



A simple statistical treatment of multiphoton absorption

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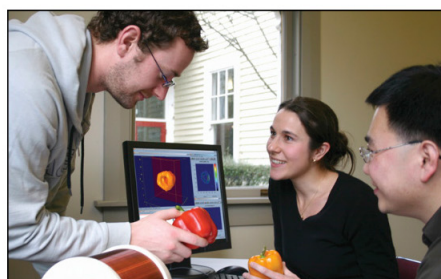
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A simple statistical treatment of multiphoton absorption

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Multiphoton absorption is a process involving the concerted absorption by individual atoms or molecules of two or more photons from an intense beam of light. It is a topic which is currently the subject of a great deal of research effort, and for which an increasing number of practical applications are being found. These range from nonlinear spectroscopy to isotope separation; from the detection of single atoms and molecules to photochemical synthesis.¹ There are, moreover, a number of unique features associated with the physics of multiphoton absorption which distinguish it from conventional absorption processes in which photons are absorbed singly. These include unusual selection rules, a dependence on the coherence properties of laser radiation, and the ability to cancel out the Doppler shift in frequency usually experienced by gas molecules.²

While many of these subjects can be discussed readily in a qualitative way in an undergraduate class, it is difficult to go into the theory underlying the absorption process unless the students have a sound background in time-dependent perturbation theory or related quantum mechanical methods. However, several important quantitative features of the process can be conveyed by an elementary statistical treatment described in this article. The basis of this treatment is the simple assumption that *the probability of a molecule undergoing n-photon absorption is proportional to the probability of finding n photons within the volume it occupies at any moment in time.* Underlying this assumption is the understanding that the molecule possesses a suitable set of energy levels such that all possible multiphoton transitions are allowed with equal intensity by the selection rules.

The first step, then, is to relate the mean number of photons within a molecular volume to the irradiance (energy per unit area per unit time) of the laser beam. Consider a cubic volume of space of length l , much less than the beam width, through which the laser light passes. If the mean number of photons within this volume at any time is m , then the mean energy in the box is mhc/λ , where λ is the wavelength. Since the cross-sectional area is l^2 , and the time taken for each photon to pass through the box is l/c , then the irradiance $I = (mhc/\lambda)/(l^3/c)$. Hence,

$$m = IV\lambda / hc^2, \tag{1}$$

where V is the volume. Since the mean volume occupied by one molecule of a liquid is the molar volume V_m divided by Avogadro's constant, we thus have

$$m = IV_m\lambda / Lhc^2. \tag{2}$$

As an example, consider a liquid with a molar volume equal to that of trichloromethane ($V_m = 8.07 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) irradiated by a mode-locked laser operating at 444 nm, and producing peak intensities of 10^{15} Wm^{-2} in each pulse. From Eq. (2), the mean number of photons per mo-

lecular volume at the instant of peak intensity is approximately 1×10^{-3} .

We now have to find the probability P_n of finding an integer number of photons n in the molecular volume. At this stage, it is necessary to choose a suitable distribution function to model the statistical properties of the radiation. The most appropriate function for coherent laser light is the Poisson distribution,³

$$P_n^{(\text{laser})} = (m^n/n!)e^{-m}. \tag{3}$$

For the example given, we thus find the probability P_1 of finding one photon is approximately 1×10^{-3} , and the probability P_2 of finding two photons is 5×10^{-7} . Hence, whereas approximately one molecule in a thousand experiences the transit of a single photon at any instant, the number which experience simultaneously the transit of two photons is approximately one in two million. This illustrates the fact that even with a high photon flux, the probability of two-photon absorption is very much smaller than that of conventional single-photon absorption.

However, P_1 and P_2 depend in different ways on the intensity of light. For example, if the laser intensity is quadrupled so that $m \approx 4 \times 10^{-3}$, then $P_1 \approx 4 \times 10^{-3}$ and $P_2 \approx 8 \times 10^{-6}$. In other words, while the probability of finding a single photon has also quadrupled, the probability of finding two has increased by a factor of 16. Again, this reflects the well-known I^n intensity dependence of n -photon absorption.⁴

Another distinctive feature of multiphoton absorption is revealed if we consider an alternative form for the probability distribution P_n . If light is produced by a thermal source, it is more appropriate to use the Bose-Einstein distribution,³

$$P_n^{(\text{thermal})} = m^n/(m + 1)^{n+1}. \tag{4}$$

If we reconsider the original example where $m \approx 1 \times 10^{-3}$, then, while we again find $P_1 \approx 1 \times 10^{-3}$, we now have $P_2 \approx 1 \times 10^{-6}$. Thus while the probability of finding one photon in the molecular volume is independent of the statistical properties of the light, the probability of finding two photons is twice as large in the case of a thermal source as it is for a coherent source of the same mean intensity. This is precisely the behavior observed for one- and two-photon absorption, reflecting the general dependence on the degree of n th-order coherence in the case of n -photon absorption. (The degree of first-order coherence is unity both for thermal and coherent light, whereas the degree of second-order coherence has the value 2 for thermal light, and 1 for coherent light.)⁵

With exceptionally intense light, the mean number of photons m per molecule may in principle approach integer

values, and in such a situation, the probabilities P_n may be very similar for different values of n . This has to be interpreted as reflecting the point at which many different multiphoton processes become equally likely; in other words, where the interactions between the molecules and the radiation are too strong for perturbation theory to apply. If we specifically consider the case $m = 2$, which leads to the result $P_1 = P_2$ in Eq. (3), then we find the corresponding irradiance is of the order of $2 \times 10^{18} \text{ Wm}^{-2}$. Using the formula

$$E = (I/2c\epsilon_0)^{1/2}, \quad (5)$$

we find the corresponding amplitude E for the electric field of the radiation is approximately $2 \times 10^{10} \text{ Vm}^{-1}$, which is by no means insignificant compared with the electrostatic field binding the electrons to the nuclear framework (10^{11} Vm^{-1}). Hence, at this level of intensity, radiative interactions are comparable to electron-nucleus interactions, and perturbation theory is indeed inapplicable.

It would be unwise to pursue this argument too far; clearly, the exact details of both intramolecular and molecule-radiation interactions depend on the quantum mechanics of the molecule. Also worth noting is the fact that, even with lower intensities, the mean number of photons m

per molecule may still approach integer values if macromolecules are considered. In such cases, however, excitation is usually localized in a much smaller chromophore unit, and so it is more appropriate to consider the mean number of photons per chromophore, rather than per molecule.

In summary, the model described in this article is undoubtedly oversimplistic, and should not be regarded as anything more than a conceptual aid. Nonetheless, it does provide an easily understood introduction to the subject of multiphoton absorption, and it enables some useful quantitative results to be obtained without recourse to detailed quantum mechanical calculations.

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³W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).

⁴P. Lambropoulos and M. Lambropoulos, *Electron and Photon Interactions with Atoms*, edited by H. Kleinpoppen and M. R. C. McDowell (Plenum, New York, 1976), p. 525.

⁵R. Loudon, *The Quantum Theory of Light* (Oxford U.P., Oxford, England, 1973).

Distinction between center of mass and center of gravity—Oscillation of rod-shaped satellite as an example

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The confusion between the meaning of the center of mass and the center of gravity of a body is well known, but there are few examples where the difference between the two is significant. The center of mass is the point on the body which moves in the same way that a single particle subject to the same external forces would move. If the body is rotating in free-space under the action of no external forces, it is that point of the body which is stationary or traveling in a straight line. The center of gravity is the point in the body where the resultant of all the gravitational forces on that body appears to act. Normally, we assume that the center of mass and center of gravity are identical, so it is perhaps useful to give a case where the fact that the two are not the same leads to a very important result.

The LDEF satellite was launched from the space shuttle on 7 April 1984. This passive satellite,^{1,2} which takes the form of a cylinder 30 ft long by 14 ft in diameter and is approximately 20 000 lb, orbits the earth at an altitude of approximately 400 km for about a year, being recovered by a subsequent shuttle flight and brought back to earth. It is required that one end of the satellite face the earth for the period it is in orbit. Let us assume the satellite is a rod of density ρ per unit length, and of length $2L$. The center of mass will lie at the center L from each end. If θ is the instantaneous value of angle of inclination of the rod to a line joining its center to the center of the earth, (distant \bar{R}), as shown in Fig. 1, the gravitational force on an element of the rod of length $dx/\cos \theta$ due to the earth's mass M_e will be

$$dF = G M_e \rho \frac{dx}{R^2} \cos \theta,$$

where R is the distance from this element to the earth's center and G is the universal gravitational constant. (For derivations, see, for example, French.³)

Now, $G M_e / (\bar{R})^2 = g$, the gravitational acceleration of the satellite, so that

$$dF = \rho g dx \secant(\theta) (\bar{R} / R)^2.$$

For the satellite to be maintained in its orbit, pointing toward the earth, the angular velocity ω of each part of the rod about the earth, must be the same. This entails a radial acceleration of $g R / \bar{R}$ for each element. It is the force associated with this difference in the radial dependence of gravity and centripetal acceleration which produces the

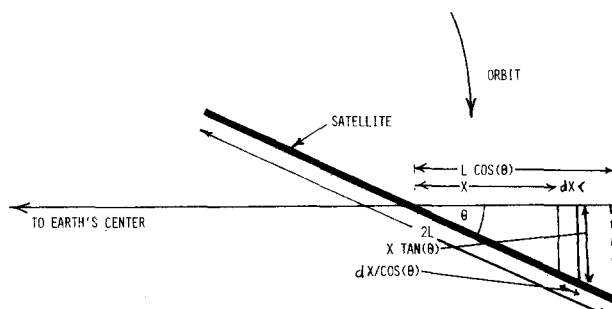


Fig. 1. Orientation of rod-shaped satellite pitching in orbit.