The pressure dependence of ΔF, β_r, and β_0 (or velocity), which are structure dependent, suggests that the structure of alcohols changes to a greater extent at lower pressures than at higher pressures. In the beginning, the number of hydrogen bonds broken increases abruptly with pressure, but as the pressure is increased, the tendency of hydrogen bonds breaking is reduced resulting in a slow pressure variation of structural absorption and associated parameters at high pressures. In case of water, on the other hand, the pressure variation of these quantities is not so brisk at lower pressures, while at higher pressures, the variation is similar to that of alcohols.

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[1] L. Hall, Phys. Rev. 73, 775 (1948).

[2] S. K. Kor, Gulshan Rai, and O. N. Awasthi, Phys. Rev. 186, 105 (1969).

[3] S. K. Kor, S. C. Deorani, and B. K. Singh, Phys. Rev. A 3, 1780 (1971).

[4] S. K. Kor, S. C. Deorani, B. K. Singh, R. Prasad, and U. S. Tandon, Phys. Rev. A 4, 1299 (1971).

[5] T. A. Litovitz and E. H. Carnevale, J. Appl. Phys. 26, 816 (1955).

[6] E. H. Carnevale and T. A. Litovitz, J. Acoust. Soc. Am. 27, 547 (1955).

[7] S. K. Kor, O. N. Awasthi, Gulshan Rai, and S. C. Deorani, Phys. Rev. A 3, 390 (1971).

[8] D. Sette, Phys. Rev. 78, 476 (1950).

[9] S. Hawley, J. Allegra, and G. Holton, J. Acoust. Soc. Am. 47, 137 (1970).

[10] S. K. Kor and S. C. Deorani, Phys. Rev. A (to be published).

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Excitation Spectrum of Liquid Helium by Small-Angle Scattering of Nuclear Gamma Rays

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Considerable difficulty has been evidenced recently in determining and understanding the excitations in liquid helium and their interactions. Small-angle scattering of nuclear gamma rays is suggested for studying the excitations, which should complement the investigations using inelastic neutron scattering. The theory is presented and experimental problems are discussed. The differential cross section for small-angle scattering of nuclear gamma rays for single excitations is related to the x-ray liquid structure factor. The shift in energy of the nuclear gamma rays is expressed in terms of a Doppler shift which is shown to be comparable to the velocities used in nuclear resonance fluorescence. Scattering angles, linewidths, count rates, and resolution are evaluated.

I. INTRODUCTION

The energy-momentum relation of an elementary excitation in liquid helium was first deduced by Landau[1] predicting that the energy $E(p)$ of an excitation should rise linearly with slope v (v is the speed of sound), pass through a maximum, drop to a local minimum at some value p_0, and then rise again. For small p the excitations are phonons and the excitations near p_0 are called rotons. A Landau-type curve has also been obtained from the substitution of a trial function into a variational principle for the energy.[2,3] The measurement of the excitation spectrum by inelastic neutron scattering by Henshaw and Woods,[4] suggested previously by Cohen and Feynman,[5] substantiated the general predicted features. A good four-term fit[6] to the data of Henshaw and Woods[4] up to momenta $p \sim 2.4$ Å^{-1} at a temperature $1.12\,^\circ$K is

$$E^2 = A_1 p^2 + A_2 p^4 + A_3 p^6 + A_4 p^8 , \qquad (1)$$

with $A_1 = 328$, $A_2 = -189$, $A_3 = 36.6$, $A_4 = -2.17$. Large variations of the excitation spectrum as a function of temperature, however, were observed. $E(p_0)$ was found to vary by almost a factor of 2 as the temperature varied from $1.12\,^\circ$K to the λ temperature, the change of $E(p_0)$ at the λ temperature being discontinuous. The linewidth also was found to change rapidly as the temperature varied, again changing discontinuously at the λ temperature.

In the long-wavelength limit where only phonons should be important, the excitation spectrum can be written as

$$E = vp(1 - \gamma p^2 + \cdots) . \qquad (2)$$

The main effort until now for studying the long-wavelength region has been centered on investigating the properties of the propagation of sound. The simplest assumption theoretically is to treat sound attenuation as the scattering of sound phonons by thermal phonons, valid for $\omega\tau \gg 1$ where τ is a relaxation time. From energy and momentum conservation it is easily shown from (2) that for $\gamma \neq 1$ the three-phonon process is forbidden. If, however, the phonon lifetime is taken into account and $3\gamma \bar{p}^2 \omega\tau \ll 1$ where $\bar{p}$ is the average thermal momentum $\bar{p} = 3kT/v$, the three-phonon process is allowed and the attenuation of sound is given by[7, 8]

$$\alpha = \frac{\pi^2}{30} \frac{(u+1)^2}{\rho \hbar^3} \frac{(kT)^4}{v^6} \omega \left[\tan^{-1} \omega\tau - \tan^{-1}\left(\tfrac{3}{2} \gamma \bar{p}^2 \omega\tau\right)\right], \tag{3}$$

where ρ is the density, and

$$u = \frac{\rho}{v} \frac{\partial v}{\partial \rho} . \tag{4}$$

When $\omega\tau \ll 1$ the general formalism of the Boltzmann or kinetic equation is needed which is valid for $\omega\tau \ll 1$ as well as for the simpler situation $\omega\tau \gg 1$. In studying the collision integral, Khalatnikov and Chernikova[9] employed a wide-angle scattering time τ_{pp} and assumed that the collinear scattering time t_{pp} is very much smaller, or $t_{pp} \ll \tau_{pp}$. For $\omega\tau_{pp} \gg 1$, the temperature and frequency dependence of the sound velocity was determined as

$$\Delta v = \frac{\pi^2}{60} \frac{(u+1)}{\rho \hbar^3} \left(\frac{kT}{v}\right)^4 \ln\left[\frac{1 + (2\omega\tau_{pp})^2}{1 + (3\gamma \bar{p}^2 \omega\tau_{pp})^2}\right] . \tag{5}$$

Disatnick,[10] in studying the collision integral, employed a general phonon-phonon relaxation time τ. If $\tau = \tau_{pp}$ he obtains the relation (5). Similarly for $\tau = \tau_{pp}$, Disatnick[10] and Khalatnikov and Chernikova[9] obtain (3).

The measured experimental attenuation[6, 11, 12] is larger than (3) when the measured value of μ is used.[13] The change of the sound velocity with temperature also disagrees with theory although in this case the measured change is smaller than the predicted value.[14] This change is observed to be smaller at higher frequencies which is opposite to that predicted by theory. The calculation of the velocity shift has been extended recently and is now in better agreement.[15] However, the frequency effect still remains at variance with experiment. In order to make experiment agree with theory it was pointed out recently[16] that a negative value of γ with $|3\gamma \bar{p}^2 \omega\tau| \gg 1$ would lead to twice the attenuation. However, recent inelastic neutron scattering measurements[17] indicate that the magnitude of γ is less than 10^{36} in cgs units, which in the low-temperature and frequency range makes the inequality only marginally satisfied. Also, the high-frequency data show that the attenuation is increasing less than linearly with frequency, whereas a negative value of γ would require a higher than linear dependence. The pressure dependence of the attenuation has been recently studied and again it was found that theory and experiment are in disagreement.[18]

It is obvious from the above that the excitations and their interactions in liquid helium are far from being understood. We suggest the use of small-angle scattering of nuclear gamma rays for studying the excitations which should compliment the investigations which have and will be done using inelastic neutron scattering. In Sec. II the theory is presented and in Sec. III experimental problems are discussed.

II. THEORY

The vector potential A_u of a photon in second quantization is

$$A_u = \sum_{k\lambda} \left(\frac{2\pi\hbar c^2}{V\omega}\right)^{1/2} \epsilon_u^\lambda \left(C_{\vec{k}\lambda} e^{ikx} + C_{\vec{k}\lambda}^\dagger e^{-ikx}\right) , \tag{6}$$

where $kx = \omega t - \vec{k} \cdot \vec{r}$, V is the normalization volume, and ϵ_u^λ is the u component of the λ polarization vector. The creation and destruction operators, respectively, obey the Bose commutation relation $[C_{\vec{k}\lambda}, C_{\vec{k}'\lambda'}^\dagger] = \delta_{\vec{k}\vec{k}'} \delta_{\lambda\lambda'}$. The interaction Hamiltonian of the electromagnetic field with nonrelativistic electrons is $(e/mc)\vec{p} \cdot \vec{A} + (e^2/2mc^2)A^2$. In photon scattering, to lowest order, the A^2 term predominates, and the transition matrix element is

$$M_{if} = (e^2/2mc^2)\langle f(t)\, k\lambda | A^2 | i(t)\, k_0 \lambda_0 \rangle , \tag{7}$$

where $|i(t)\rangle$, $|f(t)\rangle$ is the initial and final states of the liquid helium, respectively, k_0, k, are the energy momentum of the initial and final gamma, respectively, and λ_0, λ their polarizations.

Introducing (6) into (7) and carrying out the necessary operations (taking $\hbar = 1$), we obtain

$$M_{if} = \frac{e^2}{mc^2} \frac{2\pi c^2}{V} (\omega\omega_0)^{1/2} \vec{\epsilon}^{\lambda} \cdot \vec{\epsilon}^{\lambda_0} \times \langle f(t) | e^{-i(k-k_0)x} | i(t) \rangle . \tag{8}$$

Using $|i(t)\rangle = e^{-iE_i t} |i\rangle$, $|f(t)\rangle = e^{-iE_f t} |f\rangle$, $\Delta\omega = \omega_0 - \omega$, $\vec{q} = \vec{k}_0 - \vec{k}$, (8) becomes

$$M_{if} = \frac{e^2}{mc^2} \frac{2\pi c^2}{V} (\omega\omega_0)^{-1/2} \langle f | e^{i\vec{q}\cdot\vec{r}} | i \rangle \times \delta(E_f - E_i - \Delta\omega) , \tag{9}$$

where E_i is the initial energy of the liquid helium and E_f its final energy.

From Fermi's golden rule, the transition probability is $2\pi |M_{if}|^2 \rho_f$, where ρ_f is the density of final states given by $V d^3k (2\pi)^3 = d\Omega\, d\omega\, \omega^2 V/(2\pi)^3 c^3$, where $d\Omega$ is the differential solid angle of the scattered gamma and ω its energy. The cross section $d\sigma$ is equal to the transition rate divided by the incident flux, where upon using (9) we obtain

$$\frac{d^2\sigma}{d\omega\, d\Omega}=\left(\frac{e^2}{mc^2}\right)^2(\vec{\epsilon}^{\lambda}\cdot\vec{\epsilon}^{\lambda_0})^2\frac{\omega}{\omega_0}\times\sum_f |\langle f|e^{i\vec{q}\cdot\vec{r}}|i\rangle|^2\delta(E_f-E_i-\Delta\omega)\ . \quad (10)$$

The term $(e^2/mc^2)^2(\vec{\epsilon}^{\lambda}\cdot\vec{\epsilon}^{\lambda_0})^2$ is just the Thomson cross section, $d\sigma_T/d\Omega$. Averaging over the initial polarizations and summing over the final polarization, we have $\langle(\vec{\epsilon}^{\lambda}\cdot\vec{\epsilon}^{\lambda_0})^2\rangle_{\mathrm{av}}=\frac{1}{2}(1+\cos^2\theta)$, where θ is the angle of scattering.

The wave functions $|i\rangle$ and $|f\rangle$ are the electronic wave functions of the liquid helium in the initial and final states, respectively. The vector $\vec{r}$ is the position of one of the electrons, equal to $\vec{R}_j+\vec{r}_{jk}$, where $\vec{R}_j$ is the position of the center of the jth atom and $\vec{r}_{jk}$ is the relative position of the kth electron ($k=1,2$) of the jth atom. Assuming that $\vec{r}_{jk}$ is independent of $\vec{R}_j$, or $\vec{r}_{jk}=\vec{r}_k$, we can write the initial wave function in the form

$$\psi_i=\psi_i(\vec{R}_1\cdots\vec{R}_N)\psi_{\mathrm{He}}\ , \quad (11)$$

where ψ_{He} is the helium atomic electronic wave function and $\psi_i(\vec{R}_1\cdots\vec{R}_N)$ is the initial wave function of the liquid helium.

We assume that E_f-E_i in (11) is sufficiently small ($|E_f-E_i|<\delta$) such that the wave function ψ_{He} is unchanged in the scattering. This then neglects processes in which in the final state an electron is transferred to an excited state of the helium atom or is expelled from the atom. It does allow for all forms of bulk excitations (e.g., phonons and rotons). The final state then can also be written in the form (11), and (10) becomes

$$\frac{d\sigma_s}{d\omega\, d\Omega}=\frac{d\sigma_T}{d\Omega}F_{\mathrm{He}}^2\sum_f\times\left|\sum_{j=1}^{N}\int\psi_f^*(\vec{R}_1\cdots\vec{R}_N)e^{i\vec{q}\cdot\vec{R}_j}\psi_i(\vec{R}_1\cdots\vec{R}_N)\times d\vec{R}_1\cdots d\vec{R}_N\right|^2\delta(E_f-E_i-\Delta\omega)\ , \quad (12)$$

where F_{He} is the helium atomic structure factor defined as[19]

$$F_{\mathrm{He}}(q)=\sum_{k=1}^{2}\int\psi_{\mathrm{He}}^*(\vec{r}_k)e^{i\vec{q}\cdot\vec{r}_k}\psi_{\mathrm{He}}(\vec{r}_k)\,d\vec{r}_k \quad (13)$$

and ω_0 is assumed to obey $\omega_0\gg\delta$.

Assuming ψ_i is the liquid-helium ground state and single excitation predominates in the sum over final states in (12), we obtain, after integrating on ω,

$$\frac{d\sigma_s}{d\Omega}=\frac{d\sigma_T}{d\Omega}F_{\mathrm{He}}^2(q)NS_s(q)\ , \quad (14)$$

where

$$S_s(q)=\left|\sum_{j=1}^{N}\int\psi_s^*(\vec{R}_1\cdots\vec{R}_N)e^{i\vec{q}\cdot\vec{R}_j}\times\psi_0(\vec{R}_1\cdots\vec{R}_N)\,d\vec{R}_1\cdots d\vec{R}_N\right|^2\ . \quad (15)$$

The liquid structure factor is defined as

$$\frac{d\sigma_{\mathrm{coh}}}{d\Omega}=\frac{d\sigma_T}{d\Omega}F_{\mathrm{He}}^2(q)NS(q)\ , \quad (16)$$

where $d\sigma_{\mathrm{coh}}/d\Omega$ is the coherent differential cross section. It has been measured recently for small momentum transfers.[20] Comparing (14) and (16) we have in general $S_s(q)\leq S(q)$. If the assumption that single excitation predominates is a good one, then $S_s(q)\simeq S(q)$. The assumption that the initial state is the ground state is strictly true only at absolute zero. It should be a fairly good assumption at finite temperatures, however, if $(E_f-E_i)\gg kT$ such that the Bose statistical factor obeys $(e^{E_f-E_i/kT}-1)^{-1}\ll 1$.

For single excitation, conservation of energy and momentum gives

$$\omega_0-\omega\equiv\Delta\omega=E\equiv E_f-E_i\ , \quad (17)$$

$$\vec{k}_0-\vec{k}\equiv\vec{q}=\vec{p}\ , \quad (18)$$

$$q=2k_0\sin(\theta/2)=p\ . \quad (19)$$

E can be expressed in terms of the Doppler velocity V necessary to cause an energy shift $\Delta\omega$. Using (17)–(19) in (1), we obtain

$$V^2=A_1 4\sin^2(\theta/2)+A_2 16\sin^4(\theta/2)(\omega_0/c^2)+A_3 64\sin^6(\theta/2)(\omega_0/2)^4+A_4 256\sin^8(\theta/2)(\omega_0/c)^6\ . \quad (20)$$

Similarly from (2) we obtain

$$V=2v\sin(\theta/2)-\gamma v 8\sin^3(\theta/2)(\omega_0/c)^6-\delta v 16\sin^4(\theta/2)(\omega_0/c)^2, \quad (21)$$

where a term $-\delta p^3$ has been included in the expansion. It is to be noted in (21) that for γ and δ zero, the velocity V is independent of the incident energy ω_0, and is equal to the velocity of sound times $2\sin(\theta/2)$. Thus at a given scattering angle and using two incident energy gamma rays, γ and δ become sensitive functions of the difference of the Doppler velocities.

III. EXPERIMENTAL

Let us first estimate the velocity V and scattering angle θ needed in (20) and (21). A q of order 1.0 Å^{-1} and an incident gamma ray of order 10 keV corresponds to a scattering angle of 10° and a Doppler velocity of order 25 m/sec. Such Doppler velocities of nuclear gamma-ray sources have been used in experiments of nuclear resonance fluorescence. In general when a nucleus emits a gamma ray it recoils and when a nucleus absorbs a gamma ray it also recoils. Thus for a nucleus of mass M emitting a gamma ray of energy ω_0, the gamma source must be Doppler shifted by an energy ω_0^2/Mc^2 for it to resonantly scatter. For gamma ray energies of order 500 keV in heavy nucleii, this amounts to Doppler velocities of several hundred meters per second. Moon[21] achieved these Doppler velocities and thereby resonance fluorescence by using a centrifuge. Typical arrangements can be seen in Moon and Storruste[22] and Knapp.[23]

A typical velocity spectrum of resonance fluorescence using the centrifuge method can be seen in the measurement of Davey and Moon[24] of the 411-keV level of ^{198}Hg. The peak resonance effect occurs at 700 m/sec and the spectrum has a width of 500 m/sec due to the thermal motion of the source and resonant scatterer.

In using nuclear resonance fluorescence for studying the excitation spectrum of liquid helium, the liquid helium is placed between the gamma source and the resonant scatterer. The count rate can be appreciably increased by using recoilless Mössbauer transitions.[25] The observed Doppler shift is then just due to the excitation energy of the helium. The width of the velocity spectrum is determined by the angular resolution. For example, an angle θ of 10° and $\frac{1}{2}$° resolution would give a velocity width of order 1 m/sec.

The number of reported Mössbauer transitions are relatively plentiful.[26] We are interested in the low-energy Mössbauer transitions in order that the scattering angle should not be too small. There are seven reported transitions less than 23 keV. They are ^{149}Sm(22.5), ^{151}Eu(21.55), ^{57}Fe(14.39), ^{133}Ba(12.29), ^{83}Kr(9.3), ^{169}Tm(8.42), and ^{181}Ta(6.21). For a scattering angle θ in the liquid helium of 10°, the corresponding momentum transfers are (in units of Å^{-1}) ^{144}Sm(2.06), ^{151}Eu(1.96), ^{57}Fe(1.28), ^{133}Ba(1.10), ^{83}Kr(0.84), ^{169}Tm(0.76), and ^{181}Ta(0.56). (A scattering angle of 5° would give half the above momentum transfers.)

It is of interest to estimate the expected count rate. Since it is small, it is advisable to use a ring counter. Assuming a 100 mCi source, a 10° scattering angle, and $\frac{1}{2}$° resolution, the expected count rate is of the order of a count per second. If 1° resolution is taken, the count rate is increased by an order of magnitude.

It is to be noted that, in principle, knowing the velocity of sound v and using just one scattering angle, both γ and δ can be obtained from (21) using just two gamma sources.

It is also to be noted that not only the parameters γ and δ or A_1, A_2, A_3, $A_4, \ldots$ and their temperature dependence can be obtained in the experiment, but also the lifetime of the excitations τ. Though the center of the velocity spectrum is given by (20) and (21), the width of the velocity spectrum is given by $c/\tau\omega_0$.

From the above, the small-angle scattering of nuclear gamma rays is seen to be competitive with the inelastic scattering of neutrons for studying the excitations in liquid helium. In particular it is to be noted that since a neutron scatters from the helium nucleus while the gamma ray from the electrons of the atom, we can expect that the coupling to the excitations will not be exactly the same.

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[1] L. Landau, J. Phys. (USSR) 5, 71 (1941); 11, 91 (1947).

[2] R. P. Feynman, Phys. Rev. 94, 262 (1954).

[3] R. P. Feynman and M. Cohen, Phys. Rev. 102, 1189 (1956).

[4] D. G. Henshaw and A. D. B. Woods, Phys. Rev. 121, 1266 (1961).

[5] M. Cohen and R. P. Feynman, Phys. Rev. 107, 13 (1957).

[6] B. M. Abraham, Y. Eckstein, J. B. Ketterson, M. Kuchnir, and J. P. Vignos, Phys. Rev. 181, 347 (1969).

[7] P. C. Kwok, P. C. Martin, and P. B. Miller, Solid State Commun. 3, 181 (1965).

[8] C. P. Pethick and D. ter Haar, Physica 32, 1905 (1966).

[9] I. M. Khalatnikov and D. M. Chernikova, Zh. Eksperim. i Teor. Fiz. 49, 1957 (1965); 50, 411 (1966) [Sov. Phys. JETP 22, 1336 (1966); 23, 274 (1966)].

[10] Y. Disatnick, Phys. Rev. 158, 62 (1967).

[11] B. M. Abraham, Y. Eckstein, J. B. Ketterson, and J. M. Vignos, Phys. Rev. Letters 16, 1039 (1966).

[12] B. W. Waters, D. J. Watmough, and J. Wilks, Phys. Letters 26A, 12 (1967).

[13] B. M. Abraham, Y. Eckstein, J. B. Ketterson, M. Kuchnir, and P. R. Roach, Phys. Rev. A 1, 250 (1970).

[14] S. G. Eckstein, Y. Eckstein, J. B. Ketterson, and J. H. Vignos, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1970), Vol. 6, and references therein.

[15] A. F. Andreev and I. M. Khalatnikov, J. Low Temp. Phys. 2, 173 (1970).

[16] H. J. Maris and W. E. Massey, Phys. Rev. Letters 25, 220 (1970).

[17] A. D. B. Woods and R. A. Cowley, Phys. Rev. Letters 24, 646 (1970).

[18] P. R. Roach, J. B. Ketterson, and M. Kuchnir, Phys. Rev. Letters 25, 1002 (1970).

[19] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (Van Nostrand, New York, 1935).

[20] R. B. Hallock, Phys. Rev. Letters 23, 830 (1969).

[21] P. B. Moon, Proc. Phys. Soc. (London) A64, 76 (1951).

[22] P. B. Moon and A. Storruste, Proc. Phys. Soc. (London) A66, 585 (1953).

[23] V. Knapp, Proc. Phys. Soc. (London) A70, 142 (1957).

[24] W. G. Davey and P. B. Moon, Proc. Phys. Soc. (London) A66, 956 (1953).

[25] H. Frauenfelder, *The Mössbauer Effect* (Benjamin, New York, 1963).

[26] *Mössbauer Effect Data Index*, edited by J. G. Stevens and V. E. Stevens (Plenum Data Corp., New York, 1970).

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Quantum-Mechanical Transport Equation for Atomic Systems*

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A quantum-mechanical transport equation (QMTE) is derived which should be applicable to a wide range of problems involving the interaction of radiation with atoms or molecules which are also subject to collisions with perturber atoms. The equation follows the time evolution of the macroscopic atomic density matrix elements of atoms located at classical position $\vec{R}$ and moving with classical velocity $\vec{v}$. It is quantum mechanical in the sense that all collision kernels or rates which appear have been obtained from a quantum-mechanical theory and, as such, properly take into account the energy-level variations and velocity changes of the active (emitting or absorbing) atom produced in collisions with perturber atoms. The QMTE represents a somewhat different formulation of the problem than that considered in earlier works. The present formulation is better suited to problems involving high-intensity external fields, such as those encountered in laser physics.

I. INTRODUCTION

In two previous papers[1,2] (hereafter referred to as QMI and QMII), a theory of pressure effects was developed which enables one to follow the time evolution of a moving atom which was interacting with some external radiation field and undergoing collisions with perturber atoms. Quantization of the atom's center-of-mass motions proved to be a key feature of this theory since it permitted a consistent treatment of both the energy-level variations and velocity changes of the active (emitting or absorbing) atom caused by collisions with perturber atoms. One drawback of the approach of QMII was that it was formulated in terms of a perturbation expansion in powers of the external field so that, in its present form, the approach was not well suited to problems involving high-intensity fields. In this paper, based on the results of QMI and QMII, we shall derive a quantum-mechanical transport equation (QMTE) which will not possess this drawback.

The equation to be derived is termed a transport equation because it will describe the evolution of the macroscopic density matrix (or distribution function) of the ensemble of active atoms specified by the classical variables $\vec{R}$, $\vec{v}$, t. On the other hand, the equation will be quantum mechanical in the sense that all collisions kernels and rates which appear will have been obtained by inference from the quantum-mechanical collision results of QMI and II. The fact that all our collision kernels are well-defined quantum-mechanical quantities distinguishes our theory from others[3] which make use of a similar equation with phenomenological (and sometimes incorrect) kernels based on a classical rather than quantum-mechanical description of the atomic center-of-mass motion.[4]

Of what use is the QMTE? Typically, transport equations enable one to determine the approach to equilibrium of an ensemble of atoms initially described by a nonequilibrium velocity distribution. However, although applicable to problems of this kind, the QMTE will be developed in a manner directed towards application to a different class of problems. Specifically, we have in mind a situation where the active and perturber atoms are permitted to reach some sort of thermal equilibrium. At that point, an excitation or external field interaction is "turned on" and tends to alter the equilibrium distribution of the active atoms. The QMTE will trace the evolution of the active atom density matrix from the original equilibrium to the new steady state.

In turn, the macroscopic density matrix elements obtained as solutions of the QMTE will, in general, enable one to calculate values for quantities of physical interest in a given problem. For example, in laser problems, the atomic polarization which serves as a driving function for the classical laser electric field is directly related to off-diagonal density matrix elements.[1,2] Similarly, spontaneous-emission spectral profiles are determined by the diagonal density matrix elements