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Isothermal and Isolated Susceptibilities for a Nonlinear Refractive Index

M. Takatsuji

Hitachi Central Research Laboratory, Kokubunji, Tokyo, Japan

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Using a canonical-transformation method, a formal expression for the isothermal polarization induced by an arbitrarily time-varying field is obtained which includes the population change due to the energy shift which is proportional to the field intensity. The result is applied to the static linear susceptibility and nonlinear refractive index induced by an intense laser beam. It is shown for the latter that the lowest- (third-) order isolated susceptibility of an isotropic medium is a lower bound for the isothermal susceptibility if both the polarizations and frequencies of the laser beam and the probe light are the same.

I. INTRODUCTION

The concepts of the isothermal and isolated susceptibilities of electric or magnetic media are well established. In the isothermal process, the system is in thermal contact with the heat bath and maintains its temperature constant at all times when the field is applied, while in the isolated process the system was in thermal contact with the heat bath at the infinite past which was then isolated from its surroundings. The field is applied very slowly (adiabatically in Ehrenfest's sense), and the isolated motion of the system obeys the Liouville equation. Quantum mechanically, the population of a given energy level must be held constant for the isolated process, while for the isothermal process the population change is possible. The difference of the two susceptibilities arises from this fact.

The quantum-statistical formulations of both the isolated susceptibility for a time-varying field[1] and the static isothermal susceptibility[2] have been accomplished to every order in the applied field. However, there seems to be no general formulation of the isothermal susceptibility for an arbitrarily time-varying field. The main purpose of the present paper is to deal with this problem by a quantum-statistical method.

Performing a canonical transformation on the Liouville equation, the rapidly oscillating part of the Hamiltonian is eliminated. The density matrix for the isolated system is then driven by a time-independent Hamiltonian at time t, when the system is again brought into contact with the heat bath so that it is represented by a new equilibrium density matrix. It is found in Sec. II that the isothermal expectation value of an operator is obtained by replacing the equilibrium density matrix at the infinite past by the new one in the expression for the isolated expectation value of the operator. In Sec. III, the result is applied to the well-known problem of static linear susceptibilities. Those for the nonlinear refractive index induced by an intense laser beam are discussed in Sec. IV.

II. GENERAL FORMULATION

The isolated system is described by the Liouville equation for the density matrix σ,

$$i\hbar\frac{\partial\sigma}{\partial t}=[H,\sigma]\ ,\quad H=H_0+V\ , \tag{1}$$

where the Hamiltonian H consists of the unperturbed part H_0 and the perturbation V,

$$V=-\vec{\mathrm{P}}\cdot\vec{\mathrm{E}}e^{\eta t}\ , \tag{2}$$

which is turned on very slowly in the infinite past. In Eq. (2), $\vec{\mathrm{P}}$ is the electric dipole-moment operator, $\vec{\mathrm{E}}$ the applied electric field, and η a small positive quantity which is set equal to zero at the end of the calculation. In this paper, $\vec{\mathrm{E}}$ with frequency ω,

$$\vec{\mathrm{E}}=\tfrac{1}{2}\vec{\epsilon}\,(E^{\omega}e^{-i\omega t}+E^{-\omega}e^{i\omega t})\ , \tag{3}$$

is treated classically, where $\vec{\epsilon}$ is the unit polarization vector.

Now the following canonical transformation is performed on σ:

$$\rho=e^{-iS}\sigma e^{iS}\ , \tag{4}$$

where S is an Hermitian operator. ρ then obeys

$$i\hbar\frac{\partial\rho}{\partial t}=[K,\rho]\ . \tag{5}$$

The transformed Hamiltonian K is given by

$$K=e^{-iS}He^{iS}+\hbar\dot{S},\quad \dot{S}\equiv\frac{\partial S}{\partial t}\ . \tag{6}$$

The original Hamiltonian is divided into three parts:

$$H=H^{(0)}+H^{(1)}+H^{(2)}\ , \tag{7}$$

where $$H^{(0)}=H_0+H^{\alpha}+H^{\gamma}\ , \tag{8}$$

$$H^{(1)}=V-H^{\alpha}\ , \tag{9}$$

and $$H^{(2)}=-H^{\gamma}\ . \tag{10}$$

As shown in the following, H^{α} and H^{γ} represent the first- and second-order energy shifts by static and time-varying fields, respectively. $H^{(0)}$ is a renormalized unperturbed Hamiltonian taking into account the energy shifts. K and S are similarly expanded according to the order of the perturbation,

$$K=K^{(0)}+K^{(1)}+K^{(2)}+\cdots\ , \tag{11}$$

$$S=S^{(1)}+S^{(2)}+\cdots\ . \tag{12}$$

Substituting Eqs. (7)–(12) into (6), and using the expansion for any operator D,

$$e^{-iS}De^{iS}=D-i[S,D]-\tfrac{1}{2}\Big[S,[S,D]\Big]+\cdots\ , \tag{13}$$

we obtain $$K^{(0)}=H^{(0)}\ , \tag{14}$$

$$K^{(1)}=H^{(1)}-i[S^{(1)},H^{(0)}]+\hbar\dot{S}^{(1)}\ , \tag{15}$$

$$K^{(2)}=H^{(2)}-i[S^{(1)},H^{(1)}]-i[S^{(2)},H^{(0)}]-\tfrac{1}{2}\Big[S^{(1)},[S^{(1)},H^{(0)}]\Big]+\hbar\dot{S}^{(2)}\ , \tag{16}$$

and higher-order equations which we neglect here.

We choose $S^{(1)}$, $S^{(2)}$, H^{α}, and H^{γ} so that $K^{(1)}$ and $K^{(2)}$ vanish. For a sufficiently rapidly time-varying field, H^{α} does not contribute to the energy shift so that the elimination of $K^{(1)}$ results in

$$\hbar\dot{S}^{(1)}-i[S^{(1)},H^{(0)}]+V=0\ \text{(time-varying)}. \tag{17}$$

For a static field, H^{α} and $S^{(1)}$ are chosen in the form

$$H^{\alpha}_{mn}=V_{mn}\qquad\text{for } W_{mn}\equiv W_m-W_n=0\ , \tag{18}$$

$$\hbar\dot{S}^{(1)}_{mn}+i\,W_{mn}S^{(1)}_{mn}+V_{mn}=0\quad\text{for } W_{mn}\neq 0\ , \tag{19}$$

where the subscript mn means the matrix element between states m and n in the representation diagonalizing $H^{(0)}$, and W_m is the energy of the state m. We neglect the second-order energy shift in the static field, and choose $H^{(2)}$ and $S^{(2)}$ in the form

$$H^{(2)}_{mn}=\tfrac{1}{2}i\langle[S^{(1)},V]_{mn}\rangle_t\qquad\text{for } W_{mn}=0\ , \tag{20}$$

$$\hbar\dot{S}^{(2)}_{mn}+i\,W_{mn}S^{(2)}_{mn}-\tfrac{1}{2}i[S^{(1)},V]_{mn}+H^{(2)}_{mn}=0\ , \tag{21}$$

where $\langle\ \rangle_t$ means the time average over many cycles of the time-varying frequency. This choice is readily seen to eliminate $K^{(2)}$ if one notes the unitarity of e^{-iS}, namely, $[S^{(1)},\dot{S}^{(1)}]=0$. Integration of Eq. (17) from $-\infty$ to t yields, with the use of Eqs. (2) and (3),

$$S^{(1)}_{mn}=\tfrac{1}{2}(i\,P_{mn}e^{\eta t})\times\left(\frac{E^{\omega}e^{-i\omega t}}{W_{nm}+\hbar\omega+i\hbar\eta}+\frac{E^{-\omega}e^{i\omega t}}{W_{nm}-\hbar\omega+i\hbar\eta}\right)\ , \tag{22}$$

where $P=\vec{\mathrm{P}}\cdot\vec{\epsilon}$.

Then, $H^{(2)}_{mn}$ is calculated from Eq. (20) as

$$H^{(2)}_{mn}=\sum_l\frac{e^{2\eta t}P_{ml}P_{ln}}{4\hbar}\times\left(\frac{(\omega_{lm}-\omega)E^{-\omega}E^{\omega}}{(\omega_{lm}-\omega)^2+\eta^2}+\frac{(\omega_{lm}+\omega)E^{\omega}E^{-\omega}}{(\omega_{lm}+\omega)^2+\eta^2}\right)\ ,\quad W_{mn}=0, \tag{23}$$

where $\omega_{lm}=W_{lm}/\hbar$, and for classical field

$$E^{-\omega}E^{\omega}=E^{\omega}E^{-\omega}=2\langle E^2\rangle_t\ .$$

It is noted here that since H^{α} and $H^{\gamma}=-H^{(2)}$ are diagonal in the energy representation of $H^{(0)}$, the quantities $H^{(0)}$, H_0 , and $H^{\alpha,\gamma}$ commute with each other as is readily seen by taking the matrix elements of the commutators in the same representation. Then, they are diagonalized simultaneously by a complete set of the eigenfunctions. $H^{\gamma} = -H^{(2)}$ in Eq. (23) includes the perturbed energies W_m's, and therefore higher-order terms than the second in the applied field. H^{γ} is not a true second-order term. The higher-order terms are, however, parts of the higher-order corrections to the energy shift, and may be neglected in our approximation. The condition $W_{mn}=0$ in Eqs. (18) and (23) means that the perturbed states m and n are degenerate of $n \neq m$. Then, except for an accidental degeneracy, corresponding unperturbed states will also be degenerate. Thus, we can hereafter reinterpret W_m's as the eigenenergies of the unperturbed Hamiltonian H_0, and through secular equations for degenerate perturbation theory, expressions for H^{α} and H^{γ} exactly determine the first- and the second-order energy shifts caused, respectively, by static and time-varying fields.

At the infinite past, the density matrix is assumed to be in thermal equilibrium with the heat bath,

$$\sigma^0 = e^{-\beta H_0}, \quad \mathrm{Tr}\sigma^0 = 1 \ , \tag{24}$$

where β is the inverse of the temperature times Boltzmann's constant. Then the system was isolated, and has evolved according to the Liouville equation so that at time t the transformed density matrix is described by a time-independent Hamiltonian $H^{(0)}$,

$$i\hbar \frac{\partial \rho}{\partial t} = [H^{(0)}, \rho] \ . \tag{25}$$

Considering the commutability of $H^{(0)}$ and H_0 , the solution of Eq. (25) is simply

$$\rho = U^{(0)} \sigma^0 U^{(0)\dagger} = \sigma^0 \ , \tag{26}$$

$$\text{where} \quad U^{(0)} = (-i\hbar^{-1} \textstyle\int_{-\infty}^{t} H^{(0)}\, dt) \ . \tag{27}$$

However, to obtain the isothermal density matrix, one must again bring the system into thermal contact with the heat bath at time t. Then, while the field is applied, many incoherent transitions will occur among the various renormalized states (eigenstates of $H^{(0)}$) of the system, and the system will approach the new thermal equilibrium after a sufficiently long time.[3] Then, the boundary value of Eq. (25) is not σ^0, but will be

$$\sigma^e = \exp(-\beta H^{(0)}) \ , \tag{28}$$

which makes a time-independent solution of Eq. (25). Since H_0 and $H^{\alpha,\gamma}$ commute, σ^e is written

$$\sigma^e = \sigma^0 \exp[-\beta(H^{\alpha} + H^{\gamma})] \ . \tag{29}$$

Expanding $\exp[-\beta(H^{\alpha}+H^{\gamma})]$ in powers of β, and writing

$$\sigma^e = \sigma^0 + \sigma', \quad (\mathrm{Tr}\sigma^e)^{-1} = 1 + \mathrm{Tr}\sigma'' \ , \tag{30}$$

σ' and σ'' are given explicitly only for the first terms as

$$\sigma' = -\sigma'' = -\beta\sigma^0 (H^{\alpha} + H^{\gamma}) \ . \tag{31}$$

The isothermal ensemble average of the operator $\vec{\mathrm{P}}$ is thus given by

$$\langle \vec{\mathrm{P}} \rangle_T = \mathrm{Tr}\sigma^e e^{-iS} \vec{\mathrm{P}} e^{iS} / \mathrm{Tr}\sigma^e \ , \tag{32}$$

where the temperature must be held constant. Now the solution of Eq. (1) is formally written

$$\sigma = U \sigma^0 U^{\dagger} \ , \tag{33}$$

$$\text{where} \quad U = T \exp[-i\hbar^{-1} \textstyle\int_{-\infty}^{t} H(t')\, dt']$$

$$= U_0 + \sum_{l=1}^{\infty} U^{(l)} \ , \tag{34}$$

$$U_0 = \exp(-i\hbar^{-1} H_0 t) \ , \tag{35}$$

$$U^{(l)} = U_0 (i\hbar)^{-l} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{l-1}} dt_l \times [\tilde{V}(t_1) \tilde{V}(t_2) \cdots \tilde{V}(t_l)] \ , \tag{36}$$

$$\tilde{V} = U_0^{\dagger} V U_0 \ , \tag{37}$$

$U^{\dagger}$ is the Hermitian adjoint to U, and T is the time-ordering operator. From Eqs. (4), (26), and (33), e^{iS} is given by

$$e^{iS} = U U^{(0)\dagger} \ . \tag{38}$$

Expanding the both sides of Eq. (38) into the power series of the applied field, we have

$$U^{(1)} U_0^{\dagger} = iS^{(1)} - i\hbar \int_{-\infty}^{t} H^{\alpha}\, dt, \tag{39}$$

$$U^{(2)} U_0^{\dagger} = iS^{(2)} - \tfrac{1}{2} S^{(1)2} + \hbar S^{(1)} \int_{-\infty}^{t} H^{\alpha}\, dt - i\hbar \times \int_{-\infty}^{t} H^{\gamma}\, dt - \tfrac{1}{2}\hbar^{-2} \left(\int_{-\infty}^{t} H^{\alpha}\, dt\right)^2 . \tag{40}$$

Substituting Eq. (38) into (32), and using the cyclic-invariance property of the trace, we finally have for $\langle \vec{\mathrm{P}} \rangle_T$

$$\langle \vec{\mathrm{P}} \rangle_T = \mathrm{Tr}\sigma^e U^{\dagger} \vec{\mathrm{P}} U / \mathrm{Tr}\sigma^e \ . \tag{41}$$

In Eq. (41), use is made of the commutability of $U^{(0)}$ and σ^e. This is a formal expression for the isothermal polarization correct to the first- and second-order energy shifts caused, respectively, by static and rapidly time-varying fields. On the other hand, the isolated ensemble average of $\vec{\mathrm{P}}$ is given by

$$\langle \vec{\mathrm{P}} \rangle_S = \mathrm{Tr}\sigma P / \mathrm{Tr}\sigma \ . \tag{42}$$

With Eq. (33), $\langle \vec{\mathrm{P}} \rangle_S$ is rewritten

$$\langle \vec{\mathrm{P}} \rangle_S = \mathrm{Tr}\sigma^0 U^{\dagger} \vec{\mathrm{P}} U \ . \tag{43}$$

As seen from Eqs. (41), (43), and (24), the isothermal polarization is given by simply replacing σ^0 by σ^e in the expression for the isolated polarization. The difference of the two polarizations arises from the population change included in $\langle \vec{\mathrm{P}} \rangle_T$, and is written, using Eq. (30),

$$\langle \vec{\mathrm{P}} \rangle_T - \langle \vec{\mathrm{P}} \rangle_S = \mathrm{Tr}\sigma' U^\dagger \vec{\mathrm{P}} U + \mathrm{Tr}\sigma^0 U^\dagger \vec{\mathrm{P}} U \,\mathrm{Tr}\sigma'' + \mathrm{Tr}\sigma' U^\dagger \vec{\mathrm{P}} U \,\mathrm{Tr}\sigma'' \,. \tag{44}$$

Equations (41) and (44) with (29) are the main results of this section. Now we apply them to the static linear susceptibilities and nonlinear refractive index. In both cases, we neglect any resonance phenomenon, namely, we discard imaginary δ-function terms which arise as we set $\eta \to 0$ at the end of the calculation. Local field corrections are also not considered explicitly.

III. STATIC LINEAR SUSCEPTIBILITIES

For the static case, only the linear term H^α is considered in Eq. (29). From Eqs. (44) and (31), we have for the static linear isothermal susceptibility χ_T^L,

$$\chi_T^L = \chi_S^L + \lim_{\eta \to 0} (\mathrm{Tr}\sigma' U_0^\dagger P' U_0 + \mathrm{Tr}\sigma^0 U_0^\dagger P' U_0 \,\mathrm{Tr}\sigma'')/E \,, \tag{45}$$

where $P' = \vec{\mathrm{P}} \cdot \vec{\epsilon}\,'$, ϵ' is the unit vector of $\vec{\mathrm{P}}$, and the static linear isolated susceptibility χ_S^L is given by

$$\chi_S^L = \lim_{\eta \to 0} \mathrm{Tr}\sigma^0 (U_0^\dagger P' U^{(1)} + U^{\dagger(1)} P' U_0)/E \,. \tag{46}$$

χ_S^L is explicitly calculated using Eqs. (39) and (22) with $\omega = 0$, and the relation

$$\lim_{\eta \to 0} \frac{1}{W_{nm} + i\hbar\eta} = \mathcal{P} \frac{1}{W_{nm}} - i\pi\,\delta(W_{nm}) \tag{47}$$

as

$$\chi_S^L = \mathcal{P} \sum_{m,n} \frac{\sigma_n^0 - \sigma_m^0}{W_{mn}} P_{mn} P'_{nm} \,, \tag{48}$$

where $\mathcal{P}$ is the principal-value operator. Note that for χ_S^L the contribution

$$\lim_{W_{mn}=0} \frac{\sigma_n^0 - \sigma_m^0}{W_{mn}} = \beta \sigma_m^0 \tag{49}$$

is excluded by the $\mathcal{P}$ operator. Substitution of Eqs. (31) and (18) into (45) yields

$$\chi_T^L = \chi_S^L + \beta \Bigg[\sum_{m,n;\; W_{mn}=0} \sigma_m^0 P_{mn} P'_{nm} - \Big(\sum_m \sigma_m^0 P_{mm} \Big) \Big(\sum_n \sigma_n^0 P'_{nn} \Big) \Bigg] \,. \tag{50}$$

Equation (50) is the same with the result obtained by the usual method.[1,2] For media whose symmetries allow the relation $\vec{\epsilon} = \vec{\epsilon}\,'$ and thus $P = P'$, the difference of the two susceptibilities can be written as

$$\chi_T^L - \chi_S^L = \beta \Bigg[\sum_m \sigma_m^0 P_{mm}^2 - \Big(\sum_m \sigma_m^0 P_{mm} \Big)^2 \Bigg] + \beta \sum_{m \neq n \;\, W_{mn}=0} \sigma_m^0 P_{mn}^2 \,. \tag{51}$$

In Eq. (51), the first term is non-negative from the Schwarz inequality, while the second term is also non-negative for positive temperature. χ_S^L is thus a lower bound for χ_T^L, as found recently by Falk[4] for the magnetic susceptibility.

It will be seen from the above calculation that the isothermal susceptibility may formally be obtained from the isolated-susceptibility formulation, namely, from Eq. (42) by neglecting the $\mathcal{P}$ operator. The neglect in Eq. (48) yields an additional term which is equivalent to the first term in the bracket of Eq. (50). This neglect, of course, violates the unitarity of U, and one has another additional term from the expansion

$$(\mathrm{Tr}\sigma)^{-1} = 1 - \mathrm{Tr}\sigma^{(1)} - \mathrm{Tr}\sigma^{(2)} + (\mathrm{Tr}\sigma^{(1)})^2 + \cdots \,, \tag{52}$$

where $\sigma^{(1)}$ and $\sigma^{(2)}$ are the first- and second-order density matrices in the applied field, respectively, and obtained by expanding σ in Eq. (33). Similarly neglecting the $\mathcal{P}$ operator, the second term in Eq. (52), combined with the term $\mathrm{Tr}\sigma^0 P$, is seen to contribute to the second term in the bracket of Eq. (50). Kubo[1] discussed the condition for which $\chi_T^L = \chi_S^L$ in terms of the ergodicity of the system.

IV. SUSCEPTIBILITIES FOR A NONLINEAR REFRACTIVE INDEX

The classical theory of a nonlinear refractive index has recently been investigated widely for liquids.[5] The following discussion, however, may also cover other kinds of media. In the case of a nonlinear refractive index, an intense laser beam with frequency ω_L induces changes in the refractive index which may be probed by another light with frequency ω_S. The electric field thus consists of

$$\vec{\mathrm{E}}^L = \tfrac{1}{2} \vec{\epsilon}^{\,L} (E^{\omega_L} e^{-i\omega_L t} + E^{-\omega_L} e^{i\omega_L t}) \tag{53}$$

and

$$\vec{\mathrm{E}}^S = \tfrac{1}{2} \vec{\epsilon}^{\,S} (E^{\omega_S} e^{-i\omega_S t} + E^{-\omega_S} e^{i\omega_S t}) \,, \tag{54}$$

where $\vec{\epsilon}^{\,L}$ and $\vec{\epsilon}^{\,S}$ are unit polarization vectors. $\vec{\mathrm{E}}^L$ changes so rapidly that we need not consider the linear term H^α. Substituting Eq. (31) into (44), and using (10), we obtain $\langle \vec{\mathrm{P}} \rangle_T$ for the lowest-order (second in $\vec{\mathrm{E}}^L$ and first in $\vec{\mathrm{E}}^S$) nonlinear refractive index as

$$\langle \vec{\mathrm{P}} \rangle_T^{\mathrm{NL}} = \langle \vec{\mathrm{P}} \rangle_S^{\mathrm{NL}} + \lim_{\eta \to 0} \beta \Bigg[\sum_{m,n;\; W_{mn}=0} \sigma_m^0 H_{mn}^{(2)} \times (U^{\dagger(1)} \vec{\mathrm{P}} U_0 + U_0^\dagger \vec{\mathrm{P}} U^{(1)})_{nm} - \mathrm{Tr}\sigma^0 H^{(2)} \times \mathrm{Tr}\sigma^0 (U^{\dagger(1)} \vec{\mathrm{P}} U_0 + U_0^\dagger \vec{\mathrm{P}} U^{(1)}) \Bigg] \,. \tag{55}$$

In Eq. (55), $U^{(1)}$ should be calculated using Eq. (39), where the perturbation V is due to the probe light. Explicit calculation with the use of Eq. (23) gives for the nonlinear isothermal susceptibility

$$\chi_T^{\mathrm{NL}}=\chi_S^{\mathrm{NL}}+\tfrac{1}{2}\beta\Bigg[\sum_{m,n;\ W_{mn}=0}\sigma_m^0\ \mathcal{H}_{mn}^{L}\ \mathcal{H}_{nm}^{S} -\Big(\sum_m \sigma_m^0\mathcal{H}_{mm}^{L}\Big)\Big(\sum_n \sigma_n^0\mathcal{H}_{nn}^{S}\Big)\Bigg]\ , \tag{56}$$

where

$$\mathcal{H}_{mn}^{L}=\sum_l\frac{P_{ml}^{L}P_{ln}^{L}}{\hbar}\mathcal{P}\left(\frac{2\omega_{lm}}{\omega_{lm}^2-\omega_L^2}\right)\ , \tag{57}$$

$$\mathcal{H}_{mn}^{S}=\sum_l\frac{P_{ml}^{S}P_{ln}}{\hbar}\mathcal{P}\left(\frac{2\omega_{lm}}{\omega_{lm}^2-\omega_S^2}\right)\ ,\qquad P^L\equiv\vec{\mathrm{P}}\cdot\vec{\epsilon}^{\,L}\ ,\ \text{ and } P^S\equiv\vec{\mathrm{P}}\cdot\vec{\epsilon}^{\,S}\ . \tag{58}$$

The difference between the two susceptibilities is now written as

$$\chi_T^{\mathrm{NL}}-\chi_S^{\mathrm{NL}}=\tfrac{1}{2}\beta\Bigg[\sum_m\sigma_m^0\mathcal{H}_{mm}^{L}\mathcal{H}_{mm}^{S}-\Big(\sum_m\sigma_m^0\mathcal{H}_{mm}^{L}\Big)\Big(\sum_n\sigma_n^0\mathcal{H}_{nn}^{S}\Big)\Bigg]+\tfrac{1}{2}\beta\sum_{m\neq n,W_{mn}=0}\sigma_m^0\mathcal{H}_{mn}^{L}\mathcal{H}_{nm}^{S}\ . \tag{59}$$

If the medium is isotropic, $P=P^S$, and further, both the polarizations and frequencies of the laser and probe lights are the same, $\vec{\epsilon}^{\,L}=\vec{\epsilon}^{\,S}$ and $\omega_L=\omega_S$, the first and the second terms of Eq. (59) are nonnegative by the same argument as the linear case. Thus, under the above conditions, χ_S^{NL} is a lower bound for χ_T^{NL},

$$\chi_T^{\mathrm{NL}}\geqq\chi_S^{\mathrm{NL}}\ . \tag{60}$$

The equality holds when the system is nondegenerate and $\mathcal{H}_{mm}^{L}$ is independent of m.

The isolated susceptibility χ_S^{NL} may be calculated from Eq. (42). Using unitarity of U, namely,

$$U^{(1)}U_0^{\dagger}+U_0U^{(1)\dagger}=0\ ,$$

and

$$U^{(2)}U_0^{\dagger}+U^{(1)}U^{(1)\dagger}+U_0U^{(2)\dagger}=0\ ,$$

the second-order density matrix $\sigma_{mn}^{(2)}$ is written as

$$\sigma_{mn}^{(2)}=(U^{(2)}U_0^{\dagger})_{mn}(\sigma_n^0-\sigma_m^0)+\textstyle\sum_l U_{ml}^{(1)}U_{ln}^{(1)\dagger}(\sigma_l^0-\sigma_m^0)\ . \tag{61}$$

The time average of $(U^{(2)}U_0^{\dagger})_{mn}$ is explicitly calculated from Eqs. (39) and (22) as

$$\langle(U^{(2)}U_0^{\dagger})_{mn}\rangle_t=\frac{e^{2\eta t}}{W_{mn}-2i\hbar\eta}\sum_l\frac{P_{ml}P_{ln}\langle E^{L2}\rangle_t}{2\hbar}\times\frac{2\omega_{ln}-2i\eta}{\omega_{ln}^2-\omega^2-2i\eta\omega_{ln}-\eta^2}\ . \tag{62}$$

Equations (62) and (47) show that $\langle(U^{(2)}U_0^{\dagger})_{mn}\rangle_t$ with $W_{mn}=0$ does not contribute to the nonlinear refractive index of the isolated system. However, in a way similar to that in the linear case, one may formally obtain the isothermal susceptibility from Eq. (42) by neglecting the $\mathcal{P}$ operator. The neglect in the limit of $\eta\to 0$ in Eq. (62) yields an additional term which is equivalent to the first term in the bracket of Eq. (56). The third term in Eq. (52) similarly contributes to the second term in the bracket of Eq. (56). The author[6] has previously calculated the isothermal nonlinear refractive index by neglecting the $\mathcal{P}$ operator and retaining suitable terms for the population change due to the energy shift.

V. CONCLUSIONS

We have shown that the isothermal susceptibility for arbitrarily time-varying field can be formulated by a canonical-transformation method. The formulation has been explicitly discussed for the static linear susceptibility and nonlinear refractive index of dielectric media, but it may cover also other media such as magnetic and other higher-order effects in the applied field intensity. This formulation may also be used when resonance phenomena occur. For example, stimulated absorption and emission are given by taking the imaginary δ function in Eq. (22) which arises as we set $\eta\to 0$. Multiquantum absorption and stimulated Raman scattering are similarly given by taking the imaginary δ function in the limit of the solution of Eq. (21). For coherent resonance phenomena, the population change should not be taken into account since the applied pulse is short compared with the phase memory time and thus the longitudinal relaxation time, although the energy shift itself may affect them appreciably in certain cases.[7]

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that χ_S^L is also a lower bound for the adiabatic susceptibility which may be obtained from Eq. (32) by making the entropy constant (the constant entropy does not mean, in general, the constant population).

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Effective Mass and Spin Splitting in $Hg_{1-x}Cd_xTe$

G. A. Antcliffe

Texas Instruments Incorporated, Dallas, Texas 75222

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Shubnikov-de Haas measurements have been performed on single-crystal n-type $Hg_{1-x}Cd_xTe$ ($x = 0.204$) alloys with carrier concentration from 2×10^{15} to 1×10^{16} cm^{-3}. Comparison of the electron effective mass as a function of Fermi energy with $\vec{k}\cdot\vec{p}$ theory yields the following band parameters: band-edge mass $m_0^* = 5.60\pm0.25\times10^{-3}\,m_0$, interband matrix element $E_p = 17\pm1.4$ eV, and direct energy gap (at $k=0$) $E_g = 0.0635\pm0.008$ eV. We also observed spin splitting of the $N=1$, 2, and 3 Landau levels, from which the electron g factor was determined as a function of energy between 8 and 23 meV from the conduction band edge, with $g = 164\pm16$ at the band edge.

I. INTRODUCTION

The $Hg_{1-x}Cd_xTe$ alloy system is of considerable interest from several viewpoints. $Hg_{1-x}Cd_xTe$ at $X=0$ is a semimetal which exhibits a semiconductor-semimetal transition at $x\simeq0.18$, which is not yet completely understood.[1] As x is increased further, the energy gap at $k=0$ between a Γ_6 conduction band and the Γ_8 valence bands increases to about 0.10 eV at $x\simeq0.21$[2] and around this composition sensitive 8–14-μ photoconductors have been reported.[3] For an excellent summary of earlier work and for a discussion of the variation in band structure through the $Hg_{1-x}Cd_xTe$ system, we refer the reader to two excellent reviews[4] and references cited therein. We will be concerned in this paper only with one alloy composition — $Hg_{0.796}Cd_{0.204}Te$, where the conduction band has Γ_6 character. While there is agreement that this Γ_6 band is nonparabolic and should be described adequately by Kane's $\vec{k}\cdot\vec{p}$ theory,[4–6] developed for the Γ_6 band of InSb,[7] there is, at present, no systematic confirmation of this near the band edge for the semiconducting alloys ($x>0.18$). Interest has generally centered on investigations of the physical properties as functions of Cd concentration, with detailed measurements being rare due to the difficulty in attaining homogeneity in this system.[4] For example, the recent helicon propagation results[8] in low carrier concentration $Hg_{1-x}Cd_xTe$ still do not allow complete characterization of the Γ_6 band. We present in this paper the first detailed measurements on single-crystal low-concentration n-type $Hg_{1-x}Cd_xTe$ ($x=0.204$) using the Shubnikov–de Haas effect at liquid-helium temperatures. The experiments are aimed specifically at a determination of the Γ_6-band parameters, at *one* alloy composition, where the energy gap is close to 0.064 eV at 4.2 °K. The single-crystal alloys used in the present study had electron concentrations between 2×10^{15} cm^{-3} and 1×10^{16} cm^{-3} and electron mobilities greater than 2×10^5 cm^2/V sec at helium temperatures. We have determined the electron effective mass over this carrier concentration range and observed spin splitting of the lower quantum number Landau levels, which has allowed us to determine the energy dependence of the electron g factor. Limits have also been placed on the sphericity of the Fermi surface from the angular dependence of the Shubnikov–de Haas period.

We describe in Sec. II the experimental details together with a discussion of criteria which must be considered to ensure reliable Shubnikov–de Haas data. The results are presented in Sec. III together with a comparison with Kane's $\vec{k}\cdot\vec{p}$ theory. The relevant formulas from the theory are well known and summarized in the Appendix.

II. EXPERIMENTAL DETAILS

The single-crystal $Hg_{1-x}Cd_xTe$ alloys from which the experimental samples were cut were grown