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Where Semiclassical Radiation Theory Fails

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Semiclassical radiation theory provides parallel derivations of spontaneous emission and of spontaneous incoherent scattering of radiation. In the latter case, in constrast to the former, the theory is in clear disagreement with established experimental data since it predicts equal intensity for Stokes and anti-Stokes lines in Raman scattering. A new postulate of *semiquantization* is proposed to restore agreement with experiment without quantizing the electromagnetic field.

Jaynes and collaborators[1] have reopened the question of the limit of validity of semiclassical radiation theory, in which matter is described by the Schrödinger equation, without second quantization, and the electromagnetic Maxwell field is not quantized. This classical coupled-field theory has been shown to contain a description of spontaneous emission and of radiative level shifts that differs from quantum electrodynamics but cannot be ruled out by existing experimental data.[1] Following this work, a somewhat more general derivation of these results has been carried out, and the implications with regard to Planck's radiation law have been examined.[2] It is concluded that the semiclassical theory must be complemented by an additional statistical hypothesis in order to provide an internally consistent theory of thermal equilibrium between matter and radiation, but this hypothesis restores agreement with Planck's law.

In the present note, the formal similarity of the theories of spontaneous emission and of spontaneous incoherent scattering will be emphasized. In incoherent scattering, absorption of radiation of frequency ω is accompanied by essentially *spontaneous* emission of radiation of shifted frequency ω', since no exciting field of this frequency is present. The semiclassical theory of these two phenomena leads to formulas that differ from quantum electrodynamics in exactly the same way. In the case of incoherent scattering, it will be shown here that this leads to a clear disagreement with experimental data on Raman scattering. Agreement with experiment can be restored by quantizing only the Schrödinger field (second quantization), but not the Maxwell field. Such a *semiquantized* radiation theory is proposed here as an empirical extension of semiclassical theory, without assuming the full postulates of quantum electrodynamics.

The time-dependent wave function for an isolated molecule can be written in the form

$$\psi(t) = \sum_b \varphi_b c_b(t) \exp(E_b t/i\hbar), \tag{1}$$

where φ_b is a stationary-state wave function with unperturbed energy E_b. If the wave function contains two different components φ_a and φ_b, the cross terms in the expansion of the electric dipole moment $\vec{\mu}$ give Fourier coefficients

$$\vec{\mu}_\omega = \vec{\mu}_{ab} c_a^* c_b, \tag{2}$$

where

$$\omega = \omega_{ab} = (E_b - E_a)/\hbar. \tag{3}$$

It is assumed that $E_b > E_a$, so that spontaneous emission is associated with the transition $b \to a$. In the formalism of semiclassical radiation theory, this oscillatory dipole moment produces an

electromagnetic field described by the vector potential, assuming retarded potentials,

$$\vec{A}_\omega(P) = c^{-1} r_P^{-1} \exp(i\omega r_P/c)(-i\omega\vec{\mu}_\omega), \tag{4}$$

where r_P is the distance from the emitting molecule to the field point P. The emitted radiation is determined by the transverse component $\vec{A}_\omega{}^{tt}$. The total rate of energy emission, obtained by integrating the normal component of the Poynting vector obtained from $\vec{A}_\omega{}^{tt}$ over a spherical surface, is

$$\frac{dW}{dt} = \frac{4\omega^4}{3c^3}\mu_\omega{}^2 = \frac{4\omega_{ab}{}^4}{3c^3}\mu_{ab}{}^2|c_a|^2|c_b|^2. \tag{5}$$

In quantum electrodynamics, the corresponding spontaneous energy emission rate is

$$\frac{dW}{dt} = \hbar\omega_{ab}A(b,a)|c_b|^2 = \frac{4\omega_{ab}{}^4}{3c^3}\mu_{ab}{}^2|c_b|^2, \tag{6}$$

where $A(b,a)$ is Einstein's coefficient of spontaneous emission. Equations (5) and (6) differ by the factor $|c_a|^2$, the weight coefficient or occupation number of the final state of the transition. When this can be set equal to unity, as in the case of emission to the ground state, the two formulas are not experimentally distinguishable.

In the semiclassical theory of spontaneous incoherent scattering, incident radiation of angular frequency ω causes transitions between unperturbed states a and a' of a molecule, through virtual excitation of intermediate states φ_b. Radiation at frequency ω' is emitted such that

$$E_a + \hbar\omega = E_{a'} + \hbar\omega'. \tag{7}$$

The unperturbed wave function is assumed to contain both φ_a and $\varphi_{a'}$, and the scattering arises from cross terms in the electric dipole moment with Fourier coefficients of the form

$$\vec{\mu}_{\omega'} = \alpha_{a'a}(\omega',\omega)\vec{E}_\omega c_{a'}{}^* c_a, \tag{8}$$

where $\vec{E}_\omega$ is a Fourier coefficient of the incident electric field intensity.

An outline of the derivation of Eq. (8) is given below. Equation (8) has the same formal structure as Eq. (2) for spontaneous emission. It implies, by a similar argument, that the energy emission rate, and hence the incoherent scattering cross section, is proportional to $|c_{a'}|^2|c_a|^2$. This result differs from the cross section derived from quantum electrodynamics by the additional factor $|c_{a'}|^2$, the weight coefficient of the final state of the transition. In quantum electrodynamics the cross section is weighted only by the weight coefficient of the initial state of the transition.

In Raman spectroscopy, an incident beam of sharply defined frequency ω produces displaced lines at frequencies

$$\omega' = \omega \pm \omega_{aa'}. \tag{9}$$

If $E_{a'} > E_a$, the line of reduced frequency $\omega - \omega_{aa'}$, known as the Stokes line, corresponds to absorption of energy $\hbar\omega_{aa'}$ by a target molecule in a transition from E_a to the higher level $E_{a'}$. The line $\omega + \omega_{aa'}$, the anti-Stokes line, requires de-excitation from $E_{a'}$ to E_a. Since the anti-Stokes transition is weighted by $|c_{a'}|^2$ (in quantum electrodynamic theory), the equilibrium ratio $|c_{a'}|^2/|c_a|^2$ is the Boltzmann factor $\exp(-\hbar\omega_{aa'}/kT)$, which reduces the relative intensity of the anti-Stokes line. This intensity weighting is observed in vibrational Raman spectra.[3] Because of the coefficient $|c_{a'}|^2|c_a|^2$ in the cross section the semiclassical radiation theory implies equal intensity for Stokes and anti-Stokes lines for the same transition. This is in clear disagreement with observed Raman spectra and invalidates the semiclassical theory.

Equation (8) can be derived by considering virtual excitation of intermediate states φ_b induced by an incident plane-wave, plane-polarized field with Fourier coefficients

$$\vec{E}_\omega = E_k\hat{e}\exp(i\vec{k}\cdot\vec{x}). \tag{10}$$

An approximate steady-state solution of the time-dependent Schrödinger equation gives

$$c_b(t) = \sum_{\pm\omega}(b|V_\omega|a)c_a(t)(E_a - E_b + \hbar\omega)^{-1}\exp[(E_a - E_b + \hbar\omega)t/i\hbar]$$
$$+\sum_{\mp\omega}(b|V_{-\omega}|a')c_{a'}(t)(E_{a'} - E_b - \hbar\omega)^{-1}\exp[(E_{a'} - E_b - \hbar\omega)t/i\hbar], \tag{11}$$

for $b \neq a$ or a'. For electric dipole transitions, the required transition matrix elements are

$$(b|V_\omega|a) = -(\omega_{ab}/\omega)\vec{\mu}_{ba}\cdot\hat{e}E_k, \quad (a'|V_\omega|b) = (\omega_{ab}/\omega)\vec{\mu}_{a'b}\cdot\hat{e}E_k. \tag{12}$$

The electric dipole moment $\vec{\mu}$ contains cross terms proportional to $c_{a'}{}^* c_b$ as well as to $c_b{}^* c_a$. From

Eqs. (11) and (12), with ω' given by Eq. (7), assuming $E_{a'}>E_a$, the Fourier coefficient $\vec{\mu}_{\omega'}$ is given by Eq. (8) with a tensor polarizability, in dyadic form,

$$\overleftrightarrow{\alpha}_{a'a}(\omega',\omega)=\sum_b\frac{1}{\hbar\omega}\left[\frac{\omega_{ab}\vec{\mu}_{a'b}\vec{\mu}_{ba}}{\omega_{ab}-\omega}-\frac{\omega_{a'b}\vec{\mu}_{ba}\vec{\mu}_{a'b}}{\omega_{a'b}+\omega}\right], \tag{13}$$

where

$$\omega_{a'b}=(E_b-E_{a'})/\hbar. \tag{14}$$

The scalar polarizability in Eq. (8) is obtained by rotational averaging.

A theory intermediate between semiclassical theory and quantum electrodynamics can be obtained by quantizing the Schrödinger amplitude field ψ but not the Maxwell field. This intermediate theory can be called *semiquantized* radiation theory. In its most primitive form, the N-particle nonrelativistic Schrödinger field can be quantized by simply postulating that the coefficients $c_b(t)$ in Eq. (1) are anticommuting operators such that

$$\{c_a(t),c_b^{\dagger}(t)\}=c_a(t)c_b^{\dagger}(t)+c_b^{\dagger}(t)c_a(t)=\delta_{ab}, \tag{15}$$

independent of t. Here a dagger is used to indicate the Hermitian conjugate of an operator; an asterisk is used for the complex conjugate of a number. The ordinary rules of fermion quantization apply to the ψ field, which satisfies the usual time-dependent Schrödinger equation.

The semiquantized theory of spontaneous emission follows the semiclassical theory in detail, except that Eq. (2) becomes

$$\vec{\mu}_{\omega}=\vec{\mu}_{ab}c_a^{\dagger}(t)c_b(t), \tag{16}$$

so that $\vec{\mu}_{\omega}$ is an operator, acting on the Schrödinger-field state vector, in a Heisenberg picture (the state vector remains constant while the operators vary in time). A very interesting and important implication of Eq. (4) is that the electromagnetic vector potential, while not separately quantized, becomes an *operator*, also acting on the Schrödinger-field state vector. The electromagnetic field energy becomes an operator in the same sense, postulated to be

$$W_{\mathrm{op}}=\tfrac{1}{4}\pi^{-1}\int\sum_{\omega}(\vec{\mathrm{E}}_{\omega}^{\dagger}\cdot\vec{\mathrm{E}}_{\omega}+\vec{\mathrm{B}}_{\omega}^{\dagger}\cdot\vec{\mathrm{B}}_{\omega})d\tau, \tag{17}$$

summed over non-negative ω.

When the commutation rules, Eq. (15), are respected, Eq. (5) must be written as operator equation,

$$\frac{dW_{\mathrm{op}}}{dt}=\frac{4\omega_{ab}^{4}}{3c^{3}}\mu_{ab}^{2}(c_a^{\dagger}c_b)^{\dagger}(c_a^{\dagger}c_b)$$
$$=\frac{4\omega_{ab}^{4}}{3c^{3}}\mu_{ab}^{2}n_b(1-n_a), \tag{18}$$

where n_a and n_b are the number operators

$$n_a=c_a^{\dagger}c_a,\quad n_b=c_b^{\dagger}c_b \tag{19}$$

such that

$$c_ac_a^{\dagger}=1-n_a,\quad c_bc_b^{\dagger}=1-n_b \tag{20}$$

from the commutation rules. The normalization of ψ requires that

$$\sum_a n_a=1. \tag{21}$$

The state vector can be written in the form

$$\Psi=\sum_b\gamma_b\Phi_b, \tag{22}$$

where Φ_b is an eigenstate of the number operators, with $n_a=\delta_{ab}$ for all a, and the γ_b are numerical coefficients. The operator $n_b(1-n_a)$ has the value unity in state Φ_b. The physical energy emission rate, obtained by taking the mean value of dW_{op}/dt with respect to the state vector Ψ, is a sum of terms

$$\frac{dW}{dt}=\frac{4\omega_{ab}^{4}}{3c^{3}}\mu_{ab}^{2}|\gamma_b|^{2}, \tag{23}$$

for each transition $b\rightarrow a$.

Equation (23) agrees with the usual result of quantum electrodynamics, Eq. (6), if $|\gamma_b|^2$ is interpreted as the weight coefficient of state Φ_b, This result leads to Planck's radiation law. Clearly the same analysis applies in the case of spontaneous incoherent scattering; and the semiquantized theory, in accord with quantum electrodynamics, agrees with the observed intensity ratio of anti-Stokes to Stokes lines in Raman spectra.

Equation (4), a direct consequence of the coupled-field equations in the Heisenberg picture, represents a fundamental mathematical difficulty in quantum electrodynamics. If the Maxwell field is seqarately quantized as a boson field, Eq. (4) equates entitities from two essentially different algebras, an obvious inconsistency in the formalism. The semiquantized formalism proposed here removes this inconsistency by quantizing only the fermion field. A similar procedure might be considered in elementary-particle theory, quantizing only fermion fields, and representing

boson fields in terms of quadratic fermion source densities.

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Evidence for Large-Molecular-Cluster Formation of Nuclear Reaction Recoils Thermalized in Helium*

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It has been found that nuclear reaction recoils ejected from a target and thermalized in helium attach to large molecular clusters produced from impurities by the intense ionization generated by the beam passing through helium. When the clusters containing the recoils are entrained in a room-temperature sonic helium flow, they attain kinetic energies of up to 700 keV on account of their high molecular weights which were found to be as high as 10^8 u. Highly efficient separations of nuclear reaction recoils from helium carrier gas have been achieved as a result of the formation of these large clusters.

When a heavy-projectile beam (e.g., protons, α particles, heavy ions) passes through a thin target, nuclear reaction recoils are ejected from the target as a result of momentum transfer to the target nuclei. If the target is surrounded by a gas such as helium, the recoils are very quickly thermalized and can be collected using electrostatic fields[1] or differential pumping.[2] The beam also produces a plasma in the helium, and the interaction of the plasma and high free-electron density with the thermalized nuclear reaction recoils can give rise to positive, negative, and neutral species almost independent of the chemistry of the recoil. This has been observed in previous studies.[3,4] Many other related strange phenomena have been reported over the years, reflecting the complexity of the physical and chemical processes taking place. A better understanding of the interactions of nuclear reaction recoils in thermalizing media is not only of interest in learning more about reactions occurring in plasmas, but is also of considerable practical importance in developing recoil collection techniques for high-vacuum applications such as in rapid "on-line" mass separation of nuclear reaction products. We report here some significant observations on the problem in a study carried out using ^{8}Li recoils produced in the ^{7}Li(d,p) reaction and collected by differential pumping of helium (the helium-jet recoil-transport method).

A target of ^{7}Li (1 mg/cm^2) enriched to 99% was bombarded with a 12.5-MeV deuteron beam (500 nA) from the Texas A&M University cyclotron to produce the 0.85-sec, β-delayed, α emitter ^{8}Li. The ^{8}Li recoils were thermalized in 1.3 atm of He (99.999% purity) and transferred to a Teflon capillary tube (0.8 mm inside diameter, 5 m long) by differential pumping. The pressure gradient in the tube was sufficient to achieve sonic or near sonic flow of the helium near the end of the tube which terminated in a vacuum chamber. Under these conditions, there was a velocity equilibration of the recoils with the helium and a kinetic-energy enhancement in the direction of flow equal to the ratio of the mass of the recoil to that of the He atom.[5] If the recoil underwent a chemical reaction or attached itself to impurities in the helium, the energy enhancement would be proportionately larger because of the increased effective mass. The helium jet emerging from the tip of the capillary was allowed to expand freely into a vacuum chamber (20 μm pressure), and the properties of the ^{8}Li beam were studied using a Si(Au) detector which was sensitive to the α particles from ^{8}Li decay. The angular divergence of the ^{8}Li beam was found to be 0.5° (full width at half-maximum), considerably smaller than would be expected for a mass-8 beam emerging from a He stream. Under identical conditions except for the presence of a deuteron beam, a beam of thermalized ^{220}Rn α recoils was found to have an angular divergence of 30° (full width