A Simple Model for Molecular Rayleigh and Raman Scattering

George A. Hagedorn
Department of Mathematics, and
Center for Statistical Mechanics, Mathematical Physics, and
Theoretical Chemistry
Virginia Tech
Blacksburg, VA 24061–0123

(Joint work with Virginia Tech Chemistry Professor Edward Valeev)

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Outline

1. What is Raman scattering?
2. Description of our model.
3. Results.
4. Outline of the proofs.

What is Molecular Raman Scattering?

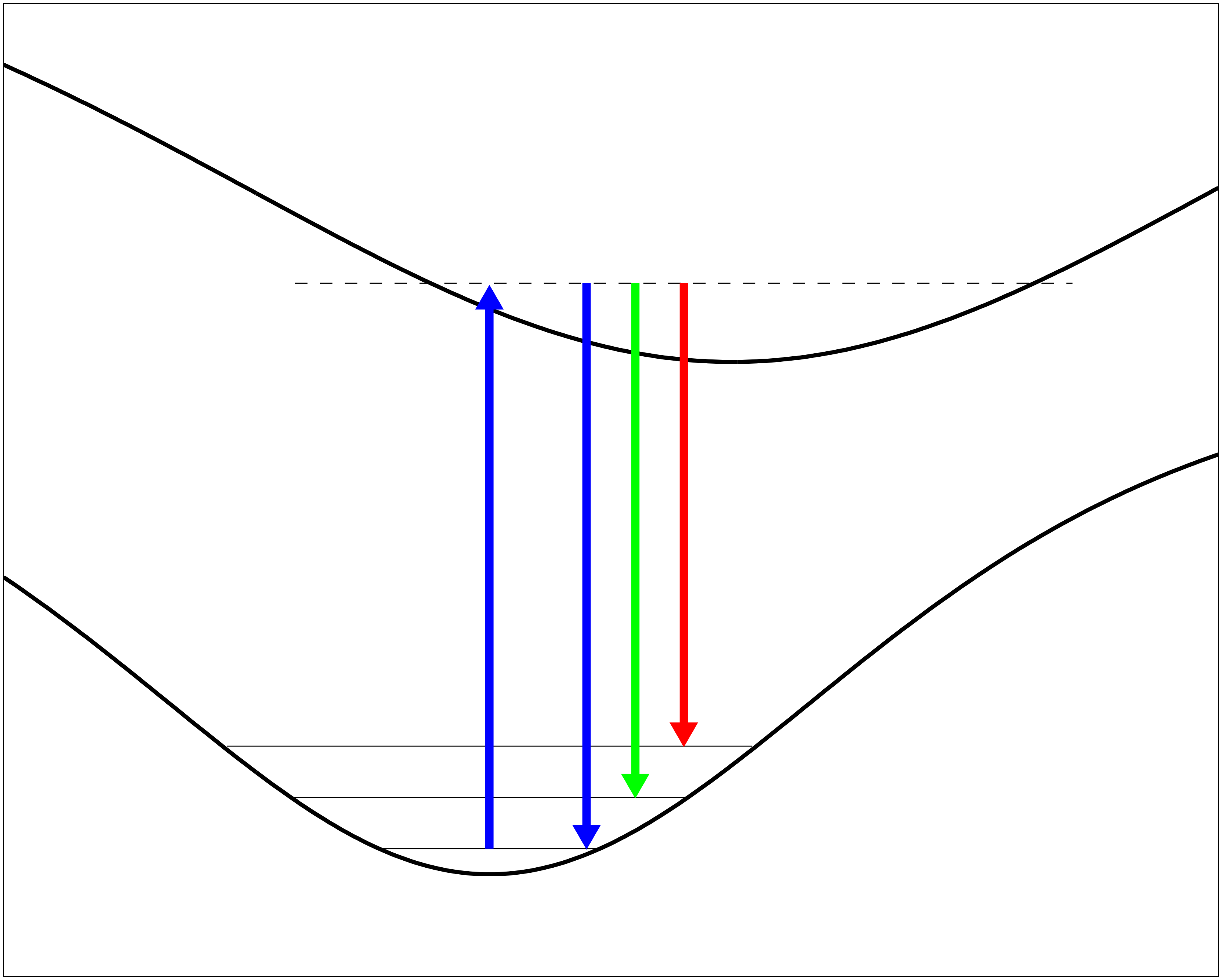
Suppose we shine light on a molecule, and suppose the light
has frequency high enough to interact significantly with the electrons
in the molecule (typically, visible or ultraviolet).

The molecule may produce light of the same or a different frequency.

If the frequency is the same, we have Rayleigh scattering.
It causes the sky to be blue.

If the frequency is different, we have Raman scattering.
To conserve energy, the molecule must change its state.
Typically, the molecule changes its vibrational state,
although there is also a rotational Raman effect.

In Resonance Raman scattering the energy of the incident photons
is tuned to an electronic transition energy of the molecule.



Our Model

We can handle more general situations, but for today, assume the molecule's nuclei have just one degree of freedom, and the electrons have just two electronic states.

The molecule's Hamiltonian

Assume the nuclear masses are proportional to ϵ^{-4}, so the molecule's Hamiltonian is $H_0(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial x^2} \;+\; \begin{pmatrix} V_0(x) & 0 \\ 0 & V_1(x) \end{pmatrix}$.

Assume V_0 has unique global minimum at $x = 0$,

$V_0(0) = V_0'(0) = 0, \qquad V_0''(0) = \omega_0^2 > 0, \qquad \liminf_{|x|\to\infty} V_0(x) > 0,$

$V_1(0) = \gamma > 0, \qquad \text{and} \qquad V_1'(0) = \beta \neq 0.$

The molecule with the laser pulse.

Our goal is to study solutions to the time–dependent Schrödinger equation

$$i\,\epsilon^2\,\frac{\partial\psi}{\partial t} \;=\; H_0(\epsilon)\,\psi \;+\; \mu\,f(t)\;\cos\!\left(\frac{\omega\,t}{\epsilon^2}\right)\,\begin{pmatrix} 0 & g(x) \\ g(x) & 0 \end{pmatrix}\psi.$$

The function $f(t) \geq 0$ is the envelope for the laser pulse.

The time–scale for the electronic motion is ϵ^2.
The laser frequency ω/ϵ^2 is tuned to be close to the transition energy for the electrons.

The function $g(x)$ is the laser coupling between the electronic levels. It can depend on the nuclear position x.

Remarks

1. The electromagnetic field is not quantized.

2. We study molecular state changes instead of the scattered light.

3. We shall start with the molecule in its ground state.
Its final state is the same or higher energy.

4. We assume f is smooth, with compact support in $[-T, T]$.
We shall assume T is sufficiently small. For realistic applications, this may mean a femtosecond laser pulse.

5. We assume both ϵ and μ are small parameters, and we assume we are at least close to the resonance condition $\omega = \gamma$.

6. We obtain explicit formulas for the Rayleigh scattering amplitude and Raman scattering amplitudes to leading order in μ and ϵ.

Results for Short Laser Pulses in the Resonance Case $\omega = \gamma$.

Assume

- the above situation with $g(0) \neq 0$ and $\omega = \gamma$.
- $\dfrac{2T}{\tau} \leq C < 1$, where τ is the period of the solution to $\ddot{x} = -V_1'(x)$ with $x(0) = x'(0) = 0$.
- $\mu \ll \epsilon^2 \ll 1$.

Then the resonance Rayleigh transition amplitude is

$$T_0(\mu, \epsilon) = -\frac{\mu^2}{4\,\epsilon^3} \frac{\sqrt{\pi\,\omega_0}\; g(0)^2}{|\beta|} \int_{-\infty}^{\infty} f(t)^2\, dt + O\left(\frac{\mu^2}{\epsilon^2}\right) + O\left(\frac{\mu^4}{\epsilon^8}\right).$$

If j is odd, the resonance Raman transition amplitude to vibrational state j is

$$T_j(\mu,\,\epsilon) \;=\; \frac{\mu^2}{4\,\epsilon^3}\;\frac{i\;(-1)^{\frac{j-1}{2}}\sqrt{\omega_0}\;g(0)^2}{\beta}\quad\frac{2^{j/2}\,\left(\left(\frac{j-1}{2}\right)!\right)}{(j!)^{1/2}}\;\int_{-\infty}^{\infty}e^{ij\omega_0 t}\;f(t)^2\,dt$$

$$+\quad O\left(\frac{\mu^2}{\epsilon^2}\right)\;+\;O\left(\frac{\mu^4}{\epsilon^8}\right).$$

If $j \geq 2$ is even, the resonance Raman transition amplitude to vibrational state j is

$$T_j(\mu,\,\epsilon) \;=\; \frac{\mu^2}{4\epsilon^3}\;\frac{(-1)^{\frac{j+2}{2}}\sqrt{\omega_0}\,g(0)^2}{|\beta|}\;\frac{\sqrt{\pi}\,(j!)^{1/2}}{2^{j/2}\,\left(\left(\frac{j}{2}\right)!\right)}\int_{-\infty}^{\infty}e^{ij\omega_0 t}\;f(t)^2\;dt$$

$$+\quad O\left(\frac{\mu^2}{\epsilon^2}\right)\;+\;O\left(\frac{\mu^4}{\epsilon^8}\right).$$

Comparisons with a Numerical Simulation

For $\mu = 0.001$, $\epsilon = 0.05$, $\beta = 1$, $\omega = \gamma = 1$, $\omega_0 = 1$, $g(0) = 1$ and $f(t) = e^{-5t^2/2}$ (cut off for $|t| > 1.5$), and $j = 0, 1, \cdots, 9$, the following chart compares these second order theoretical values for $10^5 \, |T_j(\mu, \epsilon)|$ with computer simulations for $10^5 \, |T_j(\mu, \epsilon)|$.

Theory	281	213	162	117	77.3	46.9	26.0	13.1	5.99	2.49
Simulation	280	211	159	113	74.3	44.7	24.5	12.2	5.52	2.26

For the smallest values of j, the differences are about 1%, and the percent errors increase as j increases (as one would expect). The behavior is qualitatively correct, and the behavior of the phases is also qualitatively correct.

Results for Short Laser Pulses in the Non–Resonance Case but with the light frequency ω close to γ

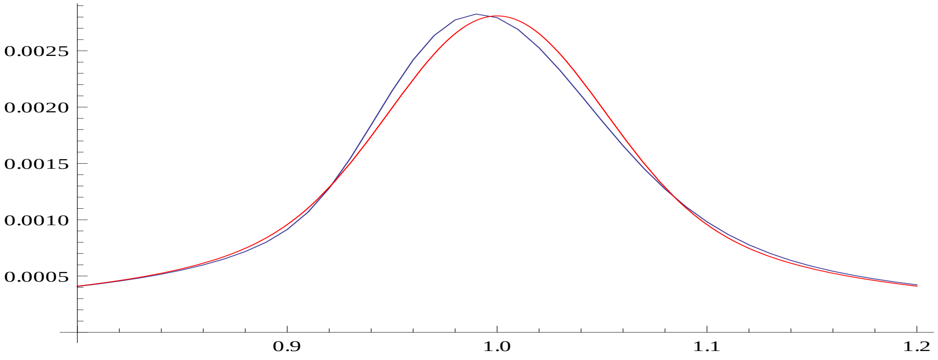
The non–resonance Rayleigh scattering amplitude to leading order is

$$T_0(\mu, \epsilon) \approx -\frac{\mu^2}{\epsilon^3}\, g(0)^2 \left(1 + \mathrm{erf}\left(\frac{i\sqrt{\omega_0}\,(\omega-\gamma)}{|\beta|\,\epsilon}\right)\right) \times \quad \exp\left(-\frac{\omega_0\,(\omega-\gamma)^2}{\beta^2\,\epsilon^2}\right) \frac{\sqrt{\pi\,\omega_0}}{4\,|\beta|} \int_{-\infty}^{\infty} f(s)^2\, ds.$$

Similar, rather messy formulas can be obtained for the leading order non–resonance Raman scattering amplitudes.

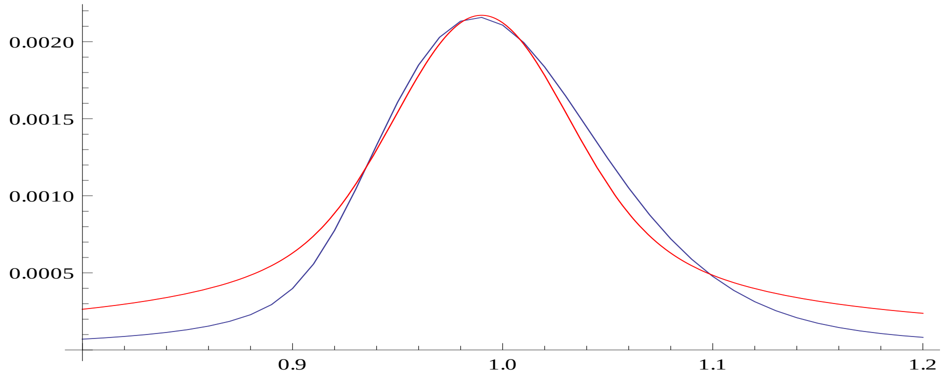
All of these formulas agree with the simpler resonance results if one takes the limit $\omega \to \gamma$.

Here are plots of the absolute value of the Rayleigh transition amplitude for a numerical simulation (blue) and our leading order formula above (red).



Comparison plot for $|T_0|$.

Here are plots of the absolute value of the Raman transition amplitude to the $j = 1$ state
for a numerical simulation (blue)
and our leading order formula (red).



Comparison plot for $|T_1|$.

Outline of the Proof in the Resonance Case

We do a formal perturbation expansion in powers of μ.

$$\psi(x,\,t) \;=\; \psi_0(x,\,t) \;+\; \mu\,\psi_1(x,\,t) \;+\; \mu^2\,\psi_2(x,\,t) \;+\; \cdots\,.$$

If g is bounded, this series is convergent for our simple model.

We substitute this expansion into the Schrödinger equation and equate terms of the same order in μ.

Order 0 in μ

$$\psi_0(x,\,t) \;=\; e^{-i(t+T)H_0(\epsilon)/\epsilon^2}\;\psi_0(x,\,-T)$$

The ground state is known to any given order in powers of ϵ,
so we know $\psi_0(x,\,-T)$ up to an $O\left(\epsilon^N\right)$ error.
We also know how to propagate this state with an $O\left(\epsilon^N\right)$ error.

Thus, we know $\psi_0(x,\,t)$ up to an $O\left(\epsilon^N\right)$ error, uniformly for $t \in [-T,\,T]$.

Explicitly, $\psi_0(x,\,s) \;=\; e^{-isE_0(\epsilon)/\epsilon^2}\;\phi_0(x)$, where

$$\phi_0(x) \;=\; \begin{pmatrix} 1 \\ 0 \end{pmatrix}\; \pi^{-1/4}\,\epsilon^{-1/2}\,\omega_0^{1/4}\,e^{-\,\omega_0\,x^2/(2\epsilon^2)} \;+\; O(\epsilon).$$

The other low-lying bound states (which we shall need) are

$$\phi_j(x) \;=\; 2^{-j/2}\,(j!)^{-1/2}\,H_j\left(\frac{\sqrt{\omega_0}\,x}{\epsilon}\right)\;\phi_0(x) \;+\; O(\epsilon), \quad \text{where} \quad j > 0.$$

The energy of the j^{th} state is

$$E_j(\epsilon) \;=\; \left(j+\frac{1}{2}\right)\omega_0\,\epsilon^2 \;+\; O\left(\epsilon^4\right).$$

The ϕ_j are precisely the states we know how to propagate quite explicitly to order ϵ^N by semiclassical methods. Even if the two electronic levels have non–trivial coupling, we have similar results by time–dependent Born–Oppenheimer methods.

Order 1 in μ

$$\psi_1(x,\, t)$$

$$= \frac{-\,i}{\epsilon^2} \int_{-T}^{t} f(r)\ \cos\left(\frac{\omega\, r}{\epsilon^2}\right) e^{-i(t-r)H_0(\epsilon)/\epsilon^2} \begin{pmatrix} 0 & g(x) \\ g(x) & 0 \end{pmatrix} \psi_0(x,\, r)\, dr.$$

Order 2 in μ

$$\psi_2(x,\, t)$$

$$= \frac{-\,i}{\epsilon^2} \int_{-T}^{t} f(s)\ \cos\left(\frac{\omega\, s}{\epsilon^2}\right) e^{-i(t-s)H_0(\epsilon)/\epsilon^2} \begin{pmatrix} 0 & g(x) \\ g(x) & 0 \end{pmatrix} \psi_1(x,\, s)\, ds$$

$$= \frac{-\,1}{\epsilon^4} \int_{-T}^{t} ds \int_{-T}^{s} dr\, f(s)\, f(r) \cos\left(\frac{\omega\, s}{\epsilon^2}\right)\ \cos\left(\frac{\omega\, r}{\epsilon^2}\right)\ e^{-i(t-s)H_0(\epsilon)/\epsilon^2}$$

$$\times \quad \begin{pmatrix} 0 & g(x) \\ g(x) & 0 \end{pmatrix} e^{-i(s-r)H_0(\epsilon)/\epsilon^2} \begin{pmatrix} 0 & g(x) \\ g(x) & 0 \end{pmatrix} \psi_0(x,\, r).$$

The Rayleigh scattering amplitude is obtained by taking the inner product of the solution at any time $t \geq T$ with $\psi_0(x,\,t)$. (The laser is off after time T, and there is no spontaneous emission in our model.)

The lowest order non-zero term in μ comes from the $O(\mu^2)$ term in the expansion above. That term is explicitly

$$
\begin{aligned}
&T_0(\epsilon,\,\mu)\\
&\approx\;\langle\,\psi_0(x,\,T),\;\mu^2\,\psi_2(x,\,T)\,\rangle\\
&=\;\frac{-\,\mu^2}{\epsilon^4}\int_{-T}^{T}ds\int_{-T}^{s}dr\,f(s)\,f(r)\,\cos\left(\frac{\omega\,s}{\epsilon^2}\right)\,\cos\left(\frac{\omega\,r}{\epsilon^2}\right)\\
&\qquad\qquad\qquad\times\quad\left\langle\begin{pmatrix}0 & g(x)\\ g(x) & 0\end{pmatrix}e^{-i(s-T)H_0(\epsilon)/\epsilon^2}\;\psi_0(x,\,T),\right.\\
&\qquad\qquad\qquad\qquad\left.e^{-i(s-r)H_0(\epsilon)/\epsilon^2}\begin{pmatrix}0 & g(x)\\ g(x) & 0\end{pmatrix}\psi_0(x,\,r)\right\rangle.
\end{aligned}
$$

We now begin approximating this term.

We first note that the $e^{-i(s-T)H_0(\epsilon)/\epsilon^2}\ \psi_0(x,\,T)$ on the left hand side of the inner product and the $\psi_0(x,\,r)$ on the right hand side of the inner product are both highly localized around $x=0$.

Some estimates with Taylor series show that we obtain the leading order in ϵ if we replace $g(x)$ everywhere in the integrand by $g(0)$.

After we do that, we can do the $e^{-i(s-r)H_0(\epsilon)/\epsilon^2}$ propagation to arbitrarily high order in ϵ. (To leading order, this is semiclassical propagation in the upper potential V_1.)

Next, we write the product of cosines in terms of complex exponentials:

$$\cos\left(\frac{\omega\, s}{\epsilon^2}\right)\ \cos\left(\frac{\omega\, r}{\epsilon^2}\right)$$
$$=\ \frac{1}{4}\ \left(e^{i\omega(s+r)/\epsilon^2}+e^{i\omega(s-r)/\epsilon^2}+e^{i\omega(-s+r)/\epsilon^2}+e^{-i\omega(s+r)/\epsilon^2}\right).$$

When we substitute this into the integral, three of the four resulting terms are rapidly oscillating integrals without stationary phase points. Integrations by parts show that they do not contribute to leading order.

The remaining term (which intuitively corresponds to absorbing and then later emitting a photon) is not rapidly oscillating. It yields

$$T_0(\mu,\, \epsilon)$$
$$\approx\ \frac{-\,\mu^2\, g(0)^2}{4\,\epsilon^4}\ \int_{-T}^{T} ds \int_{-T}^{s} dr\ f(s)\ f(r)\ e^{i(s-r)\omega_0/2}$$
$$\times\quad \langle \psi_0(x,\, 0),\, e^{-i(s-r)(H_0^{(1)}(\epsilon)-\omega)/\epsilon^2}\psi_0(x,\, 0)\rangle.$$

To leading order in ϵ, the inner product in this integrand is an inner product of two complex Gaussians at each s and r.

It can be computed explicitly, and it is $\dfrac{2\,\epsilon\,\sqrt{\pi\,\omega_0}}{|\beta|}$ times an approximate Dirac delta in $s-r$.

Because the approximate Dirac delta is symmetric and the r integral has upper limit s, we obtain only half of the Dirac delta.

Thus, we obtain our expression for the leading order Rayleigh scattering amplitude

$$T_0(\mu,\,\epsilon) \;=\; -\,\frac{\mu^2}{4\,\epsilon^3}\quad\frac{\sqrt{\pi\,\omega_0}\;\,g(0)^2}{|\beta|}\quad\int_{-\infty}^{\infty}\,f(t)^2\,dt$$

$$+\quad O\left(\frac{\mu^2}{\epsilon^2}\right)\;+\;O\left(\frac{\mu^4}{\epsilon^8}\right).$$

The analysis of the leading order resonance Raman transition amplitudes follows exactly the same reasoning.

Remarks

1. We could handle laser pulses longer than the period of vibration in the upper level by evaluating the double integral numerically.

However, this would require knowing the excited potential energy surface $V_1(x)$, its derivative, and second derivative, accurately for a large range of values of x.
Such detailed information is rarely available.
The results would involve some complicated interferences.

2. Allowing more degrees of freedom for the nuclei is not a significant problem.

Proof Modifications for the Non–Resonance Case

We assume we are close to resonance. In this situation, all four of the terms from the product of cosines involve oscillatory integrals. However, one oscillates much more slowly than the others; it gives the leading term.

The double integral to leading order has the integrand

$$f(s)\, f(r)\ \exp\left(i\,(\omega-\gamma)(s-r)/\epsilon^2\right)\ \exp\left(-\ \frac{\beta^2\,(s-r)^2}{4\,\epsilon^2}\right)$$

instead of

$$f(s)\, f(r)\ \exp\left(-\ \frac{\beta^2\,(s-r)^2}{4\,\epsilon^2}\right),$$

and again we have $s > r$.

This change gives rise to

$$\frac{\epsilon\sqrt{\pi}}{|\beta|}\;\left(1+\mathrm{erf}\left(\frac{i\,(\omega-\gamma)}{|\beta|\,\epsilon}\right)\right)\;\exp\left(-\;\frac{(\omega-\gamma)^2}{\beta^2\,\epsilon^2}\right)$$

times the approximate Dirac delta in $(s-r)$ instead of $\epsilon\sqrt{\pi}/|\beta|$ times the approximate Dirac delta.

The more complicated factor arises from the integral

$$\int_{-\infty}^{0}\;e^{i(\omega-\gamma)t/\epsilon^2}\;e^{-\,\beta^2\,t^2/(4\,\epsilon^2)}\;dt.$$

Otherwise, the analysis is the same as in the resonance case.

Summary

- For this simple, two level model, we have simple formulas for the Rayleigh and Raman scattering amplitudes in the resonance case for short laser pulses.

- When the laser is only close to resonance, we still have formulas, but they are somewhat more complicated.

- We are unaware of any such simple formulas in the mathematics, physics, or chemistry literatures.

- The main drawback to our results is that the laser pulse must be very short.

Thank you!