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## Onsager Symmetry Relations and the Spectral Distribution of Scattered Light

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The Onsager symmetry relations, used in conjunction with appropriate linear transformations of the hydrodynamic variables, allow one to analyze the distribution of the eigenvalues of the hydrodynamic matrix and to establish symmetry characteristics of its diagonalizing matrices. The implications of these results for the analysis of the spectral distribution of the polarized component of scattered light are pointed out.

### I. INTRODUCTION

In recent years there has been considerable activity, both experimentally as well as theoretically, in the study of the spectral distribution of scattered light.<sup>1</sup> The most commonly used approach to calculate the spectrum is based on Onsager's assumption concerning the regression of fluctuations.<sup>2,3</sup> The number of peaks in the spectrum can be established by determining the number of complex eigenvalues of the hydrodynamic matrix. For a more detailed analysis one may undertake a normal-mode decomposition of the spectral distribution. It is the purpose of this paper to show that the Onsager symmetry relations used in conjunction with appropriate linear transformations of hydrodynamic variables allow one to determine the maximum number of

complex roots of the hydrodynamic matrix and to establish symmetry characteristics of the diagonalizing matrices. The distribution of eigenvalues establishes that the spectrum of light scattered from an ordinary fluid can have at most three peaks. The symmetry of the diagonalizing matrices of the hydrodynamic matrix results in a simplification in the normal-mode decomposition.

### II. SPECTRUM OF SCATTERED LIGHT

As is well known,<sup>4</sup> the spectral-intensity distribution of the polarized component of scattered light  $I(\vec{k}, \Omega + \omega)$  is proportional to the scattering function  $S_e(\vec{k}, \omega)$ , where  $S_e(\vec{k}, \omega)$  is the spectral density of  $\Delta\epsilon(\vec{k}, t)$  the  $\vec{k}$ th spatial Fourier component of the fluctuation in the local dielectric constant. Here  $\vec{k}$  is the change in wave vector,  $\omega$  the change in fre-

quency upon scattering, and  $\Omega$  the frequency of the incident light. The dielectric constant can be considered as a function of the thermodynamic state of the system and thus  $\Delta\epsilon$  can be expressed in terms of the fluctuations in the thermodynamic state variables. Consequently, the scattering function can be written as

$$S_\epsilon(\vec{k}, \omega) = \sum_{i,j=1}^n \left( \frac{\partial\epsilon}{\partial A_i} \right) \left( \frac{\partial\epsilon}{\partial A_j} \right) S_{ij}(\vec{k}, \omega), \quad (1)$$

where  $A_1, \dots, A_n$  are the thermodynamic state variables and  $S_{ij}(\vec{k}, \omega)$  is the  $i, j$ th element of the spectral-density matrix of the  $\vec{k}$ th spatial Fourier component of the fluctuations in the local-state variables.

The Wiener-Khinchin theorem states that the spectral densities and the time-correlation functions are each others' temporal Fourier transforms. The time-correlation functions can be calculated conveniently using Onsager's assumption that the average regression of fluctuations will obey the same laws as the corresponding macroscopic irreversible processes,<sup>5-8</sup> i.e.,

$$\frac{\partial}{\partial t} \langle \alpha(\vec{k}, t) \rangle_{\alpha(\vec{k}, 0)} = -\underline{M}(\vec{k}) \langle \alpha(\vec{k}, t) \rangle_{\alpha(\vec{k}, 0)}, \quad (2)$$

where  $\alpha(\vec{k}, t)$  is a column vector whose elements  $\alpha_i(\vec{k}, t)$  are the  $\vec{k}$ th spatial Fourier components of the local fluctuations in  $A_i$ , and  $\underline{M}(\vec{k})$  is the hydrodynamic matrix. The notation  $\langle \dots \rangle_{\alpha(\vec{k}, 0)}$  indicates a conditional average, with initial values  $\alpha(\vec{k}, 0)$ . It will be assumed that the scattering system is isotropic and therefore the thermodynamic variables are only coupled to  $\text{div } \vec{v}$ , where  $\vec{v}$  is the velocity of the fluid. Although it will be assumed that the dielectric constant is independent of  $\text{div } \vec{v}$ , and thus one does not need to know the spectral density of this quantity, it has to be included in the set of variables  $\alpha$  in the coupled regression equations (2). Thus the column vector contains  $n+1$  elements with  $\alpha_{n+1} = \text{div } \vec{v}$ . Since in the present case the variables  $\alpha$  are scalars, then for spatially invariant systems the spectral densities, the time-correlation functions, and the hydrodynamic matrix do not depend on the direction of  $\vec{k}$ . Further, it can easily be shown that the time-correlation functions and the hydrodynamic matrix are real.

Using the regression equations (2) one easily obtains the time-correlation functions and, upon Fourier transformation, the spectral densities. For the spectral densities of the even variables one obtains

$$S_{ij}(k, \omega) \sim \text{Re} \{ [ \underline{M}(k) + i\omega \underline{I} ]^{-1} \underline{X}(k) \}_{ji}, \quad i, j = 1 \dots n \quad (3)$$

where  $\underline{X}(k)$  is the matrix of mean-square fluctuations<sup>9</sup>

$$\underline{X}(k) = \langle \alpha(\vec{k}) \alpha(\vec{k})^\dagger \rangle. \quad (4)$$

The complexity of the elements of the matrix  $[ \underline{M}(k) + i\omega \underline{I} ]^{-1}$  makes a direct analysis of the spectral densities given by (3) difficult. However, a normal-mode decomposition allows a more ready assessment of the dependence of the spectral densities on  $k$  and  $\omega$ . Since it seems reasonable on physical grounds, we assume that the eigenvalues of  $\underline{M}(k)$  are all distinct and thus  $\underline{M}(k)$  can be diagonalized by a similarity transformation. We have

$$\underline{S}^{-1} \underline{M} \underline{S} = \underline{\Lambda}, \quad (5)$$

where  $\underline{\Lambda}$  is a diagonal matrix with elements  $\lambda_1 \dots \lambda_{n+1}$  which are the eigenvalues of  $\underline{M}(k)$ . It can be shown<sup>10</sup> that

$$[ \underline{M}(k) + i\omega \underline{I} ]^{-1} = \sum_{f=1}^{n+1} \frac{\underline{G}^{(f)}}{\lambda_f + i\omega}. \quad (6)$$

The constituent matrices  $\underline{G}^{(1)} \dots \underline{G}^{(n+1)}$  are given by

$$\underline{G}^{(f)} = \underline{S}_f (\underline{S}^{-1})^f, \quad (7)$$

where  $\underline{S}_f$  is the  $f$ th column of  $\underline{S}$  and  $(\underline{S}^{-1})^f$  is the  $f$ th row of  $\underline{S}^{-1}$ . Substitution of  $[ \underline{M}(k) + i\omega \underline{I} ]^{-1}$ , given by (6), into (3) completes the normal-mode decomposition of the spectral densities. The normal modes themselves, i.e., the linear combination of variables  $\alpha(\vec{k}, t)$  for which the hydrodynamic matrix is diagonal, are given by

$$\gamma(\vec{k}, t) = \underline{S}^{-1} \alpha(\vec{k}, t). \quad (8)$$

### III. ONSAGER RELATIONS AND LINEAR TRANSFORMATION OF VARIABLES

In the present case the Onsager symmetry relations<sup>5,6,11</sup> can be written as

$$[ \underline{M}(k) \underline{X}(k) ]^T = \underline{E} \underline{M}(k) \underline{X}(k) \underline{E}, \quad (9)$$

where  $\underline{E}$ , the so-called signature matrix, is a diagonal matrix with elements  $E_i$  equal to +1 when  $A_i$  is an even variable, and equal to -1 when  $A_i$  is an odd variable under the time-reversal transformation. In the present case  $A_1, \dots, A_n$  are thermodynamic variables and thus even, while  $A_{n+1} = \text{div } \vec{v}$  is odd.

It has been recognized in the study of light scattering that it is convenient to select the hydrodynamic variables such that their fluctuations are statistically independent<sup>12</sup> and normalized.<sup>13,14</sup> It appears, however, that the significance of such variables used in conjunction with the Onsager symmetry relations has not been fully realized.

Since the matrix  $\underline{X}(k)$  is real, symmetric, and positive definite, the transformation to statistically independent normalized random variables  $\beta(\vec{k}, t)$  can be specified by

$$\beta(\vec{k}, t) = \underline{U} \underline{X}^{-1/2} \alpha(\vec{k}, t), \quad (10)$$

where  $\underline{U}$  is an arbitrary unitary matrix. For our purposes we restrict  $\underline{U}$  to those which satisfy

$$\underline{E} \underline{U} \underline{E} = \underline{U}; \quad (11)$$

that is, the transformation in (10) does not mix thermodynamic variables with  $\text{div} \vec{v}$ . The regression equations for the variables  $\beta(\vec{k}, t)$  can be written in the same form as (2) with a hydrodynamic matrix  $\underline{K}(k)$  related to  $\underline{M}(k)$  by

$$\underline{K}(k) = \underline{U} \underline{X}(k)^{-1/2} \underline{M}(k) \underline{X}(k)^{1/2} \underline{U}^\dagger. \quad (12)$$

From (10) and the fact that

$$\underline{X}(k) = \underline{E} \underline{X}(k) \underline{E}, \quad (13)$$

which follows from the principle of microscopic reversibility, it is clear that  $\underline{K}(k)$  has the symmetry

$$\underline{K}^T = \underline{E} \underline{K} \underline{E}. \quad (14)$$

This representation of the Onsager symmetry relations, achieved by the linear transformation of variables (10), will be utilized in Secs. IV and V.

#### IV. EIGENVALUES OF HYDRODYNAMIC MATRIX

The normal-mode decomposition of the spectral densities presented at the end of Sec. II indicates that the spectrum of scattered light exhibits maxima for  $\omega$  values equal to the imaginary part of the eigenvalues of the hydrodynamic matrix. The number of complex eigenvalues has been a question of some concern in the recent literature on light scattering.<sup>15</sup> Although it has been generally assumed<sup>14</sup> that there can be only two such roots, a rigorous proof does not appear to have been stated. The symmetry of  $\underline{K}$  can be used to establish the maximum number of complex eigenvalues.

From (14) it follows that, without loss of generality, we may choose the unitary matrix  $\underline{U}$  to be real and orthogonal and such that  $\underline{K}$  has the form

$$\underline{K} = \begin{bmatrix} a_1 & & 0 & & b_1 \\ & \ddots & & & \vdots \\ 0 & & & & a_n \\ & & & & b_n \\ -b_1 & \cdots & -b_n & a_{n+1} & \end{bmatrix}, \quad (15)$$

where the elements of  $\underline{K}$  are real. The characteristic polynomial of  $\underline{K}$  can then be written as

$$\begin{aligned} p(\lambda) &= |\underline{K} - \lambda \underline{I}| \\ &= \prod_{i=1}^{n+1} (a_i - \lambda) + \sum_{j=1}^n b_j^2 \prod_{i \neq j} (a_i - \lambda). \end{aligned} \quad (16)$$

For convenience it will be assumed that the elements  $a_1, \dots, a_n$  are all distinct<sup>16</sup> and without loss of generality one may take them to be ordered such that  $a_1 < a_2 < \dots < a_n$ . It then follows directly from the expression for the characteristic polynomial (16) that  $p(a_1), p(a_3), \dots$  are positive and  $p(a_2), p(a_4), \dots$  are negative.<sup>17</sup> Thus  $p(\lambda)$  changes sign at least  $n-1$  times for real values of  $\lambda$ . Therefore  $\underline{K}$  has a minimum of  $n-1$  real roots. These  $n-1$

real roots  $\lambda_1, \dots, \lambda_{n-1}$ , lie between  $a_1$  and  $a_n$ ; indeed  $a_i < \lambda_i < a_{i+1}$  for  $1 < i < n-1$ .

Whether the remaining two roots are real or complex depends on the relative magnitude of  $a_1, \dots, a_{n+1}$  and  $b_1, \dots, b_n$ . For light scattering in ordinary fluids the  $b_i$  are much larger than the  $a_i$  and there are two complex roots.

#### V. DIAGONALIZING MATRICES OF HYDRODYNAMIC MATRIX

The calculation of the matrices  $\underline{G}^{(1)}, \dots, \underline{G}^{(n+1)}$  required for the evaluation of the intensities of the normal-mode contributions can be simplified by establishing a symmetry relation between the diagonalizing matrices  $\underline{S}$  and  $\underline{S}^{-1}$  of the hydrodynamic matrix  $\underline{M}(k)$ . The symmetry evident in the transformed hydrodynamic matrix  $\underline{K}$  can be used to this end.

The similarity transformation which diagonalizes  $\underline{K}$  can be written as

$$\underline{V}^{-1} \underline{K} \underline{V} = \underline{\Lambda}. \quad (17)$$

Taking the transpose of (17) and using the symmetry of  $\underline{K}$  given by (14) one obtains

$$\underline{V}^T \underline{E} \underline{K} (\underline{V}^T \underline{E})^{-1} = \underline{\Lambda}. \quad (18)$$

Since it is assumed that the eigenvalues of  $\underline{M}$  and therefore those of  $\underline{K}$  are all distinct, it follows from (17) and (18) that the product of  $\underline{V}$  and  $\underline{V}^T \underline{E}$  is a diagonal matrix. Hence, by imposing the normalization condition

$$\sum_{i=1}^{n+1} V_{if}^2 E_i = 1, \quad (19)$$

we have that

$$\underline{V}^{-1} = \underline{V}^T \underline{E}. \quad (20)$$

Clearly in the case that all variables are even the symmetry relation is simply that of an orthogonal transformation, whereas in the case of both even and odd variables the symmetry, although well defined, is rather less simply classified. It might also be remarked that in the latter case the symmetry relation expressed by (20) implies that the transformation of the variables  $\beta(\vec{k}, t)$  to normal modes is not unitary and hence in view of (10) the normal-modes are not statistically independent.

Since the matrix  $\underline{K}$  is related to  $\underline{M}$  by a similarity transformation, it follows that the relation (20) implies a simple symmetry relation between  $\underline{S}$  and  $\underline{S}^{-1}$ , the diagonalizing matrices of  $\underline{M}$ . With an appropriate normalization condition analogous to (19) the symmetry relation can be written as<sup>18</sup>

$$\underline{S}^{-1} = \underline{S}^T \underline{X}^{-1} \underline{E}. \quad (21)$$

The constituent matrices  $\underline{G}^{(f)}$  can now be obtained directly from the diagonalizing matrix  $\underline{S}$  with an attendant simplification in the evaluation of (6).

## VI. CONCLUDING REMARKS

Some of the implications of the Onsager symmetry relations for the study of the spectral distribution of scattered light have been explored. It has been shown that the hydrodynamic matrix, describing the temporal behavior of  $n$  even variables and 1 odd variable, has at most two complex eigenvalues, and hence the spectrum of light scattered from ordinary fluids contains at most two frequency-shifted lines. Further, a symmetry relation between the diagonalizing matrices of the hydrodynamic matrix

was found, which should be useful in the calculation of the intensities of the normal-mode contributions to the spectrum of scattered light.

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<sup>17</sup>The authors wish to thank Dr. L. J. Dickey, Department of Pure Mathematics, University of Waterloo, for pointing this out.

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## Extremal Properties of Resonance Eigenvalues

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The minimax theorem for the eigenvalues of Hermitian operators is reviewed and its inverse (maxmini) theorem is derived. The connection between the Hylleraas-Undheim theorem (HUT) and the minimax theorem is clarified, and an extension of the HUT to compound resonance states is obtained. Thus, rigorous upper bounds on the resonance energies may be obtained *without* the explicit use of the exact open-channel projection operators. The exchange and re-arrangement problems are also considered.

## I. INTRODUCTION

In recent years, many narrow compound resonance levels have been discovered experimentally in various complex atomic systems, and highly accurate calculations of these levels for the simple two-electron systems have been carried out. The theoretical procedure involves, to a good first approximation, construction of an operator  $QHQ$ , where  $Q$  is the projection onto a subspace orthogo-

nal to all the open channels at a fixed total energy  $E$ . Once the continuum spectrum which is degenerate to that of  $QHQ$  is eliminated, the usual Ritz variational procedure may be applied to the Hermitian operator  $QHQ$  and obtain progressively improved upper bounds on the resonance energies  $E_n^Q$ . In a rigorous sense, this procedure is then applicable only when the operator  $Q$  is explicitly available.

It has not been possible so far to write down ex-