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Molecular theory of optical polarization and light scattering in dielectric fluids. I. Formal theory

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A molecular theory, based on first principles, is introduced for the systematic study of the effects of intermolecular forces on optical properties of dielectric molecular fluids. This theory covers a broad range of applications, including (polarized and depolarized) Rayleigh and Raman scattering, absorption spectra, and nonlinear optics. A canonical transformation is presented by which externally applied coherent fields can be separated from internal radiation fields, thus enabling the introduction of radiative corrections (such as retardation) to the intermolecular forces. The polarization of the medium is expressed in terms of a many-body polarizability (or nonlocal susceptibility) operator. The latter quantity contains implicitly all so-called local-field effects (modification of the molecular polarizability by electromagnetic fields due to neighboring molecules). The dipolar contributions, when summed to all orders, yield the familiar Lorentz-Kirkwood factor, involving the retarded dipole tensor.

I. INTRODUCTION

Much of the information we have on molecular interactions in fluids is obtainable from spectral studies of the propagation and scattering of light. Recent improvements in light-scattering techniques,[1-3] using monochromatic laser sources, make it possible to study in some detail effects of intermolecular forces on molecular correlations,[4-6] collision-induced depolarization,[7] forbidden Raman transitions,[8,9] resonance fluorescence,[10,11] higher-harmonics generation,[12-15] etc., in dielectric fluids. The theoretical procedure usually employed is to start from the independent-molecule picture and add, in an *ad-hoc* fashion, various terms pertaining to the effects of the supposedly relevant intermolecular forces. The lack of a deductively applicable formulation of the theory of light scattering, based on first principles, makes it practically impossible to judge the sufficiency of the *ad-hoc* procedures.

Various attempts have been made to formulate microscopic or phenomenological theories of optical polarization and light scattering.[7,16-63] Recently, Fulton[40] has developed a fully quantized microscopic formalism in which he uses Schwinger's method of functional derivatives[64,65] with respect to an artificially introduced classical field in order to obtain equations of motion for the relevant correlation functions. In this powerful extension of Kubo's method of linear response,[66] expressions can be derived for correlation functions pertaining to any power of the interaction with the transverse radiation field (treated as a perturbation) in which the Coulombic longitudinal fields in the matter are fully incorporated.

We find this approach lacking, however, in two ways. First, on the practical side, there is still a need for an exposition in which effects of the various intermolecular forces are spelled out in more explicit fashion, enabling the derivation of expressions of a more readibly applicable nature in specific cases. What we need is a systematic way, starting from first principles, of adding many-body effects to the molecular optical polarizability, expressing them in terms of couplings between multipole-multipole polarizabilities and multipole-induced-multipole hyperpolarizabilities of the kind introduced by Buckingham and Stephen[24,25] and by Kielich.[26-29]

Second, on a more fundamental level, there are certain effects of the transverse radiative fields that are present in the absence of an externally applied radiation beam and may not be treated satisfactorily on a perturbative level along with the applied field. What we have in mind, for example, are the retardation effects on intermolecular forces produced by the transverse fields,[67-71] which can be quite essential under near-critical conditions where long-range correlations prevail.[32,35,36] The distinction between internal fields with their retardative effects and the externally applied fields poses, however, a serious dilemma regarding their separability. We can conveniently separate transverse from longitudinal fields with the help of the Coulomb gauge[70,71] (although at the cost of losing covariance in a perturbative treatment). But how do we separate internal from externally applied transverse fields? Suppose we simply add to the nonrelativistic quantum-electrodynamical Hamiltonian, considered as adequately representing the interaction of radiation with matter in the absence of applied fields, an extra term representing the applied beam (in, say, the classical-field approximation). Are not we then in danger of "counting things twice?"

An obviously correct statement of the light-scattering problem, in which internal radiations are allowed for, is one in which the same Hamiltonian is considered whether external fields are applied or not, leaving the effect of external fields to the boundary conditions. This approach is unlike the conventional procedure in scattering theory, where the Hamiltonian is unambiguously divided into terms pertaining to the beam, the target, and their mutual interaction.[72] It is nevertheless possible,[73] under certain conditions, to introduce a canonical transformation which transfers the effect of the external fields from the boundary conditions to the Hamiltonian. This will result in the addition of an extra term, representing the external fields, to the Hamiltonian, with the requirement that the correlation functions be calculated with boundary conditions appropriate to the isolated material system in the absence of applied fields.

In Sec. II we present the canonical transformation that justifies the addition of the external field (as a classical field) to the fully quantized Hamiltonian in which internal radiation fields are already incorporated. In Sec. III an expression is obtained for the electric dipole polarization in the optical frequency range. The polarization is related in the linear-response approximation to a many-body polarizability operator (or nonlocalized susceptibility operator) whose propagators depend on the full (external-field-free) Hamiltonian. This many-body polarizability has the same form as the familiar Kramers-Heisenberg molecular polarizability, except that it depends on dynamical variables pertaining to the real (interacting) fluid rather than to an isolated molecule. The use of Liouville-space operator techniques allows us to perform operator expansions in powers of the intermolecular forces, which can be reexpressed as molecular cluster series of increasing cluster size. Certain approximations pertaining to the optical polarization of slowly moving, neutral, stable molecules are systematically introduced, allowing the expression of intermolecular interactions in terms of molecular multipoles. The effect of retaining fully only dipole-dipole terms in the interaction is demonstrated. In Sec. IV, using the Coulombic (instant-action) limit, the Lorentz-Kirkwood relation[18,41] is rederived. In Sec. V radiative corrections are included which result in the replacement of the Coulombic dipole propagator by a retarded one. Several generalizations and applications of the present formalism are set forth in the following paper[74] (henceforth to be referred to as II).

II. EXTERNAL-FIELD APPROXIMATION

Consider the quantum-electrodynamical nonrelativistic Hamiltonian of a system of charged particles (electrons and nuclei) interacting with electromagnetic radiation (neglecting spin interactions). In the Coulomb gauge, using rationalized Gaussian units, the Hamiltonian can be written[70,71]

$$H=\sum_i \frac{1}{2m_i}\left(\vec{p}_i-\frac{e_i}{c}\vec{A}(\vec{r}_i)\right)^2 + \frac{1}{8\pi}\sum_{\substack{i,j\\ i\neq j}}\frac{e_i e_j}{|\vec{r}_i-\vec{r}_j|}+H_R\,. \tag{1}$$

Here

$$H_R=\sum_{\vec{k}}\sum_{\lambda=1,2}\hbar\omega_{\vec{k}}(a^\dagger_{\vec{k}\lambda}a_{\vec{k}\lambda}+\tfrac{1}{2}) =\frac{1}{2}\int[\vec{E}(\vec{r})^2+\vec{B}(\vec{r})^2]\,d\vec{r} \tag{2}$$

is the free-radiation Hamiltonian. Particle i is characterized by its charge e_i, mass m_i, position $\vec{r}_i$, and momentum $\vec{p}_i$. The second-quantized vector potential $\vec{A}$ is given by

$$\vec{A}(\vec{r})=\sum_{\vec{k}}\sum_{\lambda=1,2}\left(\frac{\pi\hbar c}{2Vk}\right)^{1/2}\vec{\epsilon}_{\vec{k}\lambda}(a_{\vec{k}\lambda}e^{i\vec{k}\cdot\vec{r}}+a^\dagger_{\vec{k}\lambda}e^{-i\vec{k}\cdot\vec{r}})\,. \tag{3}$$

The transverse part of the electric field, $\vec{E}(\vec{r})$, and the magnetic field, $\vec{B}(\vec{r})$, are derivable from $\vec{A}(\vec{r})$ in the usual manner,

$$\vec{E}(\vec{r})=-(1/c)\vec{A}(\vec{r})\,, \tag{4}$$

$$\vec{B}(\vec{r})=\vec{\nabla}\times\vec{A}(\vec{r}). \tag{5}$$

V is the volume of the material sample, the $\vec{k}$'s over which one sums are determined by box normalization, $\omega_{\vec{k}}$ and $\vec{k}$ obey the vacuum dispersion relation

$$\omega_{\vec{k}}=ck, \tag{6}$$

and $\vec{\epsilon}_{\vec{k}\lambda}$ $(\lambda=1,2)$ are the two polarization vectors compatible with each allowed $\vec{k}$ value, and in the Coulomb gauge they obey

$$\vec{k}\cdot\vec{\epsilon}_{\vec{k}\lambda}=0,\quad \lambda=1,2, \tag{7}$$

where

$$\vec{\nabla}\cdot\vec{A}(\vec{r})=0. \tag{8}$$

The operators $a_{\vec{k}\lambda}$ and $a^\dagger_{\vec{k}\lambda}$ are the annihilation and creation operators of a photon of wave vector $\vec{k}$ and polarization $\vec{\epsilon}_{\vec{k}\lambda}$ and they obey the usual commutation relations

$$[a_{\vec{k}\lambda}, a^{\dagger}_{\vec{k}'\lambda'}] = \delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'}, \tag{9}$$

etc. The Coulomb gauge is convenient for dealing with problems of chemical physics even when the effect of internal transverse radiation fields is a significant correction to the description of matter as dominated by Coulomb forces.[70,71]

The problem of light scattering by a sample of interacting charges can be dealt with in two different approaches. The more practically appealing approach is to add to the Hamiltonian (1) a term $V(t)$ describing the interaction of the sample with the externally applied field (usually treated as a classical field).[66] This approach conveniently enables one to distinguish between "target" and "beam" and treat light scattering in the manner in which scattering phenomena are usually treated.[72] However, this distinction becomes dubious if internal fields, present in the sample even in the absence of the external field, are taken into account. From a purist point of view, a fully quantized theory does not allow us to distinguish internal photons from external ones. This problem is avoided by using the second approach, in which the same Hamiltonian (1) is used whether the external field is applied or not. The effect of the external field is then introduced through the boundary conditions, by defining an initial density matrix in which the asymptotic state of the applied beam photons is represented by a nonequilibrium steady-state distribution. By doing so we lose, however, much of the intuitive insight provided by the first approach. This is particularly unsatisfactory in cases where the applied field should be treated only to first order while certain effects of the internal fields are independently retained to arbitrary powers, as in a fully retarded description of intermolecular forces.[67–71]

It is therefore desirable to find a procedure by which the effect of the external fields is transformed from the density matrix into the Hamiltonian. Such a procedure can be shown to exist if the initial state of the beam modes can be described by a Glauber coherent state.[75,76] Such states are known to form a good representation of coherent quasiclassical radiation fields,[75,76] and are therefore most appropriate for dealing with the scattering of laser radiation.[73,77]

Suppose the laser radiation is represented by the single-mode Glauber state[75]

$$|\,\alpha_i\rangle = D^{\dagger}(\alpha_i)\,|\,0_{\vec{k}_i\lambda_i}\rangle, \tag{10}$$

where α_i is a complex c number (related to the field amplitude) and $|\,0_{\vec{k}_i\lambda_i}\rangle$ is the vacuum state pertaining to the laser mode with wave vector $\vec{k}_i$ and polarization index λ_i. This can be easily generalized to more than one mode, replacing α_i by a set of numbers $\{\alpha_i\}$ $(i=1,\ldots,j)$ and $D^{\dagger}(\alpha_i)$ by the corresponding product. The unitary displacement operator relating $|\,\alpha_i\rangle$ to $|\,0_{\vec{k}_i\lambda_i}\rangle$ is[75]

$$D^{\dagger}(\alpha_i) = \exp(\alpha_i a^{\dagger}_{\vec{k}_i\lambda_i} - \alpha_i^{*} a_{\vec{k}_i\lambda_i}). \tag{11}$$

Consider now a function of the vector potential of the type that will appear in later calculations. The averaging of this function over the Glauber state can be transformed into a vacuum average,

$$\begin{aligned}\langle \alpha_i\,|\,f(\vec{A})\,|\,\alpha_i\rangle &= \langle 0_{\vec{k}_i\lambda_i}\,|\,D(\alpha_i)f(\vec{A})D^{\dagger}(\alpha_i)\,|\,0_{\vec{k}_i\lambda_i}\rangle \\ &= \langle 0_{\vec{k}_i\lambda_i}\,|\,f\{D(\alpha_i)\vec{A}D^{\dagger}(\alpha_i)\}\,|\,0_{\vec{k}_i\lambda_i}\rangle .\end{aligned} \tag{12}$$

Since[75]

$$D(\alpha_i)a_{\vec{k}\lambda}D^{\dagger}(\alpha_i) = a_{\vec{k}\lambda} + \alpha_i\delta_{\vec{k}\vec{k}_i}\delta_{\lambda\lambda_i}, \tag{13}$$

we have

$$D(\alpha_i)\vec{A}(\vec{r})D^{\dagger}(\alpha_i) = \vec{A}(\vec{r}) + \langle \vec{A}(\vec{r})\rangle_{\alpha_i}, \tag{14}$$

where

$$\begin{aligned}\langle \vec{A}(\vec{r})\rangle_{\alpha_i} &= \langle \alpha_i\,|\,\vec{A}(\vec{r})\,|\,\alpha_i\rangle \\ &= (\pi\hbar c/2Vk_i)^{1/2}\vec{\epsilon}_{\vec{k}_i\lambda_i}(\alpha_i e^{i\vec{k}_i\cdot\vec{r}} + \alpha_i^{*}e^{-i\vec{k}_i\cdot\vec{r}}).\end{aligned} \tag{15}$$

This displacement operator thus transforms the vector potential (and hence the Hamiltonian) into a new form in which the term $\langle\vec{A}(\vec{r})\rangle_{\alpha_i}$, representing the external field, is added. However, the averaging procedure now involves the vacuum, i.e. the averaging can now be made as if no external field is present in the density matrix.

This transformation can now be employed in the calculation of (several-) time correlation functions of the type that we shall deal with in the following sections, e.g.,

$$\langle R(t)\rangle_{\alpha} = \mathrm{Tr}[\rho_{\alpha}(t_0)U^{\dagger}(t,t_0)R(t_0)U(t,t_0)], \tag{16}$$

$$\begin{aligned}\langle R(t)Q(t')\rangle_{\alpha} = \mathrm{Tr}\{&\rho_{\alpha}(t_0)U^{\dagger}(t,t_0)R(t_0)U(t,t_0) \\ &\times U^{\dagger}(t',t_0)Q(t_0)U(t',t_0)\}.\end{aligned} \tag{17}$$

Here $U(t,t_0)$ is the time-evolution operator

$$U(t,t_0) = \exp[-(i/\hbar)\,H(t-t_0)]. \tag{18}$$

The initial value of the density matrix $\rho_{\alpha}(t_0)$ is specified at time t_0, at which moment the Heisenberg and the Schrödinger representations are chosen to coincide. The Heisenberg operators $R(t)$ and $Q(t)$ correspond to dynamical variables of the material medium; e.g., if we take as R and Q the dipole-moment density operator, then (16) occurs in the theory of the dielectric constant and (17) in light-scattering theory.

Assume now that the interaction between the sample and the laser field is adiabatically switched on at time t_0 and that at this time the density operator ρ_{α} is separable into a factor pertaining to the laser modes and a factor ρ' pertaining to the matter in thermal equilibrium with all the other radiation modes,

$$\rho_\alpha = \rho' \mid \alpha_i\rangle\langle\alpha_i \mid . \tag{19}$$

This assumption requires the laser modes be sufficiently intense so as to be unaffected by the reaction of the matter on them (the external-field approximation). Also assume that the frequency of the laser mode is high enough ($\hbar\omega_i \gg k_B T$) so that at thermal equilibrium (i.e., in the absence of the external field) any occupation numbers $n_{\vec{k}_i\lambda_i} > 0$ can be ignored (by Planck's distribution law). Then

$$\rho_0 \equiv \rho' \mid 0_{\vec{k}_i\lambda_i}\rangle\langle 0_{\vec{k}_i\lambda_i} \mid \tag{20}$$

can be approximately identified with the grand-canonical distribution for the entire molecular and radiative system. Under these assumptions (16) reduces to

$$\langle R(t)\rangle_\alpha = \mathrm{Tr}[\rho_0(t_0) D(\alpha_i) U^\dagger(t,t_0) \times R(t_0) U(t,t_0) D^\dagger(\alpha_i)] . \tag{21}$$

The desired transformation of the Hamiltonian is obtained from the identity

$$D(\alpha_i) U^\dagger(t,t_0) = X^\dagger(t,t_0) D(\alpha_i(t-t_0)) , \tag{22}$$

where

$$X(t,t_0) = \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} H(t')\,dt'\right), \tag{23}$$

$$H(t) = H + V(t), \tag{24}$$

$$V(t) = \sum_j \left[-\frac{e_j}{m_j c}\left(\vec{\mathrm{p}}_j - \frac{e_j}{c}\vec{\mathrm{A}}(\vec{\mathrm{r}}_j)\right)\cdot\langle\vec{\mathrm{A}}(\vec{\mathrm{r}}_j)\rangle_{\alpha_i(t)} + \frac{e_j^2}{2m_j c^2}\langle\vec{\mathrm{A}}(\vec{\mathrm{r}}_j)\rangle^2_{\alpha_i(t)}\right], \tag{25}$$

$$\alpha_i(t) = \alpha_i e^{-i\omega_i t}, \qquad \omega_i \equiv \omega_{\vec{k}_i} ; \tag{26}$$

i.e., H is replaced by $H(t)$ by writing $\vec{\mathrm{A}}(\vec{\mathrm{r}}) + \langle\vec{\mathrm{A}}(\vec{\mathrm{r}})\rangle_{\alpha(t)}$ in (1) instead of $\vec{\mathrm{A}}(\vec{\mathrm{r}})$. In order to prove Eq. (22), one has to introduce an interaction picture in terms of the free-radiation Hamiltonian H_R, disentangle (as per Feynman[78]) the exponential operator

$$\exp\left(\frac{i}{\hbar}H(t-t_0)\right) = \left[T_< \exp\left(\frac{i}{\hbar}\int_{t_0}^{t} H_m(t')\,dt'\right)\right]\exp\left(\frac{i}{\hbar}H_R(t-t_0)\right), \tag{27}$$

where $T_<$ denotes positive time-ordering and

$$H_m(t') = \exp[(i/\hbar)H_R(t'-t_0)](H - H_R) \times \exp[-(i/\hbar)H_R(t'-t_0)], \tag{28}$$

and finally use Eqs. (14) and (29),

$$D(\alpha_i)e^{iH_R t/\hbar} = e^{iH_R t/\hbar} D(\alpha_i(t)). \tag{29}$$

For operators R that do not depend on photon-field operators, Eq. (21) thus reduces to

$$\langle R(t)\rangle_\alpha = \mathrm{Tr}[\rho_0(t_0) X^\dagger(t,t_0) R(t_0) X(t,t_0)] . \tag{30}$$

The transformation outlined here is trivially extended to several-time correlation functions such as (17). Equations (16) and (30) personify the two approaches earlier referred to[79]:

(a) In Eq. (16), the dynamics of the system is governed by the Hamiltonian (1) and the presence of the external field is manifested in the density operator ρ_α. Although this is the conventional approach in quantum electrodynamics (Dirac treatment of absorption and emission, Kramers-Heisenberg treatment of Rayleigh and Raman scattering),[70,71,41] it is not the most convenient one in problems where we want to maintain a distinction between external and internal photons.

(b) In Eq. (30), one starts from the Hamiltonian (24), which incorporates the external field, and calculates all statistical averages with the equilibrium density matrix ρ_0. This equation provides the appropriate starting point for Kubo-type expansions in powers of the external field.[66]

To this end, an interaction picture in terms of H is introduced, and subsequently the time-evolution operator (23) is expanded in powers of $V(t)$:

$$X^\dagger(t,t_0) = \left[T_< \exp\left(\frac{i}{\hbar}\int_{t_0}^{t} V_I(t')\,dt'\right)\right]\exp\left(\frac{i}{\hbar}H(t-t_0)\right), \tag{31}$$

where

$$V_I(t') = \exp[(i/\hbar)H(t'-t_0)]\,V(t') \times \exp[-(i/\hbar)H(t'-t_0)] . \tag{32}$$

The interaction-picture operator corresponding to R is given by

$$R(t) = \exp[(i/\hbar)H(t-t_0)]R(t_0)\exp[-(i/\hbar)H(t-t_0)], \tag{33}$$

and the corresponding Heisenberg operator which includes, in addition, the dynamics of the external field can be expanded as

$$\langle R'(t)\rangle_\alpha = \mathrm{Tr}\left[\rho_0(t_0)\left(R(t) + \frac{i}{\hbar}\int_{t_0}^{t} dt_1 [V_I(t_1), R(t)] + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 [V_I(t_2),[V_I(t_1),R(t)]] + \cdots\right)\right]. \tag{34}$$

This equation will be taken as the starting point of our discussion of polarization and scattering phenomena in dielectric fluids in Sec. III.

III. MANY-BODY POLARIZABILITY OPERATOR

In dealing with optical polarization phenomena in dielectric fluids, we are concerned with the time development of the dipole-moment-density operator of the entire fluid

$$\vec{\mathrm{M}}(\vec{\mathrm{r}}) = \sum_A \vec{\mu}_A \delta(\vec{\mathrm{r}} - \vec{\mathrm{r}}_A), \tag{35}$$

where

$$\vec{\mu}_A = \sum_{i\in A} e_i \vec{\mathrm{r}}_i \tag{36}$$

is the dipole-moment operator of molecule A and $\vec{\mathrm{r}}_A$ is its position operator. For neutral molecules whose spatial extensions are small compared with the wavelength of the external optical field, it is justified to introduce the dipole approximation[80,81,70] for the interaction term $V(t)$ of Eq. (25),

$$V(t) = -\int d\vec{\mathrm{r}}\vec{M}(\vec{\mathrm{r}})\cdot\vec{\mathrm{E}}_{\mathrm{ext}}(\vec{\mathrm{r}},t), \tag{37}$$

where

$$\begin{aligned}\vec{\mathrm{E}}_{\mathrm{ext}}(\vec{\mathrm{r}},t) &\equiv \langle\vec{\mathrm{E}}(\vec{\mathrm{r}})\rangle_{\alpha_i(t)}\\ &= \vec{\mathrm{E}}_{\mathrm{ext}}(\vec{\mathrm{r}})e^{i\omega_i t} + \vec{\mathrm{E}}^*_{\mathrm{ext}}(\vec{\mathrm{r}})e^{-i\omega_i t},\end{aligned} \tag{38}$$

$$\vec{\mathrm{E}}_{\mathrm{ext}}(\vec{\mathrm{r}}) = \mathcal{E}_i\vec{\epsilon}_i e^{-i\vec{\mathrm{k}}_i\cdot\vec{\mathrm{r}}}, \quad (\vec{\epsilon}_i \equiv \vec{\epsilon}_{\vec{\mathrm{k}}_i\lambda_i}), \tag{39}$$

and [see Eq. (4)]

$$\mathcal{E}_i = -i\left(\frac{\pi\hbar k_i}{2Vc}\right)^{1/2}\alpha_i^*. \tag{40}$$

In Liouville-operator notation,[82,83] Eq. (34) for the average of the Heisenberg operator $\vec{\mathrm{M}}'(\vec{\mathrm{r}},t)$ corresponding to $\vec{\mathrm{M}}(\vec{\mathrm{r}})$ is

$$\begin{aligned}\langle\vec{\mathrm{M}}'(\vec{\mathrm{r}},t)\rangle_\alpha = \mathrm{Tr}\Bigg[\rho_0\Bigg(\vec{\mathrm{M}}(\vec{\mathrm{r}},t) &+ i\int_{-\infty}^{t} dt_1 L_I(t_1)\vec{\mathrm{M}}(\vec{\mathrm{r}},t)\\ &+ i^2\int_{-\infty}^{t} dt_1\int_{-\infty}^{t_1} dt_2 L_I(t_2)L_I(t_1)\\ &\times\vec{\mathrm{M}}(\vec{\mathrm{r}},t)+\ldots\Bigg)\Bigg].\end{aligned} \tag{41}$$

Here, the interaction-picture operators $\vec{\mathrm{M}}(\vec{\mathrm{r}},t)$ and $V_I(t)$ are given by

$$\vec{\mathrm{M}}(\vec{\mathrm{r}},t) = e^{iLt}\vec{\mathrm{M}}(\vec{\mathrm{r}}), \tag{42}$$

$$V_I(t) = e^{iLt}V(t), \tag{43}$$

while the Liouville operators L and $L_I(t)$ are related to H and $V_I(t)$ as

$$LX = \hbar^{-1}[H,X], \tag{44}$$

$$L_I(t)X = \hbar^{-1}[V_I(t),X] \tag{45}$$

(X is any Hilbert-space operator here). Liouville-operator techniques have found wide application in molecular relaxation and transport problems[82–84] and they will be profitably applied throughout the present work. In Eq. (41) we have made use of the commutativity of H with ρ_0 to eliminate all dependence of the exponential operators on t_0 [compare (42) and (43) with (32) and (33)] and we have used the arbitrariness in t_0 to put $t_0 = -\infty$ in the lower limits of the integrals in (41).

In the remainder of this section, we shall be concerned with the linear term in (41). We introduce the operator

$$\vec{\mathrm{P}}(\vec{\mathrm{r}},t) = i\int_{-\infty}^{t} dt_1 L_I(t_1)\vec{\mathrm{M}}(\vec{\mathrm{r}},t) \tag{46}$$

whose average, as the linear-response polarization, is related to the dielectric constant of the sample, and whose two-point average Tr $[\rho_0\vec{\mathrm{P}}(\vec{\mathrm{r}},t)\vec{\mathrm{P}}(\vec{\mathrm{r}}',t')]$ is related to the intensity of scattered light (see paper II[74]). The quadratic term in (41) is related to second-harmonic generation, and this will also be discussed in II.

The time-integration in (46) is easily performed, allowing us to express $\vec{\mathrm{P}}$ in terms of a many-body polarizability operator $\mathcal{A}$,

$$\begin{aligned}P^\alpha(\vec{\mathrm{r}},t) &= e^{i(\omega_i+L)t}\int d\vec{\mathrm{r}}_1\,\mathcal{A}^{\alpha\beta}(\vec{\mathrm{r}},\vec{\mathrm{r}}_1;\omega_i)E^{\beta}_{\mathrm{ext}}(\vec{\mathrm{r}}_1)\\ &\quad + e^{i(-\omega_i+L)t}\int d\vec{\mathrm{r}}_1\,\mathcal{A}^{\alpha\beta}(\vec{\mathrm{r}},\vec{\mathrm{r}}_1;-\omega_i)E^{\beta*}_{\mathrm{ext}}(\vec{\mathrm{r}}_1),\end{aligned} \tag{47}$$

where greek indices denote Cartesian components and $\mathcal{A}$ is defined as[41]

$$\mathcal{A}^{\alpha\beta}(\vec{\mathrm{r}},\vec{\mathrm{r}}';\omega) \equiv \hbar^{-1}[M^\alpha(\vec{\mathrm{r}}),G(\omega)M^\beta(\vec{\mathrm{r}}')]. \tag{48}$$

Here

$$G(\omega) = \lim_{\epsilon\to 0^+}(\omega+L-i\epsilon)^{-1} = P[1/(\omega+L)] + i\pi\delta(\omega+L) \tag{49}$$

is the retarded tetradic Green's function.[82–84] The formula (48) for $\mathcal{A}$ is a many-body generalization of the Kramers-Heisenberg form for the molecular polarizability,[70]

$$\overleftrightarrow{\alpha}_A(\omega) = \hbar^{-1}[\vec{\mu}_A, G_A(\omega)\vec{\mu}_A], \tag{50}$$

where $G_A(\omega)$ is defined as in (49) but with L replaced by L_A, the Liouvillian of the (isolated) molecule A. The operator $\mathcal{A}$ can be split into a dispersive part and a dissipative part using the separation in (49) of the Green's function into a Cauchy principal part and a δ function, respectively. Far away from resonance frequencies of the system the dissipative part can be disregarded.

A specific space-time Fourier component of $\vec{P}(\vec{r}, t)$ corresponds to scattering with a wave vector $\vec{k}_s$ and frequency ω_s (in keeping with our aim to include both Raman and quasielastic Rayleigh scattering we allow for ω_s different from ω_i):

$$P^\alpha(\vec{k}_s, \omega_s) = 2\pi\delta(\omega_i + L - \omega_s)\mathcal{A}^{\alpha\beta}(\vec{k}_s, -\vec{k}_i; \omega_i)\mathcal{E}_i\epsilon_i^\beta + 2\pi\delta(-\omega_i + L - \omega_s)\mathcal{A}^{\alpha\beta}(\vec{k}_s, \vec{k}_i; -\omega_i)\mathcal{E}_i^*\epsilon_i^\beta, \tag{51}$$

where

$$\mathcal{A}^{\alpha\beta}(\vec{k}, \vec{k}'; \omega) \equiv \hbar^{-1}[M^\alpha(\vec{k}), G(\omega)M^\beta(\vec{k}')], \tag{52}$$

$$\vec{M}(\vec{k}) = \sum_A \vec{\mu}_A e^{i\vec{k}\cdot\vec{r}_A}. \tag{53}$$

The δ function in (51) expresses energy conservation between the initial state $|a\rangle$ with energy E_a and the final state $|b\rangle$ with energy E_b, namely, for the first term of (51),

$$E_{ab} \equiv E_a - E_b = \hbar(\omega_s - \omega_i). \tag{54}$$

For the second term, one has

$$E_{ab} = \hbar(\omega_s + \omega_i). \tag{55}$$

Although of little significance in light scattering, the latter term is retained in order to maintain the Hermiticity of $\vec{P}(\vec{r}, t)$. In Appendix A a symmetry property of $\mathcal{A}$ and its like is established, resembling the Onsager symmetry relations for related macroscopic quantities.

The main interest in the operator $\mathcal{A}$ lies in the fact that it contains all intermolecular forces fully and to all orders (implicit in the many-body Liouvillian L). The expression (48) thus offers a rigorous starting point for a cluster-type expansion of $\mathcal{A}$ in terms of molecular moments and quantities referring to intermolecular interactions. This is achieved by separating the fluid Hamiltonian (1) into intra- and intermolecular parts. The more familiar contribution to the forces comes from the Coulomb term. However, effects may result from the contribution of the transverse (radiative) terms ($\vec{p}\cdot\vec{A}$ and A^2) to the intermolecular forces. Consider, for example, the effect of the $\vec{p}\cdot\vec{A}$ term to second order. Physically, this can be pictured as the emission of a virtual photon by particle i (through a matrix element of $\vec{p}_i\cdot\vec{A}_i$) followed by its reabsorption by particle j (through $\vec{p}_j\cdot\vec{A}_j$). This introduces a term dependent on the distance $\vec{r}_{ij}$ between particles i and j. The inclusion of such terms will be shown to cause a modification of the static result (obtained if one would take into account only the Coulomb terms) to include retardation effects.

The results anticipated here will be presented in two stages. First, a static calculation will be performed, neglecting all radiative effects (Sec. IV). This will also be included in Sec. V. To this end, the Hamiltonian (1) is divided into a zero-order (noninteracting) part H_0 and perturbative parts H_1, H_2, and H_3, as follows:

$$H = H_0 + H_1 + H_2 + H_3, \tag{56}$$

$$H_0 = \sum_A H_A + H_R, \tag{57}$$

$$H_A = \sum_{i\in A} \frac{p_i^2}{2m_i} + \frac{1}{8\pi} \sum_{\substack{i\in A\\(i\neq j)}} \sum_{j\in A} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|}, \tag{58}$$

$$H_1 = \frac{1}{8\pi} \sum_{A\neq B} \sum_{\substack{i\in A\\ j\in B}} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|} \simeq \frac{1}{2}\int d\vec{r}\int d\vec{r}'\, \vec{M}(\vec{r})\cdot\overleftrightarrow{T}(\vec{r}-\vec{r}')\cdot\vec{M}(\vec{r}'), \tag{59}$$

$$H_2 = -\frac{1}{c}\sum_i \frac{e_i}{m_i}\vec{p}_i\cdot\vec{A}(\vec{r}_i), \tag{60}$$

$$H_3 = \frac{1}{2c^2}\sum_i \frac{e_i^2}{m_i}\vec{A}(\vec{r}_i)^2. \tag{61}$$

As before, subscripts $i, j, \ldots$ stand for electrons and nuclei, while $A, B, \ldots$ designate different molecules. At this early stage, the discussion is restricted to intermolecular dipole forces in Eq. (59). The inclusion of higher multipoles does not constitute an essential difficulty and will be discussed in II.[74] The T tensor appearing in (59) is the static dipole-dipole tensor defined as

$$\overleftrightarrow{T}(\vec{r}) \equiv -(\vec{\nabla}\vec{\nabla} - \tfrac{1}{3}\nabla^2)\frac{1}{4\pi r} = \frac{1}{4\pi r^3}(1 - 3\hat{r}\hat{r}), \qquad \hat{r} = \frac{\vec{r}}{r}. \tag{62}$$

The inclusion of the Laplacian term $(-\frac{1}{3}\nabla^2)$ serves to remove the δ-function singularity at $\vec{r} = 0$. This is necessary to avoid the appearance of self-interactions in the Hamiltonian, as we deal here with intermolecular forces only. This point will turn out to be of importance in the comparison of our molecular theory with phenomenological theories[31] (see paper II[74]).

IV. DIPOLE APPROXIMATION (COULOMBIC LIMIT)

In this section H_2 and H_3 will be neglected. The separation of $\mathcal{A}$ into intra- and intermolecular parts is effected by means of a Dyson-type expansion of the resolvent operator appearing in $\mathcal{A}$, namely

$$G = G_0 - G_0 L_1 G. \tag{63}$$

Here, omitting further explicit reference to the common argument ω_i, we write

$$G \equiv (\omega_i + L - i\epsilon)^{-1}, \tag{64}$$

$$G_0 \equiv (\omega_i + L_0 - i\epsilon)^{-1}, \tag{65}$$

where L, L_0, and L_1 are, respectively, the Liouville operators corresponding to H, H_0, and H_1. Simple commutator algebra yields

$$\begin{aligned} \mathfrak{A}^{\alpha\beta}(\vec{r}_1, \vec{r}_2; \omega_i) = \hbar^{-1}[M^\alpha(1), GM^\beta(2)] = \hbar^{-1}[M^\alpha(1), G_0 M^\beta(2)] &- (2\hbar^2)^{-1}[M^\alpha(1), G_0 M^\gamma(3) T^{\gamma\delta}(34)[M^\delta(4), GM^\beta(2)]] \\ &- (2\hbar^2)^{-1}[M^\alpha(1), G_0[M^\gamma(3), GM^\beta(2)] T^{\gamma\delta}(34) M^\delta(4)] \\ &- (2\hbar^2)^{-1}[M^\alpha(1), G_0 M^\gamma(3)[T^{\gamma\delta}(34), GM^\beta(2)] M^\delta(4)]. \end{aligned} \tag{66}$$

Here the shorthand notation $\vec{M}(1) = \vec{M}(\vec{r}_1)$ and $\overleftrightarrow{T}(34) = \overleftrightarrow{T}(\vec{r}_3 - \vec{r}_4)$ has been employed. Also, integration over $\vec{r}_3$ and $\vec{r}_4$ is implicit, i.e., we use a "summation convention" over both repeated space labels and repeated tensorial indices.

Let us analyze more closely the four terms on the right-hand side of (66). The first term can be written in the form

$$\begin{aligned} \overleftrightarrow{\mathfrak{A}}_0(\vec{r}_1, \vec{r}_2; \omega_i) &\equiv \hbar^{-1}[\vec{M}(1), G_0\vec{M}(2)] \\ &\simeq \hbar^{-1} \sum_{A,B} [\vec{\mu}_A, G_0\vec{\mu}_B]\delta(\vec{r}_1 - \vec{r}_A)\delta(\vec{r}_2 - \vec{r}_B), \end{aligned} \tag{67}$$

where the extraction of the spatial δ functions from the commutator involves an error of the order v/c (a Doppler shift; see Appendix B). Notice that H_A commutes with H_B and with H_R, and therefore all $A \neq B$ terms vanish. $\mathfrak{A}_0$ then reduces to a sum of single-molecule contributions,

$$\overleftrightarrow{\mathfrak{A}}_0(r_1, r_2; \omega_i) = \sum_A \overleftrightarrow{\alpha}_A(\omega_i)\delta(\vec{r}_1 - \vec{r}_A)\delta(\vec{r}_1 - \vec{r}_2), \tag{68}$$

where $\alpha_A(\omega_i)$ is the Kramers-Heisenberg polarizability (50). This simple result follows from the neglect of the $\vec{p}\cdot\vec{A}$ terms in H_0. As was already stated, these terms introduce in second order couplings between the various charges. These couplings include both intramolecular effects (when the coupled charges belong to the same molecule) and intermolecular effects. The former cause small radiative corrections to the molecular energy levels, which will not be discussed here. The latter, however, contribute retardation corrections (see Sec. V) to the intermolecular forces. Consequently, if we do not separate H_2 from H_0 in the present calculation, the sum $\sum_{A,B}$ in (67) would not reduce to a sum of single-particle terms. Besides, α_A would remain an operator in the space of photon states. In the present approximation it is an operator only on the internal degrees of freedom of molecule A.

The last term in (66) can be neglected compared with the second or third term. It is proven in Appendix B that their ratio is of order v/c, or even smaller.

Analysis of the second term of (66) is complicated by the fact that the leftmost resolvent G_0 operates both on $\vec{M}(3)$ and on $[\vec{M}(4), G\vec{M}(2)]$ [its action on $T(34)$ produces, again, Doppler-like contributions, and is hence ignored]. Generally the action of $(\omega + L)^{-1}$ on a product of two operators A and B can be disentangled as follows:

$$(\omega + L)^{-1}AB = \frac{1}{\omega}\sum_{n=1}^{\infty}\sum_{m=0}^{n}\binom{n}{m}\left[\left(-\frac{L}{\omega}\right)^{n-m}A\right] \times\left[\left(-\frac{L}{\omega}\right)^{m}B\right]. \tag{69}$$

By this general rule the second term of Eq. (66) can be factorized as

$$\begin{aligned} -\frac{1}{2\hbar^2\omega_i}\sum_{n=0}^{\infty}\sum_{m=0}^{n}\binom{n}{m}\Bigg(\left[M^\alpha(1), \left\{\left(-\frac{L_0}{\omega_i}\right)^{n-m} M^\gamma(3)\right\}\right] T^{\gamma\delta}(34)\left\{\left(-\frac{L_0}{\omega_i}\right)^{m}[M^\delta(4), GM^\beta(2)]\right\} \\ + \left\{\left(-\frac{L_0}{\omega_i}\right)^{m} M^\gamma(3)\right\} T^{\gamma\delta}(34)\,[M^\alpha(1), \{(-L_0/\omega_i)^{n-m}[M^\delta(4), GM^\beta(2)]\}]\Bigg). \end{aligned} \tag{70}$$

In Appendix C it is shown that if the photon scattering process is quasielastic, i.e., when the energy $|E_a - E_b|$ of the transition from the initial state $|a\rangle$ to the final state $|b\rangle$ is small with respect to the photon energy $\hbar\omega_i$, then only the $m = 0$ term in the summation over m in Eq. (70) contributes significantly. Consequently, Eq. (70) can be simplified to yield

$$\begin{aligned} -(1/2\hbar^2)\{[M^\alpha(1), G_0 M^\gamma(3)]\, T^{\gamma\delta}(34)[M^\delta(4), GM^\beta(2)] \\ + M^\gamma(3) T^{\gamma\delta}(34)[M^\alpha(1), G_0[M^\delta(4), GM^\beta(2)]]\}. \end{aligned} \tag{71}$$

The third term on the right-hand of Eq. (66) can be factorized similarly. Finally, collecting all the terms, one has

$$\mathcal{A}^{\alpha\beta}(12)=\mathcal{A}_0^{\alpha\beta}(12)-\tfrac{1}{2}[\mathcal{A}_0^{\alpha\gamma}(13)T^{\gamma\delta}(34)\mathcal{A}^{\delta\beta}(42)+\mathcal{A}^{\gamma\beta}(32)T^{\gamma\delta}(34)\mathcal{A}_0^{\alpha\delta}(14)$$
$$+M^{\gamma}(3)T^{\gamma\delta}(34)B^{\alpha\delta\beta}(142)+B^{\alpha\gamma\beta}(132)T^{\gamma\delta}(34)M^{\delta}(4)]\,, \qquad (72)$$

where

$$\mathcal{A}^{\alpha\beta}(12)\equiv\mathcal{A}^{\alpha\beta}(\vec{r}_1,\vec{r}_2;\omega_i), \qquad (73)$$

$$B^{\alpha\beta\gamma}(123)\equiv\hbar^{-2}\big[M^{\alpha}(\vec{r}_1),(\omega_i+L_0)^{-1}$$
$$\times[M^{\beta}(\vec{r}_2),(\omega_i+L)^{-1}M^{\gamma}(\vec{r}_3)]\big]\,. \qquad (74)$$

The latter expression (74) is closely related to the second-harmonic susceptibility tensor (see paper II[74]). Although its appearance in the perturbation expansion of the linear polarizability might seem strange, it really has a simple physical explanation: under the joint action of the external field at position $\vec{r}_A$ and the (static) dipolar field of a neighboring molecule B, an oscillating dipole with frequency ω_i can be induced in molecule A if it has a nonvanishing $B^{\alpha\beta\gamma}$. Further expansion of the many-body resolvent G in Eq. (74) would show that the expression (72) for $\mathcal{A}$ depends not only on the molecular second-harmonic tensor B_0 but on all molecular *higher*-harmonic susceptibilities as well (see paper II[74]). The significance of these hyperpolarizabilities has been noted and thoroughly investigated by Buckingham and Stephen[24,25] and by Kielich.[26–29] Here we simply confine ourselves to noting that for atoms and for molecules whose point group includes an element of inversion symmetry (nonpolar molecules) the terms in Eq. (72) that depend on M and B vanish by symmetry arguments, and in that case Eq. (72) can be further simplified. Using

$$T^{\alpha\beta}(\vec{r})=T^{\beta\alpha}(\pm\vec{r}) \qquad (75)$$

and assuming that $\mathcal{A}_0$ and $\mathcal{A}$ commute, one has

$$\mathcal{A}^{\alpha\beta}(12)=\mathcal{A}_0^{\alpha\beta}(12)-\mathcal{A}_0^{\alpha\gamma}(13)T^{\gamma\delta}(34)\mathcal{A}^{\delta\beta}(42), \qquad (76)$$

or, in $3N$-dimensional matrix notation,

$$\overleftrightarrow{\mathcal{A}}=\overleftrightarrow{\mathcal{A}}_0-\overleftrightarrow{\mathcal{A}}_0\cdot\overleftrightarrow{T}\cdot\overleftrightarrow{\mathcal{A}}. \qquad (77)$$

This can be formally solved by writing

$$\overleftrightarrow{\mathcal{A}}=(1+\overleftrightarrow{\mathcal{A}}_0\cdot\overleftrightarrow{T})^{-1}\cdot\overleftrightarrow{\mathcal{A}}_0. \qquad (78)$$

Thus the many-body polarizability operator $\mathcal{A}$ is related in a closed form to the single-particle operator $\mathcal{A}_0$.[18–23,41,47] This relation is central to the work of Kirkwood on dielectrics and, going even further back, it is implicit in the work of Lorentz. The exact relation between (78) and the Clausius-Mossotti equation of classical dielectric theory[31,33] is further explored in II. The main generalization lies in the fact that (78) is an operator equation involving operators in the Hilbert space of internal (electronic, etc.) molecular states. Hence (78) applies as well to Raman as to Rayleigh scattering, the only difference between these two cases being the choice of matrix elements. More attention will be given to applications to Raman scattering in paper II.[74]

V. RETARDATION EFFECTS

We shall now proceed to consider the terms H_2 and H_3, neglected so far in the Dyson expansion of $\mathcal{A}$, which, as was remarked previously, bring about retardation effects. In the present section only nonpolar molecules will be considered, so that we need not worry, for the time being, about such contributions as the *MTB* term. Also, the dipole approximation will be retained. In addition to truncating the expansion of the Coulomb term as in (59), this implies replacing $\vec{A}(\vec{r}_i)$, the vector potential at the position of electron i, by $\vec{A}(\vec{r}_A)$, its value at the center of mass of molecule A to which electron i belongs.

This is not as trivial an assumption as it looks. True as it may be with regard to the slowly varying *external* field, it is not at all obvious that the same assumption can be made for the quantum electrodynamics (QED) $\vec{A}$, remembering that the QED definition of $\vec{A}$ contains a sum over all $\vec{k}$ [see Eq. (13)], while the dipole approximation implies that $\vec{k}$ is an *optical* wave vector. The justification for this procedure lies herein that $\vec{A}$ will finally appear only in commutators of the type $[\vec{A},(\omega+L_0)^{-1}\vec{A}]$, which, owing to the dispersion relations obeyed by the radiation field, contribute mostly when $k\simeq\omega/c$ (see, e.g., Power[85]).

First-order contributions (and likewise all odd orders) in H_2 vanish. The reason is that diagonal matrix elements of $\vec{A}$ (or of all odd powers of $\vec{A}$) between pure photon states (in the occupation-number representation) vanish. This point of view is justified by the results of Sec. II: all matrix elements are to be computed with the equilibrium density matrix, and for optical modes this means that in all calculations the vacuum expectation value is to be taken. The first nonvanishing contributions (first order from H_1 and H_3 and second order from H_2) are all of order e^2 (where e is the electronic charge). The first-order contribution of H_3 depends on the commutator

$$[\vec{A}(\vec{r}_B),G_0\mu_A^{\dagger}], \qquad (79)$$

and the only reason why this does not vanish identically is that the center-of-mass kinetic-energy operator contained in G_0 does not commute with $\vec{A}(\vec{r}_B)$. This produces, again, only Doppler-like corrections (of order $\beta = v/c$), which are negligible if ω_i is far from resonance.

The second-order contribution of H_2 is given by

$$\frac{1}{c^2\hbar^3}\sum_{i,j}\Big[\mu_A^\alpha, (\omega_i + L_0)^{-1}\big[(e_i/m_i)p_i^\gamma A_i^\gamma, (\omega_i + L_0)^{-1}[(e_j/m_j)p_j^\delta A_j^\delta, (\omega_i + L_0)^{-1}\mu_B^\beta]\big]\Big], \quad A \neq B. \tag{80}$$

Neglecting commutators of the type (79), this reduces to

$$\frac{1}{c^2\hbar^3}\sum_{\substack{i\in A\\ j\in B}}[\mu_A^\alpha, (\omega_i + L_0)^{-1}(e_i/m_i)p_i^\gamma][A_A^\gamma, (\omega_i + L_0)^{-1}A_B^\delta][(e_j/m_j)p_j^\delta, (\omega_i + L_0)^{-1}\mu_B^\beta]. \tag{81}$$

Again assuming that the center-of-mass motion has a negligible effect, we can write

$$(1/\hbar)[A_A^\alpha, (\omega_i + L_0)^{-1}A_B^\beta] \simeq (1/\hbar)[A_A^\alpha, (\omega_i + L_R)^{-1}A_B^\beta] \equiv D^{\alpha\beta}(\vec{r}_A - \vec{r}_B, \omega_i), \tag{82}$$

where L_R is the free photon-field Liouvillian corresponding to H_R [Eq. (2)]. The quantity D, the temporal Fourier transform of the retarded two-point commutator of the vector potential, is a well-known object in quantum electrodynamics and it is known to be a c number in photon space.[70,71] In the Coulomb gauge it is given by[70]

$$(\omega^2/c^2)\overleftrightarrow{D}(\vec{r}, \omega) = \overleftrightarrow{T}(\vec{r}) - \overleftrightarrow{F}(\vec{r}, \omega), \tag{83}$$

Where T is the static dipole propagator [Eq. (62)] and F is the retarded dipole propagator

$$\overleftrightarrow{F}(\vec{r}, \omega) = -\left(\vec{\nabla}\vec{\nabla} - \tfrac{1}{3}\nabla^2 + \frac{\omega^2}{c^2}\right)\frac{e^{-i\omega r/c}}{4\pi r} = \frac{e^{-i\omega r/c}}{4\pi}\left[\frac{\omega^2}{c^2 r}(\hat{r}\hat{r} - 1) + \left(\frac{i\omega}{cr^2} + \frac{1}{r^3}\right)(1 - 3\hat{r}\hat{r})\right]. \tag{84}$$

The appearance of the static dipole tensor T in (83) will be shown to effect the cancellation of the contribution of H_1 and to replace it by a term containing only the retarded propagator F. To recast Eq. (81) in the desired form, we use the identity

$$\sum_{i\in A}\frac{e_i}{m_i}\vec{p}_i = iL_0\vec{\mu}_A. \tag{85}$$

It follows that

$$\sum_{i\in A}[\vec{\mu}_A, (\omega_i + L_0)^{-1}(e_i/m_i)\vec{p}_i] = -i\omega_i[\vec{\mu}_A, (\omega_i + L_0)^{-1}\vec{\mu}_A], \tag{86}$$

as can be shown by adding to the left-hand side the null operator $-i[\vec{\mu}_A, \vec{\mu}_A]$. Then (81) reduces to

$$\overleftrightarrow{\alpha}_A\cdot(\overleftrightarrow{T}_{AB} - \overleftrightarrow{F}_{AB})\cdot(1 + L_0/\omega_i)\overleftrightarrow{\alpha}_B. \tag{87}$$

In consistency with our present approximation scheme in which we consider only quasielastic scattering [see discussion following Eq. (70)], we replace (87) by

$$\overleftrightarrow{\alpha}_A\cdot(\overleftrightarrow{T}_{AB} - \overleftrightarrow{F}_{AB})\cdot\overleftrightarrow{\alpha}_B. \tag{88}$$

When this effect of H_2 is added to the first-order contribution of H_1, one clearly sees that this amounts to replacing $\mathfrak{A}_0 T\mathfrak{A}_0$ by $\mathfrak{A}_0 F\mathfrak{A}_0$.

It is straightforward to extend this calculation to all orders, always taking the nth-order term in H_1 together with the $2n$th-order term in H_2. A word of caution is appropriate here. Although it is true that in the dipole approximation the contribution from H_3 is vanishingly small to all orders, one should make certain that mixing terms between H_2 and H_3 may be ignored as well. For example, if H_2 is taken to second and H_3 to first order, the resulting complex commutator expression can be reduced to

$$\frac{1}{\omega_i^2}\left(\sum_{j\in B}\frac{e_j^2}{2m_jc^2}\right)\overleftrightarrow{\alpha}_A\cdot\overleftrightarrow{D}_{AB}\cdot\overleftrightarrow{D}_{BC}\cdot\overleftrightarrow{\alpha}_C. \tag{89}$$

However, in comparison with the term $\alpha_A F_{AB}\alpha_B$, the quantity above is about 22 orders of magnitude smaller, so that it certainly can be neglected.

Summing the results to all orders one finally obtains the retarded Lorentz-Kirkwood formula

$$\overleftrightarrow{\mathfrak{A}} = \overleftrightarrow{\mathfrak{A}}_0\cdot(1 + \overleftrightarrow{F}\cdot\overleftrightarrow{\mathfrak{A}}_0)^{-1} \tag{90}$$

as a generalization of (78). To remind the reader, this result was obtained under the following assumptions: (a) the dipole approximation; (b) neglect of hyperpolarizabilities (exact for nonpolar molecules); (c) neglect of Doppler-type terms under off-resonance conditions; and (d) quasielastic scattering (i.e., $|\omega_i - \omega_s| \ll \omega_i$). In paper II[74] several ramifications of the present formalism, removing some of these restrictions, will be discussed.

APPENDIX A: EXTENDED ONSAGER SYMMETRY RELATIONS

In this appendix we shall investigate those symmetry properties of matrix elements of operators with the general structure

$$p_{ij} = (1/\hbar)[O_i, (\omega + L - i\epsilon)^{-1} O_j], \quad \epsilon \to 0^+, \tag{A1}$$

that are implied by time-reversal symmetry. The discussion will be closely modeled after that of Landau and Lifshitz.[86] The operators O_i and O_j are Hermitian and have well-defined signature under time reversal. We shall distinguish between the two cases where O_i and O_j have equal (case I) and opposite (case II) sign under time reversal. Matrix elements of such operators are either purely real or purely imaginary, implying

$$\langle g|O_i|f\rangle = \langle f|O_i|g\rangle^* = \pm\langle f|O_i|g\rangle, \tag{A2}$$

where the sign depends on whether O_i has positive or negative signature under time reversal. This result is only strictly true when the states $|f\rangle$ and $|g\rangle$ are not degenerate. For an interacting many-body system confined to a finite volume (broken rotational symmetry) there are no *exact* degeneracies, so that (A2) may be taken to hold generally.[86]

The operator p_{ij} can now be decomposed as follows:

$$\mathrm{Re}\,p_{ij} = q^+_{ij} + i r^+_{ij}, \tag{A3}$$

$$\mathrm{Im}\,p_{ij} = -i q^-_{ij} + r^-_{ij}, \tag{A4}$$

where [see Eq. (49)]

$$q^{\pm}_{ij} = (1/2\hbar)\{[O_i, \mathrm{P}(\omega + L)^{-1} O_j] \pm [O_i, \mathrm{P}(-\omega + L)^{-1} O_j]\} \tag{A5}$$

(P denotes the Cauchy principal part) and

$$r^{\pm}_{ij} = (\pi/2\hbar)\{[O_i, \delta(\omega + L) O_j] \pm [O_i, \delta(-\omega + L) O_j]\} \tag{A6}$$

have matrix elements

$$\hbar\langle g|q^+_{ij}|f\rangle = \sum_e \left(\frac{\langle g|O_i|e\rangle\langle e|O_j|f\rangle\omega_{ef}}{\omega_{ef}^{\,2} - \omega^2} + \frac{\langle g|O_j|e\rangle\langle e|O_i|f\rangle\omega_{eg}}{\omega_{eg}^{\,2} - \omega^2}\right), \tag{A7}$$

$$\hbar\langle g|q^-_{ij}|f\rangle = \sum_e \left(\frac{-\langle g|O_i|e\rangle\langle e|O_j|f\rangle\omega}{\omega_{ef}^{\,2} - \omega^2} + \frac{\langle g|O_j|e\rangle\langle e|O_i|f\rangle\omega}{\omega_{eg}^{\,2} - \omega^2}\right), \tag{A8}$$

$$\begin{aligned}\hbar\langle g|r^{\pm}_{ij}|f\rangle = \frac{\pi}{2}\sum_e \big(&\langle g|O_i|e\rangle\langle e|O_j|f\rangle\delta(\omega + \omega_{ef}) - \delta(\omega + \omega_{ge})\langle g|O_j|e\rangle\langle e|O_i|f\rangle \\ &\pm\langle g|O_i|e\rangle\langle e|O_j|f\rangle\delta(-\omega + \omega_{ef}) \mp \delta(-\omega + \omega_{ge})\langle g|O_j|e\rangle\langle e|O_i|f\rangle\big).\end{aligned} \tag{A9}$$

For *diagonal* matrix elements ($|f\rangle = |g\rangle$) we have in case I (O_i and O_j of equal time-reversal type)

$$\langle g|\mathrm{Re}\,p_{ij}|g\rangle = \langle g|q^+_{ij}|g\rangle = \langle g|q^+_{ji}|g\rangle, \tag{A10}$$

$$\langle g|\mathrm{Im}\,p_{ij}|g\rangle = \langle g|r^-_{ij}|g\rangle = \langle g|r^-_{ji}|g\rangle, \tag{A11}$$

as a result of which

$$\langle g|p_{ij}|g\rangle = \langle g|p_{ji}|g\rangle. \tag{A12}$$

As special examples of this equality we have the dipole-dipole (many-body polarizability

$$\langle g|\mathfrak{A}^{\alpha\beta}(\vec{r}_1, \vec{r}_2; \omega)|g\rangle = \langle g|\mathfrak{A}^{\beta\alpha}(\vec{r}_2, \vec{r}_1; \omega)|g\rangle \tag{A13}$$

and the dipole-quadrupole hyperpolarizability [for definitions of C and C', see paper II,[74] Eqs. (48) and (49)]

$$\langle g|C^{\alpha,\beta\gamma}(\vec{r}_1, \vec{r}_2; \omega)|g\rangle = \langle g|C'^{\beta\gamma,\alpha}(\vec{r}_2, \vec{r}_1; \omega)|g\rangle. \tag{A14}$$

In case II, we have

$$\langle g|\mathrm{Re}\,p_{ij}|g\rangle = i\langle g|r^+_{ij}|g\rangle = -i\langle g|r^+_{ji}|g\rangle, \tag{A15}$$

$$\langle g|\mathrm{Im}\,p_{ij}|g\rangle = -i\langle g|q^-_{ij}|g\rangle = i\langle g|q^-_{ji}|g\rangle, \tag{A16}$$

hence

$$\langle g|p_{ij}|g\rangle = -\langle g|p_{ji}|g\rangle. \tag{A17}$$

Equations (A12) and (A17) are typical Onsager reciprocal relations. As an example of (A17), we can quote the electric-dipole–magnetic-dipole hyperpolarizability [for definitions of D and D', see paper II,[74] Eqs. (50) and (51)],

$$\langle g|D^{\alpha\beta}(\vec{r}_1, \vec{r}_2; \omega)|g\rangle = -\langle g|D'^{\beta\alpha}(\vec{r}_2, \vec{r}_1; \omega)|g\rangle. \tag{A18}$$

Next we consider off-diagonal elements $\langle g|p_{ij}|f\rangle$ for which $\omega_{fg} \ll \omega$, as is the case in vibrotational Raman scattering. We shall in the following ignore the dissipative contributions $r^{\pm}_{ij}$. For the dispersive contributions $q^{\pm}_{ij}$, which are dominant in ordinary off-resonance Raman scattering, the symmetry relations (A12) and (A17) can be extended to (not too inelastic) off-diagonal elements as follows:

$$\langle g | q^{+}_{ij} | f \rangle = \pm \langle f | q^{+}_{ji} | g \rangle [1 + O(\xi)], \tag{A19}$$

$$\langle g | q^{-}_{ij} | f \rangle = \pm \langle f | q^{-}_{ji} | g \rangle [1 + O(\eta)], \tag{A20}$$

where the sign ± again depends on whether O_i and O_j have equal or opposite time-reversal signature. From Eqs. (A7) and (A8) it follows that the relative correction terms ξ and η are typically given by

$$\xi = \frac{[\omega_{ef}/(\omega_{ef}{}^2 - \omega^2) - \omega_{eg}/(\omega_{eg}{}^2 - \omega^2)]}{[\omega_{ef}/(\omega_{ef}{}^2 - \omega^2) + \omega_{eg}/(\omega_{eg}{}^2 - \omega^2)]} = \frac{\omega_{fg}}{\omega_{ef} + \omega_{eg}}, \tag{A21}$$

$$\eta = \frac{[\omega/(\omega_{ef}{}^2 - \omega^2) - \omega/(\omega_{eg}{}^2 - \omega^2)]}{[\omega/(\omega_{ef}{}^2 - \omega^2) + \omega/(\omega_{eg}{}^2 - \omega^2)]}$$

$$= \frac{\omega_{fg}(\omega_{eg} + \omega_{ef})}{\omega_{eg}{}^2 + \omega_{ef}{}^2 - 2\omega^2}. \tag{A22}$$

In the sum over all intermediate states $|e\rangle$ in (A7) and (A8) the important contributions usually come from highly excited states $|e\rangle$ with $\omega_{eg} \gtrsim \omega$, hence $\xi \lesssim \omega_{fg}/\omega$. The same holds for η provided, however, that ω does not lie close to one of the excited states $|e\rangle$, so that the denominator in (A22) is not small for any $|e\rangle$. We can conveniently regard ω_{fg}/ω as the appropriate small parameter. It thus appears that the Onsager symmetry relations still hold in an approximate fashion for vibrotational Raman scattering (where $\omega_{fg} \ll \omega$), but are invalid in electronic Raman scattering (where $\omega_{fg} \gtrsim \omega$). Some additional observations are made in Appendix C about inelasticity corrections of a rather different nature from those discussed here.

APPENDIX B: DOPPLER-TYPE CORRECTIONS

At several points in Secs. IV and V certain terms are referred to as Doppler-type corrections and are neglected. It is claimed that their order of magnitude relative to the corresponding leading term is v/c, v being the average center-of-mass molecular velocity. The argument is based on the structure of the resolvent G_0 of Eq. (65). The Liouvillian L_A [see Eq. (58)] contains both a part L_A^{int} operating on the internal (electronic, vibrational, rotational) states of molecule A and the center-of-mass kinetic operator L_A^{cm},

$$L_A^{\text{cm}} X = (1/\hbar)[p_A{}^2/2m_A, X], \tag{B1}$$

where $\vec{p}_A$ and m_A are the center-of-mass linear momentum and mass of molecule A. In the expression

$$[\vec{\mu}_A e^{i\vec{k}_s \cdot \vec{r}_A}, (\omega_i + L_A^{\text{int}} + L_A^{\text{cm}})^{-1} \vec{\mu}_A e^{-i\vec{k}_i \cdot \vec{r}_A}], \tag{B2}$$

L_A^{int} operates only on $\vec{\mu}_A$ and L_A^{cm} only on the exponential, i.e.,

$$L_A^{\text{cm}} e^{-i\vec{k}_i \cdot \vec{r}_A} = (1/2m_A)(\vec{p}_A \cdot \vec{k}_i e^{-i\vec{k}_i \cdot \vec{r}_A} + e^{-i\vec{k}_i \cdot \vec{r}_A} \vec{p}_A \cdot \vec{k}_i) \tag{B3}$$

(for ease of presentation, the spatial density factors are written in the $\vec{k}$ rather than in the $\vec{r}$ representation). Matrix elements of $L_A^{\text{int}} \vec{\mu}_A$ produce energy differences that are smaller than or of the same order of magnitude as ω_i (for vibrotational and electronic intermediate states, respectively). Provided ω_i is *not* close to one of the resonance frequencies of the molecular spectrum, we may thus compare (B3) with ω_i in order to estimate its relative importance:

$$\beta \simeq \vec{p}_A \cdot \vec{k}_i / m_A \omega_i \simeq \frac{v_A}{c} \simeq 10^{-5} \tag{B4}$$

(at room temperature). We may thus justifiably neglect L_A^{cm} in (B2), so that the exponentials can be taken out of the commutator, as is done in Eq. (67). The same kind of analysis leads to the neglect of the commutator of Eq. (79).

Also, the neglect of the fourth term of (66), as compared with the second one in the same equation, is justified with an appeal to the same kind of argument. The ratio between these two terms is essentially given by

$$\beta = \frac{[T_{AB}^{\alpha\beta}, (\omega_i + L_B)^{-1} \mu_B^{\alpha} e^{i\vec{k}_i \cdot \vec{r}_B}] \mu_B^{\beta}}{\hbar\, T_{AB}^{\alpha\beta} \alpha_B^{\beta\alpha}(\omega_i) e^{i\vec{k}_i \cdot \vec{r}_B}}. \tag{B5}$$

By use of (B3) we have, to first order in L_B,

$$[\overleftrightarrow{T}_{AB}, (\omega_i + L_B)^{-1} \vec{\mu}_B e^{i\vec{k}_i \cdot \vec{r}_B}] \simeq (1/\omega_i^2)[\overleftrightarrow{T}_{AB}, \vec{p}_B \cdot \vec{k}_i / m_B] \vec{\mu}_B e^{i\vec{k}_i \cdot \vec{r}_B}. \tag{B6}$$

A very rough estimate of β can be obtained by ignoring the commutator character of the expression on the right-hand side above, doing similarly for $\overleftrightarrow{\alpha}_B$ $(\simeq \vec{\mu}_B \vec{\mu}_B / \hbar\omega_i)$, where $\beta \simeq v/c$. The value of β is even further reduced if the commutator in (B6) is handled more carefully; namely, by taking into account that

$$(1/\hbar)[\overleftrightarrow{T}_{AB}, \vec{p}_B \cdot \vec{k}_i / m_B] = i(\vec{k}_i / m_B) \cdot \vec{\nabla}_B \overleftrightarrow{T}_{AB}, \tag{B7}$$

one gets a more accurate estimate for β, i.e., $\beta \simeq \hbar / mcR$, where R is a typical intermolecular distance. For a fluid of H atoms, $\beta \simeq 2 \times 10^{-6}/R$ (R in Å), so that for liquid densities, $\beta \simeq 10^{-6}$, and for dilute gases, $\beta \simeq 10^{-8}$. For heavier molecules, β will be even smaller. By the same reasoning, the action of G_0 on $T(34)$ in Eq. (66) is consistently ignored; when compared with the result of operating with G_0 on the other (electronic) factors, the former is of relative order of magnitude β.

One should not confuse these neglected Doppler corrections to $\mathfrak{A}$ with the contribution of the center-of-mass motion to the low-frequency $(\omega_i - \omega_s)$ Fourier components of the $\langle \mathfrak{A}(0)\mathfrak{A}(t)\rangle$ correlation function, which is very essential to the interpretation of light-scattering experiments.[37,39] This (*non-negligible*) Doppler modulation derives from the spatial δ functions in Eq. (67). It is thus important to realize that in (67) we have extracted the δ functions from the commutator, but we did not neglect them altogether, so that our formalism retains all of the basic ingredients for a correct hydrodynamic or kinetic description of Doppler-broadened Rayleigh-Brillouin spectra.

APPENDIX C: INELASTICITY CORRECTIONS

The algebra in the Coulomb-limit calculation in Sec. IV is considerably simplified by the neglect of the $m \neq 0$ terms in Eq. (70). It is the purpose of this Appendix to investigate under which conditions this approximation is justified. Consider a matrix element of the complicated operator expression (70),

$$-\frac{1}{2\hbar^2\omega_i}\sum_{n=0}^{\infty}\sum_{m=0}^{n}\binom{n}{m}\sum_c \{\langle a|\,[M^{\alpha}(1),\{(-L_0/\omega_i)^{n-m}M^{\gamma}(3)\}]\,|c\rangle T^{\gamma\delta}(34)\langle c|\,\{(-L_0/\omega_i)^{m}[M^{\delta}(4),GM^{\beta}(2)]\}\,|b\rangle$$
$$+\langle a|\,\{(-L_0/\omega_i)^{m}M^{\gamma}(3)\}\,|c\rangle T^{\gamma\delta}(34)\langle c|\,[M^{\alpha}(1),\{(-L_0/\omega_i)^{n-m}[M^{\delta}(4),GM^{\beta}(2)]\}]\,|b\rangle\}, \qquad \text{(C1)}$$

and note that the states $|a\rangle$ and $|b\rangle$ satisfy the energy-conservation condition (54). The parameter $\xi \equiv |\omega_{ab}|/\omega_i = |E_a - E_b|/\hbar\omega_i$ is introduced as a measure of the degree of inelasticity in the photon scattering event. One should distinguish between quasielastic $(\xi < 1)$ and strongly inelastic $(\xi \gtrsim 1)$ scattering. Rayleigh $(\xi \simeq 10^{-5}-10^{-4})$, rotational Raman $(\xi \simeq 10^{-3}-10^{-2})$, and usually also vibrational Raman $(\xi \simeq 10^{-2}-10^{-1})$ scattering belong to the first category. Electronic Raman scattering $(\xi \simeq 1-10)$, on the other hand, should be considered separately. It will be argued that the approximation implied by neglecting the $m \neq 0$ terms in Eq. (C1) is justified in the quasielastic case, to which we now restrict our attention.

In the first term of Eq. (C1) an intermediate state $|c\rangle$ occurs whose energy E_c might seem to be possibly very different from E_a and E_b. However, this is *not* so in most cases of interest, by virtue of the fact that L_0 is diagonalized in the molecular indices. This is most clearly seen by taking a matrix element of the second term of (66) to lowest order in the interaction L_1

$$\langle a|[M^{\alpha}(1),G_0M^{\gamma}(3)T^{\gamma\delta}(34)\mathfrak{A}^{\delta\beta}(42)]|b\rangle$$
$$\simeq \sum_{A\neq B}\langle a_Aa_B|[\mu_A^{\alpha},G_0\mu_A^{\gamma}T_{AB}^{\gamma\delta}\alpha_B^{\delta\beta}]|b_Ab_B\rangle$$
$$=\sum_{A\neq B}\langle a_A|[\mu_A^{\alpha},G_0\mu_A^{\gamma}T_{AB}^{\gamma\delta}\langle a_B|\alpha_B^{\delta\beta}|b_B\rangle]|b_A\rangle$$
$$=\sum_{A\neq B}\langle a_A|\alpha_A^{\alpha\gamma}|b_A\rangle T_{AB}^{\gamma\delta}\langle a_B|\alpha_B^{\delta\beta}|b_B\rangle, \qquad \text{(C2)}$$

where the states $|a_A\rangle$ and $|a_B\rangle$ of molecules A and B are not coupled (to lowest order in L_1). In most cases of practical interest (e.g., depolarized scattering by isotropic molecules[7]) it is sufficient to consider L_1 only to first order. In higher-order terms, whenever a particular molecular label (A, etc.) occurs more than once, the previous argument does not appear to hold anymore. Consider, for example, the expression

$$\sum_{A\neq B}\langle a_Aa_B|\,\mu_A^{\alpha}G_0\mu_A^{\gamma}T_{AB}^{\gamma\delta}\alpha_B^{\delta\epsilon}T_{BA}^{\epsilon\eta}\alpha_A^{\eta\beta}|b_Ab_B\rangle$$
$$=\sum_{A\neq B}\sum_{c_A}\langle a_A|\,\mu_A^{\alpha}G_0\mu_A^{\gamma}|\,c_A\rangle T_{AB}^{\gamma\delta}$$
$$\times\langle a_B|\,\alpha_B^{\delta\epsilon}|b_B\rangle T_{BA}^{\epsilon\eta}\langle c_A|\,\alpha_A^{\eta\beta}|b_A\rangle, \qquad \text{(C3)}$$

where we have taken only one term of the commutator bracket. Here it would seem that the sum over all states $|c_A\rangle$ also includes highly excited states of molecule A. However, in this sum the dominant contribution comes from $|c_A\rangle \simeq |b_A\rangle$, since quite generally $\langle c|\,\alpha|b\rangle$ decreases in magnitude as ω_{cb} (the energy difference between the states $|b\rangle$ and $|c\rangle$) increases. (The latter property is reflected in the facts that Rayleigh is stronger than Raman scattering and that vibrational Raman scattering, in turn, is stronger than electronic Raman scattering.) It is thus true—to first order in L_1 rigorously and to higher orders in L_1 approximately—that the intermediate state $|c\rangle$ appearing in Eq. (70) is no "new" state but is composed of the same molecular states as $|a\rangle$ and $|b\rangle$ [e.g., in Eq. (C1), $|c\rangle = |b_Aa_B\rangle$].

Since $|c\rangle$ is energetically close to $|a\rangle$ and $|b\rangle$, the matrix element

$$\langle c(L_0/\omega_i)^m[M^\delta(4), GM^\beta(2)]|b\rangle = (\omega_{cb}/\omega_i)^m\langle c|[M^\delta(4), GM^\beta(2)]|b\rangle \quad \text{(C4)}$$

occurring in Eq. (C1) is a rapidly decreasing function of m, so that the neglect of all terms $m \geqslant 1$ is well justified in the quasielastic case. Notice that the $m = 1$ term corresponds to a polarizability current $\dot{\overleftrightarrow{\alpha}}_A \equiv iL_A\overleftrightarrow{\alpha}_A$. In strongly inelastic scattering, the effects of such currents could therefore become important. In Appendix A it is shown that under the same conditions ($\xi \gtrsim 1$) the polarizability has an antisymmetric part ($\mathfrak{a}^{\alpha\beta} \neq \mathfrak{a}^{\beta\alpha}$). This point seems to have been raised in 1934 by Placzek[87]; more recently, such effects have been discussed and actually measured in electronic Raman spectra of lanthanide crystals by Mortensen and Koningstein.[88,89] The present discussion suggests the possibility of observing similar inelasticity corrections in collision-induced scattering in compressed gases. It must be added that these terms are absent in the usual (classical) theories of collision-induced light scattering.

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