Luminescent Materials and Applications

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Luminescent Materials and Applications

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Series Preface

WILEY SERIES IN MATERIALS FOR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

This book series is devoted to the rapidly developing class of materials used for electronic and optoelectronic applications. It is designed to provide much-needed information on the fundamental scientific principles of these materials, together with how these are employed in technological applications. The books are aimed at (postgraduate) students, researchers and technologists, engaged in research, development and the study of materials in electronics and photonics, and industrial scientists developing new materials, devices and circuits for the electronic, optoelectronic and communications industries.

The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such titles as electrical conduction in solids, optical properties, thermal properties, etc., all with applications and examples of materials in electronics and optoelectronics. The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure-property relationships have always been fundamentally and intrinsically important to materials science and engineering.

Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials and new applications. It is not unusual to find scientists with chemical engineering background working on materials projects with applications in electronics. In selecting titles for the series, we have tried to maintain the interdisciplinary aspect of the field, and hence its excitement to researchers in this field.

PETER CAPPER
SAFA KASAP
ARTHUR WILLOUGHBY

Preface

Luminescence is a subject that continues to play a major technological role for humankind. We greatly value the ability to create well-illuminated indoor and outdoor spaces. We have whole-heartedly embraced light emitting flat panel displays. We continue to dream about new light sources such as flexible sheets of light that may one day replace glass tubes or glass-based displays.

This book reviews key types of solid-state luminescence that are of current interest, including organic light emitting materials and devices, inorganic light emitting diode materials and devices, down-conversion materials, nanomaterials that exhibit interesting quantum confinement effects, and powder and thin film electroluminescent phosphor materials and devices.

This book employs a science-based approach, and the chapter authors all have a strong interest in the fundamental physics that forms a basis for the phenomenon of luminescence. As such, this book may be used as a starting point to gain an understanding of various types and mechanisms of luminescence for students and professionals.

It may also be used to gain an understanding of the implementation of various types and mechanisms of luminescence into practical devices. The book presents both the physics as well as the materials aspects of the field of solid-state luminescence. Without the achievement of materials having purity and suitable morphology as well as manufacturability, solid-state luminescence would become a curiosity only.

Solid-state luminescence is now set to significantly displace gas discharge luminescence in many areas in much the same way that gas discharges have displaced tungsten filament incandescence already. One can say this with confidence owing to the high conversion efficiencies now demonstrated for inorganic and organic light emitting diodes. Efficiency values well over 100 lumens per watt are now achievable in fully solid state light emitters. It is our hope that this book not only educates, but that it also stimulates further progress in this rapidly evolving field.

I would like to thank the chapter authors for their outstanding cooperation with the rather arduous book-creating process, and would also like to thank the excellent staff at Wiley for their professionalism and dedication in bringing this book to life.

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1 Principles of Luminescence

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1.1 INTRODUCTION

Technologically important forms of luminescence may be split up into several categories (Table 1.1). Although the means by which the luminescence is excited varies, all luminescence is generated by means of accelerating charges. The portion of the electromagnetic spectrum visible to the human eye is in wavelengths from 400 to 700 nm. The evolution of the relatively narrow sensitivity range of the human eye is complex, but is intimately related to the solar spectrum, the absorbing behavior of the terrestrial atmosphere, and the reflecting properties of organic materials. Green is the dominant color in nature and, not surprisingly, the wavelength at which the human eye is most sensitive. In this chapter, we cover the physical basis for radiation and radiation sources in solids that produce visible light.

1.2 RADIATION THEORY

A stationary point charge has an associated electric field E (Figure 1.1). A charge moving with uniform velocity relative to the observer gives rise to a magnetic field (Figure 1.2). Electric and magnetic fields both store energy, and the total energy density is given by

$$\mathscr{E} = \frac{1}{2}\varepsilon_0 E^2 + \frac{1}{2\mu_0} B^2$$

Luminescent Materials and Applications Edited by Adrian Kitai

Table 1.1 Luminescence types, applications and typical efficiencies (visible output power/electrical input power)

Luminescence type	Typical application	Luminous efficiency
Blackbody radiation	Tungsten filament lamp	~5%
Photoluminescence	Fluorescent lamp	~20%
Cathodoluminescence	Television screen	~10%
Electroluminescence	Light-emitting diode, flat panel display	0.1–50%

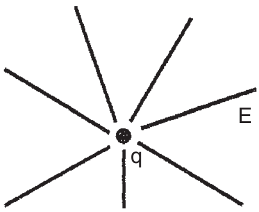

Figure 1.1 The lines of electric field E due to a point charge q. Solid State Luminescence, Adrian Kitai, Copyright 1993 with kind permission from Springer Science and Business Media

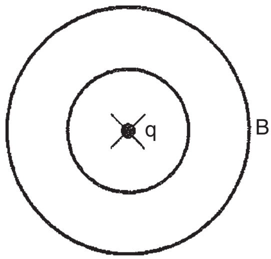

Figure 1.2 The lines of magnetic field B due to a point charge q moving into the page with uniform velocity. Solid State Luminescence, Adrian Kitai, Copyright 1993 with kind permission from Springer Science and Business Media

It is important to note that the energy density moves with the charge so long as the charge is either stationary or undergoing uniform motion; this is evident since a new reference frame may be constructed in which the observer is stationary with respect to the charge.

However, for an accelerated charge, energy continuously leaves the charge to compensate exactly for the work done in causing the charge to accelerate. Consider the charge q in Figure 1.3. Initially at rest in position **A**, it then accelerates to position **B** and stops there. The electric field lines now emanate from position **B,** but would, if further out, have emanated from position A, since the field lines cannot convey information about the location of the charge at speeds greater than the velocity of light c. This results in kinks in the lines of electric field which propagate away from q with velocity c. Each time q accelerates, a new series of propagating kinks is generated. Each kink is made up of a component of E that is transverse to the direction of expansion, which we call $E_{\perp}$. If the velocity of the charge during its acceleration does not exceed a small fraction of c, then for r:

$$E_{\perp} = \frac{qa}{4\pi\varepsilon_0 c^2 r}\sin\theta$$

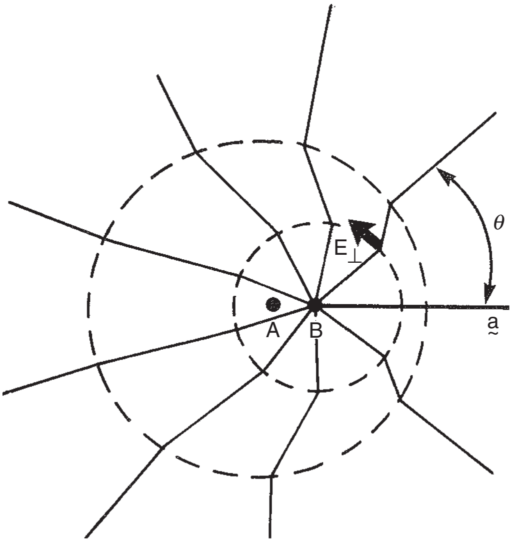

Figure 1.3 Lines of electric field emanating from an accelerating charge (after Eisberg and Resnick [1]). Solid State Luminescence, Adrian Kitai, Copyright 1993 with kind permission from Springer Science and Business Media

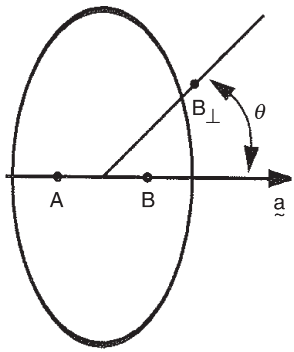

Figure 1.4 Lines of magnetic field *B* emanating from an accelerating charge. *B* is perpendicular to the page. Solid State Luminescence, Adrian Kitai, Copyright 1993 with kind permission from Springer Science and Business Media

Here, a is acceleration, and r is the distance between the charge and the position where the electric field is evaluated. The strongest transverse field occurs in directions normal to the direction of acceleration (Figure 1.3).

Likewise, a transverse magnetic field $B_\perp$ is generated during the acceleration of the charge (Figure 1.4), given by

$$B_\perp = \frac{\mu_0 q a}{4\pi c r}\sin\theta$$

The two transverse fields propagate outwards with velocity c each time q undergoes acceleration, giving rise to the electromagnetic radiation, the frequency of which matches the frequency with which q accelerates. Note that $E_\perp$ and $B_\perp$ are perpendicular to each other. The energy density of the radiation is

$$\mathscr{E} = \frac{1}{2}\varepsilon_0 E_\perp^2 + \frac{1}{2\mu_0} B_\perp^2$$

The Poynting vector or energy flow per unit area (radiation intensity) is

$$\begin{aligned} S &= \frac{1}{\mu_0} \boldsymbol{E}_\perp \times \boldsymbol{B}_\perp \\ &= \frac{q^2 a^2}{16\pi\varepsilon_0 c^3 r^2} \sin^2\theta \hat{r} \end{aligned}$$

where $\hat{r}$ is a unit radial vector.

Maximum energy is emitted in a ring perpendicular to the direction of acceleration, but no energy is emitted along the line of motion. To obtain the *total* radiated energy per unit time or power P leaving q due to its acceleration, we integrate S over a sphere surrounding q to obtain

$$P = \int S(\theta)\,\mathrm{d}A = \int_0^\pi S(\theta) 2\pi r^2 \sin\theta\,\mathrm{d}\theta$$

since dA is a ring of area $2\pi r^2 \sin^\theta \theta d\theta$.

Substituting for $S(\theta)$, we obtain

$$P = \frac{1}{4\pi\varepsilon_0} \frac{2}{3} \frac{q^2 a^2}{c^3}$$

1.3 SIMPLE HARMONIC RADIATOR

If a charge q moves about the origin of the x-axis with position $x = A \sin \omega t$, then we can easily calculate the average power radiated away from the oscillating charge. Note that

$$a = \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = -A\omega^2 \sin\omega t$$

and

$$P = \frac{2q^2 A^2 \omega^4 \sin^2 \omega t}{4\pi\varepsilon_0 3c^3}$$

Now, average power $\overline{P}$ is the root-mean-square power, which gives

$$\bar{P} = \frac{q^2 A^2 \omega^4}{4\pi\varepsilon_0 3c^3} \tag{1.1}$$

If we now consider that an equal and opposite stationary charge $-q$ is located at $x = 0$, then we have a dipole radiator with electric dipole moment of amplitude $p = qA$. Now we may write

$$\bar{P} = \frac{p^2 \omega^4}{12\pi\varepsilon_0 c^3}$$

Non-oscillatory radiation also exists; the synchroton radiation source is an example of a radiator that relies on the constant centripetal acceleration of an orbiting charge. Quadrupole and higher-order poles may exist, even in the absence of a dipole moment, but they have lower rates of energy release.

1.4 QUANTUM DESCRIPTION

A charge q (possibly an electron) does not exhibit energy loss or radiation when in a stationary state or eigenstate of a potential energy field. This requires that no net acceleration of the charge occurs, in spite of its uncertainty in position and momentum dictated by the Heisenberg uncertainty principle. However, experience tells us that radiation may be produced when a charge moves from one stationary state to another. It will be the purpose of this section to show that radiation may only be produced if an oscillating dipole results from a charge moving from one stationary state to another.

Consider a charge q initially in stationary state φ_n and eventually in state $\varphi_{n'}$. During the transition, a superposition state is created which we call φ_s:

$$\psi_2 = a\psi_n + b\psi_{n'}, \quad |a|^2 + |b|^2 = 1$$

where a and b are time-dependent coefficients. Initially, $a = 1$, $b = 0$ and finally, $a = 0$, $b = 1$.

Quantum mechanics allows us to calculate the expected value of the position $\langle r \rangle$ of a particle in a quantum state. For example, for stationary state φ_s,

$$\langle r \rangle_n = \langle \psi_n | r | \psi_n \rangle = \int_v |\psi_n|^2 r \, \mathrm{d}V$$

provided φ_n is not normalized, and V represents all space. Since, by definition, $|\varphi_n|^2$ is not a function of time because φ_n is a stationary state, the answer to this integral is always time independent and may be written as r_0. Note that the time dependence of a stationary state is given by $|e^{(\mathrm{i}E/h)t}|^2 = e^{(1E/h)t} e^{(-1E/h)t} = 1$. If we now calculate the expectation value of the position of q for the superposition state φ_s, we obtain

$$\begin{aligned}\langle r \rangle_s &= \langle a\psi_n + b\psi_{n'} | r | a\psi_n + b\psi_{n'} \rangle \\ &= |a|^2 \langle \psi_n | r | \psi_n \rangle + b^2 \langle \psi_{n'} | r | \psi_{n'} \rangle + a * b \langle \psi_n | r | \psi_{n'} \rangle + b * a \langle \psi_{n'} | r | \psi_n \rangle\end{aligned}$$

We let

$$\psi_n = \phi_n \exp\left(-\mathrm{i}\frac{E_n}{\hbar}t\right)$$

where ϕ_n is the spatially dependent part of φ_n. Hence

$$\begin{aligned}\langle r(t)\rangle_s &= a*b\langle\phi_n|r|\phi_{n'}\rangle \exp\left[\frac{\mathrm{i}(E_n - E_{n'})}{\hbar}t\right] + b*a\langle\phi_{n'}|r|\phi_n\rangle \exp\left[\frac{\mathrm{i}(E_n - E_{n'})}{\hbar}t\right] \\ &= 2\,\mathrm{Re}\left\{a*b\langle\phi_n|r|\phi_{n'}\rangle \exp\left[\frac{\mathrm{i}(E_n - E_{n'})}{\hbar}t\right]\right\}\end{aligned}$$

since the position must be a real number. This may be written as

$$\begin{aligned}\langle r(t)\rangle_s &= 2|a*b\langle\phi_n|r|\phi_{n'}\rangle|\cos(\omega_{nn'}t+\delta) \\ &= 2|r_{nn'}|\cos(\omega_{nn'}t+\delta)\end{aligned} \qquad (1.2)$$

Note that we have introduced the relationship $E = \hbar\omega$ that defines the energy of one photon generated by the charge q as it moves from φ_n to $\varphi_{n'}$. Note also that $\langle r(t)\rangle$ is oscillating with frequency $\omega_{nn'} = (E_n - E_{n'})/\hbar$ such that the required number of oscillations at the required frequency releases one photon having energy $E = \hbar\omega_{nn'}$ from the oscillating charge. The term $r_{nn'}$ also varies with time, but does so slowly compared with the cosine term. Consider that an electron oscillates about $x = 0$ with amplitude $A = 1$ Å to produce a photon with $\lambda = 550$ nm. From Equation (1.1)

$$\bar{P} = \frac{(1.6\times10^{-19})^2\times(10^{-10})^2\,(2\pi)^4\times(3\times10^8)}{12\pi\,(8.85\times10^{-12})(5.5\times10^{-7})^4} = 4\times10^{-12}\,\mathrm{W}$$

since

$$\omega = \frac{2\pi c}{\lambda}$$

One photon of this wavelength has energy $E = hc/\lambda = 3\times10^{-19}$ J. Hence, the approximate length of time taken to release the photon is $(3\times10^{-19}\,\mathrm{J})/(4\times10^{-12}\,\mathrm{J\,s^{-1}}) = 7.7\times10^{-8}$s. Since the period of electromagnetic oscillation is $T = \lambda/c = 1.8\times10^{-15}$s, approximately 10^7 oscillations take place. We have assumed $|r_{nn'}|$ to be a constant, which will be shown not to be the case in a later section.

We may define a photon emission rate $R_{nn'}$ of a continuously oscillating charge. We use Equations (1.1) and (1.2) and $E = \hbar\omega$ to obtain

$$R_{nn'} = \frac{\bar{P}}{\hbar\omega} = \frac{q^2\omega^3}{3\pi\varepsilon_0 c^3\hbar}|r_{nn'}|^2 \text{ photons s}^{-1}$$

1.5 SELECTION RULES

A particle cannot change quantum states without conserving energy. When energy is released as electromagnetic radiation, we can determine whether or not a particular transition is allowed by calculating the term $|r_{nn'}|$, and seeing whether it is zero or non-zero. The results over a variety of possible transitions give selection rules that name allowed and forbidden transitions.

The transitions involved in the hydrogen atom are of particular importance. We will now derive the well-known selection rules for the electron in hydrogen states, or more generally in one-electron atomic states. We use polar coordinates and begin by calculating r_{nn}:

$$r_{nn'} = \langle n|r|n'\rangle = \int_{\text{all space}} \psi_{\text{n}}^{*} r \psi_{n'} \mathrm{d}V$$
$$= \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \psi_n^{*}(r,\theta,\phi) r \psi_{n'}(r,\theta,\phi) r^2 \sin\theta \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r$$

Note that since we are working in three dimensions, we must consider r in vector form, and let $\varphi(r,\ \theta,\ \phi) = R_n(r)\Theta_{lm}(\theta)\Phi_m(\phi)$. Now

$$r_{nn'} = \int_0^{\infty} R_{n'}(r) r^3 R_n(r) \mathrm{d}r \left[\int_0^{2\pi}\int_0^{\pi} \Theta_{l'm'}(\theta)\Theta_{lm}(\theta) \sin\theta r \Phi_m^{*}(\phi)\Phi_{m'}(\phi) \mathrm{d}\theta \mathrm{d}\phi\right]$$

The term in brackets may be broken up into orthogonal components of unit vector $r = \sin\theta\cos\phi \boldsymbol{x} + \sin\theta \sin\phi \boldsymbol{y} + \cos\theta \boldsymbol{z}$, to obtain three terms:

$$\begin{aligned}&\int_0^{\pi} \sin^2\theta \Theta_{l'm'}(\theta)\Theta_{lm}(\theta) \mathrm{d}\theta \int_0^{2\pi} \Phi_m^{*}(\phi)\Phi_{m'}(\phi)\cos\phi \mathrm{d}\phi \boldsymbol{x}\\ &+\int_0^{\pi} \sin^2\theta \Theta_{l'm'}(\theta)\Theta_{lm}(\theta) \mathrm{d}\theta \int_0^{2\pi} \Phi_m^{*}(\phi)\Phi_{m'}(\phi)\sin\phi \mathrm{d}\phi \boldsymbol{y}\\ &+\int_0^{\pi} \sin^2\theta\cos\theta \Theta_{l'm'}(\theta)\Theta_{lm}(\theta) \mathrm{d}\theta \int_0^{2\pi} \Phi_m^{*}(\phi)\Phi_{m'}(\phi) \mathrm{d}\phi \boldsymbol{z}\end{aligned} \tag{1.3}$$

Since $\Phi_m(\phi) = \mathrm{e}^{im\phi}$, the three integrals in ϕ may be written as

$$I_1 = \int_0^{2\pi} \cos\phi e^{\mathrm{i}(m-m')\phi} \mathrm{d}\phi$$
$$I_2 = \int_0^{2\pi} \sin\phi e^{\mathrm{i}(m-m')\phi} \mathrm{d}\phi$$
$$I_3 = \int_0^{2\pi} \mathrm{e}^{\mathrm{i}(m-m')\phi} \mathrm{d}\phi$$

I_3 is zero unless $m' = m$.
I_1 may be written as

$$I_1 = \frac{1}{2}\int_0^{2\pi} [\mathrm{e}^{\mathrm{i}(m-m'+1)\phi} + \mathrm{e}^{\mathrm{i}(m-m'-1)\phi}] \mathrm{d}\phi$$

which is zero unless $m' = m \pm 1$. I_2 gives the same result.

Now consider the integrals in θ, which multiply I_1, I_2 and I_3. We shall name them J_1, J_2, and J_3, If I_3 is non-zero, then $m' = m$. Hence we obtain

$$J_3 = \int_0^{\pi} \sin\theta \cos\theta \, \Theta_{l'm}^{*}(\theta)\Theta_{lm}(\theta)\,\mathrm{d}\theta$$

The integral:

$$\int_0^{\pi} \Theta_{l'm}^{*}(\theta)\Theta_{lm}(\theta)\,\mathrm{d}\theta$$

is zero unless $l' = 1$, a property of the associated Legendre polynomials which, being eigen-functions, are orthogonal to each other [2]. Since $\cos\theta$ is an odd function over the range $0 \le \theta \le \pi$, the parity is reversed in J_3 and hence $J_3 = 0$ unless $l' = l \pm 1$.

If I_1 is non-zero, then $m' = m \pm 1$. Hence, we obtain

$$J_1 = \int_0^{\pi} \sin^2\theta \, \Theta_{l',m\pm1}^{*}(\theta)\Theta_{lm}(\theta)\,\mathrm{d}\theta$$

Using the properties of associated Legendre polynomials once again, we note that it is always possible to write $\Theta_{lm}(\theta) = a\Theta_{l-1,m+1}(\theta) + b\Theta_{l+1,m+1}(\theta)$, where a and b are constants. Choosing $m' = m + 1$, we obtain

$$J_1 = \int_0^{\pi} \sin^2\theta \, \Theta_{l',m\pm1}(\theta)[a\Theta_{l-1,m+1}(\theta) + \mathrm{b}\Theta_{l+1,m+1}(\theta)]\mathrm{d}\theta$$

For a non-zero result, $l' = 1 \pm 1$ using the orthogonality property. The same conclusion is obtained from the case $m' = m - 1$ and from the J_2 integral. Therefore, we have shown that the selection rules for a one-electron atom are

$$\Delta m = 0, \ \pm 1 \quad \text{and} \quad \Delta l = \pm 1$$

Note that we have neglected spin-orbit coupling here. Its inclusion would give

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta j = 0, \ \pm 1$$

Selection rules do not absolutely prohibit transitions that violate them, but they are far less likely to occur. Transitions may take place from oscillating magnetic dipole moments, or higher-order electric pole moments.

These alternatives are easily distinguished from allowed transitions since they occur much more slowly, resulting in photon release times of milliseconds to seconds rather than nanoseconds as calculated earlier. It is important to realize that practical phosphors having atomic luminescent centers often release photons via ‘forbidden’ transitions. The surrounding atoms in a crystal may lift the restrictions of ideal selections rules because they lower the symmetry of atomic states.

1.6 EINSTEIN COEFFICIENTS

Consider that an ensemble of atoms has electrons in quantum states k of energy E_k, which may make transitions to states 1 of energy E_l with the release of photons (Figure 1.5).

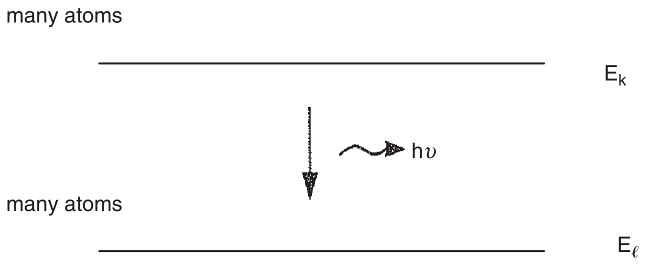

Figure 1.5 The decay of an electron from state *k* to state *l* results in the release of a photon. Solid State Luminescence, Adrian Kitai, Copyright 1993 with kind permission from Springer Science and Business Media

In order to begin making such transitions, something is needed to perturb the electrons in states *k*, otherwise they would not initiate the transitions, and would not populate superposition states φ_s. The study of quantum electrodynamics shows that there is always some electromagnetic field present in the vicinity of an atom, at whatever frequency is required to induce the charge oscillations and to initiate the radiation process. This is because electromagnetic fields are quantized and hence a zero-point energy exists in the field. We call this process **spontaneous emission**.

Alternatively, the transition may be initiated by applied photons (an applied electromagnetic field), which give rise to **stimulated emission**. It is also possible to excite electrons in state *l* to state *k* by using photons of suitable energy.

These ideas may be summarized as follows. The rate, at which atoms in the E_k state decay, is W_{kl}. This is proportional to the number of photons of frequency ω supplied by the radiation field, which is proportional to photon energy density $u(v)$ and to the number of atoms in the E_k state. The spontaneous process occurs without supplying radiation, and hence its rate is determined simply by the number of atoms in the E_k state, N_k. We may write

$$W_{kl} = [A_{kl} + B_{kl}u(v)]N_k = \omega_{kl}N_k \tag{1.4.a}$$

The proportionality constants *A* and *B* are called the Einstein *A* and *B* coefficients, and ω_{kl} is the rate on a per atom basis.

Atoms in the E_l state may not spontaneously become excited to the E_k state, whereas photons of energy $E_k - E_l$ may be absorbed. Hence:

$$W_{kl} = B_{lk}u(v)N_l = \omega_{lk}N_l \tag{1.4.b}$$

At this point, the idea of stimulated emission needs to be developed in order to explain why transition rates are proportional to $u(v)$. However, it is clear that A_{kl} is simply another name for $R_{nn'}$, the photon emission rate, in the case of dipole radiation.

1.7 HARMONIC PERTURBATION

Consider an atom possessing electron levels *k* and *I* that experiences a weak electromagnetic field. By 'weak' we require that the potential energy experienced by the electrons due to this field is small compared with the Coulomb potential from the nucleus and other electrons. The total Hamiltonian is given by the sum of the atomic term $H_o(r)$ and the perturbation term $H'(r, t)$:

$$H(r,t) = H_0(r) + H'(r,t) \quad \text{with} \quad H'(r,t) = H'(r)f(t)$$

If the field is turned on at $t = 0$ with frequency ω, then

$$H'(r,t) = \begin{cases} 0 & t < 0 \\ 2H'(r)\cos\omega t & t \geq 0 \end{cases}$$

Time-dependent perturbation theory [2] may be used to determine the wavefunction that results from the perturbation which is harmonic in this case. Assume the electron is initially in eigenstate $\varphi_l(r, t)$. In general, if $\varphi_k(r, t)$ are all eigenstates of $H_o(r)$ then the wavefunctions after the perturbation term $H'(r, t)$ is added will be of the form:

$$\psi(r,t) = \sum_k C_k(t)\psi_k(r,t)$$

where

$$C_k = \frac{(\phi_k|H'(r)|\phi_l)}{\mathrm{i}\hbar}\int_0 \mathrm{e}^{\mathrm{i}\omega_{kl}t'} f(t')\,\mathrm{d}t'$$

and

$$\psi(r,t) = \phi_k(r)\mathrm{e}^{\mathrm{i}\omega_k t}$$

The probability of a transition from the initial eigenstate $\varphi_l(r, t)$ to a new eigenstate $\varphi_k(r, t)$ is given simply by $|C_k(t)|^2$. We write

$$P_{l-k}(t) = |C_k(t)|^2 = \left(\frac{H'_{kl}}{\mathrm{i}\hbar}\right)^2 \left|\int_0^t \mathrm{e}^{\mathrm{i}\omega_{kl}t'} f(t')\,\mathrm{d}t'\right|^2$$

Because of the weak electromagnetic field, f(t) = 2cos ωt, and therefore

$$\begin{aligned} C_k(t) &= \frac{H'_{kl}}{\mathrm{i}\hbar}\int_0^t \mathrm{e}^{\mathrm{i}\omega_{kl}t'}(\mathrm{e}^{-\mathrm{i}\omega t'} + \mathrm{e}^{\mathrm{i}\omega t'})\,\mathrm{d}t' \\ &= -\frac{H'_{kl}}{\hbar}\left[\frac{\mathrm{e}^{\mathrm{i}(\omega_{kl}-\omega)t'} - 1}{\omega_{kl} - \omega} + \frac{\mathrm{e}^{\mathrm{i}(\omega_{kl}+\omega)t'} - 1}{\omega_{kl} + \omega}\right] \\ &= \frac{2\mathrm{i}H'_{kl}}{\hbar}\left\{\frac{\mathrm{e}^{\mathrm{i}(\omega_{kl}-\omega)t/2}\sin[(\omega_{kl}-\omega)t/2]}{\omega_{kl}-\omega} + \frac{\mathrm{e}^{\mathrm{i}(\omega_{kl}+\omega)t/2}\sin[(\omega_{kl}+\omega)t/2]}{\omega_{kl}+\omega}\right\} \end{aligned}$$

Resonance occurs when $\omega_{kl} = \pm\,\omega$. The two signs signify either a stimulated absorption process ($\omega_{kl} = \omega$) or a stimulated emission process ($\omega_{kl} = -\omega$) since energy is then released (E_{kl} negative). If $\omega_{kl} = \omega$:

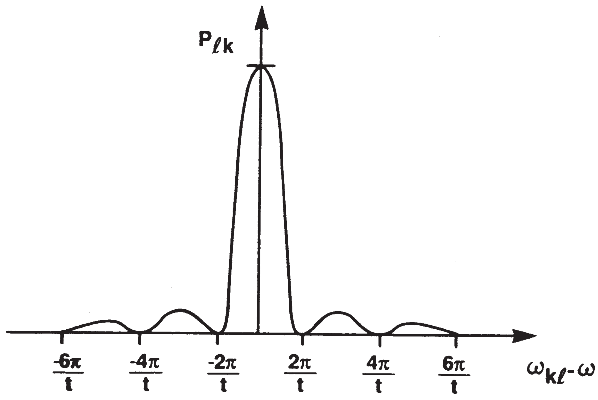

Figure 1.6 Dependence of transition probability on $\omega_{kl} - \omega$ as a result of harmonic perturbation. Solid State Luminescence, Adrian Kitai, Copyright 1993 with kind permission from Springer Science and Business Media

$$P_{lk} = |C_k|^2 = \frac{4|H'_{kl}|^2}{\hbar^2(\omega_{kl}-\omega)^2}\sin^2\left[\frac{1}{2}(\omega_{kl}-\omega)t\right] \tag{1.5}$$

The probability of the transition (stimulated emission or absorption) is always proportional to $|H'_{kl}|^2$. P_{lk} is shown in Figure 1.6, which should be thought of as a graph that grows rapidly in height with time t. Note, however, that being taller to begin with, the central peak grows faster than the others with time, and the function resembles a delta function for long time evolution. This is consistent with the uncertainty relationship $\Delta E\ \Delta t \geq h/2$ since, as time increases, the uncertainty in energy approaches zero.

The term $|H'_{kl}|^2$ may be expressed in terms of the electric field E of the electromagnetic perturbation. If p is the dipole moment of the electron as it undergoes the lk transition, then

$$H' = |-\boldsymbol{p}\cdot\boldsymbol{E}| \propto |E|.$$

Since energy density $u(v)$ is proportional to $|E|^2$, it is clear that $|H'_{kl}|^2 \propto u(v)$, and so we have shown that the Einstein B coefficients must be multiplied by $u(v)$, as in Equations 1.4a and 1.4b.

When we wish to describe the time evolution of the rate of emission for an ensemble of N atoms undergoing stimulated emission, we may use

$$W_{lk}\,(\text{transitions s}^{-1}) = \frac{N_l P_{lk}\,(\text{transitions})}{t\,(\text{s})}$$

Thus it is evident that when $P_{lk} \infty t^2$, then the transition rate increases linearly with time. This situation obtains for small *t,* since from Equation (1.5) we see that

$$P_{lk} \propto \lim_{n\to\infty} = \frac{\sin^2[\frac{1}{2}(\omega_{kl}-\omega)t]|H'_{kl}|^2}{(\omega_{kl}-\omega)^2} = \frac{1}{4}t^2$$

Of course, for long times, W_{lk} becomes constant as equilibrium is reached. Note that

$$B_{lk} = B_{kl} \text{ since } P_{lk} = P_{kl}.$$

1.8 BLACKBODY RADIATION

If an ensemble of electron states are in equilibrium, $W_{lk} = W_{kl}$. However, the spontaneous emission process may only take place in one direction, and we can write

$$[A_{kl} + B_{kl}u(v)]N_k = W_{kl} = W_{lk} = B_{lk}u(v)N_l = B_{kl}u(v)N_l$$

Therefore

$$\frac{N_l}{N_k} = \frac{A_{kl} + B_{kl}u(v)}{B_{kl}u(v)}$$

and

$$u(v) = \frac{A_{kl}N_k}{B_{kl}N_l - B_{kl}N_k}$$

Since the populations of atoms having excited states of certain energies will obey Boltzmann statistics:

$$\frac{N_l}{N_k} = \mathrm{e}^{(E_k-E_l)/kT} = \mathrm{e}^{\hbar\omega/kT}$$

it follows that

$$u(v) = \frac{A/B}{e^{\hbar\omega/kT} - 1} \tag{1.6}$$

where subscripts have been dropped.

Consider a cavity with metallic walls uniformly heated to temperature *T*. If we could observe the cavity through a small hole the wall, we would detect electromagnetic radiation due to the thermally agitated electrons in the cavity walls.

For analysis, suppose the cavity is cubic with edge length *a*, and principal axes *x*, *y* and *z* (Figure 1.7). Since the cavity walls are electrically conductive, the electric field in the

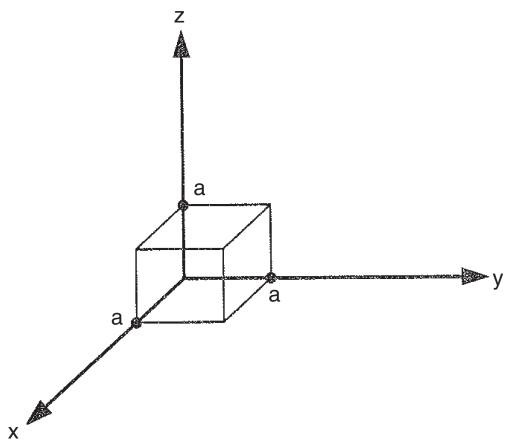

Figure 1.7 Cavity of cubic shape with edge length a (after Solymar and Walsh, [3]). Solid State Luminescence, Adrian Kitai, Copyright 1993 with kind permission from Springer Science and Business Media

radiation field must be zero at the cavity walls, and because of electromagnetic reflections at metallic surfaces, standing waves will only exist in equilibrium. Hence, the E field for waves traveling in the x-direction will be given by

$$E(x,t) = E_0 \sin\left(\frac{2\pi x}{\lambda}\right)\sin(2\pi\nu t) \quad \text{where } \nu = \frac{c}{\lambda}$$

To satisfy boundary conditions, $E(a, t) = 0$, and therefore

$$\frac{2\pi a}{\lambda} = n_x\pi, \quad \lambda_x = \frac{2a}{n} \quad \text{and} \quad \nu_n = \frac{cn_x}{2a}$$

Note that the frequencies are quantized and may be counted using integers n_x. Similar expressions may be written for E_y and E_z. Consider an artificial space having axes (n_x, n_y, n_z). Such a space consists of a lattice of points, each of which uniquely describes a particular three-dimensional radiation pattern or mode. It is easy to show that all points (n_x, n_y, n_z), at a given distance $r = 2a\nu/c$ from the origin, represent standing waves of the same frequency ν, but along different directions within the cavity [1]. We can then count the number of cavity modes between spheres of radii $2a\nu/c$ and $2a(\nu + d\nu)/c$ (Figure 1.8). Since each point occupies a unit 'volume', the number of points in the spherical shell is shell volume $4\pi r w^2 \, dr = 4\pi(2a/c)^3 \nu^2 \, d\nu$. Since we wish only to consider positive values of n, we divide by 8 to count only one octant of the shell, and multiply by 2 because each standing wave has two possible polarizations. Hence, the number of modes over frequency range $d\nu$ is

$$N(\nu) = \frac{8\pi a^3}{c^3}\nu^2 d\nu = \frac{8\pi V}{c^3}\nu^2 d\nu$$

Because each mode has a degree of freedom, namely the choice of electric field amplitude, on average each mode will have the same energy E which, from classical kinetic

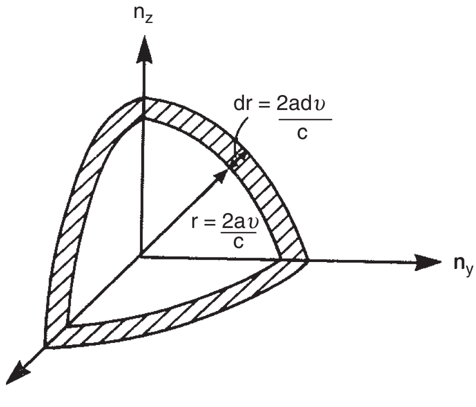

Figure 1.8 Spherical shell enclosing points in (n_x, n_y, n_z) space lattice that represent standing waves that range in frequency from v to v + dv (after Solymar and Walsh [3]). Solid State Luminescence, Adrian Kitai, Copyright 1993 with kind permission from Springer Science and Business Media

theory, is $E = kT$. Should one mode gain in E, it would lose it owing to collisions of electrons in the cavity walls, which would transfer it to other modes. Therefore the energy per unit cavity volume over the frequency interval dv may be expressed in terms of the energy density $u(v)$ as

$$u(v)\mathrm{d}v = \frac{8\pi v^2}{c^3} kT\mathrm{d}v \tag{1.7}$$

This expression clearly differs from Equation (1.6). This is because our classical wave theory assumes that the energy of each cavity mode is continuously variable as just stated, even though the allowed cavity modes have discrete frequencies v. However, in our treatment leading to Equation (1.6), we treated the energy levels giving rise to modes at frequency v as discrete, such that $hv = \Delta E$. Starting with lowest frequency mode, for example along the x-direction, $n_x = 1$ and $v_1 = c/2a$. If $n_x = 2$, then $v_2 = c/a$. This implies a pair of discrete energy levels, $E_1 = hv_1$ and $E_2 = hv_2$ with difference $\Delta E = hc/2a$. So long as $\Delta E = kT$, there is no real problem with the classical treatment. However, for higher-order modes, or for lower temperatures, the energy spacing between modes may by far exceed kT and it becomes essential to take the energy of each mode as discrete. Since Equation (1.7) gives the correct result for

$$\lim_{v\to\infty} u(v) = \lim_{v\to\infty} \frac{8\pi v^2 kT}{c^3} \tag{1.8}$$

we can now evaluate A/B in Equation (1.6) by requiring that

$$\lim_{v\to\infty} \frac{A/B}{\mathrm{e}^{hv/kT} - 1} = \frac{A/B}{hv/kT} = \frac{8\pi v^2 kT}{c^3}$$

Therefore