambda'}(\mathbf{rp}t)$ is the Wigner operator at position $\mathbf{r}$ and momentum $\mathbf{p}$ at time t corresponding to internal states labeled by λ and λ', then G is related to the correlation function of two f's[12] by

$$G(\mathbf{kp'}z)f_0(\mathbf{p}') = (1/i)\int_0^\infty dt\, d(\mathbf{r}-\mathbf{r}')[\exp(izt)]\{\exp[-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')]\}$$
$$\times \langle\{[f(\mathbf{rp}t) - \langle f(\mathbf{rp}t)\rangle], [f(\mathbf{r}'\mathbf{p}'t') - \langle f(\mathbf{r}'\mathbf{p}'t')\rangle]\}\rangle \quad (2)$$

where the labels λ, λ' are implicit, the brackets $\langle\ \rangle$ denote the equilibrium expectation value, and

$$f_0(\mathbf{p}) = \langle f(\mathbf{rp}t)\rangle = (n/Q^{\text{int}})(\beta/2\pi m)^{3/2}\exp\{-\beta[(p^2/2m) + H^{\text{int}}]\} \quad (3)$$

H^{int} is the single-particle contribution to the internal-state Hamiltonian and $Q^{\text{int}} = \operatorname{tr}\exp(-\beta H^{\text{int}})$ is the internal-state partition function. In Eq. (1) the notation $\int d\bar{\mathbf{p}}$ is used to denote simultaneously integration over $\bar{\mathbf{p}}$ and a trace over internal variables. The kernal Ω of Eq. (1) consists of two parts:

$$\Omega(\mathbf{pp}') = [H^{\text{int}}, 1_2]\,\delta(\mathbf{p}-\mathbf{p}') + \Omega^c(\mathbf{pp}') \equiv \Omega^{\text{int}}(\mathbf{pp}') + \Omega^c(\mathbf{pp}') \quad (4)$$

The first term contains all the single-particle contributions of the internal variables to the dynamics, while Ω^c contains the effects of two-body collisions. The explicit form of Ω^c in terms of the full two-particle transition matrix of the system is given in Appendix A.

Equation (1) is consistent for low frequencies and long wavelengths with the correct hydrodynamic behavior in terms of the transport coefficients calculated from the same equation. However, since the terms discarded in deriving Eq. (1)[12] are of higher order in the density, we expect it to be a good approximation for dilute gases for all frequencies and wavelengths in the same sense that the ordinary Boltzmann equation is a good approximate equation for all frequencies and wavelengths for atomic gases. We therefore examine the solution of (1) as a function of $\mathbf{k}$ and z. In particular we shall be interested in the density–density correlation function $S(\mathbf{k}\omega)$, which is related to G by

$$S(\mathbf{k}\omega) = -2\operatorname{Im}\int d\mathbf{p}\, d\mathbf{p}'\, G(\mathbf{kpp}'\omega + i\epsilon)f_0(\mathbf{p}') \quad (5)$$

and which is directly measured in neutron scattering and polarized light scattering.

For depolarized light scattering we shall be concerned with the orientational correlation function

$$S^{l}_{mm'}(\mathbf{k}\omega) = -2\,\mathrm{Im} \int d\mathbf{p}\, d\mathbf{p}'\, Y^{\dagger}_{lm}(\theta\phi)\, G(\mathbf{kpp}'\omega + i\epsilon)\, Y_{lm'}(\theta\phi) f_0(\mathbf{p}') \quad (6)$$

where $Y_{lm}(\theta\phi)$ is a spherical harmonic of the molecular orientation specified by the angles θ and ϕ. It can be shown(13) that $S^{2}_{mm'}$ describes the depolarized light scattering for a gas of linear molecules.

In order to examine the nature of the solution to Eq. (1), assume that the Hamiltonian consists of two parts

$$H^{\mathrm{int}} = H^{\mathrm{int}}_0 - \gamma \mathbf{J} \cdot \mathbf{H} \quad (7)$$

where **J** is the total internal angular momentum of a molecule and **H** is a static magnetic field. H^{int}_0 is the internal Hamiltonian in the absence of any external field. H^{int}_0 is therefore rotationally invariant and hence commutes with **J**:

$$[\mathbf{J}, H^{\mathrm{int}}_0] = 0 \quad (8)$$

In Eq. (7) $\gamma = g_J \mu_N$ ($\hbar = 1$) is the gyromagnetic ratio with g_J the Landé g factor and μ_N the nuclear magneton. In general g_J should be treated as a scalar operator in the internal-state space. However, for simplicity g_J is treated as a constant. The generalization to include the operator character of g_J is straightforward and can be handled by the method introduced in Ref. 7.

It is readily shown that Eq. (1) is consistent with the conservation laws of particles, momentum, and energy.[6] This can be seen since

$$\int d\mathbf{p} \begin{pmatrix} 1 \\ \mathbf{p} \\ p^2/2m + H^{\mathrm{int}} \end{pmatrix} \Omega(\mathbf{pp}') = 0 \quad (9)$$

It is convenient therefore to think of Eq. (1) in terms of the Hilbert space defined by the set of all functions of **p** and internal variables with scalar product defined by

$$\langle \psi \mid \Phi \rangle = (1/n) \int d\mathbf{p}\, \psi(\mathbf{p})\, \Phi(\mathbf{p}) f_0(\mathbf{p}) \equiv \langle \psi(\mathbf{p})\, \Phi(\mathbf{p}) \rangle \quad (10)$$

where n is the number density.

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[6] Equation (1) is not, however, consistent with conservation of angular momentum. This point has been discussed extensively in Ref. 12.

The conserved variables form a five-dimensional subspace of this Hilbert space. We represent this subspace in terms of the orthonormal basis functions

$$\begin{gathered}\langle \mathbf{p} \mid 1\rangle \equiv \psi_1(\mathbf{p}) = 1, \qquad \langle \mathbf{p} \mid 2\rangle \equiv \psi_2(\mathbf{p}) = (\beta/m)^{1/2}\,\mathbf{p} \\ \langle \mathbf{p} \mid 3\rangle \equiv \psi_3(\mathbf{p}) = (\beta/\sqrt{c_v})[(p^2/2m) - (3/2\beta) + H^{\text{int}} - \langle H^{\text{int}}\rangle]\end{gathered} \tag{11}$$

where c_v is the specific heat of the gas.

Equation (1) can be projected into this subspace to give a "matrix" equation of the form

$$[z\delta_{\alpha\beta} - \Sigma_{\alpha\gamma}(\mathbf{k}z)]\, G_{\gamma\beta}(\mathbf{k}z) = \delta_{\alpha\beta} \qquad \alpha, \beta, \gamma = 1, 2, 3 \tag{12}$$

where a summation convention is employed over repeated indices,

$$\begin{aligned} G_{\alpha\beta}(\mathbf{k}z) &= \langle \alpha \mid G(\mathbf{k}z) | \, \beta\rangle \equiv \langle \alpha \mid 1/[z - (\mathbf{p}\cdot\mathbf{k}/m) - \Omega] | \, \beta\rangle \\ &= (1/n) \int d\mathbf{p}\, d\mathbf{p}'\, \psi_\alpha(\mathbf{p})\, G(\mathbf{k}\mathbf{p}\mathbf{p}'z)\, \psi_\beta(\mathbf{p}') \end{aligned}$$

and "mass operator"

$$\begin{aligned} \Sigma_{\alpha\beta}(\mathbf{k}\mathbf{z}) \equiv & \left\langle \alpha \,\middle|\, \frac{\mathbf{p}\cdot\mathbf{k}}{m} \,\middle|\, \beta \right\rangle \\ & + \left\langle \alpha \,\middle|\, \frac{\mathbf{p}\cdot\mathbf{k}}{m}\, Q\, \frac{1}{z - Q[(\mathbf{p}\cdot\mathbf{k}/m) + \Omega]\, Q}\, Q\, \frac{\mathbf{p}\cdot\mathbf{k}}{m} \,\middle|\, \beta \right\rangle \end{aligned}$$

with $Q = 1 - P$ and $P = \sum_{\alpha=1}^{3} | \, \alpha\rangle\langle\alpha \, |$. Formally, Eq. (12) is an exact projection of Eq. (1) onto the subspace of conserved quantities. In effect all we have done is to shift the emphasis from calculating the operator

$$G(\mathbf{k}z) = 1/[z - (\mathbf{p}\cdot\mathbf{k}/m) - \Omega] \tag{13}$$

to calculating the memory operator

$$K(\mathbf{k}z) = Q\, \frac{1}{z - Q(\mathbf{p}\cdot\mathbf{k}/m) + \Omega}\, Q = Q\, \frac{1}{z - Q(\mathbf{p}\cdot\mathbf{k}/m)\, Q - \Omega}\, Q \tag{14}$$

since $P\Omega = \Omega P = 0$.

Equation (12) is exactly equivalent to Eq. (1). Our method of approximate solution for K will be outlined later. We first notice that the Σ matrix can be put into the especially suggestive form

$$\begin{pmatrix} 0 & \left(\dfrac{m}{\beta}\right)^{1/2} \dfrac{\mathbf{k}}{m} & 0 \\ \left(\dfrac{m}{\beta}\right)^{1/2} \dfrac{\mathbf{k}}{m} & -i\, \dfrac{\mathbf{k}\cdot\boldsymbol{\eta}(\mathbf{k}z)\cdot\mathbf{k}}{mn} & \left(\dfrac{m}{\beta c_v}\right)^{1/2} \dfrac{\mathbf{k}}{m} - \left(\dfrac{\beta}{mc_v}\right)^{1/2} \mathbf{k}\cdot\mathbf{B}_{TJ_q}(\mathbf{k}z) : \mathbf{k}\mathbf{k} \\ 0 & \left(\dfrac{m}{\beta c_v}\right)^{1/2} \dfrac{\mathbf{k}}{m} - \left(\dfrac{\beta}{mc_v}\right)^{1/2} \mathbf{k}\mathbf{k} : \mathbf{B}_{J_qT}(\mathbf{k}z)\cdot\mathbf{k} & -i\, \dfrac{\mathbf{k}\cdot\boldsymbol{\varkappa}(\mathbf{k}z)\cdot\mathbf{k}}{c_v k_B n} \end{pmatrix} \tag{15}$$

where

$$\boldsymbol{\eta}(\mathbf{k}z) = in\,\beta \left\langle T \,\middle|\, Q \frac{1}{z - Q(\mathbf{p}\cdot\mathbf{k}/m)\,Q - \Omega}\, Q \,\middle|\, T \right\rangle$$

$$\boldsymbol{\varkappa}(\mathbf{k}z) = in\,\frac{\beta}{T} \left\langle J_\epsilon \,\middle|\, Q \frac{1}{z - Q(\mathbf{p}\cdot\mathbf{k}/m)\,Q - \Omega}\, Q \,\middle|\, J_\epsilon \right\rangle$$

$$\mathbf{B}_{TJ_q}(\mathbf{k}z) = -n\beta \left\langle T \,\middle|\, Q \frac{1}{z - \Omega}\, Q \frac{p}{m}\, Q \frac{1}{z - Q(\mathbf{p}\cdot\mathbf{k}/m)\,Q - \Omega}\, Q \,\middle|\, J_\epsilon \right\rangle$$

$$\mathbf{B}_{J_qT}(\mathbf{k}z) = -n\beta \left\langle J_\epsilon \,\middle|\, Q \frac{1}{z - \Omega}\, Q \frac{p}{m}\, Q \frac{1}{z - Q(\mathbf{p}\cdot\mathbf{k}/m)\,Q - \Omega}\, Q \,\middle|\, T \right\rangle$$

The stress tensor T and heat current J_ϵ are represented by

$$\langle \mathbf{p} \mid T \rangle = \mathbf{pp}/m \tag{16a}$$

and

$$\langle \mathbf{p} \mid J_\epsilon \rangle = [(p^2/2m) + H^{\text{int}}]\,\mathbf{p} \tag{16b}$$

$\boldsymbol{\eta}$, $\boldsymbol{\varkappa}$, and the **B**'s are generalized transport coefficients defined such that

$$\lim_{z\to 0}\lim_{\mathbf{k}\to 0} \boldsymbol{\eta}(\mathbf{k}z) = \boldsymbol{\eta} \equiv \eta_v \mathbf{11} + \boldsymbol{\eta}_s \tag{17a}$$

the viscosity, a fourth-rank tensor (η_v is the bulk viscosity and $\boldsymbol{\eta}_s$ the shear viscosity),

$$\lim_{z\to 0}\lim_{\mathbf{k}\to 0} \boldsymbol{\varkappa}(\mathbf{k}z) = \boldsymbol{\varkappa} \tag{17b}$$

the thermal conductivity a second-rank tensor, and

$$\lim_{z\to 0}\lim_{\mathbf{k}\to 0} \mathbf{B}_{TJ_q}(\mathbf{k}z) = \mathbf{B}_{TJ_q} = \mathbf{B}_{J_qT} \tag{17c}$$

The **B**'s are fourth-rank tensors and are usually called Burnett⁽¹⁴⁾ coefficients.

The equations of motion of the conserved variables are of the form of generalized Burnett equations. This is to be contrasted with the usual treatments of "generalized hydrodynamics"⁽¹⁵⁾ which are generalizations of the Navier–Stokes equations. However, when pushed to full generality the generalized hydrodynamic procedure must yield equations very similar to ours.⁽¹⁶⁾ Once we have an expression for K we can solve Eq. (12); in particular we would obtain the density correlation function

$$S(\mathbf{k}\omega) = -2n\,\mathrm{Im}\,G_{11}(\mathbf{k}\omega + i\epsilon) \tag{17d}$$

3. HYDRODYNAMIC LIMIT

It is clear from (14) that in the limit of low frequencies and long wavelengths our equations reduce to the ordinary linearized Navier–Stokes equations. In the presence of a magnetic field the transport coefficients are no longer isotropic. There are five independent components of the shear viscosity and three independent components of the thermal conductivity. As a result the damping coefficients implied by the Navier–Stokes equations will depend upon the direction of the vector **k** relative to the magnetic field **H**. With this in mind it is straight forward to generalize the treatment of the hydrodynamic behavior of correlations of conserved quantities as presented by Kadanoff and Martin(17) to include anisotropic transport coefficients. Since the field effects on the transport coefficients are typically of the order of a few per cent, the mixing of transverse and longitudinal modes due to the field can be neglected. Thus we obtain for the density–density correlation function

$$S(\mathbf{k}\omega) = \frac{n}{\beta}\left(\frac{\partial n}{\partial p}\right)_T \left\{\frac{D_2k^2[1-(c_v/c_p)]}{\omega^2+(D_2k^2)^2} + \frac{D_1k^4c_1(2c_v/c_p) - D_2k^2(\omega^2-c_1{}^2k^2)[1-(c_v/c_p)]}{(\omega^2-c_1{}^2k^2)^2+(D_1k^2\omega)^2}\right\} \tag{18}$$

where

$$D_1 = \frac{\eta_{3333}}{m\eta} + \frac{\kappa_{33}}{m\eta}\left(\frac{1}{c_v}-\frac{1}{c_p}\right), \qquad D_2 = \frac{\kappa_{33}}{mc_p}, \qquad c_1{}^2 = \frac{1}{m}\left(\frac{\partial p}{\partial n}\right)_s$$

The elements of the transport coefficients are calculated in the Cartesian basis defined by the three unit vectors

$$\hat{e}_3 = \hat{k}, \qquad \hat{e}_1 = (\hat{H} - \cos\theta\hat{k})/\sin\theta, \qquad \hat{e}_2 = (\hat{k}\times\hat{H})/\sin\theta$$

with $\cos\theta = \hat{k}\cdot\hat{H}$.

It was shown in Ref. 7 that a convenient representation for the transport coefficients is

$$\boldsymbol{\kappa} = \kappa_{\|}\hat{H}\hat{H} + \kappa_{\perp}(1-\hat{H}\hat{H}) + \kappa_{\mathrm{tr}}\boldsymbol{\epsilon}\cdot\hat{H}$$

and

$$\boldsymbol{\eta} = \eta_v\mathbf{11} + \sum_{\mu}\eta_\mu\mathbf{e}_\mu\mathbf{e}_\mu \tag{19}$$

$\boldsymbol{\epsilon}$ is the isotropic third-rank tensor and

$$\{\mathbf{e}_\mu\}: \qquad \mathbf{e}_0 = \sqrt{\tfrac{3}{2}}\,(\hat{H}\hat{H}-\tfrac{1}{3}\mathbf{1}), \qquad \mathbf{e}_{\pm1} = (1/\sqrt{2})\{\hat{e}_\pm, \hat{H}\}$$

$$\mathbf{e}_{\pm2} = \hat{e}_\pm\hat{e}_\pm, \qquad \hat{e}_\pm = (1/\sqrt{2})(\hat{e}_3\sin\theta - \hat{e}_1\cos\theta \pm i\hat{e}_2)$$

In terms of this basis the appropriate components of the transport coefficients are

$$\eta_{3333} = \eta_v + \tfrac{3}{2}\eta_0(\cos^2\theta - \tfrac{1}{3})^2 + \tfrac{1}{4}(\eta_1+\eta_{-1})\sin^2\theta + \tfrac{1}{4}(\eta_2+\eta_{-2})\sin^4\theta$$

$$\kappa_{33} = \kappa_{11}\cos^2\theta + \kappa_{\perp}\sin^2\theta \tag{20}$$

The corresponding expressions for the density–energy correlation function $S_{n\epsilon}(k\omega)$ and energy–energy correlation function $S_{\epsilon\epsilon}(\mathbf{k}\omega)$ are

$$\begin{aligned} S_{n\epsilon}(\mathbf{k}\omega) &= \left(\frac{\partial n}{\partial \beta}\right)_p \left(\frac{D_2k^2}{\omega^2 + (D_2k^2)^2} - \frac{D_1k^2(\omega^2 - c_1{}^2k^2)}{(\omega^2 - c_1{}^2k^2)^2 + (D_1k^2\omega)^2}\right) \\ &\quad + \frac{\epsilon + p}{n} S_{nn}(\mathbf{k}\omega) \qquad (21) \\ S_{\epsilon\epsilon}(\mathbf{k}\omega) &= \frac{mnc_pD_2k^2}{\omega^2 + (D_2k^2)^2} + 2\,\frac{\epsilon + p}{n} S_{n\epsilon}(\mathbf{k}\omega) + \left(\frac{\epsilon + p}{n}\right)^2 S_{nn}(\mathbf{k}\omega) \end{aligned}$$

where n, ϵ, and p are the number density, energy density, and pressure of the equilibrium system, respectively.

Even though the coupling of the transverse and longitudinal modes is negligible, we must take into account the splitting of the usual twofold degenerate transverse diffusive modes(17) due to the presence of the field. In terms of the basis defined in (2) the transverse momentum correlation functions are of the form

$$\begin{aligned} S^T_{gg}(\mathbf{k}\omega) &= \frac{mn/\beta}{[\omega^2 + (D^1k^2)^2][\omega^2 + D^2k^2)^2]} \\ &\times \begin{pmatrix} \omega^2D^{11}k^2 + [D^{11}D^{22} - (D^{12})^2]\,D^{22}k^6 & -D^{12}k^2\{\omega^2 - k^4[D^{11}D^{22} - (D^{12})^2]\} \\ -D^{12}k^2\{\omega^2 - k^4[D^{11}D^{22} - (D^{12})^2]\} & \omega^2D^{22}k^2 + [D^{11}D^{22} - (D^{12})^2]\,D^{11}k^6 \end{pmatrix} \end{aligned} \qquad (22)$$

where

$$D^{11} = \eta_{3113}/mn, \qquad D^{12} = \eta_{3123}/mn, \qquad D^{22} = \eta_{3223}/mn$$

and

$$\left.\begin{matrix} D^1 \\ D^2 \end{matrix}\right\} = \frac{D^{11} + D^{22} \pm [(D^{11} - D^{22})^2 - 4(D^{12})^2]^{1/2}}{2}$$

In terms of our invariant representation of the transport coefficients the components of the viscosity are

$$\begin{aligned} \eta_{3113} &= [\tfrac{3}{8}\eta_0 + \tfrac{1}{16}(\eta_2 + \eta_{-2})] \sin^2 2\theta + \tfrac{1}{4}(\eta_1 + \eta_{-1}) \cos^2 2\theta \\ \eta_{3223} &= \tfrac{1}{4}(\eta_1 + \eta_{-1}) \cos^2 \theta + \tfrac{1}{4}(\eta_2 + \eta_{-2}) \sin^2 \theta \qquad (23) \\ \eta_{3123} &= -\tfrac{1}{4}i(\eta_1 - \eta_{-1}) \cos 2\theta \cos \theta - \tfrac{1}{8}i(\eta_2 - \eta_{-2}) \sin 2\theta \sin \theta \end{aligned}$$

The specific expressions for the transport coefficients in the presence of the magnetic field are approximately given by (7,8)

$$\begin{aligned} \eta_\mu &= 2\eta \left[1 - \xi^2 \frac{i\mu h_s/\Gamma_{88}}{1 + (i\mu h_s/\Gamma_{88})}\right], \qquad \kappa_\parallel = \kappa \left[1 - a_0 \frac{(h_s/\Gamma_{99})^2}{1 + (h_s/\Gamma_{99})^2}\right] \\ \kappa_\perp &= \kappa \left[1 - a_0 \left(\frac{1}{2} \frac{(h_s/\Gamma_{99})^2}{1 + (h_s/\Gamma_{99})^2} + \frac{(2h_s/\Gamma_{99})^2}{1 + (2h_s/\Gamma_{99})^2}\right)\right] \end{aligned} \qquad (24)$$

Table I[a]

Gas	ξ^2	a_0/ξ^2	h_s/Γ_{88}	Γ_{88}/Γ_{99}
N_2	0.003	3.5	$0.000144H/P$	0.490
CO	0.00375	2.19	$0.000110H/P$	0.570
CH_4	0.00077	3.57	$0.0000485H/P$	0.288

[a] H in Oe, P in Torr.

where η and κ are the viscosity and thermal conductivity of the gas in the absence of the field; $h_s = \gamma H$ is the precession frequency of the molecular magnetic moment; Γ_{88} and Γ_{99} are molecular collision frequencies which will be defined in the next section; ξ^2 and a_0 are dimensionless parameters of the order of the square of the deviation from sphericity of the molecules.

The parameters in Eq. (24) can be obtained from direct transport measurements in the presence of a magnetic field. Typical values of these parameters as determined from experiments by Korving *et al.*(18) are given in Table I. Since $S(\mathbf{k}\omega)$ gives the spectrum of polarized light, the magnetic field effects on the transport coefficients should be seen in the experimental linewidths of light scattering experiments.

4. EXTENSION TO SHORTER WAVELENGTHS

In order to solve Eq. (12) for arbitrary frequencies and wave numbers, certain assumptions about the form of the collision kernal Ω^c must be made. This must be done in a way which is consistent with approximate calculations of transport coefficients. This assures that the solution will have the correct hydrodynamic limit. Assume that Ω^c is of the form

$$\Omega^c = \Omega_0 + Q_0(\delta\Omega)\, Q_0 \tag{25}$$

where Ω_0 is a constant and Q_0 is a projector on a subspace of the Q subspace. If $\Omega_0 = 0$ and $Q_0 = Q$, Eq. (25) is exact. By keeping only a finite subset Q_0 of Q, it is hoped that all of the important physics of the collective properties will be retained. By projecting out the conserved variables, we have separated all the slowly decaying quantities at long wavelengths from all the other nonconserved variables which must decay more rapidly. As discussed elsewhere,(19) it is just this separation of time scales which implies the hydrodynamic equations at low frequencies and longwavelengths. The assumption that Q_0 corresponds to a finite subspace is equivalent to terminating Mori's(20) continued fraction representation at a finite number. In order to obtain the correct hydrodynamic limit which gives the magnetic field effects, we include in Q_0 not only the currents of the conserved variables, but also internal variables which couple with the currents and also to the magnetic field. As stressed in Ref. 7, these internal variables should contain the internal angular momentum **J** in terms of a second-rank tensor. Thus as in Ref. 7 we assume

$$Q_0 = \sum_{\alpha=4}^{9} | \alpha \rangle \langle \alpha | \tag{26}$$

where

$$\langle \mathbf{p} \mid 4 \rangle \equiv \psi_4(\mathbf{p}) = \left(\frac{c_v}{c^{\text{int}} c_v{}^0} \right)^{1/2} \beta \left[\frac{c^{\text{int}}}{c_v} \left(\frac{p^2}{2m} - \frac{3}{2\beta} \right) - \frac{c_v{}^0}{c_v} (H^{\text{int}} - \langle H^{\text{int}} \rangle) \right]$$

$$\langle \mathbf{p} \mid 5 \rangle \equiv \psi_5(\mathbf{p}) = \frac{\beta}{\sqrt{2}\, m} [\mathbf{p}]^{(2)},$$

$$\langle \mathbf{p} \mid 6 \rangle \equiv \psi_6(\mathbf{p}) = \left(\frac{\beta}{m c_p{}^0} \right)^{1/2} \beta \left(\frac{p^2}{2m} - \frac{5}{2\beta} \right) \mathbf{p}$$

$$\langle \mathbf{p} \mid 7 \rangle \equiv \psi_7(\mathbf{p}) = (\beta / m c^{\text{int}})^{1/2} \beta (H^{\text{int}} - \langle H^{\text{int}} \rangle)\, \mathbf{p}$$

$$\langle \mathbf{p} \mid 8 \rangle \equiv \psi_8(\mathbf{p}) = (30 / \langle 4J^4 - 3J^2 \rangle)^{1/2} [\mathbf{J}]^{(2)}$$

$$\langle \mathbf{p} \mid 9 \rangle \equiv \psi_9(\mathbf{p}) = (30\beta / m \langle 4J^4 - 3J^2 \rangle)^{1/2} [\mathbf{J}]^{(2)}\, \mathbf{p}$$

where c^{int} is the internal contribution to the specific heat in units of k_B, $c_v{}^0 = \frac{3}{2}$, $c_p{}^0 = \frac{5}{2}$, $[\mathbf{p}]_{ij}^{(2)} = p_i p_j - \frac{1}{3} \delta_{ij} p^2$, and $[\mathbf{J}]_{ij}^{(2)} = \frac{1}{2}\{J_i, J_j\} - \frac{1}{3} \delta_{ij} J^2$. The currents of the conserved quantities are given in terms of the ψ's by

$$\begin{aligned} \langle \mathbf{p} \mid Q \mid T \rangle &= (1/\beta)(c^{\text{int}}/c_v c_v{}^0)^{1/2} \psi_4(\mathbf{p})\, \mathbf{1} + (\sqrt{2}/\beta)\, \psi_5(\mathbf{p}) \\ \langle \mathbf{p} \mid Q \mid J_\epsilon \rangle &= (c_p{}^0 / m\beta^3)^{1/2} \psi_6(\mathbf{p}) + (c^{\text{int}}/m\beta^3)\, \psi_7(\mathbf{p}) \end{aligned} \tag{27}$$

When discussing depolarized light scattering we also need

$$\langle \mathbf{p} \mid 2m \rangle = \psi_{2m}(\mathbf{p}) = Y_{2m}(\theta, \phi) / \langle Y_{2m} \mid Y_{2m} \rangle^{1/2} \tag{28}$$

For simplicity the coupling of the Y_{2m} to the ψ_α, $\alpha = 4,9$, will be neglected. That is, we assume Y_{2m} is outside of the Q_0 subspace. This is almost certainly not the case. In fact ψ_{2m} is not even orthogonal to ψ_8. A more correct treatment would assign the part of ψ_{2m} which is orthogonal to ψ_8 as a separate vector in the finite vector space and then keep the contributions of both vectors along with their possible coupling to the depolarized scattering. However, it will greatly simplify the analysis if ψ_{2m} is treated separately from the ψ_α, $\alpha = 4, 9$. As more depolarized light scattering data become available, it may be necessary to carry out this more complete analysis to obtain quantitative agreement with experiments.

The matrix elements of Ω^c are parameterized in a particularily convenient way. From the requirement that the collision operator be isotropic we obtain the following nonvanishing matrix elements of Ω^c:

$$
\begin{gathered}
i\Omega^c_{44} = \Gamma_{44}\,, \qquad i\Omega^c_{55} = \Gamma_{55}\mathbf{I}^s, \qquad i\Omega^c_{66} = \Gamma_{66}\mathbf{1}, \\
i\Omega^c_{58} = \Gamma_{58}\mathbf{I}^s, \qquad i\Omega^c_{67} = \Gamma_{67}\mathbf{I}^s, \qquad i\Omega^c_{69} = \Gamma_{67}\mathbf{I}^s \\
i\Omega^c_{77} = \Gamma_{77}\mathbf{1}, \qquad i\Omega^c_{88} = \Gamma_{88}\mathbf{I}^s, \qquad i\Omega^c_{99} = \Gamma_{99}\mathbf{I}^s\mathbf{1}, \\
i\Omega^c_{79} = \Gamma_{79}\mathbf{I}^s, \qquad i\Omega^0 = \Gamma_0
\end{gathered}
$$

where $\mathbf{I}^s_{ijkl} = \frac{1}{2}(\delta_{ik}\,\delta_{je} + \delta_{ie}\,\delta_{jk} - \frac{2}{3}\,\delta_{ij}\,\delta_{kl})$ and $i\Omega^c$ is self-adjoint and positive definite.

The Γ's are not independent. McCourt and Snider(5) have proven the following indentities among the collision matrix elements:

$$
\begin{gathered}
\Gamma_{58} = \sqrt{5}\,\Gamma_{69}\,, \qquad \Gamma_{66} = \tfrac{2}{3}\Gamma_{55} + \tfrac{5}{6}\Gamma_{44}\,, \\
\Gamma_{67} = \tfrac{1}{2}\sqrt{\tfrac{5}{2}}\,\Gamma_{44}\,, \qquad \Gamma_{44} = \tfrac{2}{3}\sqrt{30}\,\Gamma_{58}
\end{gathered}
\tag{29}
$$

In Appendix B we show that the solution for K reduces to a finite matrix equation. The evaluation of the matrix elements involves complex error functions. As a result it is useful to calculate the error functions by computer[7] and to solve the matrix equations numerically. The numerical work was done on Columbia University's IBM 360/91–360/75 computer. For calculational purposes we chose gaseous N_2 as a typical diamagnetic gas. The collision parameters can be obtained from field-dependent transport measurements.(18) We used the values deduced from these measurements by McCourt and Moraal.(22) For simplicity we assume $\Gamma_0 = \Gamma_{88} = n\sigma v_{\mathrm{rel}}$, where n is the density, $v_{\mathrm{rel}} = 4(1/\pi m\beta)^{1/2}$, and $\sigma = 23$ Å^2.

In Fig. 1 we have plotted $S(k\omega)$ versus ω for three different k's in zero field. The transition between hydrodynamic behavior at long wavelengths, kinetic theory at intermediate wavelengths, and free-particle behavior at short wavelengths is clearly seen.

At short wavelengths the Lorentzian Rayleigh–Brillouin spectrum is replaced by the Gaussian free-particle spectrum. The frequency unit used in Fig. 1 is $\bar{\omega} = \omega/kv$, where $v = (2/m\beta)^{1/2}$. As a result the position of the sound peak is independent of k and occurs at $\bar{\omega} = 0.833$. This natural dimensionless frequency unit was first used by Yip.(23) In Fig. 2 the change of $S(\mathbf{k}\omega)$ from its zero-field value for $h_s/\Gamma_{88} = 2$ is plotted. An effect on the width which is of the same order of magnitude as the Senftleban effects for long wavelengths is evident. The magnetic field effects disappear for short

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[7] We have extended the program described by Christiansen.(20)

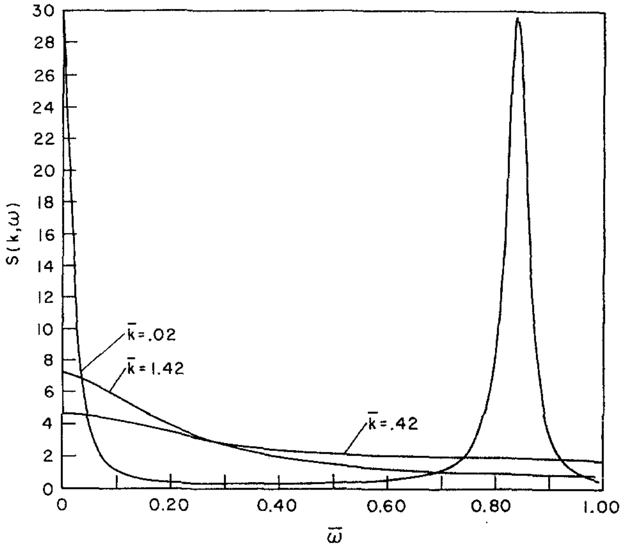

Fig. 1. The dynamic structure factor $S(\mathbf{k}\omega)$ (in units of n/Γ_0, where n is the number density and Γ_0 is a collision frequency) versus ω for three different wave vectors and parameters appropriate for nitrogen. The frequency unit is $\bar{\omega} = \omega/kv$, where $v = -2/m\beta$ is a thermal velocity. Therefore the position of the sound peak is always at $\bar{\omega} = 0.833$. The unit of wave vector is $\bar{k} = kv/\Gamma_0$.

wavelengths as soon as $kv/h_s \gg 1$. That is, the appropriate frequency describing the wavelength dependence is kv while h_s, the Larmor frequency, is the appropriate magnetic field frequency. So the kv term dominates at large k.

5. DEPOLARIZED LIGHT SCATTERING

The spectrum of depolarized light is given by(13)

$$C^2(\mathbf{k}\omega) = \int dr\,dt\,[\exp(i\omega t)][\exp(-i\mathbf{k}\cdot\mathbf{r})]\langle P_2(\hat{u}(\mathbf{r}t)\cdot\hat{u}(0,0))\rangle \tag{30}$$

where P_2 is the second Legendre polynomial and $\hat{u}(\mathbf{r}t)$ is the orientation vector of a molecule at point $\mathbf{r}$ at time t. It follows immediately from the addition theorem of spherical harmonics that C^2 is given by[8]

$$C^2(\mathbf{k}\omega) = \tfrac{1}{5}\sum_{m=-2}^{2} C_m{}^2(\mathbf{k}\omega) \tag{31}$$

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[8] If the axis of quantization is chosen to be the magnetic field direction, then matrix elements of G corresponding to $m' \neq m$ vanish.

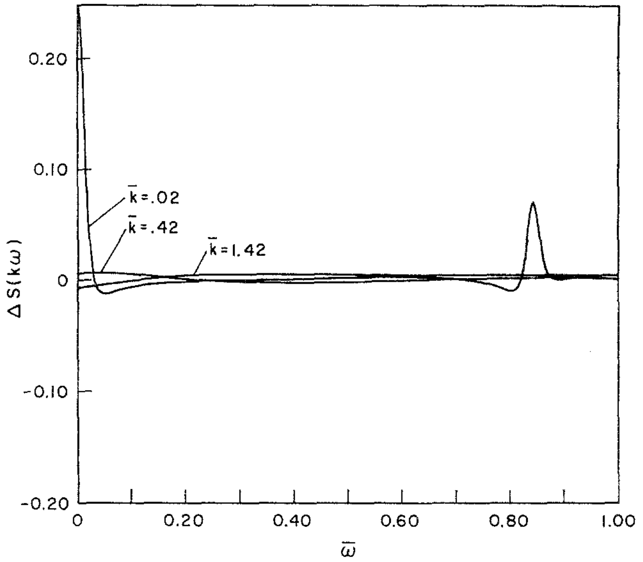

Fig. 2. The deviation $\Delta S(\mathbf{k}\omega) = S(\mathbf{k}, \omega) - S(\mathbf{k}, \omega)|_{H=0}$ of the dynamic structure factor due to a magnetic field perpendicular to $\mathbf{k}$ with magnitude such that $h_s/\Gamma = 2$; three different wavevectors and parameters chosen for nitrogen. For long wavelengths the change is the same relative order of magnitude as the Sentleben effects. However, the effects disappear rapidly for shorter wavelengths.

where

$$C_m{}^2(\mathbf{k}\omega) = \int d\mathbf{p}\, d\mathbf{p}'\, \psi_{2m}^{\dagger}(\mathbf{p})\, G(\mathbf{k}\mathbf{p}\mathbf{p}'\omega + i\epsilon)\, \psi_{2m}(\mathbf{p}')f_0(\mathbf{p}')$$

[c.f. Eq. (25) for the definition of ψ_{2m}].

In order to calculate C^2 from the transport equation (1) we make a simplifying assumption. We assume that

$$\begin{aligned} G_m{}^2(\mathbf{k}z) &= \langle 2m \mid 1/[z - (\mathbf{p} \cdot \mathbf{k}/m) - \Omega^{\text{int}} - \Omega^c] \mid 2m\rangle \\ &\approx \langle 2m \mid 1/[z - (\mathbf{p} \cdot \mathbf{k}/m) - \Omega^{\text{int}} - \Omega_2] \mid 2m\rangle \qquad (32) \end{aligned}$$

where $i\Omega_2 = \Gamma_2 = n\sigma_2 v_{\text{rel}}$. This assumption is made to simplify the analysis. It is not clear that any new information would be obtained by treating the collision operator more accurately. Nevertheless, this assumption still contains the crucial competition between physical processes.[9] The $\mathbf{v} \cdot \mathbf{k}$ term

---

[9] Treatment of the interesting questions relating to motional narrowing of the Rayleigh and Raman lines would require a modification of the kinetic equation to include memory effects, as, for example, in Ref. 12.

describes Doppler effects, Ω_2 contains collision effects, while Ω^{int} contains the effects of rotational level spacing and precession of the magnetic moments about a magnetic field. Cooper *et al.*(24) have fit the pressure dependence of Rayleigh line of N_2 with $\sigma_2 = 28$ Å^2. If we assume for N_2 that $H_0^{\text{int}} = J^2/2I$ and neglect the field dependence f f_0, then C_2 takes the form

$$C^2(\mathbf{k}z) = \sum_m \frac{1}{\langle | Y_{2m} |^2\rangle'} \frac{\pi}{ik} \frac{(m\beta)^{1/2}}{2\pi} \sum_{j_1 j_2} e^{-j_2(j_2+1)/2I} | \langle j_1 m + m_2 \mid Y_{2m} \mid j_2 m_2 \rangle |^2$$
$$w \left[\frac{1}{k} \frac{(m\beta)^{1/2}}{2} \left(z + i\Gamma_2 - \frac{j_1(j_1+1) - j_2(j_2+1)}{2I} - m h_s \right) \right] \tag{33}$$

where $\langle | Y_{2m} |^2 \rangle' = \langle | Y_{2m} |^2 \rangle \, Q^{\text{int}}$, $h_s = \gamma H$ is the molecular precession frequency, and

$$w(\xi) = (i/\pi) \int_{-\infty}^{\infty} dx \, [(\exp -x^2)/(\xi - x)] = [\exp(-\xi^2)][1 - \operatorname{erf}(-i\xi)]$$

is a standard complex error function.(25) The angular momentum matrix elements of the spherical harmonics for diamagnetic molecules can be obtained from(26)

$$\begin{aligned} &\langle j_1 m + m_2 \mid Y_{2m} \mid j_2 m_2 \rangle \\ &\quad = \int d\Omega \, Y^*_{j_1 m + m_2}(\Omega) \, Y_{2m}(\Omega) \, Y_{j_2 m_2}(\Omega) \\ &\quad = (-1)^{m+m_2} \left[\frac{5(2j_1+1)(2j_2+1)}{4\pi} \right]^{1/2} \begin{pmatrix} j_1 & 2 & j_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_1 & 2 & j_2 \\ m+m_2 & m & m_2 \end{pmatrix} \end{aligned} \tag{34}$$

From Eq. (34) it is clear that our treatment of the Rayleigh ($j_1 = j_2$) line is equivalent to Hess's(11) since the $j_1 = j_2$ matrix elements of Y_2 are proportional to the matrix elements $[J]^{(2)}$.

Using the Racah formula(26) for the $3j$ symbols we have calculated $G_m{}^2(\mathbf{k}\omega + i\epsilon)$ numerically. In Fig. 3 we have plotted $C^2(\mathbf{k}\omega)$ in zero field versus ω for $\bar{k} = kv/\Gamma_0 = 0.02$. The moment of inertia I for $\mathrm{N_2}$ is taken from spectral data.(27) Our calculations correspond to a pressure of 588 Torr at room temperature. In Fig. 4 we plot the Rayleigh part of $C^2(\mathbf{k}\omega)$ for magnetic field strength corresponding to $h_s/\Gamma_2 = 10$. We see that the simple spectral lines in zero field are split into quintets of lines corresponding to $m = 0$, ± 1, ± 2.

6. DISCUSSION AND CONCLUSIONS

We have extended the calculation of magnetic field effects on collective properties of polyatomic gases outside the hydrodynamic regime. We have

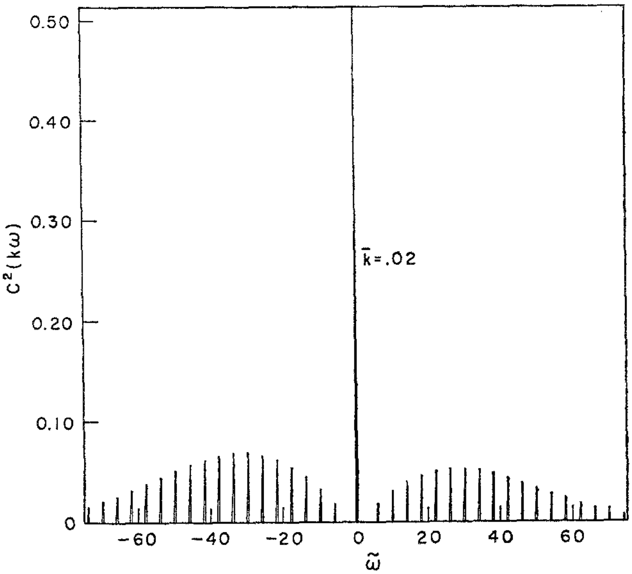

Fig. 3. The orientational correlation function for nitrogen. The Stokes and anti-Stokes rotational bands are clearly seen. The unit of frequency here is $\tilde{\omega} = 2I\omega$.

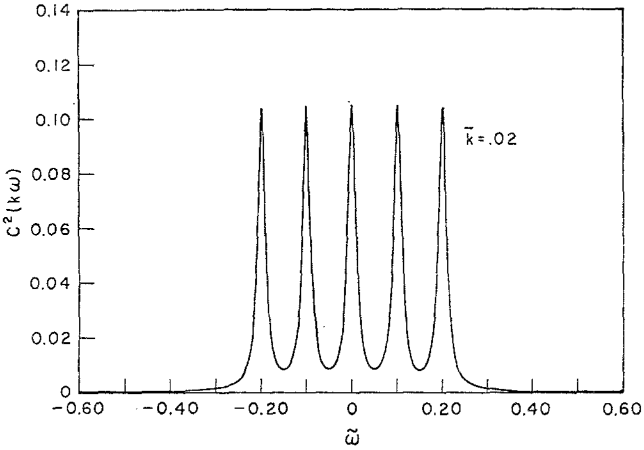

Fig. 4. The Zeeman splitting of the central line of the depolarized spectrum for nitrogen in a magnetic field $h_s/\Gamma_2 = 10$. The splitting is small for nitrogen since nitrogen is diamagnetic.

made the simplest possible assumptions which are consistent with the known behavior of the transport coefficients in a magnetic field. These calculations were applied in a straightforward manner to the calculation of the spectrum of polarized light scattering.

The depolarized spectrum has been calculated using the simplest possible assumptions consistent with pressure and Doppler broadening and internal rotational structure.

Our calculations could be improved upon in several ways. The calculation of the polarized spectrum could be improved by including more basis vectors in the Q_0 subspace. If this were done, however, it would no longer be possible to determine all the collision parameters from transport measurements. The calculation of the depolarized spectrum could be improved by retaining the coupling of the second-rank orientation tensor with the other properties of the system.

Considering the present body of experimental knowledge of polyatomic gases, we do not see at this time the point of extending our calculations beyond the approximations considered. When the experiments are more accurate and the deficiencies in our calculations are more apparent then it will be straightforward to improve our calculations.

APPENDIX A. THE COLLISION KERNAL Ω_c

The kinetic Eq. (1) was obtained⁽⁷⁾ with a collision kernal given by

$$\Omega_c(\mathbf{pp}') = i\,\delta C(\mathbf{rp}t)/\delta f(\mathbf{rp}'t) \tag{A.1}$$

where

$$\begin{aligned}2C(\mathbf{rp}t) = {} & (2\pi)^{-3} \int d\mathbf{p}_2\, d\mathbf{p}_3\, d\mathbf{p}_4\, d\omega\, 1_2^{(1)(3)} 1_2^{(2)(4)}\, \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_3 - \mathbf{p}_4) \\ & \times \{T(\mathbf{rp}_1 + \mathbf{p}_2\,,\, \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2), \tfrac{1}{2}(\mathbf{p}_3 - \mathbf{p}_4), t\omega)\, f(\mathbf{rp}_3 t)\, f(\mathbf{rp}_4 t) \\ & \times \delta(\omega - \bar{\epsilon}(p_3) - \bar{\epsilon}(p_4)) \\ & \times T^\dagger(\mathbf{r}, \mathbf{p}_3 + \mathbf{p}_4\,,\, \tfrac{1}{2}(\mathbf{p}_3 - \mathbf{p}_4), \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2)), \delta(\omega - \bar{\epsilon}(p_1) - \bar{\epsilon}(p_2))\} \\ & - \{T(\mathbf{r}, \mathbf{p}_1 + \mathbf{p}_2\,,\, \tfrac{1}{2}(\mathbf{p}_3 - \mathbf{p}_4), t, \omega)\, \delta(\omega - \bar{\epsilon}(p_3) - \bar{\epsilon}(p_4)) \\ & \times T^\dagger(\mathbf{r}, \mathbf{p}_1 + \mathbf{p}_2\,,\, \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2), \tfrac{1}{2}(\mathbf{p}_3 - \mathbf{p}_4), t, \omega), f(\mathbf{rp}_1 t)\, f(\mathbf{rp}_2 t) \\ & \times \delta(\omega - \bar{\epsilon}(p_1) - \bar{\epsilon}(p_2))\}\end{aligned} \tag{A.2}$$

where $\bar{\epsilon}(p_i) = (p_i^2/2m) + H^{(i)\mathrm{int}}$ and $T(\mathbf{rp}_1 + \mathbf{p}_2, \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2), \tfrac{1}{2}(\mathbf{p}_3 - \mathbf{p}_4), t\omega)$ is the two-particle scattering amplitude at position $\mathbf{r}$ at time t for the scattering process in which $\mathbf{p}_1$ and $\mathbf{p}_2$ are the moments of incoming and $\mathbf{p}_3$ and $\mathbf{p}_4$ the moments of the outgoing particles when the incident and final particles have total energy ω.

APPENDIX B. REDUCTION TO A FINITE MATRIX EQUATION

We wish to show that the projected function K can be obtained from a finite matrix equation if we assume (25). We illustrate this argument schematically. Using the operator identity

$$1/(A - B) = (1/A) + (1/A)\, B[1/(A - B)] \tag{B.1}$$

we see that

$$\begin{aligned} K &= Q \frac{1}{z-(\mathbf{p}\cdot\mathbf{k}/m) + \Omega^{\text{int}} + \Omega^{c})\, Q}\, Q \\ &= Q \frac{1}{(z-\Omega^{\text{int}}-\Omega_0-(\mathbf{p}\cdot\mathbf{k}/m)\, Q}\, Q + Q\frac{1}{z-\Omega^{\text{int}}-\Omega_0-(\mathbf{p}\cdot\mathbf{k}/m)\, Q} \\ &\quad \times Q_0(\delta\Omega)\, Q_0 K Q \end{aligned}$$

So we have

$$Q_0 K Q_0 = Q_0 K' Q_0 + Q_0 K' Q_0(\delta\Omega)\, Q_0 K Q_0 \tag{B.2}$$

where

$$K' = 1/[z - \Omega^{\text{int}} - \Omega_0 - (\mathbf{p}\cdot\mathbf{k}/m)\, Q_0]$$

We can evaluate K' since we have from (B.1)

$$\begin{aligned} K'Q_0 &= \frac{1}{z-\Omega^{\text{int}}-\Omega_0-(\mathbf{p}\cdot\mathbf{k}/m)}\, Q_0 - \frac{1}{z-\Omega^{\text{int}}-\Omega_0-(\mathbf{p}\cdot\mathbf{k}/m)}\, \frac{\mathbf{p}\cdot\mathbf{k}}{m}\, PK' \\ &= K^0 Q_0 - K^0(\mathbf{p}\cdot\mathbf{k}/m)\, PK'Q_0 \end{aligned} \tag{B.3}$$

where

$$K^0 = 1/[z - \Omega^{\text{int}} - \Omega_0 - (\mathbf{p}\cdot\mathbf{k}/m)]$$

thus

$$PK'Q_0 = PK^0Q_0 + PK^0(\mathbf{p}\cdot\mathbf{k}/m)\, PK'Q_0 = [P - PK^0(\mathbf{p}\cdot\mathbf{k}/m)\, P]^{-1}\, PK^0Q_0 \tag{B.4}$$

We observe that

$$K^0(\mathbf{p}\cdot\mathbf{k}/m) = -1 + K_0(z - \Omega^{\text{int}} - \Omega_0) \tag{B.5}$$

So

$$P - PK^0(\mathbf{p}\cdot\mathbf{k}/m)\, P = PK^0(z - \Omega_0)\, P$$

and

$$Q_0K^0(\mathbf{p}\cdot\mathbf{k}/m)\, P = Q_0K^0(z - \Omega_0)\, P \tag{B.6}$$

where we have used $\Omega^{\text{int}}P = 0$.

Putting these all together, we obtain

$$Q_0K'Q_0 = Q_0K^0Q_0 - Q_0K^0P(PK^0P)^{-1}\, PK^0Q_0 \tag{B.7}$$

The matrix elements of K^0 can be evaluated directly and involve complex error functions. Once $Q_0K'Q_0$ is known from (B.7), then (B.2) is a finite matrix equation in the Q_0 subspace. Its solution is formally written as

$$Q_0KQ_0 = [Q_0 - Q_0K'Q_0(\delta\Omega)\,Q_0]^{-1}\,Q_0K'Q_0 \qquad \text{(B.8)}$$

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