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Tutorial

Pedagogical Revision of Spontaneous Emission and Photons

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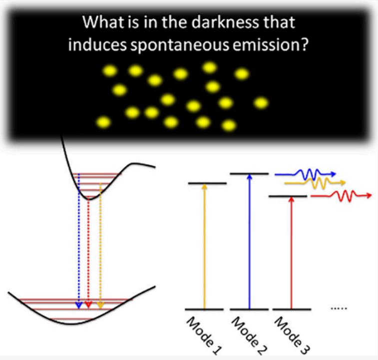
ABSTRACT: This article provides teaching material on classical and quantum electromagnetic field theory for undergraduate and graduate chemistry students. It focuses on the concepts of spontaneous emission and the photon as explained by quantum electromagnetic field theory. In general chemistry classrooms, these concepts are introduced early on using the well-known Jablonski diagram. However, we argue that the current approach to teaching spontaneous emission and the photon in chemistry needs to be re-evaluated in light of insights from quantum electromagnetic field theory. This article presents a revised proposal for teaching these topics.



KEYWORDS: *Graduate Education, Research, Tutorial, Upper Division Undergraduates, General Public, Physical Chemistry, Curriculum, Photochemistry, Quantum Chemistry, Misconception, Spontaneous Emission, Photon, Fluorescence*

■ INTRODUCTION

Spontaneous emission is an important topic in chemistry curricula for both graduate and undergraduate students. It is usually taught in the context of fluorescence. This journal has long discussed various novel approaches to teaching concepts related to fluorescence.[1−10]

Spontaneous emission processes serve as important tool for detection and technological innovation across various research fields, including chemistry, physics, and biology. For instance, fluorescence techniques enable the study of single molecules,[11] support the separation of cells into distinct populations (as seen in flow cytometry),[12] and facilitate cell visualization through fluorescence microscopy.[13] Additionally, fluorescence is crucial to many DNA sequencing methods.[14]

Recently, a new frontier in interdisciplinary research has emerged, known as quantum technology and computing, which also highlights the significance of fluorescence. A well-engineered fluorescent source that can function as a single-photon emitter is a fundamental component for numerous advanced quantum technologies,[15] including the development of a quantum Internet.[16,17] Recent literature suggests that some of the most promising types of single-photon emitters are fluorescent quantum dots[18−20] and two-dimensional materials.[21,22] The synthesis and characterization of novel quantum dots and two-dimensional materials are central to several areas of chemistry. This progress was recognized with last year's Nobel Prize in Chemistry, awarded to the pioneers for their discovery and synthesis of quantum dots".[23]

Therefore, given the traditional widespread applications of emission spectroscopy and the emerging demands of engineered single-photon emitters for the ongoing development of quantum technologies, the need for chemistry students to be exposed to the theory and practice of spontaneous emission will continue for many decades to come.

According to IUPAC recommendations, spontaneous emission is defined as *emission which occurs even in the absence of a perturbing electromagnetic field.*[24,25] Additionally, a photon is defined as *the quantum of electromagnetic energy at a given frequency. This energy, $E = h\nu$, is the product of the Planck constant (h) and the frequency of the radiation (ν).*[24,25] To the best of our knowledge, all popular undergraduate and graduate physical chemistry textbooks define spontaneous emission and the photon using these definitions.

However, this article seeks to challenge both definitions and proposes alternative ones that are necessary for introducing quantum technology to chemistry students. These alternative definitions are also important for exploring other emerging fields, such as attochemistry[26−29] and vibrational strong coupling chemistry,[30,31] in the chemistry curriculum.

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The core of alternative definitions is based on the understanding that, according to the quantum electromagnetic field theory, spontaneous emission phenomena like fluorescence are initiated by vacuum fluctuations that pervade the universe. During the emission process, *photons do not simply escape from molecules; instead, the quantized electromagnetic field undergoes a transition from its vacuum state to the single-photon state.* Many past and recent educational resources and textbooks, primarily authored by physicists, focus on these concepts.[32−34] However, we believe that these ideas are often overlooked in the of photochemistry and photophysics. In particular, quantum electromagnetic field theory has yet to be incorporated into physical chemistry textbooks or classroom discussion about photochemistry and photophysics.

At Gandhi Institute of Technology and Management (GITAM), we have developed courses to teach various concepts of quantum technology and computing to students from diverse backgrounds (science and engineering). Recently, one of our efforts to introduce quantum computing has been documented in the literature.[35,36] As a continuation of these ongoing efforts, we have designed an open elective course on basic quantum optics for sixth-semester liberal education students in science and engineering. The prerequisite for this course is the successful completion of at least one basic quantum mechanics course offered by either the chemistry or physics department. This course covers concepts, such as spontaneous emission and photons, along with their alternative definitions.

■ CONCISE PROBLEM STATEMENT

As spontaneous emission is introduced at an early stage in chemistry education, a preliminary survey was conducted to gather responses to the following two questions: (a) Are you familiar with both spontaneous emission phenomena, such as fluorescence, and the Jablonski diagram? and (b) Which of the images shown in Figure 1 best represents spontaneous emission, like fluorescence? Chemistry undergraduate and graduate students from various reputed Indian institutes, including the *Indian Institute of Science, Indian Institute of Research and Education (Mohali), Indian Association for the Cultivation of Science, Indian Institute of Technology (Kharagpur and Madras), Visva Bharati University,* and *Gandhi Institute of Technology and Management (Visakhapatnam)* voluntarily participated in this survey.

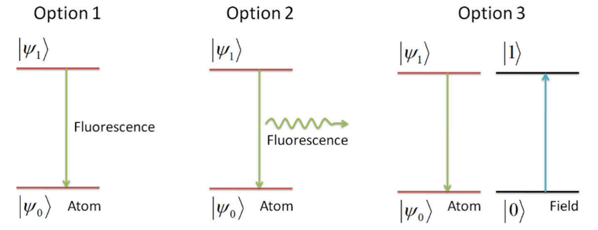

Figure 1. Different options for diagrammatical presentation of spontaneous emission are shown. The first two options utilize a traditional Jablonski diagram, while the third option is based on concepts from quantum electromagnetic field theory.

Figure 2 represents the responses of a total of 57 students. As shown in Figure 2(a), most of the students who participated in the survey are familiar with both spontaneous emission and the Jablonski diagram, which is traditionally used to depict spontaneous emission. Figure 2(b) indicates that, as expected, the majority of students selected either option 1 or 2 as the diagrammatic representation of spontaneous emission, these options are commonly found in physical chemistry textbooks. However, we argue that while both images convey part of the story concerning matter, they neglect the photon aspect. Only option 3 in Figure 1 coveys the complete message. This topic will be discussed in this article.

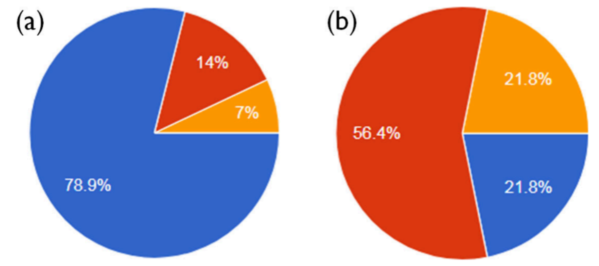

Figure 2. Responses from students regarding the following questions were recorded: (a) Are you familiar with both spontaneous emission phenomena, such as fluorescence, and the Jablonski diagram? and (b) Which of the images shown in Figure 1 best represents spontaneous emission, like fluorescence? Responses to the first question were categorized as Yes (blue), No (red) and May Be (orange). Responses to the second question were classified into three options: Option 1 (blue), Option 2 (red), and Option 3 (orange). These options are given in Figure 1.

It is not surprising that most chemistry students chose either option 1 or option 2 as the diagrammatic representation of spontaneous emission. In fact, in 1983, Milonni noted that a similar question would likely receive a comparable response from most physicists.[32] However, since 1983, pedagogical discussion about quantum electromagnetic field theory has led to a revision in physicists' responses, as seen in several physics textbooks;[33,34,37,38] Despite this, the responses from physical chemistry students, as depicted in Figure 2(b), still require improvement and revision. For further insight on this topic, see Supporting Information S1.

The present article is organized into several units, each designed to achieve specific learning outcomes. After outlining the units, we will conclude by discussing the necessary revision for a clearer presentation of spontaneous emission and photons. The content can be utilized by any instructor looking to introduce these concepts in the context of quantum electromagnetic field theory within photochemistry or photophysics courses. If someone wishes to grasp the physical concept without getting deeply into the mathematical details, they can focus on the main article, trusting that the underlying formalisms included in the Supporting Information are accurate.

■ UNIT 1A: AN INTRODUCTION TO FIELD THEORY AND THE VACUUM

Expected Learning Outcome

Students understand field theory, specifically electromagnetic field theory and its two versions (classical and quantum).

Field theory is often an unfamiliar subject for chemistry students. Therefore, it should be introduced early on using language drawn from everyday life experiences. Our approach to this introduction is documented in Supporting Information S2. The key takeaway from our discussion is that even if we do not know the object or medium that creates a "field",[39] we may able to detect or be aware of the field itself. Although we may not understand the origin of the field, we can study its general properties using various scientific methods. For example, we can investigate the Earth's magnetic field with a compass, even without knowing how its magnetization is generated or which part of the Earth is responsible for it.

The study of a field, regardless of its origin or medium, is known as *field theory*. For an engaging yet comprehensive introduction to this topic, students may refer to Strassler's book.[40] It is important to note that while there are various types of fields, this article specifically focuses on the electromagnetic field, which describes light and its interaction with matter.

The theory of electromagnetic field has two versions: (a) classical and (b) quantum. In the classical version, the electromagnetic field is treated as a purely classical mechanical entity; while in the quantum version, it is regarded as a purely quantum mechanical system.

Before students are introduced to the two versions of electromagnetic field theory, it would be beneficial to explain a commonly known but often misunderstood concept called free space, empty space or vacuum space—refer to simply as "the vacuum" from now on. This discussion will set a foundation for understanding the upcoming material.

As outlined in Supporting Information S2, students will learn that the vacuum pervades the universe. They will soon discover that the vacuum field, or more accurately, vacuum fluctuation, also fills the universe. The interaction between an atom and the vacuum creates a composite quantum system that allows for energy exchange. These concepts are not connected to our everyday experiences, so it is essential to spend time discussing them as described in Supporting Information S2. This will help chemistry students establish the right mindset and thinking-momentum as they prepare to delve into electromagnetic field theory.

After introducing the basic ideas of "The Field Theory" and "The Vacuum" using everyday language, a learning roadmap is provided to the students, as shown in Figure 3.

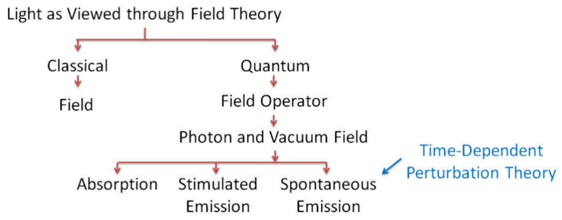

Figure 3. A guide to understanding spontaneous emission through quantum electromagnetic field theory.

UNIT 1B: CLASSICAL ELECTROMAGNETIC FIELD THEORY

Expected Learning Outcome

Students understand that when light is considered as a classical object, it can be represented (in its simplest form) as a plane monochromatic wave. The mathematical expression for the energy density of a monochromatic electromagnetic field at a specific point in space is analogous to the total energy of a harmonic oscillator. This pure mathematical equivalence leads to the development of quantum electromagnetic field theory.

It is important for students to understand the classical description of light before exploring its quantum version. The classical view lays the groundwork for essential mathematical notation and terminology that will be used later in discussing quantum electromagnetic field theory.

The fundamental learning outcome of classical electromagnetic field theory is that light, in its simplest form, can be described as a plane monochromatic wave (note that real light, such as laser light, is much more complex than this basic description). This wave consists of both electric and magnetic fields; however, *within weak-field approximation*, light can be described using only its electric field (assuming that the wave propagates along the + z-direction in the vacuum):[41] Using the complex notation

$$\tilde{E}(z, t) = E_0 e^{i(\omega_0 t - k_0 z)} = E_0 e^{i\omega_0 t} e^{-ik_0 z} = \tilde{E}(t) e^{-ik_0 z} \quad (1)$$

or using more familiar trigonometric notation

$$E(z, t) = E_0 \cos(\omega_0 t - k_0 z) \quad (2)$$

In the above context, a tilde sign (~) above letter E is used to represent the complex electric field. The symbol E_0 is the maximum electric field amplitude, while k_0 denotes the magnitude of the wave vector (here $\vec{k}_0$ which represents the propagation direction) and ω_0 is angular frequency of the plane wave. Both eqs 1 and (2) describe a monochromatic plane wave. However, when it comes to rigorous mathematical derivation, complex notation is often preferred as it simplifies the calculations compared to using trigonometric forms. For visualizing the electric field, though, the trigonometric form is utilized, with the cosine representing the real part of the complex notation. Figure 4 illustrates the trigonometric form.

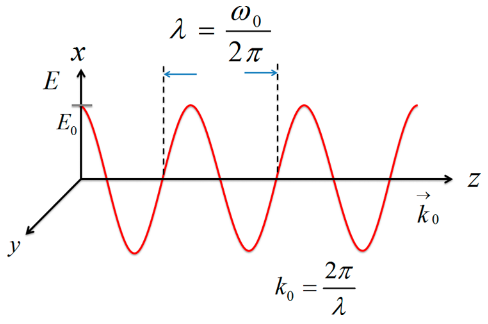

Figure 4. Oscillatory electric field of light propagating along the + z-direction. Here, E_0 represents the maximum electric field amplitude, $\vec{k}_0$ indicates the propagation direction, and λ signifies the wavelength of the monochromatic light.

For readers seeking a deeper understanding of the origins of classical electromagnetic field theory based on Maxwell's equations in the vacuum, Supporting Information S3 provides additional insights. Math-oriented students may find it beneficial to review this material.

Electromagnetic Energy Density

The final learning outcome of this unit is to obtain a mathematical expression for the total energy content of a monochromatic electromagnetic field. This section will have a direct introduction, noting that the proof is beyond the scope of this discussion. It is well-established in textbooks[42] on electromagnetic theory that the total energy content of the electromagnetic field in a volume V of the vacuum is given by

$$W = \frac{1}{4}V\varepsilon_0[\tilde{E}^*(t)\tilde{E}(t) + \tilde{E}(t)\tilde{E}^*(t)] \tag{3}$$

Note that while the electric field depends on both time (t) and space (z), eq 3 includes only the time-dependent electric field. This is because the total energy content is calculated after integrating over space (see Supporting Information S4). Furthermore, the order of $\tilde{E}(t)$ and $\tilde{E}^*(t)$ in the above equation is arranged to align with the quantum version, where the order of the corresponding field operators is significant. The constant ε_0 represents the permittivity of the vacuum. A superscript (*) is used to denote the complex conjugate. In other words, when the time-dependent part of the field is represented in its complex form as $\tilde{E}(t) = E_0 e^{i\omega_0 t}$, its complex conjugate is written as $\tilde{E}^*(t) = E_0 e^{-i\omega_0 t}$. For a detailed discussion on the origin of this equation, refer to Supporting Information S4. If readers prefer to skip mathematical rigor, it would be to accept eq 3 and proceed.

Next, students are asked to examine the expression $\tilde{E}(t) = E_0 e^{i\omega_0 t}$ more closely. This expression is technically the polar form of a complex function, representing pure time-dependent part of the electric field of a monochromatic plane wave. A complex function can be expressed in both polar ($e^{i\theta}$) and algebraic ($a + ib$) forms. For reasons that will be explained shortly, students are asked to define $\tilde{E}(t)$ in the following algebraic form:

$$\tilde{E}(t) = \frac{1}{\sqrt{\varepsilon_0 V}}(\omega_0\chi(t) - iP(t)) \tag{4}$$

where, Supporting Information S5 shows that $\chi(t) = \frac{\sqrt{\varepsilon_0 V}}{2\omega_0}[\tilde{E}(t) + \tilde{E}^*(t)]$ and $P(t) = -\frac{\sqrt{\varepsilon_0 V}}{2i}[\tilde{E}(t) - \tilde{E}^*(t)]$ are real quantities. Consequently we may write,

$$\begin{aligned}\tilde{E}^*(t)\tilde{E}(t) &= \frac{1}{\varepsilon_0 V}(\omega_0\chi(t) + iP(t))(\omega_0\chi(t) - iP(t))\\ &= \frac{1}{\varepsilon_0 V}(\omega_0^2\chi^2(t) + P^2(t))\end{aligned} \tag{5}$$

and

$$\tilde{E}(t)\tilde{E}^*(t) = \frac{1}{\varepsilon_0 V}(\omega_0^2\chi^2(t) + P^2(t)) \tag{6}$$

To understand the benefits of using the algebraic form presented in eq 4, students substitute eqs 5 and 6 into eq 3 to derive:

$$w = \frac{p^2(t)}{2} + \frac{1}{2}\omega_0^2\chi^2(t) \tag{7}$$

Equation 7 describes the energy density in an electromagnetic field at a specific point in space. An interesting piece of information is revealed in eq 7. To unravel this information, students are encouraged to visualize a harmonic oscillator with a unit mass. This concept may be familiar to those who have studied the quantum mechanics of harmonic oscillators, particularly at the level presented by McQuarrie).[43] The total energy of the oscillator, which is sum of its kinetic and potential energies, can be expressed as follows:

$$E = \frac{p^2}{2} + \frac{1}{2}\omega^2 x^2 \tag{8}$$

where, p represents the momentum of the oscillatory particle, x represents the displacement of the oscillatory particle from its equilibrium position, and ω is the oscillator's angular frequency. Furthermore, the following classical mechanical relation holds for this oscillator: $\frac{\mathrm{d}x}{\mathrm{d}t} = p$.

To understand the information conveyed in eq 7, we need to compare it with eq 8. These equations are mathematically equivalent, provided that $P(t)$ and $\chi(t)$ are connected by the expected formula, $\frac{\mathrm{d}\chi(t)}{\mathrm{d}t} = P(t)$. In fact, a mathematical derivation presented in Supporting Information S5 demonstrates this relationship.

■ UNIT II: QUANTUM ELECTROMAGNETIC FIELD THEORY AND THE UNDERSTANDING OF THE PHOTON

Expected Learning Outcome

Students understand the origin of the field operator and its two versions: single mode and multimode. A photon is simply the fundamental excitation of the electromagnetic field.

The foundation for understanding quantum electromagnetic field theory is based on a key postulate of quantum mechanics: *every observable in classical mechanics corresponds to a linear, Hermitian operator in quantum mechanics.* Students familiar with quantum chemistry, particularly at the level presented by McQuarrie,[43] are already acquainted with this postulate. In quantum mechanics, the Hamiltonian operator represents the total energy operator. Using the total energy content of a monochromatic electromagnetic field, as outlined in eq 3, we can formulate the Hamiltonian for the electromagnetic field. More specifically this applies to the **single mode electromagnetic field,**[44] which is essentially a monochromatic plane wave:

$$\hat{H} = \frac{1}{4}\varepsilon_0 V[\hat{E}^\dagger(t)\hat{E}(t) + \hat{E}(t)\hat{E}^\dagger(t)] \tag{9}$$

In the above context, the field operator $\hat{E}(t)$ is a newly introduced concept that is not commonly found in popular quantum chemistry textbooks. Students should remember that the total energy density of each individual mode of the electromagnetic field is mathematically equivalent to the total energy of a harmonic oscillator, which is a *learning outcome of Unit I.* The Hamiltonian of a harmonic oscillator can be expressed in the number state or Fock state representation as follows,

$$\hat{H} = \frac{\hbar\omega_0}{2}[\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger] \tag{10}$$

We can also say that the Hamiltonian of a single mode of the electromagnetic field can take the same mathematical form. Here $\hat{a}$ represents the annihilation operator, while $\hat{a}^\dagger$ represents the creation operator.

The concept of the number state or Fock state representation and creation/annihilation operators may seem unfamiliar to chemistry students. McQuarrie's textbook on quantum chemistry[43] includes a discussion on how to represent a harmonic oscillator problem using these operators. Similarly, Levine's quantum chemistry textbook employs raising and lowering operators, referred to as "ladder operators", in the context of angular momentum.[45] To ensure that the article is self-contained, Supporting Information S6 provides the necessary background on these topics. Refs 46 and 47 may also be useful. For students who wish to avoid mathematical complexities, they can simply proceed to the next discussion.

The established equivalence between the single mode electromagnetic field and the harmonic oscillator allows students to conclude mathematically that the Hamiltonians in eqs 9 and 10 are identical; they present two different forms of the same underlying reality. As a consequence, we can derive a mathematical expression for the field operators.

Single Mode Electromagnetic Field Operator

By comparing eqs 9 and 10, we obtain the expressions for the single mode field operators:

$$\hat{E}^{\dagger}(t) = \sqrt{\frac{2\hbar\omega_0}{\varepsilon_0 V}}\,\hat{a}^{\dagger}(t) \tag{11}$$

and

$$\hat{E}(t) = \sqrt{\frac{2\hbar\omega_0}{\varepsilon_0 V}}\,\hat{a}(t) \tag{12}$$

Next, following Euler's formula, in which the real part of a complex quantity $e^{i\theta}$ is expressed by $\frac{1}{2}(e^{i\theta} + e^{-i\theta})$, the **real** part of the single mode electromagnetic field operator is expressed by

$$Re[\hat{E}(t)] = \frac{1}{2}[\hat{E}(t) + \hat{E}^{\dagger}(t)] = \sqrt{\frac{\hbar\omega_0}{2\varepsilon_0 V}}\,[\hat{a}(t) + \hat{a}^{\dagger}(t)] \tag{13}$$

It is important to note that the creation and annihilation operators in eq 10 are not time-dependent. However, they must be time-dependent in eq 13. Supporting Information S7 explains how to obtain time-dependent creation and annihilation operators by switching between representations in time-dependent quantum mechanics - a topic that is not commonly covered in chemistry classrooms.[48] For example, the time-dependence of the annihilation operator used in eq 13 takes the following form:

$$\hat{a}(t) = \hat{a}(0)e^{-i\omega_0 t} = \hat{a}e^{-i\omega_0 t} \tag{14}$$

Students now have a clear expression for the real single-mode electromagnetic field operator:

$$Re[\hat{E}(t)] = \sqrt{\frac{\hbar\omega_0}{2\varepsilon_0 V}}\,[\hat{a}e^{-i\omega_0 t} + \hat{a}^{\dagger}e^{i\omega_0 t}] \tag{15}$$

To simplify the notation, from now on, we will express the real field operator associated with a single-mode of the electromagnetic field as $\hat{E}(t)$ (not by $Re[\hat{E}(t)]$).

Multimode Electromagnetic Field Operator

A radiation may consist of multiple frequency components made up of numerous monochromatic plane waves. This type of radiation displays a multimode electromagnetic field, which can be represented by summing all individual single mode fields:

$$\hat{E}(t) = \sqrt{\frac{\hbar}{2\varepsilon_0 V}}\sum_m \sqrt{\omega_m}\,[\hat{a}_m e^{-i\omega_m t} + \hat{a}_m^{\dagger}e^{i\omega_m t}] \tag{16}$$

Each mode, as defined by the subscript m, has an angular frequency ω_m and its characteristic creation and annihilation operators.

Introduction to the Photon

By this point, students have likely recognized that a single-mode electromagnetic field is mathematically equivalent to a harmonic oscillator. Consequently, by using the established eigenvalue expression of a harmonic oscillator, $E_n = \hbar\omega_0\left(n + \frac{1}{2}\right)$, where $n = 0, 1, 2, \ldots$, we obtain the same expression for a single-mode electromagnetic field:

$$\hat{H}|n\rangle = E_n|n\rangle = \hbar\omega_0\left(n + \frac{1}{2}\right)|n\rangle \tag{17}$$

The state $|n\rangle$ is referred to as the number states or Fock states of a single-mode electromagnetic field and n features the number of photons present in that field. This is when students come to understand that a photon is a quantized excitation in the Fock state, characterized by specific package of energy $\hbar\omega_0$.

Next, consider the following situations:

(a) When $n = 0$, $E_0 = \frac{1}{2}\hbar\omega_0$: it represents a field with no photon ($n = 0$). This state is known as the **vacuum state** or ground state of a single-mode electromagnetic field, represented by $|0\rangle$. As briefly discussed in Supporting Information S8, the absence of light—defined as absolute darkness—corresponds to a lack of **mean field strength**. However, the vacuum field may randomly appear and disappear at specific points in space and time. This phenomenon is referred to as the vacuum fluctuation.

(b) When $n = 1$, $E_1 = E_0 + \hbar\omega_0$: it represents a single-photon state, represented by $|1\rangle$. **A single photon is the fundamental excitation of the single mode electromagnetic field.** A single photon state (a Fock state with only one photon) can be created, and materials capable of generating single photons are of great interest in quantum technology. For further discussion on photons, refer to Supporting Information S9. Additionally, see ref 49 for Young's double-slit experiment at the single photon limit, which highlights the extraordinarily strange properties of photons.

(c) Similarly, $n = 2$ represents a two-photon state, and so on.

UNIT III: COMPLETE QUANTUM MECHANICAL ANALYSIS OF LIGHT-ATOM INTERACTION

Expected Learning Outcome

Students understand that spontaneous emission occurs when an excited atom returns to a lower energy state without any external radiation. In this process, the electromagnetic field undergoes transition from a vacuum state to a single-photon state. This phenomenon is induced by vacuum fluctuations.

The interaction of light with an atom is often described using a **semiclassical treatment** in popular quantum chemistry textbooks. In this method, the radiation field is treated based on classical electromagnetic field theory, while the atom is treated using quantum mechanics.[45] However, to the best our knowledge, a **fully quantum mechanical treatment,** where both the radiation field and the atom are described using quantum mechanics, is not commonly included these textbooks. We believe that *this omission significantly contributes to misconceptions about spontaneous emission and the nature of photons in the minds of chemistry students.*

The content detailing the semiclassical treatment of light-atom interactions, closely following the material in Levine's Quantum Chemistry,[45] is provided in Supporting Information S10. To understand the notation and the meanings of various terms, students are encouraged to review this material. A key learning outcome of the semiclassical treatment is its ability to explain how an atom can lead to absorption and stimulated emission processes with nonzero probability, as long as the external radiation field strength is also nonzero (i.e., $\overline{E}_0 \neq 0$). However, this approach does not offer a mathematical explanation for spontaneous emission.

For a complete quantum chemical treatment, we begin by assuming that the atom at $z = 0$ is initially in a stationary state $|\psi_n^0\rangle$ (with energy E_n^0) before the light-atom interaction process is initiated at $t = 0$. The interaction with light, represented by the interaction Hamiltonian $\hat{H}'(t) = -\overline{\mu}\cdot\overline{E}(t)$, induces a transition of the atom from its initial state $|\psi_n^0\rangle$ to another stationary state $|\psi_l^0\rangle$ (with energy E_l^0). Using the first-order time-dependent perturbation theory, which operates under the weak-field approximation, the population in the final state $|\psi_l^0\rangle$ at time $t = t_1$ (i.e., immediately after the light-atom interaction process is turned off) is given by the term, $|c_l(t_1)|^2$, where $c_l(t_1)$ is defined as (under dipole approximation or in the length gauge: these terminologies are defined in Supporting Information S10)

$$c_l(t_1) = \frac{i}{\hbar}\int_0^{t_1} e^{i\omega_{\mathrm{ln}}t}\langle\psi_l{}^0|\overline{\mu}\cdot\overline{E}(t)|\psi_n{}^0\rangle \mathrm{d}t \tag{18}$$

The term $|c_l(t_1)|^2$ provides the probability of an atom undergoing a transition from its initial state (just before the interaction process begins) to its final state (immediately after the interaction process ends).

As students will treat both the atom and the field quantum mechanically, the initial and final states in the above equation must represent "*combined atom-field*" states. We have already assumed that that the atom undergoes a transition from its initial state $|\psi_n^0\rangle$ to its final state $|\psi_l^0\rangle$. This atomic transition has $\omega_{\mathrm{ln}} = \left(\frac{E_l^0 - E_n^0}{\hbar}\right)$.

To construct a "combined atom-field" state, students may assume that the radiation in the vacuum consists of multimode fields. Just before the light-atom interaction is turned on at $t = 0$, the field is in the state $|n_{k'}\rangle$; it has n photons present in the k'-th mode, while all other modes are in their respective vacuum states. Thus, just before the onset of the light-atom interaction process, a single mode field (monochromatic plane wave) exists with n photons.

Furthermore, immediately after the light-atom interaction process is turned off (at $t = t_1$), the final field state becomes $|F_f\rangle$: at this point we do not need to specify the final state of the field; students will derive this in the subsequent analysis.

Based on the arguments presented above, we need to re-express eq 18 to account for the "*combined atom-field states*". Let us denote the initial and final combined states as $|\psi_n^0, n_{k'}\rangle$ and $|\psi_l^0, F_f\rangle$, respectively. Consequently, the matrix element of eq 18 can be rewritten as

$$\langle\psi_l{}^0, F_f|\overline{\mu}\cdot\overline{E}(t)|\psi_n{}^0, n_{k'}\rangle = \langle\psi_l{}^0|\overline{\mu}|\psi_n{}^0\rangle\cdot\langle F_f|\overline{E}(t)|n_{k'}\rangle \tag{19}$$

It is important to note that the first integral is over the spatial coordinate $(\overline{r})$ for the collection of electron in the atom, while the second integral is over the field space. Additionally, the product mentioned above technically represents a tensor product, since a combined atom-field state is expressed as the tensor product of the respective states (for example, $|\psi_n^0, n_{k'}\rangle = |\psi_n^0\rangle \otimes |n_{k'}\rangle$).

In Unit II, students have already become familiar with the multimode field operator in vacuum. By inserting eqs 16 into eq 19, students can further simplify eq 19. First, focus only on the field matrix element:

$$\begin{aligned}\langle F_f|\hat{E}(t)|n_{k'}\rangle &= \sqrt{\frac{\hbar}{2\varepsilon_0 V}}\sum_m \sqrt{\omega_m}\langle F_f|[\hat{a}_m e^{-i\omega_m t} + \hat{a}_m^{\dagger} e^{i\omega_m t}]|n_{k'}\rangle \\ &= \sqrt{\frac{\hbar}{2\varepsilon_0 V}}\sum_m \sqrt{\omega_m}\langle F_f|\hat{a}_m e^{-i\omega_m t}|n_{k'}\rangle \\ &\quad + \sqrt{\frac{\hbar}{2\varepsilon_0 V}}\sum_m \sqrt{\omega_m}\langle F_f|\hat{a}_m^{\dagger} e^{i\omega_m t}|n_{k'}\rangle\end{aligned} \tag{20}$$

Using the information presented in Supporting Information S6, S10 and S11, a pure quantum mechanical treatment reveals that the probability of transition from the initial state $|\psi_n^0\rangle$ to the final state $|\psi_l^0\rangle$ of an atom depends on the following factors:

$$\begin{aligned}|c_l(t_1)|^2 &\propto |\langle\psi_l{}^0|\overline{\mu}|\psi_n{}^0\rangle\cdot\langle F_f|n_{k'} - 1\rangle|^2 \mathrm{sinc}^2\left[\frac{(\omega_{\mathrm{ln}} - \omega_{k'})t_1}{2}\right] \\ &\propto |\langle\psi_l{}^0|\overline{\mu}|\psi_n{}^0\rangle\cdot\langle F_f|n_{k'} + 1\rangle|^2 \mathrm{sinc}^2\left[\frac{(\omega_{\mathrm{ln}} + \omega_{k'})t_1}{2}\right] \\ &\propto |\langle\psi_l{}^0|\overline{\mu}|\psi_n{}^0\rangle\cdot\langle F_f|1_m\rangle|^2 \mathrm{sinc}^2\left[\frac{(\omega_{\mathrm{ln}} + \omega_m)t_1}{2}\right]\end{aligned} \tag{21}$$

In the above context, a cardinal sine function is defined by $\mathrm{sinc}(x) = \frac{\sin(x)}{x}$. Equation 21 indicates that an atom can undergo transition from one energy level to another with a nonzero probability, provided that two matrix elements—one associated with the atom and the other with the field—are **nonzero**, along with the corresponding sinc function. The sinc function enforces the conservation of energy during the transition process, allowing for excitation or de-excitation only of a field mode that matches the energy level spacing of the atom. Additionally, the matrix element related to the field reveals nature of the photon that will be created or annihilated during the transition. Further clarification on these points can be found in Supporting Information S11. In this discussion, we will concentrate specifically on the third term, which represents spontaneous emission.

It is interesting to note that the existence of the third term does not depend on the initial field state $|n_{k'}\rangle$, *which was assumed to be present during the light-atom interaction process.* This implies that the third term can have a nonzero value even *in the absence of the initial field; in other words, we can assume that all field modes are present in their respective vacuum states before transition process begins.* As explained in Supporting Information S11, this term becomes negligible unless $\omega_{ln} = -\omega_m$ or, $E_l = E_n - \omega_m\hbar$ because of the $\mathrm{sinc}^2\left[\frac{(\omega_{\mathrm{ln}} + \omega_m)t_1}{2}\right]$ function. This indicates that the initial state of the atom must have a higher energy than the final state for this process to occur, and an energy equivalent to one photon $(\omega_m\hbar)$ associated with a specific m-th mode is released by the atom during the transition.

In addition, as explained in Supporting Information S11, the integral $\langle F_f \mid 1_m\rangle$ remains nonzero only when $|F_f\rangle = |1_m\rangle$; i.e., the field (of the specific m-th mode) must be excited from the vacuum state to its single photon state $|1_m\rangle$. Consequently, an

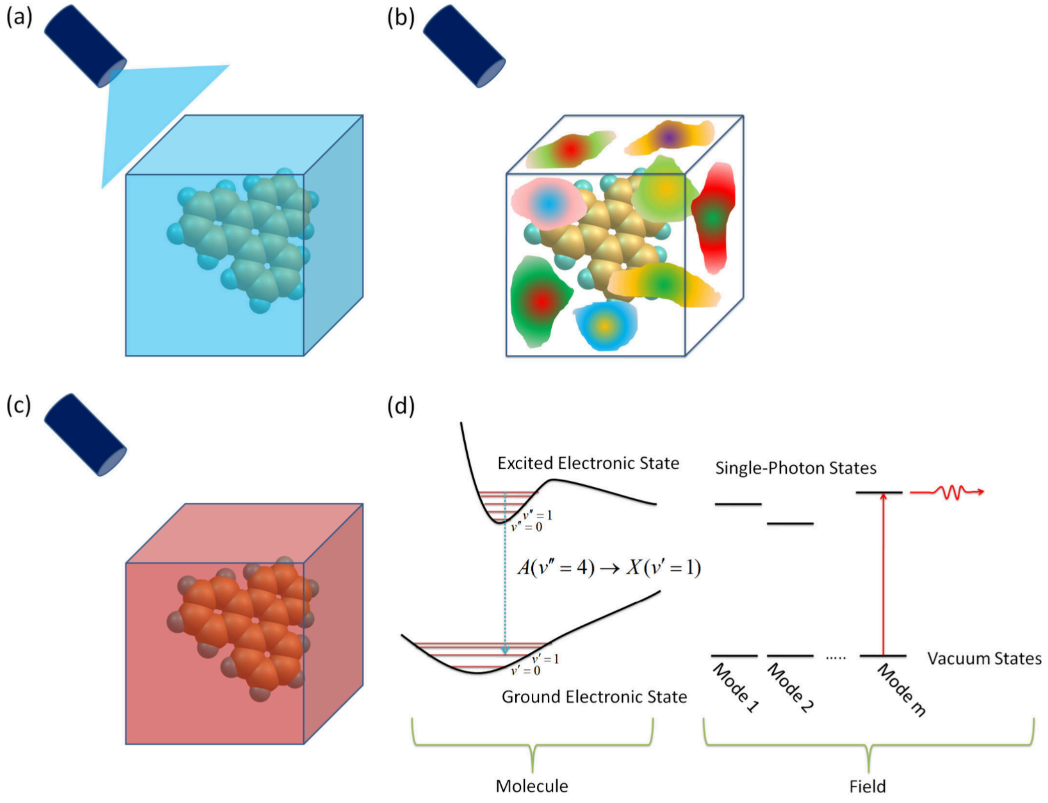

Figure 5. (a) Absorption process, where molecules are exposed to external radiation (blue). (b) Excited molecules interact with vacuum fluctuations in the absence of external radiation (in darkness). These vacuum fluctuations pervade the universe and induce spontaneous emission. (c) The spontaneous de-excitation of the excited molecule results in the emission of red. (d) The molecule and field create a composite quantum system, with the molecular and field transitions involved in spontaneous emission illustrated schematically.

atom can undergo a transition spontaneously from an excited state to a lower energy state by creating a single-photon state in a mode that corresponds to the energy level spacing of the atom. This phenomenon is known as **spontaneous emission**. It is important to note that this process cannot occur if light is not regarded as a quantum mechanical entity.

Thus, one can obtain a complete quantum mechanical understanding of spontaneous emission through the following process: Atoms/Molecules are initially excited using external radiation (absorption process, as illustrated in Figure 5(a)—external radiation is assumed to have blue color). Once the external radiation is tuned off, the excited atoms/molecules interact with vacuum fluctuation (as depicted in Figure 5(b)), occurring in the absence of light. This interaction means that the interaction Hamiltonian remains nonzero even in darkness - a concept that does not align with semiclassical treatment (refer to Supporting Information S10). These vacuum fluctuations trigger spontaneous emission (as shown in Figure 5(c) - spontaneous emission is assumed to exhibit red glow). Students can be asked: Why, when a material absorbs blue light, is the subsequent spontaneous emission observed in the red spectrum? Why is the reverse, red absorption followed by blue emission, not seen?

Figure 5(d) displays the typical potential energy curves associated vibrational states (rotational states are omitted for brevity) of the molecule in both its ground and electronically excited states, representing the molecular transition during spontaneous emission. This part of the process is illustrated in a standard Jablonski diagram. During this emission process, a specific field mode that matches the energy level spacing of the chromophore is excited from the vacuum state to the single-photon state, resulting in the creation of a photon. This aspect is mostly overlooked in traditional presentations of spontaneous emission using Jablonski diagram.

Physical Chemistry Aspects of Spontaneous Emission

Several physical chemistry aspects of spontaneous emission and the photon including exercises based on a comprehensive quantum mechanical treatment of light-matter interaction are given in Supporting Information S12. On this note, students may find ref 50 informative.

■ GENERAL CONCLUSIONS AND RECOMMENDATION OF REVISIONS

As of now, the quantum description of light successfully addresses not only the origin of the photon but also the phenomenon of spontaneous emission. The transition rate associated with spontaneous emission, calculated using quantum electromagnetic theory, exactly matches the more familiar Einstein coefficient (refer to ref 34).

According to the quantum description of light, *a photon is not just a particle moving through space*. It can be visualized in two simple ways: (a) as the fundamental excitation of the vacuum electromagnetic field that pervades the universe, or (b) as the dimmest possible flash (with the smallest permissible field amplitude) of electromagnetic field. Note that current IUPAC definition of a photon states that it is *the quantum of electromagnetic energy at a given frequency. This energy,* $E = h\nu$, *is the product of the Planck constant* (h) *and the frequency of the radiation* (ν).[24,25] However, what does it mean when we refer to it as *the quantum of electromagnetic energy*? Does this not suggest that it is a particle? Does it convey the essence of the quantum theory of light, where the energy states of electromagnetic field are quantized? The purpose of the present article is to highlight the fact that the IUPAC definition of a photon is incomplete.

Furthermore, when a molecule de-excites from a higher energy state to a lower one spontaneously (without the aid of external radiation), this process itself excites the electromagnetic field from its vacuum state to the single photon state. Therefore, option 3 in Figure 1 provides a more appropriate diagrammatic representation of spontaneous emission. Both options 1 and 2 are not only incomplete but also misleading, as a flawed representation can lead to further misunderstandings about the quantum mechanical description of spontaneous emission (a wrong picture is worth a thousand wrong words). It is worth noting that the current IUPAC definition of spontaneous emission states that it is an *emission which occurs even in the absence of a perturbing electromagnetic field.*[24,25] This definition sharply contradicts the quantum mechanical description of spontaneous emission. The interaction Hamiltonian remains nonzero in a full quantum mechanical description due to the presence of vacuum fluctuations. This article elaborates on this point to provide more comprehensive pedagogical view of spontaneous emission.

Our intention in writing this article is to initiate a pedagogical awareness of the description of the photon and spontaneous emission within chemistry classroom discussions regarding photochemistry and photophysics, as informed by quantum electromagnetic field theory. We hope that this contribution will facilitate further discussion in order to achieve agreement across disciplines (physics and chemistry) and possibly lead to a revision of the respective definitions in the IUPAC glossary of photochemistry. In this regard, reviewers and students have provided several interesting comments that are worth noting. These comments are included in Supporting Information S13 to encourage further pedagogical contribution along this line.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.4c01030.

> Supporting Information S1: The Inquiry of Professor Feynman's Father and Its Relevance to the Current Context; Supporting Information S2: General Introduction to the Field Theory and the Vacuum, Supporting Information S3: Mathematically More Involved Presentation of Classical Electromagnetic Field Theory; Supporting Information S4: Electromagnetic Energy Density versus Energy Flow; Supporting Information S5: Prove that $d\chi(t)/dt = P(t)$; Supporting Information S6: Number or Fock State Representation of Harmonic Oscillator; Supporting Information S7: Introduction to the Heisenberg Equation of Motion; Supporting Information S8: Introduction to Vacuum Fluctuation, Supporting Information S9: Pictorial Representation of the Photon S10: Semiclassical Treatment of Light-Atom Interactions; Supporting Information S11: Quantum Mechanical Treatment; Supporting Information S12: Physical Chemistry Aspects and Application Exercise; Supporting Information S13: Future Pedagogical Efforts. (PDF, DOCX)

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Notes

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