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A Simple Conceptual-Model For 2-Photon Absorption

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Demanding Lorentz invariance under a boost in the x^2 direction gives the additional equations

$$T_{\hat{0}\hat{1}} = T_{\hat{1}\hat{0}} = T_{\hat{2}\hat{3}} = T_{\hat{3}\hat{2}} = 0, \quad T_{\hat{2}\hat{2}} = -T_{\hat{0}\hat{0}} . \tag{A13}$$

At last, Lorentz invariance under a boost in the x^3 direction gives the additional equation

$$T_{\hat{3}\hat{3}} = -T_{\hat{0}\hat{0}} . \tag{A14}$$

From Eqs. (A12)–(A14) follows

$$T_{\hat{\mu}\hat{\nu}} = T_{\hat{0}\hat{0}} \, \mathrm{diag}(1, -1, -1, -1) , \tag{A15}$$

which can be written as

$$T_{\hat{\mu}\hat{\nu}} = T_{\hat{0}\hat{0}} \, \eta_{\hat{\mu}\hat{\nu}} , \tag{A16}$$

where $\eta_{\hat{\mu}\hat{\nu}}$ are the components of the Minkowski metric tensor. Transformation to an arbitrary basis $\{e_\mu\}$ gives

$$T_{\mu\nu} = T_{\hat{0}\hat{0}} \, g_{\mu\nu} . \tag{A17}$$

From the physical interpretation of the components of the energy-momentum density tensor, it follows that

$$T_{\hat{0}\hat{0}} = \rho , \tag{A18}$$

where ρ is the energy density of the system (here the vacuum). This will not be invariant under Lorentz transformations for arbitrary systems. But, the energy density *of the vacuum* is in general a scalar function of the four space-time coordinates.

In homogeneous cosmological models one demands that the density ρ measured by an observer depends only upon time. Due to the relativity of simultaneity this condition is Lorentz invariant only if $\rho = \mathrm{constant} = \rho_0$. Thus in the cosmological case the energy-momentum density tensor of the vacuum is

$$T_{\mu\nu} = \rho_0 \, g_{\mu\nu} . \tag{A19}$$

The energy density of the vacuum appears as a cosmological constant.

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A simple conceptual model for two-photon absorption

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The process of two-photon excitation of atoms is explained by a simple conceptual model which takes into account virtual states of the atom as well as photon statistics. In addition to predicting the correct dependence of the two-photon excitation probability on the intensity of incident light, the model also provides an explanation for a number of experimentally observed effects.

It is a fundamental principle of atomic theory that an atom can be raised to an excited energy state by the absorption of a photon whose energy is exactly equal to that required for the transition. Alternatively, if there exist intermediate states, this excitation can be effected in a stepwise fashion with the absorption of a single photon, of correct energy for each transition involved. However, it is also possible for an atom to "simultaneously" absorb a number of photons, each of which is not necessarily resonant with the intermediate transitions, and thereby be raised directly to

the excited state. The only requirement is that the sum of the energies of the photons absorbed be equal to the excitation energy (and that the proper selection rules be satisfied). This is called multiphoton excitation.

In this paper we consider an important subclass of the above process, that of two-photon absorption. Although the theory was first described by Goeppert-Mayer in 1929,[1] it was not until 1961 that it could be experimentally verified.[2] The reason for this delay is, as we shall see, that the process requires an intensity of incident light most readily obtained through the use of lasers. Probably the most important application of two-photon absorption is in the field of Doppler-free spectroscopy. If the two photons absorbed by the atom are traveling in opposite directions, then although their individual energies are Doppler shifted, their sum is not. This means that every atom in the sample can participate regardless of its velocity. Other methods, such as saturation spectroscopy,[3] achieve Doppler-free results by selecting only a subclass of atoms from the sample (i.e., those with zero component of velocity in the direction of the incident light). With sample sizes as low as 10^{-9} g for some artificially produced radioisotopes, this difference could be important. Other advantages of two-photon spectroscopy include the ability to reach excited states that are parity-forbidden for single-photon transitions, and more importantly the extension of the effective spectral range of the light source (in some cases all the way into the UV).

The complete quantitative description of the two-photon process requires familiarity with quantum-mechanical methods, especially second-order perturbation theory.[4] The treatment presented here is based on little more than the Heisenberg uncertainty relation, elementary statistics, and physical intuition. Nevertheless, several experimentally verified features of the process do emerge.

We begin by considering an atomic transition between two levels of energy E_i and E_f with $E_i < E_f$. Assume that a third level exists whose energy E_k differs slightly from $(E_f - E_i)/2$, i.e., E_k is nearly halfway between E_i and E_f. Now let the atom be irradiated by light of frequency ω such that $\hbar\omega = (E_f - E_i)/2$. The situation is depicted in Fig. 1(a).

Since the light is not resonant with the transition $E_i \rightarrow E_k$, the state $|k\rangle$ is not populated. However, the photon may still be absorbed, thereby raising the atom to an excited state E_v, as long as this state exists for a time limited by the Heisenberg uncertainty relation [Fig. 1(b)]. Since the nearest stationary state is $|k\rangle$, this time is given approximately by
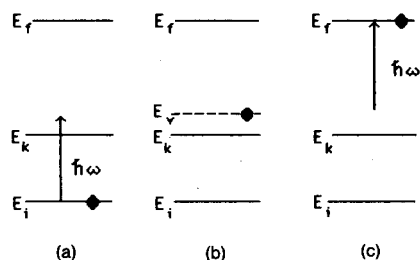
$$|E_v - E_K|\Delta t = h$$

(a)   (b)   (c)

Fig. 1. Schematic representation of two-photon absorption.

or

$$\Delta t = 1/|\omega - \omega_{i,k}|, \tag{1}$$

where $\hbar\omega_{i,k} = (E_k - E_i)$.

We call the state $|v\rangle$ a virtual atomic state, although in other perturbative treatments, they can actually enter as real stationary states. The two-photon excitation process can then be completed if a second photon of frequency ω is absorbed by the atom while it is still in the virtual state [Fig. 1(c)]. We are, therefore, led to the fundamental assumption of this model, namely, that the probability for two-photon excitation is proportional to the probability of finding two photons within the interval of time the atom spends in a virtual state.[5]

To obtain values for this probability we turn to a statistical description of the propagation of light. We ask the following question: Given a light beam of intensity I (which can be represented in terms of a photon flux of one photon per T s), what is the probability of getting two photons during a time interval Δt given by Eq. (1)? The answer, it would seem, should be provided by the Poisson distribution function[6]

$$P_n(\Delta t, T) = \exp(-\Delta t/T)(1/n!)(\Delta t/T)^n, \tag{2}$$

with $n = 2$ in our case.

All that remains is for us to relate the intensity to T. This can easily be done by recalling that intensity is simply a measure of the amount of energy per unit area per second. With this in mind we set

$$I = \hbar\omega/AT, \tag{3}$$

where T is the average time between the passage of single photons in the beam and A is an area element on the order of the cross-sectional area of the atom.

Before actually inserting the values for Δt and T from Eqs. (1) and (3), respectively, into Eq. (2), we pause briefly for two important observations. First, the exponential term in Eq. (2) can quickly be set equal to unity. To see this we note that, for typical optical transitions, the Δts as given by Eq. (1) are on the order of 10^{-15} s. This means that for the exponential term to contribute, T needs to be of the same order. This would correspond to a photon flux of about 10^{15} per second! At that intensity a perturbative treatment of the process is certainly not in order, and a completely different method would have to be employed. Second, to allow for the possible existence of more than one intermediate state $|k\rangle$, the expression in Eq. (1) should be summed over all possible values of k.

We may now obtain our result for the two-photon excitation probability $A_{i,f}$ under the assumption of this model. Using Eqs. (1)–(3), we get

$$A_{i,f} = P_2(\Delta t, T) = C\left(\sum_k \frac{A}{|\omega - \omega_{i,k}|}\right)^2 I^2,$$

where C is a constant. As a final step, we relate the classical quantity representing the area A of the atom to quantum-mechanical observables characteristic of the atomic dimension. Under these circumstances it seems that a simple product of the transition dipole moments $R_{i,k} = \langle i|r|k\rangle$ and $R_{k,f} = \langle k|r|f\rangle$ would be appropriate for this purpose. We then get, as our final result,

$$A_{i,f} = C\left(\sum_k \frac{R_{i,k} R_{k,f}}{|\omega - \omega_{i,k}|}\right)^2 I^2. \tag{4}$$

This expression bears a striking resemblance to that ob-

tained by second-order quantum-mechanical perturbation theory. Several experimental observations can be understood with reference to Eq. (4). Probably the most notable is the dependence of the two-photon process on the square of the incident light intensity. This makes such experiments difficult with light sources of low (or even moderate) power.

In addition, since the dipole-moment operator possesses odd partity, nonzero values of $R_{i,k}$ and $R_{k,f}$ will exist only if the intermediate state $|k\rangle$ is of opposite parity to $|i\rangle$ and $|f\rangle$ simultaneously. This means that $|i\rangle$ and $|f\rangle$ must have the same parity for two-photon transitions, unlike the single-photon case.

The energy denominator in Eq. (4) shows that those intermediate states closer to resonance with the incident photon participate more strongly. This effect is frequently exploited in experimental situations. For example the $3S{\rightarrow}4D$ two-photon transitions in sodium, first carried out by Cagnac et al.,[7] use the $3P_{1/2}$ and $3P_{3/2}$ levels as intermediate states. Their energies differ from that of the incident photons by about 0.1%. As such, they contribute significantly to the transition probability. The singularity which results when $\omega = \omega_{i,k}$ should not be disturbing since, in that case, excitation via single-photon transitions becomes the dominant process.

It should also be pointed out that although the intermediate state was assumed to lie nearly halfway between E_i and E_f in the model, the result [Eq. (4)] is valid in general. More specifically, there need not even be any states between E_i and E_f! In that case, the summation is carried out over all other states of the atom (discrete and continuous) for which $R_{i,k}$, and $R_{k,f}$ are not zero. The $1S$–$2S$ two-photon transition in hydrogen is such a case. There are no states with energies between E_{1S} and E_{2S}, but two-photon absorption has been observed.[8] The intermediate states which contribute in this case include the $2P$, $3P$, $4P$, etc. For hydrogen, this calculation has actually been carried out exactly by Bassani et al.[9] The relative contributions of

the intermediate states can be seen explicitly.

Finally, we should mention that the concept of a virtual atomic state is a powerful one, capable of explaining other nonlinear processes in atoms. For example, if the incident light intensity is not high enough, then the virtual state $|v\rangle$ may have a chance to decay spontaneously before the second photon comes along. If this decay is to one of the intermediate states, then a photon of frequency ω' will be emitted. But this is precisely Raman scattering. In this manner, such phenomena as third-harmonic generation and three-wave mixing can be understood.

In conclusion, we note that the model does not explain the important dependence of the process on the polarization of the two photons. This is not too surprising since nowhere in the development does the model consider the vector-field nature of the incident electromagnetic radiation. Nevertheless, the simplicity and conceptual clarity of the model help to provide a basic understanding and even appreciation of this mysterious process.

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Volume exclusion correction to the ideal gas with a lattice gas model

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The thermodynamic properties of the classical ideal gas are well known and documented. The departure of real gases from ideal behavior requires modification of the ideal equation of state. We derive an exact solution for an "excluded volume" system in which the constituent particles have nonzero volume and only one particle may occupy a specific region in space. To incorporate this volume exclusion, we propose a lattice gas model and find a simple combinatorial solution to this model. We construct the partition function, equation of state, and several other thermodynamic quantities.

I. INTRODUCTION

One description of an ideal gas is that of a collection of noninteracting particles. With the absence of interactions

as the only assumption, one may derive the familiar ideal equation of state $PV = NkT$. When this simple P–V–T dependence is not observed, or in the extreme case when the gas condenses to the liquid phase, it is clear that atomic or