Theory of stimulated emission processes in spherical microparticles

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A semiclassical theory of stimulated processes in dielectric spherical particles is formulated. The theory applies to the small-signal regime and to isotropic (but radially nonuniform) pumping. Iterative treatment of the pumped-medium susceptibility by scattering theory demonstrates the basic features observed experimentally by Chang and co-workers [H. M. Tzeng, K. F. Wall, M. B. Long, and R. K. Chang, Opt. Lett. **9**, 499 (1984); S. X. Qian and R. K. Chang, Phys. Rev. Lett. **56**, 926 (1986)], namely, the drastic reduction of the threshold for lasing and multiorder stimulated Raman processes, and the frequency pulling from Mie resonances of the inactive medium.

A series of pioneering experiments conducted by Chang and co-workers have demonstrated the occurrence of lasing[1,2] and stimulated Raman scattering[3,4] (SRS) in micrometer-sized spherical liquid droplets. Recently, lasing has been studied also by Baer[5] in millimeter-sized solid spheres. The salient features revealed in these experiments are the following. (a) Lasing occurs[1] at a number of frequencies within the emission band that are red shifted relative to the Mie resonances of light scattering by the droplet.[6,7] (b) Strong SRS can occur at multiorder Stokes lines[4] when there is a Mie resonance near each of these lines. (c) The pumping thresholds for both processes are lower by several orders of magnitude in such a droplet than in bulk. Chang and co-workers attributed this threshold reduction to the high internal reflection by the spherical dielectric boundary of amplified emission at Mie resonances and concluded (a conclusion reiterated recently by Baer[5]) that the theory of lasing from such systems must combine laser equations with Mie theory and that[4] "the normal plane-wave growth equations for SRS . . . need be modified into multipass spherical-wave nonlinear equations . . . ."

Fluorescence and Raman emission in a spherical particle have been described previously as linear response (characterized by a constant polarizability) to the pump field.[8] The self-consistent field-dipole interaction (which is essential for stimulated processes) in a sphere has been treated thus far only in the initiation regime of superfluorescence,[9,10] for a homogeneous, fully inverted emitter distribution. Resonant features of the emission and their connection with Mie theory have not been explored in these treatments.

In this paper we modify the conventional semiclassical theory of stimulated processes in the small-signal regime so as to allow for the spherical boundary of the active medium, and for radially nonuniform, isotropic pumping. Effects of Mie resonances are accounted for and results pertaining to the aforementioned experimentally observed features are emphasized.

The starting point of our treatment of lasing are the two coupled Maxwell-Bloch equations for the field $\mathbf{E}$ and polarization $\mathbf{P}$ in the semiclassical small-signal regime of lasing.[11] The Fourier components $\mathbf{E}_\lambda(\mathbf{r})$ and $\mathbf{P}_\lambda(\mathbf{r})$ associated with a positive frequency Ω_λ are then related (in the rotating-wave approximation) by the Bloch equation $\mathbf{P}_\lambda = \chi_\lambda^{(1)}(\mathbf{r})\mathbf{E}_\lambda$, where

$$\chi_\lambda^{(1)} = \mu_\omega^2 N^{(0)}(\mathbf{r})/\hbar(\Omega_\lambda - \omega - i\gamma)$$

is the first-order susceptibility and $N^{(0)}(\mathbf{r})$ is the time-dependent population inversion established by pumping and relaxation. The frequency, linewidth, and dipole moment of the fluorescing atomic or molecular transition are denoted by ω, γ, and μ_ω, respectively. On using this relation in the Maxwell (Helmholtz) wave equation for $\mathbf{E}_\lambda(\mathbf{r})$ driven by the polarization current[6] one obtains

$$[-(\nabla\times\nabla\times)+k_\lambda^2-(U_0+\Delta U)]\mathbf{E}_\lambda = 0 \; . \tag{1}$$

Here $k_\lambda = \Omega_\lambda/c$, $\Delta U(\mathbf{r}) = -4\pi k_\lambda^2 \chi_\lambda^{(1)}(\mathbf{r})$, $U_0 = k_\lambda^2(1-\epsilon_\lambda)\Theta(a-r)$, ϵ_λ being the complex dielectric index of the (optically inactive) medium in the sphere, accounting for light refraction and absorption at the frequency Ω_λ, and $\Theta(a-r)$ is the Heaviside step function for a sphere of radius a.

In general, the susceptibility $\chi_\lambda^{(1)}(\mathbf{r})$ is both anisotropic and radially-nonuniform, reflecting the spatial distribution of the pumping field. We facilitate the treatment of this susceptibility in (1) by using an iterative expansion in ΔU, i.e., taking $|\chi_\lambda^{(1)}| \ll |\epsilon - 1|$, an assumption consistent with the small-signal (near-threshold) lasing regime. Even then the anisotropy of $\chi_\lambda^{(1)}$ is a complicating factor, responsible (to first order in ΔU) for the coupling of zeroth-order field modes of different angular symmetry oscillating at the same Ω_λ. Here we limit ourselves to single-mode theory, applicable in the small-signal regime when the pumping (and thus ΔU) is nearly isotropic but nonuniform, being confined to a spherical shell. Isotropic pumping is realizable[5] on using an unpolarized pumping field whose linearly polarized components fill annular shells that are nearly isotropic in the polar angle (Y_{lm} spherical harmonics with high order l) and have different azimuthal-angle dependences (different m values). The angular modes of lasing emission are then uncoupled, and we may consider one such mode oscillating near a Mie resonance labeled by $\lambda=(l,\nu)$. By operating on Eq. (1) with $(\mathbf{L}\cdot)$, $\mathbf{L}$ being the angular momentum operator, a scalar wave equation is obtained[6,10] for $\mathbf{L}\cdot\mathbf{E}_\lambda$ with $-(\nabla\times\nabla\times)$ replaced by ∇^2. For a particular magnetic-wave (TE) mode

$$a_{lm}g_{l\nu}(r)Y_{lm}(\theta,\phi)$$

contained in $\mathbf{L}\cdot\mathbf{E}_\lambda$, the angular variables can then be eliminated and the resulting radial equation reads

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+k_\lambda^2-\frac{l(l+1)}{r^2}-U_0-\Delta U\right]g_l=0 . \tag{2}$$

This radial equation is the three-dimensional analog of the equation for single-mode lasing in a one-dimensional (e.g., Fabry-Perot) cavity with nonuniform pumping and dielectric (nonzero-transmission) boundaries. Conventional treatments[11] single out the field inside the cavity, reducing the outside field effects to a Q value for transmission losses, then consider the oscillation of modes of the internal field (normalized in the cavity). The major departure of the ensuing treatment from such methods is the use of scattering theory to describe the field inside and outside the sphere on equal footing. This allows the natural extension of the Mie theory of light scattering to the regime of stimulated emission.

The iterative solution of (2) to first order in $\Delta U(r)$ is given in many works on scattering theory in the form of the "distorted-wave Born approximation,"[12] i.e., as a small additive correction to the scattering amplitude induced by U_0. This solution, however, does not predict a shift of the resonance position due to ΔU, and is therefore inappropriate near resonance. The iteration procedure used here is an extension of Eq. (12.3.62) in Ref. 13. It consists in writing the solution of (3) for an incident signal wave of unit amplitude $j_l(k_\lambda r)$ as

$$g_l=g_l^{(0)}-k_\lambda\int\Delta U(r')[g_l^{(0)}(r)\tilde{g}_l^{(0)}(r')-g_l^{(0)}(r')\tilde{g}_l^{(0)}(r)]\times g_l(r')r'^2dr' , \tag{3}$$

where $g_l^{(0)}$ and $\tilde{g}_l^{(0)}$ are two orthogonal (independent) solutions to zeroth order in ΔU. This means that the Green's function in (3) is constructed from "distorted waves." The form of $g_l^{(0)}$ is given by the Mie theory[6,8] or scattering theory for a spherical-well potential U_0, on applying at $r=a$ the boundary conditions appropriate for a magnetic wave (TE mode) in Maxwell's equations,

$$\begin{aligned}g_l^{(0)}&=-(i/k_\lambda aM_l)j_l(\epsilon^{1/2}k_\lambda r)\Theta(a-r)\\&\quad+[1-\Theta(a-r)]e^{i\delta_l^{(0)}}\\&\quad\times[\cos\delta_l^{(0)}j_l(k_\lambda r)+\sin\delta_l^{(0)}n_l(k_\lambda r)]\\&\underset{r\to\infty}{\longrightarrow}(e^{i\delta_l^{(0)}}/k_\lambda r)\sin(k_\lambda r-l\pi/2+\delta_l^{(0)}) .\end{aligned} \tag{4}$$

Here j_l and n_l are the Bessel and Neumann spherical functions and $M_l(\epsilon^{1/2}k_\lambda a)$ is the lth magnetic-wave Mie denominator[14] measuring the amplification of the field inside the sphere (reflected wave) relative to the signal (incident) wave. The zeroth-order phase shift $\delta_l^{(0)}$ determines $e^{i\delta_l^{(0)}}\sin\delta_l^{(0)}$, which is the scattering amplitude [the ratio of the amplitude of the scattered outgoing wave having the form of a spherical Hankel function $h_l^{(1)}(k_\lambda r)$ to that of the signal wave]. The asymptotic form of $\tilde{g}_l^{(0)}$, which is orthogonal to $g_l^{(0)}$, is then

$$\begin{aligned}\tilde{g}_l^{(0)}&\sim-e^{i\delta_l^{(0)}}[\sin\delta_l^{(0)}j_l(k_\lambda r)-\cos\delta_l^{(0)}n_l(k_\lambda r)]\\&\underset{r\to\infty}{\longrightarrow}-(e^{i\delta_l^{(0)}}/k_\lambda r)\cos(k_\lambda r-l\pi/2+\delta_l^{(0)}) .\end{aligned} \tag{5}$$

The first iteration of (3) yields

$$\begin{aligned}g_l^{(1)}&=g_l^{(0)}(r)(1-\beta^{(1)})+\alpha^{(1)}\tilde{g}_l^{(0)}(r)\\&\underset{r\to\infty}{\longrightarrow}(e^{i\delta_l^{(1)}}/k_\lambda r)\sin(k_\lambda r-l\pi/2+\delta_l^{(1)}) ,\end{aligned} \tag{6}$$

where

$$\begin{aligned}\alpha^{(1)}&=k_\lambda\int\Delta U(r')g_l^{(0)^2}(r')r'^2dr' ,\\\beta^{(1)}&=k_\lambda\int\Delta U(r')\tilde{g}_l^{(0)}(r')g_l^{(0)}(r')r'^2dr' .\end{aligned} \tag{7}$$

By comparing the coefficients of $\sin(k_\lambda r-l\pi/2)$ and $\cos(k_\lambda r-l\pi/2)$ in Eqs. (4)–(6) we obtain

$$\begin{aligned}\tan\delta_l^{(1)}&\simeq\frac{\tan\delta_l^{(0)}(1-\beta^{(1)})-\alpha^{(1)}}{1-\beta^{(1)}+\alpha^{(1)}\tan\delta_l^{(0)}}\\&\simeq\tan(\delta_l^{(0)}-\alpha^{(1)})\Longrightarrow\delta_l^{(1)}\simeq\delta_l^{(0)}-\alpha^{(1)} ,\end{aligned} \tag{8}$$

where we have neglected $\beta^{(1)}\sim O(\Delta U)$ relative to 1 and have taken $\alpha^{(1)}\simeq\tan\alpha^{(1)}$. The scattering amplitude $e^{i\delta_l^{(1)}}\sin\delta_l^{(1)}$ attains a maximum at the resonance $\mathrm{Re}(\delta_l^{(1)})\simeq\pi/2$, which is shifted by $\mathrm{Re}(\alpha^{(1)})$ from the zeroth-order Mie resonance. Lasing occurs if $\mathrm{Im}(\delta_l^{(1)})<0$, because then the scattering amplitude near resonance can exceed unity (in absolute value), i.e., the scattered wave becomes amplified as compared to the incident (signal) wave.

In order to obtain quantitative estimates from (8), we rewrite $\alpha^{(1)}$ [Eq. (7)], using the definitions of $\chi^{(1)}$ and ΔU, as

$$\alpha^{(1)}=4\pi\epsilon^{-1/2}\chi_\lambda^{(1)}(\langle N_l^{(0)}\rangle)/[\rho_\lambda M_l(\rho_\lambda)]^2 , \tag{9}$$

where $\rho_\lambda=\epsilon^{1/2}k_\lambda a$ (complex size parameter) and $\chi^{(1)}$ is the bulk susceptibility for the expectation value of population inversion

$$\langle N_l^{(0)} \rangle = \int_0^{\rho_\lambda} N^{(0)}(r') j_l^2(\epsilon^{1/2} k_\lambda r') d(\epsilon^{1/2} k_\lambda r')^3 .$$

In the commonly occurring case of near-surface population inversion[1,2,5] $N^{(0)}(r) \simeq \bar{N}\delta(r-a)$, the lasing oscillation condition $\mathrm{Im}\delta_l^{(1)} < 0$ following from (8) becomes

$$\mathrm{Im}\delta_l^{(0)} < 4\pi\epsilon^{-1/2}[j_l(\rho_\lambda)/M_l(\rho_\lambda)]^2 \mathrm{Im}\chi_\lambda^{(1)}(\bar{N}) , \quad (10)$$

where $\mathrm{Im}\delta_l^{(0)}$ is of the order of the bulk absorption constant[7] times the radius a, or $\mathrm{Im}(\rho_\lambda)$. For $\rho_\lambda \gtrsim 100$ as in Ref. 1, estimating[14] $M_l(\rho_\lambda) \sim 10^{-4}$ and $j_l(\rho_\lambda) \gtrsim 10^{-2}$ for its peak value at $l \simeq \rho_\lambda$, we then find from (10) that the lasing threshold is more than 10^4 times lower than in bulk with the same inverted population density $\bar{N}$. Thus the origin of the drastic lowering of the lasing threshold observed for spherical microparticles[1,2] is seen to be the smallness of the resonant denominator M_l, expressing the highly effective field confinement in the sphere (high Q value).

The resonance shift $\rho_\lambda^{(1)} - \rho_\lambda^{(0)} = \epsilon^{1/2}(k_\lambda^{(1)} - k_\lambda^{(0)})a$ is determined from (8) by the equality $\mathrm{Re}\alpha^{(1)} \simeq \mathrm{cotan}\delta_l^{(0)}$, which can be rewritten as [Eq. (9)]

$$\begin{aligned} -4\pi\epsilon^{-1/2}&\mathrm{Re}\{\chi^{(1)}(\langle N_l^{(0)}\rangle)/[\rho_\lambda M_l(\rho_\lambda)]^2\} \\ &\simeq (\rho_\lambda^{(1)^2} - \rho_\lambda^{(0)^2})/2\rho_\lambda^{(0)}\Gamma_\lambda \\ &\simeq (\rho_\lambda^{(1)} - \rho_\lambda^{(0)})/\Gamma_\lambda . \end{aligned} \quad (11)$$

Here we have used the form[12] of $\tan\delta_l^{(0)}$ near the unperturbed resonance $\rho_\lambda^{(0)}$ whose width is Γ_λ (the imaginary part of the roots of M_l for real ϵ).[14] On using the general relationship between the real and imaginary parts of the susceptibility above threshold,[11] the lasing condition (10) combined with (11) yield the following "frequency-pulling" condition in the small-signal regime:

$$(\rho_\lambda^{(1)} - \rho_\lambda^{(0)})/\Gamma_\lambda \lesssim \langle -[(\omega - \Omega_\lambda^{(0)})/\gamma] \rangle \mathrm{Im}\delta_l^{(0)} . \quad (12)$$

The angular brackets on the right-hand side of (12) denote averaging over the ω distribution in the sphere, which is determined either by inhomogeneous broadening (in doped crystals) or by the Franck-Condon bandwidth in molecular solutions. Assuming that under conditions similar to those of Ref. 1, $\langle(\omega - \Omega_\lambda^{(0)})\rangle/\gamma \gtrsim 30$ and $\mathrm{Im}\delta_l^{(0)} \lesssim 10^{-2}$ (bulk absorption constant below $1\ \mathrm{cm}^{-1}$), we conclude from (12) that frequency pulling can exceed the width Γ_λ only for peaks well above threshold, for which the right-hand side of (12) is much smaller (in absolute value) than the left-hand side. Experiment[1] supports this conclusion.

In order to adapt the above theory to the treatment of stimulated Raman scattering, converting the incident $\Omega_{\lambda 0}$ radiation into Stokes-shifted radiation at $\Omega_{\lambda 1} \simeq \Omega_{\lambda 0} - \omega_V$, the only modification required is the replacement of $\chi_\lambda^{(1)}$ by the effective susceptibility for third-order Stokes polarization[15] $\chi_{\lambda 1}^{(3)} | E_{\lambda 0} |_{\mathrm{ref}}^2$. Here $\chi_{\lambda 1}^{(3)} \propto (\Omega_{\lambda 0} - \omega_v - \Omega_{\lambda 1} + i\gamma_v)^{-1}$ is maximal for $\Omega_{\lambda 1}$ within the Raman transition linewidth γ_v centered about $\Omega_{\lambda 0} - \omega_v$, and $(E_{\lambda 0})_{\mathrm{ref}}$ is the reflected pump wave inside the sphere, related to the incident pump wave $(E_{\lambda 0})_{\mathrm{inc}}$ as in (4).

For pumping nearly confined to the surface we then have, instead of (9),

$$\begin{aligned} \alpha_s^{(3)} = 4\pi\epsilon^{-1/2}&\chi_{\lambda 1}^{(3)}(\bar{N}^{(s)}) | E_{\lambda 0} |_{\mathrm{inc}}^2 (k_{\lambda l} a)^{-2} \\ &\times [j_l(\rho_{\lambda 0}/M_l(\rho_{\lambda 0})]^2 [j_l(\rho_{\lambda 1})/M_l(\rho_{\lambda 1})]^2 , \end{aligned} \quad (13)$$

where $\bar{N}^{(s)}$ is the Raman-transition inverted-population density.[15]

If the oscillation condition $\mathrm{Im}\alpha_s^{(3)} > \mathrm{Im}\delta_l^{(0)}$ is satisfied (as for the experimental conditions of Ref. 4), then $(E_{\lambda 1})_{\mathrm{ref}}$ grows exponentially at each boundary reflection, building up sufficient intensity to serve as a pump for the second Stokes-order frequency $\Omega_{\lambda 2} \simeq \Omega_{\lambda 0} - 2\omega_v$. The $\alpha_s^{(3)}$ factor for the latter process can be strongly enhanced compared to the corresponding bulk value if both $\Omega_{\lambda 1}$ and $\Omega_{\lambda 2}$ are removed from Mie resonances by less than γ_v. Using the same parameters as in the estimate following (10), including $M_l(\rho_{\lambda 1}) \sim M_l(\rho_{\lambda 2}) \sim 10^{-4}$, we find that

$$\alpha_s^{(3)} \sim 10^7 \chi^{(3)}(\bar{N}_s) | E_{\lambda 1} |_{\mathrm{inc}}^2 ,$$

i.e., the enhancement is even more spectacular than in lasing. The availability of closely spaced resonances up to $\Omega_{\lambda 14} \simeq \Omega_{\lambda 0} - 14\omega_v$ in the experiment of Ref. 4 yields small resonant denominators $M_l(\rho_{\lambda n})$ for orders n in the range $1 \le n \le 14$. Thereby a multiorder SRS process, in which the $\Omega_{\lambda n}$ mode pumps the consecutive $\Omega_{\lambda n+1}$ mode, can occur with much lower threshold values than in bulk.

Although the theory outlined above explains the basic observable features of stimulated processes in dielectric spheres, namely, threshold reduction in lasing and multiorder SRS and frequency pulling, it cannot provide accurate quantitative interpretation of the cited experimental results, pertaining to a multimode situation. In future works we intend to dwell on the angular and spectral features of the emission caused by intermode coupling due to pumping anisotropy and the E_λ^2 (saturation) term in the population-inversion factor of the lasing susceptibility.

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