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Principles of Solid State Luminescence

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It is useful to understand the origin of luminescence. Solid state luminescent materials and devices all rely on a common mechanism of luminescence whether they are semiconductor light emitting diodes (LEDs) or phosphors or quantum dots, and whether they are organic or inorganic materials. This is introduced in Sections 1.1–1.3 and then this chapter presents a series of more specific luminescence processes.

1.1 Introduction to Radiation from an Accelerating Charge

Light is electromagnetic radiation which can be produced by an accelerating charge. Let us first consider a stationary point charge q in a vacuum. Electric field lines are produced from the point charge with electric field lines emanating radially out from the charge as shown in Figure 1.1.

This stationary point charge does not produce electromagnetic radiation but since it does produce an electric field there is electric field energy surrounding the point charge. This energy is related to the electric field by:

$$E_\varepsilon = \frac{\epsilon_0}{2}\mathcal{E}^2$$

where ϵ_0 is the permittivity of vacuum and E_ε is the electric field energy density.

If the charge q were to move with a constant velocity v an additional magnetic field B is produced. Lines of this magnetic field form closed loops that lie in planes perpendicular to the velocity vector of the moving change as shown in Figure 1.2.

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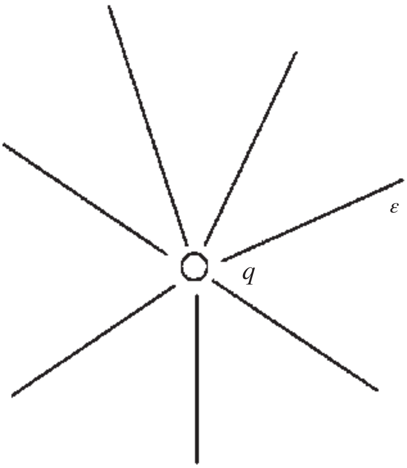


Figure 1.1 *Lines of electric field $\mathcal{E}$ produced by stationary point charge q*

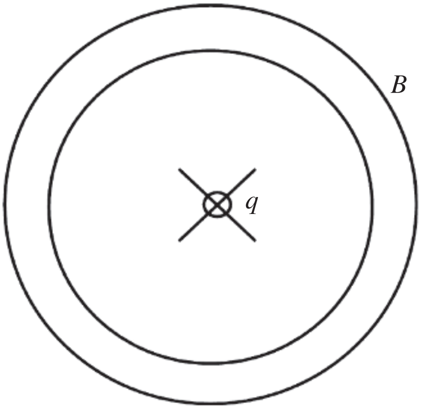


Figure 1.2 *Closed lines of magnetic field B due to a point charge q moving with constant velocity into the page*

Both magnetic and electric fields exist surrounding the charge moving with uniform velocity. The magnetic field also has an energy associated with it. The magnetic field energy density E_B is given by:

$$E_\mathrm{B} = \frac{1}{2\mu_0}B^2$$

where μ_0 is the magnetic permeability of vacuum.

The total energy density due to both fields is now:

$$E = E_\varepsilon + E_\mathrm{B} = \frac{\epsilon_0}{2}\mathcal{E}^2 + \frac{1}{2\mu_0}B^2$$

The field strengths of both the electric and the magnetic fields fall off as we move further away from the charge and therefore the energy density falls off rapidly with distance from the charge. There is no radiation from the charge.

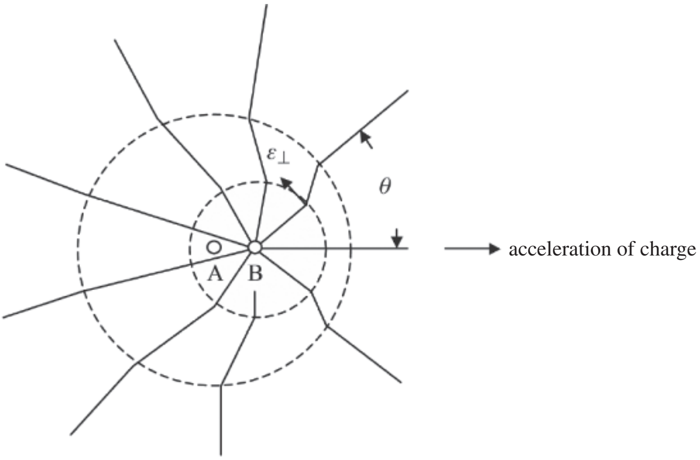


Figure 1.3 Lines of electric field emanating from an accelerating charge

The situation changes dramatically if the charge q undergoes acceleration. Consider a charge that rapidly accelerates as shown in Figure 1.3.

The electric field lines further away from the charge are still based on the original position of the charge at position A before the acceleration occurred, however electric field lines after acceleration will now emanate from the new location at position B of the charge. The new electric field lines will expand outwards and replace the original field lines. The speed at which this expansion occurs is the speed of light c because it is not possible for information on the new location of the charge to arrive at any particular distance away from the charge faster than the speed of light.

The kinks in the electric field lines in Figure 1.3 associated with this expansion must contain an electric field component $\mathcal{E}_\perp$which is perpendicular to the radial field direction. $\mathcal{E}_\perp$ propagates outwards from the accelerating charge at velocity c. Notice that the biggest kink and therefore the largest magnitudes of $\mathcal{E}_\perp$ propagate in directions perpendicular to the acceleration of the charge. In the direction of the acceleration $\mathcal{E}_\perp = 0$.

In addition, there is a magnetic field $B_\perp$ that is perpendicular to both the direction of acceleration as well as to $\mathcal{E}_\perp$. This field is shown in Figure 1.4. This magnetic field $\mathcal{E}_\perp$ propagates outwards and is also a maximum in a direction normal to the acceleration.

The combined electric and magnetic fields $\mathcal{E}_\perp$ and $B_\perp$ form a propagating electromagnetic wave that travels away from the accelerating charge.

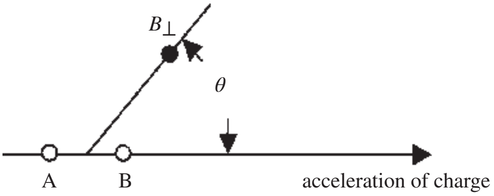


Figure 1.4 Direction of magnetic field $B_\perp$ that is perpendicular to both the direction of acceleration as well as to $\mathcal{E}_\perp$ from Figure 1.3

The magnitudes of $\mathcal{E}_\perp$ and $B_\perp$ are given by:

$$\mathcal{E}_\perp = \frac{qa}{4\pi\epsilon_0 c^2 r}\sin\theta$$

and

$$B_\perp = \frac{\mu_0 qa}{4\pi cr}\sin\theta$$

The electromagnetic radiation formed by these two fields propagates away from the accelerating charge and this radiation has a directed power flow per unit area (Poynting vector) given by:

$$\vec{S} = \frac{1}{\mu_0}\mathcal{E}_\perp \times B_\perp = \frac{q^2a^2}{16\pi^2\epsilon_0 c^3 r^2}\sin^2\theta\,\hat{r}$$

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

The total radiated energy from the accelerated charge is calculated by integrating the magnitude of the Poynting vector over a sphere surrounding the accelerating charge and we obtain:

$$P = \int_{sphere} SdA = \int_0^{2\pi}\int_0^{\pi} S(\theta)r^2\sin\theta d\theta d\phi = \int_0^{\pi} S(\theta)2\pi r^2\sin\theta d\theta$$

Substituting for $S(\theta)$,

$$P = \frac{2q^2a^2}{16\pi\epsilon_0 c^3}\int_0^{\pi}\sin^3\theta d\theta$$

Upon integration we obtain:

$$P = \frac{2q^2a^2}{12\pi\epsilon_0 c^3} \tag{1.1}$$

1.2 Radiation from an Oscillating Dipole

The manner in which a charge can accelerate can take many forms. For example, an electron orbiting in a cyclotron accelerates steadily towards the center of its orbit and radiation according to Equation 1.1 will be emitted most strongly tangentially to the orbit in a direction perpendicular to the acceleration vector. If energetic electrons are directed towards an atomic target, the rapid deceleration upon impact with atomic nuclei causes radiation called bremsstrahlung (radiation due to deceleration).

The charge acceleration that is by far the most important in luminescent solids, however, is generated by an oscillating dipole formed by an electron oscillating in the vicinity of a positive atomic nucleus. This is known as an oscillating dipole and the radiation it produces is called dipole radiation. Dipole radiation can occur within, and be very effectively released from, solids such as semiconductors or insulators that are substantially transparent to the dipole radiation.

Consider a charge q that oscillates about the origin along the x-axis having position given by:

$$x(t) = A\sin\omega t$$

The electron has acceleration $a = \frac{d^2x(t)}{dt^2}$ or

$$a(t) = -A\omega^2 \sin \omega t$$

Substituting into Equation 1.1 we can write:

$$P(t) = \frac{2q^2A^2\omega^4 \sin^2 \omega t}{12\pi\epsilon_0 c^3}$$

and averaging this power over one cycle we obtain average power

$$\overline{P} = \frac{\omega}{2\pi}\frac{2q^2A^2\omega^4}{12\pi\epsilon_0 c^3}\int_0^{\frac{2\pi}{\omega}} \sin^2 \omega t \, \mathrm{d}t$$

which yields:

$$\overline{P} = \frac{q^2A^2\omega^4}{12\pi\epsilon_0 c^3} \tag{1.2}$$

In terms of the dipole moment $p = qA$ this is written:

$$\overline{P} = \frac{p^2\omega^4}{12\pi\epsilon_0 c^3}$$

Dipole radiation may take place from atomic orbitals inside a crystal lattice or it may take place as an electron and a hole recombine. We do not think of classical oscillating electron motion because we describe electrons using quantum mechanics. We are now ready to show that the quantum mechanical description of an electron can yield oscillations during a radiation event.

1.3 Quantum Description of an Electron during a Radiation Event

Solving Schroedinger's equation for a potential $V(r)$ in which an electron may exist yields a set of wavefunctions or stationary states that allow us to obtain the probability density function and energy levels of the electron. Examples of this include the set of electron orbitals of a hydrogen atom or the electron states in a potential well. These are called stationary states because the electron will remain in a specific quantum state unless perturbed by an outside influence. There is no time dependence of measurable electron parameters such as energy, momentum or expected position. As an example of this, consider an electron in a stationary state ψ_{n} which is a solution of Schroedinger's equation. ψ_{n} may be written in terms of a spatial part of the wavefunction $\phi_{\mathrm{n}}(r)$ as:

$$\psi_{\mathrm{n}} = \phi_{\mathrm{n}}(r) \exp\left(\frac{-iEt}{\hbar}\right) \tag{1.3}$$

We can calculate the expected value of the position of this electron as:

$$\langle r \rangle (t) = \langle \psi_{\mathrm{n}} | r | \psi_{\mathrm{n}} \rangle = \int_V V \, |\psi_{\mathrm{n}}|^2 \, r \, dV$$

where V represents all space. Substituting the form of a stationary state we obtain:

$$\langle r\rangle(t) = \int_V \left[\phi(r)\exp\left(\frac{-iEt}{\hbar}\right)\ \phi(r)\exp\left(\frac{iEt}{\hbar}\right)\right] rdV = \int_V r\phi^2(r)dV$$

which is a time-independent quantity. This confirms the stationary nature of this state. A stationary state does not radiate and there is no energy loss associated with the behavior of an electron in such a state.

Note that electrons are not truly stationary in a quantum state from a classical viewpoint. It is therefore the quantum state that is described as stationary and not the electron itself. Quantum mechanics sanctions the existence of a charge that has a distributed spatial probability distribution function and yet that is in a stationary state. Classical physics fails to describe or predict this.

Experience tells us, however, that radiation may be produced when a charge moves from one stationary state to another and we can show that radiation is produced if an oscillating dipole results from a charge moving from one stationary state to another. Consider a charge q initially in normalized stationary state ψ_n and eventually in normalized stationary state $\psi_{\mathrm{n}'}$. During the transition, a superposition state is created which we shall call ψ_s:

$$\psi_\mathrm{s} = a\psi_\mathrm{n} + b\psi_{\mathrm{n}'}$$

where $|a|^2 + |b|^2 = 1$ to normalize the superposition state. Here, a and b are time-dependent coefficients. Initially $a = 1$ and $b = 0$ and after the transition, $a = 0$ and $b = 1$. If we now calculate the expectation value of the position of q for the superposition state ψ_s we obtain:

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

Of the four terms, the first two are stationary but the last two terms are not and therefore $\langle r\rangle_\mathrm{s}(t)$ may be written using Equation 1.3 as:

$$\langle r\rangle_\mathrm{s}(t) = a^*b\langle\phi_\mathrm{n}|r|\phi_{\mathrm{n}'}\rangle\exp\left(\frac{-i(E_\mathrm{n} - E_{\mathrm{n}'})t}{\hbar}\right) + b^*a\langle\phi_\mathrm{n}|r|\phi_{\mathrm{n}'}\rangle\exp\left(\frac{i(E_\mathrm{n} - E_{\mathrm{n}'})t}{\hbar}\right)$$

Using the Euler formula $e^{ix} + e^{-ix} = 2\cos x$

we have:

$$\begin{aligned}\langle r\rangle_\mathrm{s}(t) &= a^*b\langle\phi_\mathrm{n}|r|\phi_{\mathrm{n}'}\rangle\exp\left(\frac{-i(E_\mathrm{n} - E_{\mathrm{n}'})t}{\hbar}\right) + b^*a\langle\phi_\mathrm{n}|r|\phi_{\mathrm{n}'}\rangle\exp\left(\frac{i(E_\mathrm{n} - E_{\mathrm{n}'})t}{\hbar}\right) \\ &= 2a^*b\langle\phi_\mathrm{n}|r|\phi_{\mathrm{n}'}\rangle\cos\left(\frac{(E_\mathrm{n} - E_{\mathrm{n}'})t}{\hbar}\right)\end{aligned}$$

Defining $|r_{\mathrm{nn}'}| = a^*b\langle\phi_\mathrm{n}|r|\phi_{\mathrm{n}'}\rangle$ and $\omega_{\mathrm{nn}'} = \frac{(E_\mathrm{n} - E_{\mathrm{n}'})}{\hbar}$ we finally obtain:

$$\langle r\rangle_\mathrm{s}(t) = 2|r_{\mathrm{nn}'}|\cos(\omega_{\mathrm{nn}'}t) \tag{1.4}$$

Here, $|r_{\mathrm{nn}'}|$ is called the matrix element for the transition. It is seen that the expectation value of the position of the electron is oscillating with frequency $\omega_{\mathrm{nn}'} = \frac{(E_\mathrm{n} - E_{\mathrm{n}'})}{\hbar}$ which is

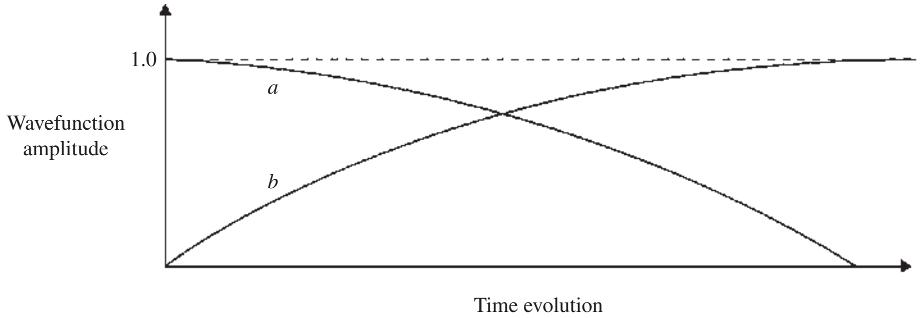


Figure 1.5 *A time-dependent plot of coefficients a and b is consistent with the time evolution of wavefunctions* ϕ_{n} *and* $\phi_{\mathrm{n}'}$. *At* $t = 0$, $a = 1$ *and* $b = 0$. *Next a superposition state is formed during the transition such that* $|a|^2 + |b|^2 = 1$. *Finally, after the transition is complete* $a = 0$ *and* $b = 1$

the required frequency to produce a photon having energy $E = E_{\mathrm{n}} - E_{\mathrm{n}'}$. The term $|r_{\mathrm{nn}'}|$ also varies with time, but does so very slowly compared with the cosine term. This is illustrated in Figure 1.5.

We may also define a photon emission rate $R_{\mathrm{nn}'}$ of a continuously oscillating charge q. We use Equations 1.2 and 1.4 and $E = \hbar\omega$ to obtain:

$$R_{\mathrm{nn}'} = \frac{\overline{P}}{\hbar\omega} = \frac{q^2\omega^3}{3\pi\epsilon_0 c^3\hbar}|r_{\mathrm{nn}'}|^2 \mathrm{photons/s}$$

The photon emission rate is only an average rate. This is because of the Heizenberg Uncertainty Principle which states that the position and the momentum of an electron cannot be precisely measured simultaneously. It also means that we cannot predict the exact time of photon creation while simultaneously knowing its exact energy. Since the energy of the photon is defined without uncertainty there will be uncertainty about the precise time of release of each photon.

1.4 The Exciton

A hole and an electron can exist as a valence band state and a conduction band state. In this model the two particles are not localized and they are both represented using Bloch functions in the periodic potential of the crystal lattice. If the mutual attraction between the two becomes significant then a new description is required for their quantum states that is valid before they recombine but after they experience some mutual attraction.

The hole and electron can exist in quantum states that are actually *within* the energy gap.

Just as a hydrogen atom consists of a series of energy levels associated with the allowed quantum states of a proton and an electron, a series of energy levels associated with the quantum states of a hole and an electron also exists. This hole–electron entity is called an *exciton*, and the exciton behaves in a manner that is similar to a hydrogen atom with one important exception: a hydrogen atom has a lowest energy state or ground state when its quantum number $n = 1$, but a exciton, which also has a ground state at $n = 1$, has an opportunity to be annihilated when the electron and hole eventually recombine.

For an exciton we need to modify the electron mass m to become the reduced mass μ of the hole–electron pair, which is given by:

$$\frac{1}{\mu} = \frac{1}{m_{\mathrm{e}}^{*}} + \frac{1}{m_{\mathrm{h}}^{*}}$$

For direct gap semiconductors such as GaAs this is about one order of magnitude smaller than the free electron mass m. In addition the excition exists inside a semiconductor rather than in a vacuum. The relative dielectric constant ϵ_{r} must be considered, and it is approximately 10 for typical inorganic semiconductors. Adapting the hydrogen atom model, the ground state energy for an exciton is:

$$E_{\mathrm{exciton}} = \frac{-\mu q^4}{8\epsilon_{\mathrm{o}}^2\epsilon_{\mathrm{r}}^2 h^2} \cong \frac{E_{\mathrm{Rydberg}}}{1000}$$

This yields a typical exciton ionization energy or binding energy of under 0.1 eV.

The exciton radius in the ground state ($n = 1$) will be given by:

$$a_{\mathrm{exciton}} = \frac{4\pi\epsilon_0 \ \epsilon_{\mathrm{r}}\hbar^2}{\mu q^2} \cong 100a_0$$

which yields an exciton radius of the order of 50 Å. Since this radius is much larger than the lattice constant of a semiconductor, we are justified in our use of the bulk semiconductor parameters for effective mass and relative dielectric constant.

Our picture is now of a hydrogen atom-like entity drifting around within the semiconductor crystal and having a series of energy levels analogous to those in a hydrogen atom. Just as a hydrogen atom has energy levels $E_{\mathrm{n}} = \frac{13.6}{n^2}$eV where quantum number n is an integer, the exciton has similar energy levels but in a much smaller energy range, and a quantum number n_{exciton} is used.

The exciton must transfer energy to be annihilated. When an electron and a hole form an exciton it is expected that they are initially in a high energy level with a large quantum number n_{exciton}. This forms a larger, less tightly bound exciton. Through *thermalization* the exciton loses energy to lattice vibrations and approaches its ground state. Its radius decreases as n_{exciton} approaches 1. Once the exciton is more tightly bound and n_{exciton} is a small integer, the hole and electron can then form an effective dipole and radiation may be produced to account for the remaining energy and to annihilate the exciton through the process of dipole radiation. When energy is released as electromagnetic radiation, we can determine whether or not a particular transition is allowed by calculating the term $|r_{\mathrm{nn}'}|$ in Equation 1.4 and determining whether it is zero or non-zero. If $|r_{\mathrm{nn}'}| = 0$ then this is equivalent to saying that dipole radiation will *not* take place and a photon cannot be created. Instead lattice vibrations remove the energy. If $|r_{\mathrm{nn}'}| > 0$ then this is equivalent to saying that dipole radiation *can* take place and a photon can be created. We can represent the exciton energy levels in a semiconductor as shown in Figure 1.6.

At low temperatures the emission and absorption wavelengths of electron–hole pairs must be understood in the context of excitons in all p-n junctions. The existence of excitons, however, is generally hidden at room temperature and at higher temperatures in

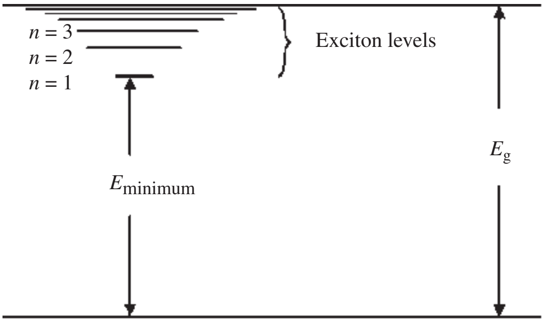


Figure 1.6 *The exciton forms a. series of closely spaced hydrogen-like energy levels that extend inside the energy gap of a semiconductor. If an electron falls into the lowest energy state of the exciton corresponding to n = 1 then the remaining energy available for a photon is* E_{minimum}

inorganic semiconductors because of the temperature of operation of the device. The exciton is not stable enough to form from the distributed band states and at room temperature kT may be larger than the exciton energy levels. In this case the spectral features associated with excitons will be masked and direct gap or indirect gap band-to-band transitions occur. Nevertheless, photoluminescence or absorption measurements at low temperatures conveniently provided in the laboratory using liquid nitrogen (77 K) or liquid helium (4.2 K) clearly show exciton features, and excitons have become an important tool to study inorganic semiconductor behavior. An example of the transmission as a function of photon energy of a semiconductor at low temperature due to excitons is shown in Figure 1.7.

In an indirect gap inorganic semiconductor at room temperature without the formation of excitons, the electron–hole pair can lose energy to phonons and be annihilated but not through dipole radiation. In a direct-gap semiconductor, however, dipole radiation can occur. The calculation of $|r_{\mathrm{nn}'}|$ is also relevant to band-to-band transitions. Since a dipole does not carry linear momentum it does not allow for the conservation of electron momentum during electron–hole pair recombination in an indirect gap semiconductor crystal and dipole radiation is forbidden. The requirement of a direct gap for a band-to-band transition that conserves momentum is consistent with the requirements of dipole radiation. Dipole radiation is effectively either allowed or forbidden in band-to-band transitions.

Not all excitons are free to move around in the semiconductor. *Bound excitons* are often formed that associate themselves with defects in a semiconductor crystal such as vacancies and impurities. In organic semiconductors *molecular exictons* form, which are very important for an understanding of optical processes that occur in organic semiconductors. This is because molecular excitons typically have high binding energies of approximately 0.4 eV. The reason for the higher binding energy is the confinement of the molecular exciton to smaller spatial dimensions imposed by the size of the molecule. This keeps the hole and electron closer and increases the binding energy compared with free excitons. In contrast to the situation in inorganic semiconductors, molecular excitons are thermally stable

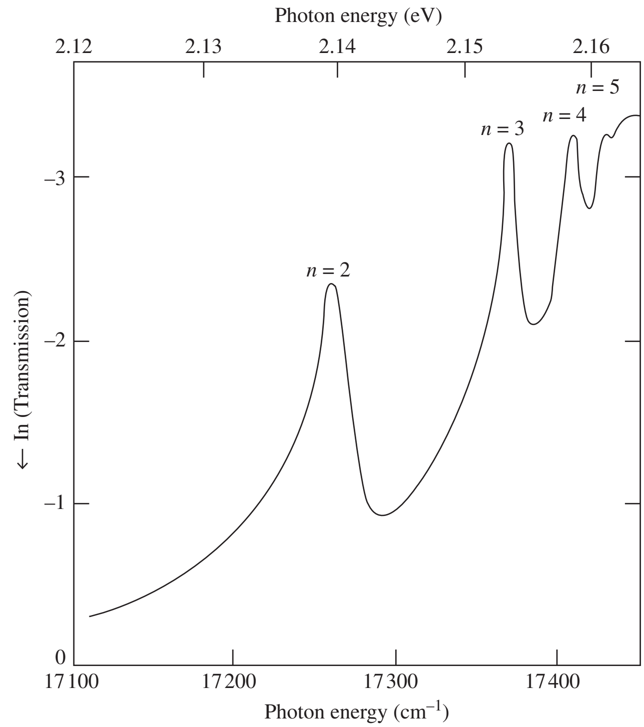


Figure 1.7 *Low-temperature transmission as a function of photon energy tor Cu_2O. The absorption of photons is caused through excitons, which are excited into higher energy levels as the absorption process takes place. Cu_2O is a semiconductor with a bandgap of 2.17 eV. Reprinted from Kittel, C., Introduction to Solid State Physics, 6e, ISBN 0-471-87474-4. Copyright (1986) John Wiley and Sons, Australia*

at room temperature and they generally determine emission and absorption characteristics of organic semiconductors in operation. The molecular exciton is fundamental to organic light emitting diode (OLED) operation. We will first need to discuss in more detail the physics required to understand excitons and optical processes in molecular materials.

1.5 Two-Electron Atoms

Until now we have focused on dipole radiators that are composed of two charges, one positive and one negative. In Section 1.3 we introduced an oscillating dipole having one positive charge and one negative charge. In Section 1.4 we discussed the exciton, which also has one positive charge and one negative charge.

However, we also need to understand radiation from molecular systems with two or more electrons, which form the basis of organic semiconductors. Once a system has two or more identical particles (electrons) there are additional and very fundamental quantum effects that we need to consider. In inorganic semiconductors, band theory gives us the tools to handle large numbers of electrons in a periodic potential. In organic semiconductors electrons are confined to discrete organic molecules and "hop" from molecule to molecule. Band theory is still relevant to electron behavior within a given molecule provided it contains repeating structural units.

Nevertheless, we need to study the electronic properties of molecules more carefully because molecules contain multiple electrons, and exciton properties in molecules are rather different from the excitons we have discussed in inorganic semiconductors. The best starting point is the helium atom, which has a nucleus with a charge of $+2q$ as well as two electrons each with a charge of $-q$. A straightforward solution to the helium atom using Schrödinger's equation is not possible since this is a *three-body* system; however, we can understand the behavior of such a system by applying the Pauli exclusion principle and by including the spin states of the two electrons.

When two electrons at least partly overlap spatially with one another their wavefunctions must conform to the Pauli exclusion principle; however, there is an additional requirement that must be satisfied. The two electrons must be carefully treated as *indistinguishable* because once they have even a small spatial overlap there is no way to know which electron is which. We can only determine a probability density $|\psi|^2 = \psi^*\psi$ for each wavefunction but we cannot determine the precise location of either electron at any instant in time and therefore there is always a chance that the electrons exchange places. There is no way to label or otherwise identify each electron and the wavefunctions must therefore not be specific about the identity of each electron.

If we start with Schrödinger's equation and write it by adding up the energy terms from the two electrons we obtain:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{\partial^2\psi_T}{\partial y_1^2}+\frac{\partial^2\psi_T}{\partial z_1^2}\right)-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_T}{\partial x_2^2}+\frac{\partial^2\psi_T}{\partial y_2^2}+\frac{\partial^2\psi_T}{\partial z_2^2}\right)+V_T\psi_T=E_T\psi_T \tag{1.5}$$

Here $\psi_T(x_1, y_1, z_1, x_2, y_2, z_2)$ is the wavefunction of the two-electron system, $V_T(x_1, y_1, z_1, x_2, y_2, z_2)$ is the potential energy for the two-electron system and E_T is the total energy of the two-electron system. The spatial coordinates of the two electrons are (x_1, y_1, z_1) and (x_2, y_2, z_2).

To simplify our treatment of the two electrons we will start by assuming that the electrons do not interact with each other. This means that we are neglecting coulomb repulsion between the electrons. The potential energy of the total system is then simply the sum of the potential energy of each electron under the influence of the helium nucleus. Now the potential energy can be expressed as the sum of two identical potential energy functions $V(x_1, y_1, z_1)$ for the two electrons and we can write:

$$V_T(x_1, y_1, z_1, x_2, y_2, z_2) = V(x_1, y_1, z_1) + V(x_2, y_2, z_2)$$

Substituting this into Equation 1.5 we obtain:

$$\begin{aligned}&-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{\partial^2\psi_T}{\partial y_1^2}+\frac{\partial^2\psi_T}{\partial z_1^2}\right)-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_T}{\partial x_2^2}+\frac{\partial^2\psi_T}{\partial y_2^2}+\frac{\partial^2\psi_T}{\partial z_2^2}\right)\\&+V(x_1,y_1,z_1)\psi_T+V(x_2,y_2,z_2)\psi_T=E_T\psi_T\end{aligned} \tag{1.6}$$

If we look for solutions for ψ_T of the form $\psi_T = \psi(x_1, y_1, z_1)\psi(x_2, y_2, z_2)$ then Equation 1.6 becomes

$$\begin{aligned}
&-\frac{\hbar^2}{2m}\psi(x_2, y_2, z_2)\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)\psi(x_1, y_1, z_1)\\
&-\frac{\hbar^2}{2m}\psi(x_1, y_1, z_1)\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)\psi(x_2, y_2, z_2)\\
&+V(x_1, y_1, z_1)\psi(x_1, y_1, z_1)\psi(x_2, y_2, z_2)\\
&+V(x_2, y_2, z_2)\psi(x_1, y_1, z_1)\psi(x_2, y_2, z_2)\\
&=E_T\psi(x_1, y_1, z_1)\psi(x_2, y_2, z_2)
\end{aligned}\tag{1.7}$$

Dividing Equation 1.7 by $\psi(x_1, y_1, z_1)\psi(x_2, y_2, z_2)$ we obtain:

$$\begin{aligned}
&-\frac{\hbar^2}{2m}\frac{1}{\psi(x_1, y_1, z_1)}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)\psi(x_1, y_1, z_1)\\
&-\frac{\hbar^2}{2m}\frac{1}{\psi(x_2, y_2, z_2)}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)\psi(x_2, y_2, z_2)\\
&+V(x_1, y_1, z_1)+V(x_2, y_2, z_2)=E_T
\end{aligned}$$

Since the first and third terms are only a function of (x_1, y_1, z_1) and the second and fourth terms are only a function of (x_2, y_2, z_2), and furthermore since the equation must be satisfied for independent choices of (x_1, y_1, z_1) and (x_2, y_2, z_2) it follows that we must independently satisfy two equations, namely

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x_1, y_1, z_1)}\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}+\frac{\partial^2}{\partial z_1^2}\right)\psi(x_1, y_1, z_1)+V(x_1, y_1, z_1)=E_1$$

and

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x_2, y_2, z_2)}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)\psi(x_2, y_2, z_2)+V(x_2, y_2, z_2)=E_2$$

These are both identical one-electron Schrödinger equations. We have used the technique of separation of variables.

We have considered only the spatial parts of the wavefunctions of the electrons; however, electrons also have spin. In order to include spin the wavefunctions must also define the spin direction of the electron.

We will write a complete wavefunction $[\psi(x_1, y_1, z_1)\psi(S)]_a$, which is the wavefunction for one electron where $\psi(x_1, y_1, z_1)$ describes the spatial part and the spin wavefunction $\psi(S)$ describes the spin part, which can be spin up or spin down. There will be four quantum numbers associated with each wavefunction of which the first three arise from the spatial part. A fourth quantum number, which can be $+1/2$ or $-1/2$ for the spin part, defines the direction of the spin part. Rather than writing the full set of quantum numbers for each wavefunction we will use the subscript *a* to denote the set of four quantum numbers. For the other electron the analogous wavefunction is $[\psi(x_2, y_2, z_2)\psi(S)]_b$ indicating that this electron has its own set of four quantum numbers denoted by subscript *b*.

Now the wavefunction of the two-electron System including spin becomes:

$$\psi_{T_1} = [\psi(x_1, y_1, z_1)\psi(S)]_a[\psi(x_2, y_2, z_2)\psi(S)]_b \tag{1.8a}$$

The probability distribution function, which describes the spatial probability density function of the two-electron system, is $|\psi_T|^2$, which can be written as:

$$\begin{aligned}|\psi_{T_1}|^2 &= \psi^*_{T_1}\psi_{T_1}\\ &= [\psi(x_1, y_1, z_1)\psi(S)]^*_a [\psi(x_2, y_2, z_2)\psi(S)]^*_b [\psi(x_1, y_1, z_1)\psi(S)]_a\\ &\quad [\psi(x_2, y_2, z_2)\psi(S)]_b\end{aligned} \tag{1.8b}$$

If the electrons were distinguishable then we would need also to consider the case where the electrons were in the opposite states, and in this case

$$\psi_{T_2} = [\psi(x_1, y_1, z_1)\psi(S)]_b[\psi(x_2, y_2, z_2)\psi(S)]_a \tag{1.9a}$$

Now the probability density of the two-electron system would be:

$$\begin{aligned}|\psi_{T_2}|^2 &= \psi^*_{T_2}\psi_{T_2}\\ &= [\psi(x_1, y_1, z_1)\psi(S)]^*_b [\psi(x_2, y_2, z_2)\psi(S)]^*_a [\psi(x_1, y_1, z_1)\psi(S)]_b\\ &\quad [\psi(x_2, y_2, z_2)\psi(S)]_a\end{aligned} \tag{1.9b}$$

Clearly Equation 1.9b is not the same as Equation 1.8b and when the subscripts are switched the form of $|\psi_T|^2$ changes. This specifically contradicts the requirement, that measurable quantities such as the spatial distribution function of the two-electron system remain the same regardless of the interchange of the electrons.

In order to resolve this difficulty, it is possible to write wavefunctions of the two-electron system that are linear combinations of the two possible electron wavefunctions.

We write a *symmetric* wavefunction ψ_S for the two-electron system as:

$$\psi_S = \frac{1}{\sqrt{2}}[\psi_{T_1} + \psi_{T_2}] \tag{1.10}$$

and an *antisymmetric* wavefunction ψ_A for the two-electron system as:

$$\psi_A = \frac{1}{\sqrt{2}}[\psi_{T_1} - \psi_{T_2}] \tag{1.11}$$

If ψ_S is used in place of ψ_T to calculate the probability density function $|\psi_S|^2$, the result will be independent of the choice of the subscripts, In addition since both ψ_{T_1} and ψ_{T_2} are valid solutions to Schrödinger's equation (Equation 1.6) and since ψ_S is a linear combination of these solutions it follows that ψ_S is also a valid solution. The same argument applies to ψ_A.

We will now examine just the spin parts of the wavefunctions for each electron. We need to consider all possible spin wavefunctions for the two electrons. The individual electron spin wavefunctions must be multiplied to obtain the spin part of the wavefunction for the two-electron system as indicated in Equations 1.8 or 1.9, and we obtain four possibilities, namely $\psi_{\frac{1}{2}}\psi_{-\frac{1}{2}}$ or $\psi_{-\frac{1}{2}}\psi_{\frac{1}{2}}$ or $\psi_{\frac{1}{2}}\psi_{\frac{1}{2}}$ or $\psi_{-\frac{1}{2}}\psi_{-\frac{1}{2}}$.

For the first two possibilities to satisfy the requirement that the spin part of the new two-electron wavefunction does not depend on which electron is which, a symmetric or an antisymmetric spin function is required. In the symmetric case we can use a linear combination of wavefunctions:

$$\psi = \frac{1}{\sqrt{2}}\left(\psi_{\frac{1}{2}}\psi_{-\frac{1}{2}} + \psi_{-\frac{1}{2}}\psi_{\frac{1}{2}}\right) \tag{1.12}$$

This is a symmetric spin wavefunction since changing the labels does not affect the result. The total spin for this symmetric system turns out to be $s = 1$, There is also an antisymmetric case for which

$$\psi = \frac{1}{\sqrt{2}}\left(\psi_{\frac{1}{2}}\psi_{-\frac{1}{2}} - \psi_{-\frac{1}{2}}\psi_{\frac{1}{2}}\right) \tag{1.13}$$

Here, changing the sign of the labels changes the sign of the linear combination but does not change any measurable properties and this is therefore also consistent with the requirements for a proper description of indistinguishable particles. In this antisymmetric system the total spin turns out to be $s = 0$.

The final two possibilities are symmetric cases since switching the labels makes no difference. These cases therefore do not require the use of linear combinations to be consistent with indistinguishability and are simply

$$\psi = \psi_{\frac{1}{2}}\psi_{\frac{1}{2}} \tag{1.14}$$

and

$$\psi = \psi_{-\frac{1}{2}}\psi_{-\frac{1}{2}} \tag{1.15}$$

These symmetric cases both have spin $s = 1$.

In summary, there are four cases, three of which, given by Equations 1.12, 1.14, and 1.15, are symmetric spin states and have total spin $s = 1$, and one of which, given by Equation 1.13, is antisymmetric and has total spin $s = 0$. Note that total spin is not always simply the sum of the individual spins of the two electrons, but must take into account the addition rules for quantum spin vectors. (See reference [1]) The three symmetric cases are appropriately called *triplet* states and the one antisymmetric case is called a *singlet* state. Table 1.1 lists the four possible states.

We must now return to the wavefunctions shown in Equations 1.10 and 1.11. The antisymmetric wavefunction ψ_A may be written using Equations 1.11, 1.8a and 1.9a as:

$$\begin{aligned}\psi_{\mathrm{A}} &= \frac{1}{\sqrt{2}}[\psi_{\mathrm{T}_1} - \psi_{\mathrm{T}_2}] \\ &= \frac{1}{\sqrt{2}}\{[\psi(x_1, y_1, z_1)\psi(S)]_{\mathrm{a}}[\psi(x_2, y_2, z_2)\psi(S)]_{\mathrm{b}} \\ &\quad -[\psi(x_1, y_1, z_1)\psi(S)]_{\mathrm{b}}[\psi(x_2, y_2, z_2)\psi(S)]_{\mathrm{a}}\}\end{aligned} \tag{1.16}$$

Table 1.1 *Possible spin states for a two-electron system*

State	Probability	Total Spin	Spin arrangement	Spin summetry	Spatial symmetry	Spatial attributes	Dipole-allowed transition to/from singlet ground state
Singlet	25%	0	$\psi_{\frac{1}{2}}\psi_{-\frac{1}{2}} - \psi_{-\frac{1}{2}}\psi_{\frac{1}{2}}$	Antisymmetric	Symmetric	Electrons close to each other	Yes
Triplet	75%	1	$\psi_{\frac{1}{2}}\psi_{-\frac{1}{2}} + \psi_{-\frac{1}{2}}\psi_{\frac{1}{2}}$ or $\psi_{\frac{1}{2}}\psi_{\frac{1}{2}}$ or $\psi_{-\frac{1}{2}}\psi_{-\frac{1}{2}}$	Symmetric	Antisymmetric	Electrons far apart	No

If, in violation of the Pauli exclusion principle, the two electrons were in the *same* quantum state $\psi_T = \psi_{T_1} = \psi_{T_2}$ which includes both position and spin, then Equation 1.16 immediately yields $\psi_A = 0$, which means that such a situation cannot occur. If the symmetric wavefunction ψ_S of Equation 1.10 was used instead of ψ_A, the value of ψ_S would not be zero for two electrons in the same quantum state. For this reason, a more complete statement of the Pauli exclusion principle is that *the wavefunction of a system of two or more indistinguishable electrons must be antisymmetric.*

In order to obtain an antisymmetric wavefunction, from Equation 1.16 either the spin part *or* the spatial part of the wavefunction may be antisymmetric. If the spin part is antisymmetric, which is a singlet state, then the Pauli exclusion restriction on the spatial part of the wavefunction may be lifted. The two electrons may occupy the same spatial wavefunction and they may have a high probability of being close to each other.

If the spin part is symmetric this is a triplet state and the spatial part of the wavefunction must be antisymmetric. The spatial density function of the antisymmetric wavefunction causes the two electrons to have a higher probability of existing further apart, because they are in distinct spatial wavefunctions.

If we now introduce the coloumb repulsion between the electrons it becomes evident that if the spin state is a singlet state, the repulsion will be higher because the electrons spend more time close to each other. If the spin state is a triplet state, the repulsion is weaker because the electrons spend more time further apart.

Now let us return to the helium atom as an example of this. Assume one helium electron is in the ground state of helium, which is the 1s state, and the second helium electron is in an excited state. This corresponds to an excited helium atom, and we need to understand this configuration because radiation always involves excited states.

The two helium electrons can be in a triplet state or in a singlet state. Strong dipole radiation is observed from the singlet state only, and the triplet states do not radiate. We can understand the lack of radiation from the triplet states by examining spin. The total spin of a triplet state is $s = 1$. The ground state of helium, however, has no net spin because if the two electrons are in the same $n = 1$ energy level the spins must be in opposing directions to satisfy the Pauli exclusion principle, and there is no net spin. The ground state of helium is therefore a singlet state. There can be no triplet states in the ground state of the helium atom.

There is a net magnetic moment generated by an electron due to its spin. This fundamental quantity of magnetism due to the spin of an electron is known as the *Bohr magneton.* If the two helium electrons are in a triplet state there is a net magnetic moment, which can be expressed in terms of the Bohr magneton since the total spin $s = 1$. This means that a magnetic moment exists in the excited triplet state of helium. Photons have no charge and hence no magnetic moment. Because of this a *dipole transition from an excited triplet state to the ground singlet state is forbidden* because the triplet state has a magnetic moment but the singlet state does not, and the net magnetic moment cannot be conserved. In contrast to this the *dipole transition from an excited singlet state to the ground singlet state is allowed* and strong dipole radiation is observed.

The triplet states of helium are slightly lower in energy than the singlet states. The triplet states involve symmetric spin states, which means that the spin parts of the wavefunctions are symmetric. This forces the spatial parts of the wavefunctions to be antisymmetric, as illustrated in Figure 1.8 and the electrons are, on average, more separated. As a result, the repulsion between the ground state electron and the excited state electron is weaker. The excited state electron is therefore more strongly bound to the nucleus and it exists in a lower energy state. The observed radiation is consistent with the energy difference between the higher energy singlet state and the ground singlet state. Direct, dipole-allowed radiation from the triplet excited state to the ground singlet state is forbidden. See Figure 1.9.

We have used helium atoms to illustrate the behavior of a two-electron system; however, we now need to apply our understanding of these results to molecular electrons, which are important for organic light emitting and absorbing materials. Molecules are the basis for organic electronic materials and molecules always contain two or more electrons in a molecular system.

1.6 Molecular Excitons

In inorganic semiconductors electrons and holes exist as distributed wavefunctions, which prevents the formation of stable excitons at room temperature. In contrast to this, holes and electrons are localized within a given molecule in *organic semiconductors*, and the *molecular exiton* is thereby both stabilized and bound within a molecule of the organic semiconductor. In organic semiconductors, which are composed of molecules, excitons are clearly evident at room temperature and also at higher operational device temperatures.

An exciton in an organic semiconductor is an excited state of the molecule. A molecule contains a series of electron energy levels associated with a series of *molecular orbitals* that are complicated to calculate directly from Schrödinger's equation because this is a multi-body problem. These molecular orbitals may be occupied or unoccupied. When a molecule absorbs a quantum of energy that corresponds to a transition from one molecular orbital to another higher energy molecular orbital, the resulting electronic excited state of the molecule is a molecular exciton comprising an electron and a hole within the molecule.

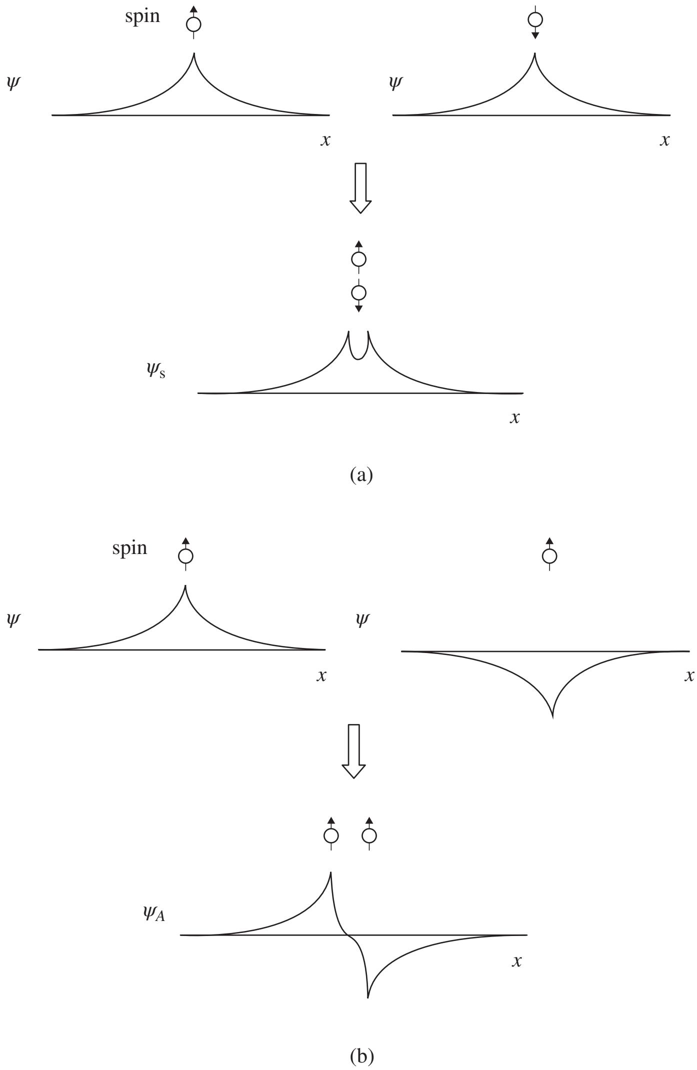


Figure 1.8 *A depiction of the symmetric and antisymmetric wavefunctions and spatial density functions of a two-electron system. (a) Singlet state with electrons closer to each other on average. (b) Triplet state with electrons further apart on average*

An electron is said to be found in the lowest unoccupied molecular orbital and a hole in the highest occupied molecular orbital, and since they are both contained within the same molecule the electron-hole state is said to be *bound.* A *bound exciton* results, which is spatially localized to a given molecule in an organic semiconductor. Organic molecule energy levels are relevant to OLEDs.

These molecular excitons can be classified as in the case of excited states of the helium atom, and either singlet or triplet excited states in molecules are possible. The results from Section 1.5 are relevant to these molecular excitons and the same concepts involving

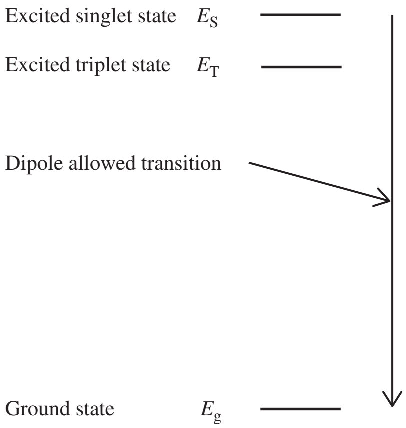


Figure 1.9 *Energy level diagram showing a ground state and excited singlet and triplet states. The excited triplet state is slightly lower in energy compared with the excited singlet state because two triplet state electrons are, on average, further apart than two singlet state electrons. Radiative emission from an electron in the excited singlet state to the ground singlet state is dipole-allowed. Radiative emission between the excited triplet state and the ground state requires an additional angular momentum exchange. See Section 1.6*

electron spin, the Pauli exclusion principle, and indistinguishability are relevant because the molecule contains two or more electrons.

If a molecule in its unexcited state absorbs a photon of light it may be excited forming an exciton in a singlet state with spin $s = 0$. These excited molecules typically have characteristic lifetimes on the order of nanoseconds, after which the excitation energy may be released in the form of a photon and the molecule undergoes *fluorescence* by a dipole-allowed process returning to its ground state.

It is also possible for the molecule to be excited to form an exciton by electrical means rather than by the absorption of a photon which is the situation in OLEDs.

Under electrical excitation the exciton may be in a singlet or a triplet state since electrical excitation, unlike photon absorption, does not require the total spin change to be zero. There is a 75% probability of a triplet exciton and 25% probability of a singlet exciton, as described in Table 1.1. The probability of fluorescence is therefore reduced under electrical excitation to 25% because the decay of triplet excitons is not dipole-allowed.

Another process may take place, however. Triplet, excitons have a spin state with $s = 1$ and these spin states can frequently be coupled with the orbital angular momentum of molecular electrons, which influences the effective magnetic moment of a molecular exciton. The restriction on dipole radiation can be partly removed by this coupling, and light emission over relatively long characteristic radiation lifetimes is observed in specific molecules. These longer lifetimes from triplet states are generally on the order of milliseconds and the process is called *phosphorescence*, in contrast with the shorter lifetime fluorescence from singlet states. Since excited triplet states have slightly lower energy levels than excited singlet states, triplet phosphorescence has a longer wavelength than singlet fluorescence in a given molecule (see Chapters 4 and 5).

In addition, there are other ways that a molecular exciton can lose energy. There are three possible energy loss processes that involve energy transfer from one molecule to another molecule. One important process is known as *Förster resonance energy transfer*. Here a molecular exciton in one molecule is established but a neighboring molecule is not initially excited. The excited molecule will establish an oscillating dipole moment as its exciton starts to decay in energy as a superposition state. The radiation field from this dipole is experienced by the neighboring molecule as an oscillating field and a superposition state in the neighboring molecule is also established. The originally excited molecule loses energy through this resonance energy transfer process to the neighboring molecule and finally energy is conserved since the initial excitation energy is transferred to the neighboring molecule *without the formation of a photon*. This is not the same process as photon generation and absorption since a complete photon is never created; however, only dipole-allowed transitions from excited singlet states can participate in Förster resonance energy transfer.

Förster energy transfer depends strongly on the intermolecular spacing, and the rate of energy transfer falls off as $\frac{1}{R^6}$ where R is the distance between the two molecules, A simplified picture of this can be obtained using the result for the electric field of a static dipole. This field falls off as $\frac{1}{R^3}$ Since the energy density in a field is proportional to the square of the field strength it follows that the energy available to the neighboring molecule falls of as $\frac{1}{R^6}$. This then determines the rate of energy transfer.

Dexter electron transfer is a second energy transfer mechanism in which an excited electron state transfers from one molecule (the donor molecule) to a second molecule (the acceptor molecule). This requires a wavefunction overlap between the donor and acceptor, which can only occur at extremely short distances typically of the order 10–20 Å.

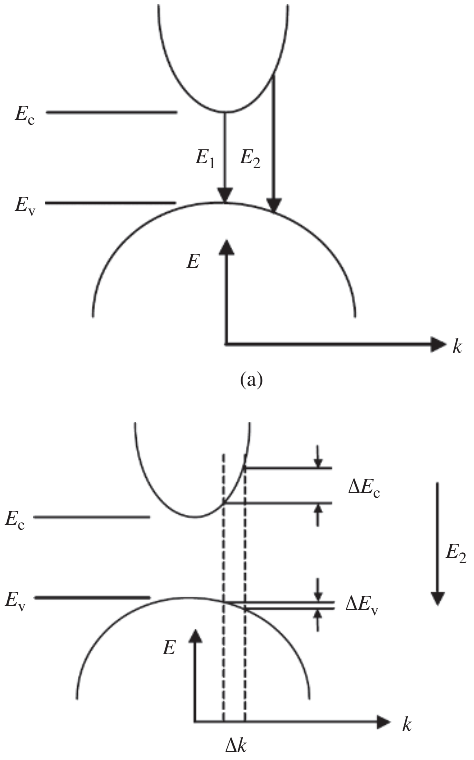
The Dexter process involves the transfer of the electron and hole from molecule to molecule. The donor's excited state may be exchanged in a single step, or in two separate charge exchange steps. The driving force is the decrease in system energy due to the transfer. This implies that the donor molecule and acceptor molecule are different molecules. This is relevant to a range of important OLED devices. The Dexter energy transfer rate is proportional to $e^{-\alpha R}$ where R is the intermolecular spacing. The exponential form is due to the exponential decrease in the wavefunction density function with distance.

Finally, a third process is radiative energy transfer. In this case a photon emitted by the host is absorbed by the guest molecule. The photon may be formed by dipole radiation from the host molecule and absorbed by the converse process of dipole absorption in the guest molecule.

1.7 Band-to-Band Transitions

In inorganic semiconductors the recombination between an electron and a hole occurs to yield a photon, or conversely the absorption of a photon yields a hole–electron pair. The electron is in the conduction band and the hole is in the valence band. It is very useful to analyze these processes in the context of band theory for inorganic semiconductor LEDs.

Consider the direct-gap semiconductor having approximately parabolic conduction and valence bands near the bottom and top of these bands, respectively, as in Figure 1.10. Two possible transition energies, E_1 and E_2, are shown, which produce two photons having



(a)

(b)

Figure 1.10 *(a) Parabolic conduction and valence bands in a direct-gap semiconductor showing two possible transitions. (b) Two ranges of energies* ΔE_v *in the valence band and* ΔE_c *in the conduction band determine the photon emission rate in a small energy range about a specific transition energy. Note that the two broken vertical lines in (b) show that the range of transition energies at* E_2 *is the sum of* ΔE_c *and* ΔE_v

two different wavelengths. Due to the very small momentum of a photon, the recombination of an electron and a hole occurs almost vertically in this diagram, to satisfy conservation of momentum. The x-axis represents the wavenumber k, which is proportional to momentum.

Conduction band electrons have energy

$$E_e = E_c + \frac{\hbar^2 k^2}{2m_e^*}$$

and for holes we have:

$$E_h = E_v - \frac{\hbar^2 k^2}{2m_h^*}$$

In order to determine the emission/absorption spectrum of a direct-gap semiconductor we need to find the probability of a recombination taking place as a function of energy E. This transition probability depends on an appropriate density of states function multiplied by probability functions that describe whether or not the states are occupied.

We will first determine the appropriate density of states function. Any transition in Figure 1.10 takes place at a fixed value of reciprocal space where k is constant. The same set of points located in reciprocal space or k-space gives rise to states both in the valence band and in the conduction band. In our picture of energy bands plotted as E versus k, a given position on the k-axis intersects all the energy bands including the valence and conduction bands. There is therefore a state in the conduction band corresponding to a state in the valence band at a specific value of k.

Therefore, in order to determine the *photon emission rate* over a specific range of photon energies we need to find the appropriate density of states function for a *transition* between a group of states in the conduction band and the corresponding group of states in the valence band. This means we need to determine the number of states in reciprocal space or k-space that give rise to the corresponding set of transition, energies that can occur over a small radiation energy range ΔE centred at some transition energy in Figure 1.10. For example, the appropriate number of states can be found at E_2 in Figure 1.10b by considering a small range of k-states Δk that correspond to small differential energy ranges ΔE_c and ΔE_v and then finding the total number of band states that fall within the range ΔE. The emission energy from these states will be centred at E_2 and will have an emission energy range $\Delta E = \Delta E_c + \Delta E_v$ producing a portion of the observed emission spectrum. The *density of transitions* is determined by the density of states in the *joint dispersion relation,* which will now be introduced.

The available energy for any transition is given by:

$$E(k) = hv = E_e(k) - E_h(k)$$

and upon substitution we can obtain the joint dispersion relation, which adds the dispersion relations from both the valence and conduction bands. We can express this transition energy E and determine the joint dispersion relation from Figure 1.10a as:

$$E(k) = hv = E_c - E_v + \frac{\hbar^2 k^2}{2m_e^*} + \frac{\hbar^2 k^2}{2m_h^*} = E_g + \frac{\hbar^2 k^2}{2\mu} \tag{1.17}$$

where

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

Note that a range of k-states Δk will result in an energy range $\Delta E = \Delta E_c + \Delta E_v$ in the joint dispersion relation because the joint dispersion relation provides the *sum* of the relevant ranges of energy in the two bands as required. The smallest possible value of transition energy E in the joint dispersion relation occurs at $k = 0$ where $E = E_g$ from Equation 1.17 which is consistent with Figure 1.10. If we can determine the density of states in the joint dispersion relation, we will therefore have the density of possible photon emission transitions available in a certain range of energies.

The density of states function for an energy conduction band is:

$$D(E) = \frac{1}{2}\pi \left(\frac{2m^*}{\pi^2 \hbar^2} \right)^{\frac{3}{2}} \sqrt{E}$$

We can formulate a *joint density of states* function by substituting μ in place of m^*.

Recognizing that the density of states function must be zero for $E < E_g$ we obtain:

$$D_{\mathrm{joint}}(E) = \frac{1}{2}\pi\left(\frac{2\mu}{\pi^2\hbar^2}\right)^{\frac{3}{2}}(E - E_g)^{\frac{1}{2}} \tag{1.18}$$

This is known as the *joint density of states* function valid for $E \geq E_g$.

To determine the probability of occupancy of states in the bands, we use Fermi–Dirac statistics. The Boltzmann approximation for the probability of occupancy of carriers in a conduction band is:

$$F(E) \cong \exp\left[-\frac{(E_e - E_f)}{kT}\right]$$

and for a valence band the probability of a hole is given by:

$$1 - F(E) \cong \exp\left[\frac{(E_h - E_f)}{kT}\right]$$

Since a transition requires both an electron in the conduction band and a hole in the valence band, the probability of a transition will be proportional to:

$$F(E)[1 - F(E)] = \exp\left(-\frac{(E_e - E_h)}{kT}\right) = \exp\left(-\frac{E}{kT}\right) \tag{1.19}$$

Including the density of states function, we conclude that the probability $p(E)$ of an electron–hole pair recombination applicable to an LED is proportional to the product of the joint density of states function and the function $F(E)[1 - F(E)]$, which yields:

$$p(E) \propto D(E - E_g)F(E)[1 - F(E)] \tag{1.20}$$

Now using Equations 1.18, 1.19, and 1.20, we obtain the photon emission rate $R(E)$ as:

$$R(E) \propto (E - E_g)^{1/2}\exp\left(-\frac{E}{kT}\right) \tag{1.21}$$

The result is shown graphically in Figure 1.11.

If we differentiate Equation 1.21 with respect to E and set $\frac{\mathrm{d}R(E)}{\mathrm{d}E} = 0$ the maximum is found to occur at $E = E_g + \frac{kT}{2}$. From this, we can evaluate the full width at half maximum to be $1.8kT$.

If we were interested in optical absorption instead of emission for a direct gap semiconductor, the absorption constant α can be evaluated using Equation 1.18 and we obtain:

$$\alpha(hv) \propto (hv - E_g)^{\frac{1}{2}} \tag{1.22}$$

We consider the valence band to be fully occupied by electrons and the conduction band to be empty. In this case the absorption rate depends on the joint density of states function only and is independent of Fermi–Dirac statistics. The absorption edge for a direct gap semiconductor is illustrated in Figure 1.12.

This absorption edge is only valid for direct gap semiconductors, and only when parabolic band-shapes are valid. If $hv \gg E_g$ this will not be the case and measured absorption coefficients will differ from this theory.

In an indirect gap semiconductor, the absorption α increases more gradually with photon energy hv until a direct gap transition can occur.

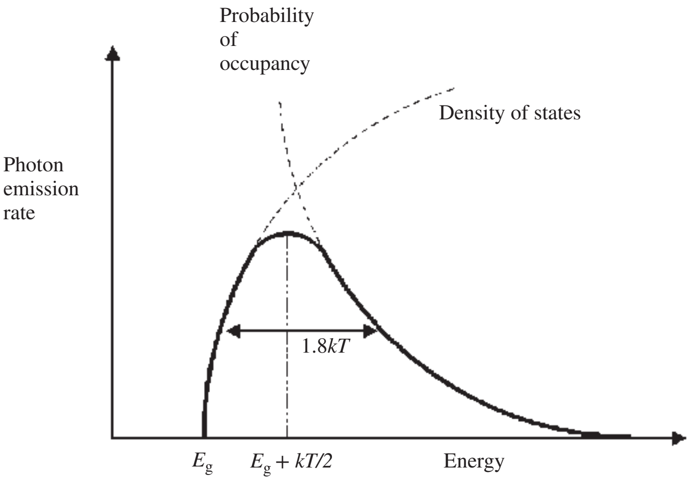


Figure 1.11 *Photon emission rate as a function of energy for a direct gap transition of an LED. Note that at low energies the emission drops off due to the decrease in the density of states term* $(E - E_g)^{\frac{1}{2}}$ *and at high energies the emission drops off due to the Boltzmann term* $\exp(-E/kT)$

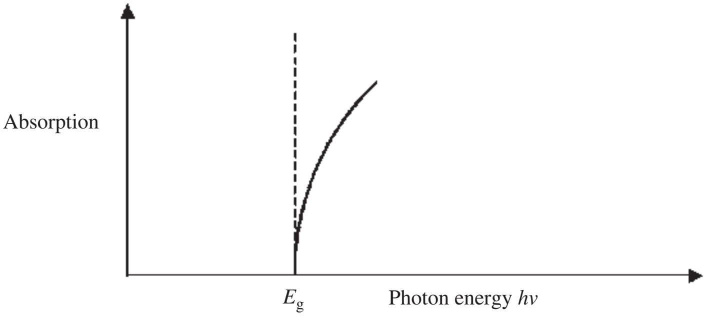


Figure 1.12 *Absorption edge for a direct gap semiconductor*

1.8 Photometric Units

The most important applications of LEDs and OLEDs are for visible illumination and displays. This requires the use of units to measure the brightness and color of light output. The power in watts and wavelength of emission are often not adequate descriptors of light emission. The human visual system has a variety of attributes that have given rise to more appropriate units and ways of measuring light output. This human visual system includes the eye, the optic nerve and the brain, which interpret light in a unique way. Watts, for example, are considered *radiometric* units, and this section introduces *photometric* units and relates them to radiometric units.

Luminous intensity is a photometric quantity that represents the perceived brightness of an optical source by the human eye. The unit of luminous intensity is the *candela* (cd).

One cd is the luminous intensity of a source that emits 1/683 watt of light at 555 nm into a solid angle of one steradian. The candle was the inspiration for this unit, and a candle does produce a luminous intensity of approximately 1 cd.

Luminous flux is another photometric unit that represents the light power of a source. The unit of luminous flux is the *lumen* (lm). A candle that produces a luminous intensity of 1 cd produces 4π lumens of light power. If the source is spherically symmetrical then there are 4π steradians in a sphere, and a luminous flux of 1 lm is emitted per steradian.

A third quantity, *luminance*, refers to the luminous intensity of a source divided by an area through which the source light is being emitted; it has units of cd m^{-2}. In the case of an LED *die* or semiconductor chip light source the luminance depends on the size of the die. The smaller the die that can achieve a specified luminous intensity, the higher the luminance of this die.

The advantage of these units is that they directly relate to perceived brightnesses, whereas radiation measured in watts may be visible, or invisible depending on the emission spectrum. Photometric units of luminous intensity, luminous flux and luminance take into account the relative sensitivity of the human vision system to the specific light spectrum associated with a given light source.

The eye sensitivity function is well known for the average human eye. Figure 1.13 shows the perceived brightness for the human visual system of a light source that emits a constant

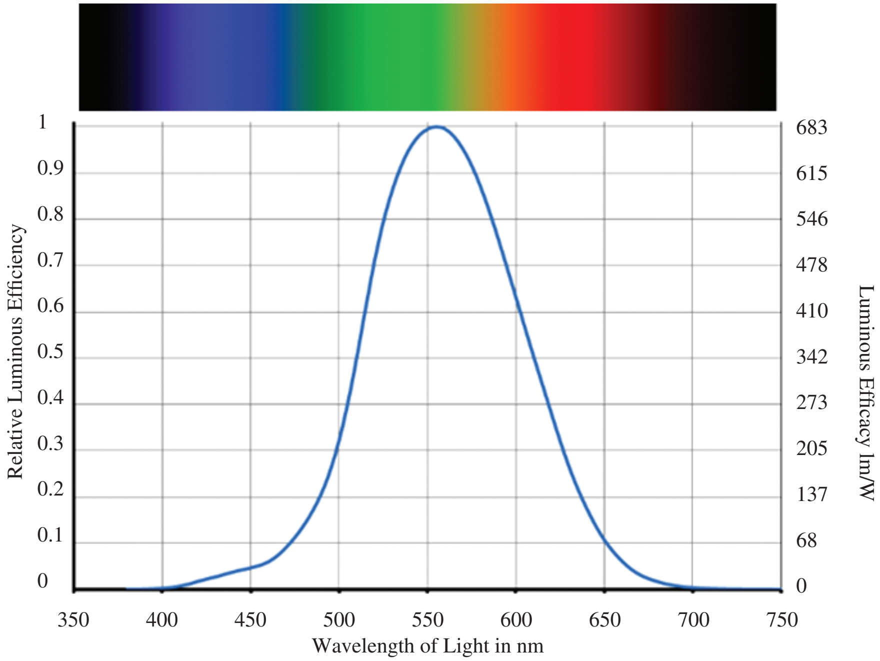


Figure 1.13 *The eye sensitivity function. The left scale is referenced to the peak of the human eye response at 555 nm. The right scale is in units of luminous efficacy. International Commission on Illumination (Commission Internationale de l'Eclairage, or CIE), 1931 and 1978*

optical power that is independent of wavelength. The left scale has a maximum of 1 and is referenced to the peak of the human eye response at 555 nm. The right scale is in units of *luminous efficacy* (lm W^{-1}), which reaches a maximum of 683 lm W^{-1} at 555 nm. Using Figure 1.13, luminous intensity can now be determined for other wavelengths of light.

An important measure of the overall efficiency of a light source can be obtained using luminous efficacy from Figure 1.13. A hypothetical monochromatic electroluminescent light source emitting at 555 nm that consumes 1 W of electrical power and produces 683 lm has an electrical-to-optical conversion efficiency of 100%. A hypothetical monochromatic light source emitting at 450 nm that consumes 1 W of electrical power and produces approximately 30 lm also has a conversion efficiency of 100%. The luminous flux of a blue LED or a red LED that consumes 1 W of electric power may be lower than for a green LED; however, this does not necessarily mean that they are less efficient.

Luminous efficiency values for a number of light sources may be described in units of lm W^{-1}, or light power divided by electrical input power. Luminous efficiency can never exceed luminous efficacy for a light source having a given spectrum.

The perceived color of a light source is determined by its spectrum. The human visual system and the brain create our perception of color. For example, we perceive a mixture of red and green light as yellow even though none of the photons arriving at our eyes is yellow.

The human eye contains light receptors on the retina that are sensitive in fairly broad bands centred at the red, the green and the blue parts of the visible spectrum. Color is determined by the relative stimulation of these receptors. For example, a light source consisting of a combination of red and green light excites the red and green receptors, as does a pure yellow light source, and we therefore perceive both light sources as yellow in color.

Since the colors we observe are perceptions of the human visual system, a color space has been developed and formalized that allows all the colors we recognize to be represented on a two-dimensional graph called the *colour space chromaticity* diagram (Figure 1.14). The diagram was created by the International Commission on Illumination (Commission Internationale de l'Éclairage, or CIE) in 1931, and is therefore often referred to as the CIE diagram. CIE *x* and *y color coordinates* are shown that can be used to specify the color point of any light source. The outer boundary of this color space refers to monochromatic light sources that emit light at a single wavelength. As we move to the center of the diagram to approach white light the light source becomes increasingly less monochromatic. Hence a source having a spectrum of a finite width will be situated some distance inside the boundary of the color space.

If two light sources emit light at two distinct wavelengths anywhere on the CIE diagram and these light sources are combined into a single light beam, the human eye will interpret the color of the light beam as existing on a straight line connecting the locations of the two sources on the CIE diagram. The position on the straight line of this new color will depend on the relative radiation power from each of the two light sources.

If three light sources emit light at three distinct wavelengths that are anywhere on the CIE diagram and these light sources are combined into a single light beam, the human eye will interpret the color of the light beam as existing within a triangular region of the CIE diagram having vertices at each of the three sources. The position within the triangle of this

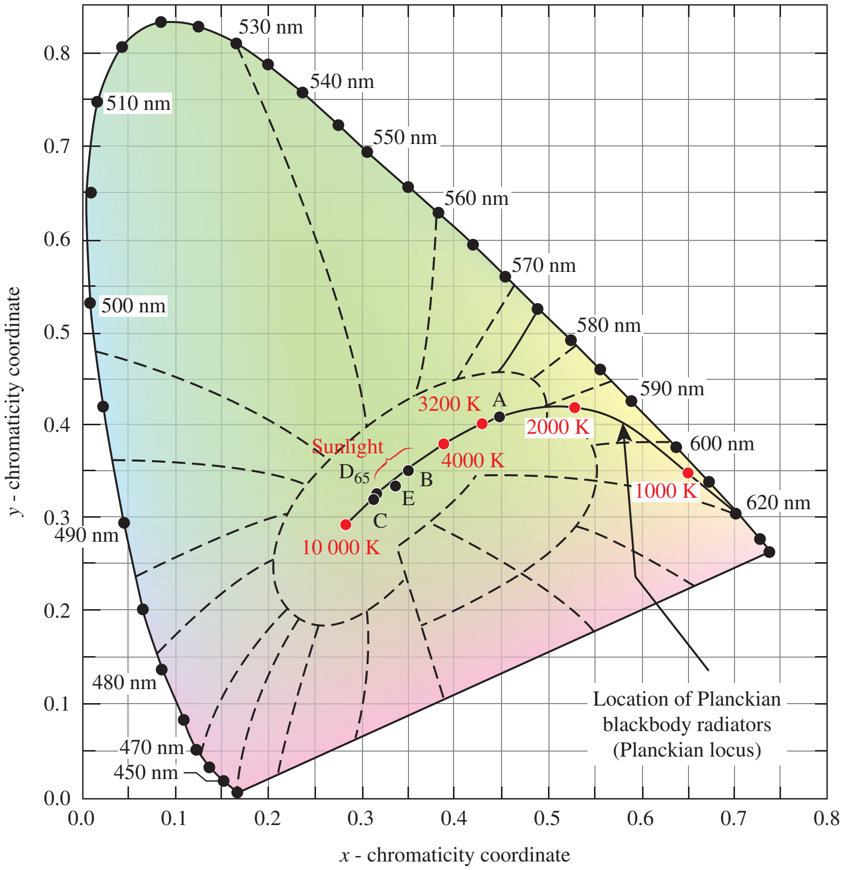


Figure 1.14 *Color space chromaticity diagram showing colors perceptible to the human eye. The center region of the diagram indicates a Planckian locus, which corresponds to the colors of emission from a blackbody source having temperatures from 1000 to 10 000 K. This locus includes the solar spectrum corresponding to a 5250 K blackbody. International Commission on Illumination (Commission Internationale de l'Eclairage, or CIE), 1931*

new color will depend on the relative radiation power from each of the three light sources. This ability to produce a large number of colors of light from only three light sources forms the basis for *trichromatic* illumination. Lamps and displays routinely take advantage of this principle. It is clear that the biggest triangle will be available if red, green and blue light sources are selected to define the vertices of the color triangle. This colour triangle is often referred to as a *color space* that is enabled by a specific set of three light emitters.

The Planckian blackbody locus is also shown in Figure 1.14. All the color points on this line represent a blackbody source of a specific given temperature. For example, a point at approximately 5000 K represents the color of the sun. A tungsten filament lamp with a filament temperature of 3000 K is also a point on this line.

Name	Appr. Munsell	Appearance under daylight	Swatch
TUS01	7,5 R 6/4	Light grayish red	🟥
TUS02	5 Y 6/4	Dark grayish yellow	🟫
TCS03	5 GY 6/8	Strong yellow green	🟩
TCS04	2,5 G 6/6	Moderate yellowish green	🟩
TCS05	10 BG 6/4	Light bluish green	🟦
TCS06	5 PB 6/8	Light blue	🟦
TCS07	2,5 P 6/8	Light violet	🟪
TCS08	10 P 6/8	Light reddish purple	🟪

Figure 1.15 *Eight standard color samples used to determine the colour rendering index*

The colors on this Planckian locus are important since they are used as reference spectra for non-blackbody light emitters such as LEDs. A measure used to quantify the closeness of an LED spectrum to a blackbody radiator is the color rendering index or CRI. Appropriately named, a CRI value indicates how well a given light source can substitute for a blackbody source in terms of illuminating a wide range of colored or pigmented objects.

The highest CRI of a light source is 100 indicating a perfect blackbody spectrum. Lamps achieving CRI values between 90 and 100 are considered “museum grade” lamps and may be used to view art, color samples, and pigments with a high degree of accuracy. For more general illumination tasks a CRI between 80 and 90 is often considered adequate.

The CRI is calculated by comparing the color rendering of the source in question to that of a blackbody radiator for sources with correlated color temperatures under 5000 K, and a phase of daylight otherwise (e.g., D65). The procedure makes use of a set of standard test color samples shown in Figure 1.15.

A simplified summary of the steps used to determine the CRI are as follows:

1. Find the chromaticity coordinates of the test source in the CIE 1960 color space. The CIE 1960 color space is a modified version of the color space in Figure 1.14.
2. Determine the correlated color temperature (CCT) of the test source by finding the closest point to the Planckian locus on the chromaticity diagram.
3. If the test source has a CCT<5000 K, use a blackbody for reference, otherwise use CIE standard illuminant D65 (daylight) shown in Figure 1.14. Both sources should have the same CCT.
4. Illuminate the first eight standard samples shown in Figure 1.15.
5. Find the coordinates of the light reflected by each sample in the CIE 1964 color space using the test source and again using the reference source.
6. For each sample, calculate the distance ΔE in CIE color space between the two sets of color coordinates.
7. For each sample, calculate the special CRI using the formula $R = 100 - 4.6\Delta E$.
8. Find the general CRI by calculating the arithmetic mean of the special CRIs.

1.9 The Light Emitting Diode

The most important means of achieving electron–hole pair recombination producing radiation is via a p-n junction diode. In this section the key concepts underlying p-n junction operation are summarized and for reference, detailed quantitative treatments are available [1–4].

First we will consider the case of a diode in equilibrium without a current or voltage applied to it. The band model of a p-n junction is shown in Figure 1.16. A built-in electric field exits at the diode junction and this field gives rise to a potential difference V_0 across the junction.

In the conduction band, equal and opposite electron currents flow comprising an electron drift current due to the built-in electric field and an opposing electron diffusion current due to the large concentration gradient of electrons across the junction. Similarly, in the valence band, equal and opposite hole currents flow comprising a hole drift current due to the built-in electric field and an opposing hole diffusion current due to the large concentration gradient of holes across the junction. The net diode current is zero.

If a potential V is now applied to the diode the built-in electric field is modified. A positive value of V which is described as a forward bias decreases the built-in electric field as shown in Figure 1.17. This results in an increase of diffusion current relative to drift current and a rapid and approximately exponential increase in net diode current occurs as V increases.

If the applied voltage is negative, then the built-in electric field increases as shown in Figure 1.18. This results in a larger potential barrier that favors drift current but not diffusion current. A net drift current flows but the drift current is small since it is only supplied by the small minority carrier concentration of electrons in the p-side and the small minority concentration of holes in the n-side of the diode. This drift current, being supply limited, saturates with increasingly negative applied voltage.

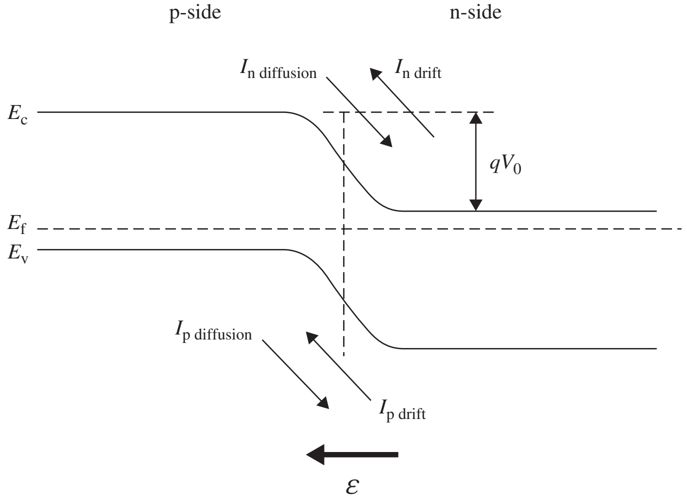


__Figure 1.16__ Band diagram of a p-n junction in equilibrium showing hole and electron currents. The net current is zero. V_0 is the built-in potential of the junction

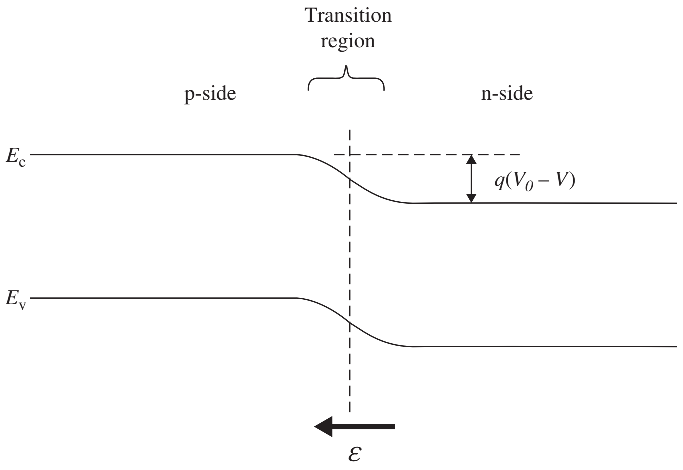


Figure 1.17 *Band diagram of p-n junction with positive bias voltage V applied. The junction potential is decreased and a net diffusion current flows*

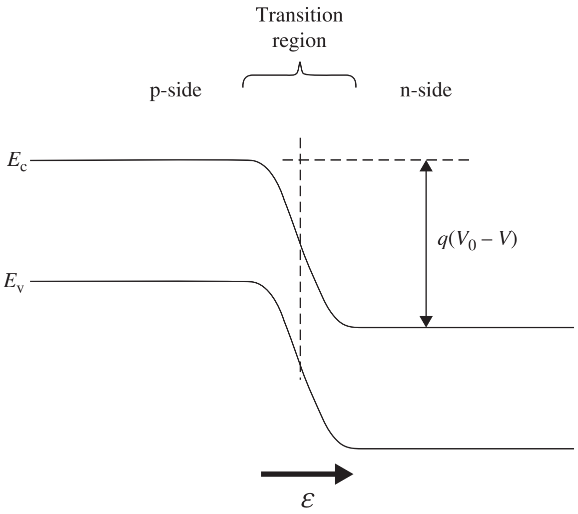


Figure 1.18 *Band diagram of p-n junction with negative bias voltage V applied. The junction potential is increased and a net drift current flows*

The resulting current–voltage characteristic of the diode is shown in Figure 1.19.

The relationship describing the curve in Figure 1.19 may be expressed using the diode equation given by:

$$I = qA\left(\frac{D_n}{L_n}n_p + \frac{D_p}{L_p}p_n\right)\left(e^{qV/kT} - 1\right)$$

where A is the junction area, D_n and D_p are the diffusion constants of electrons and holes, respectively, L_n and L_p are the diffusion lengths of electrons and holes, respectively, and

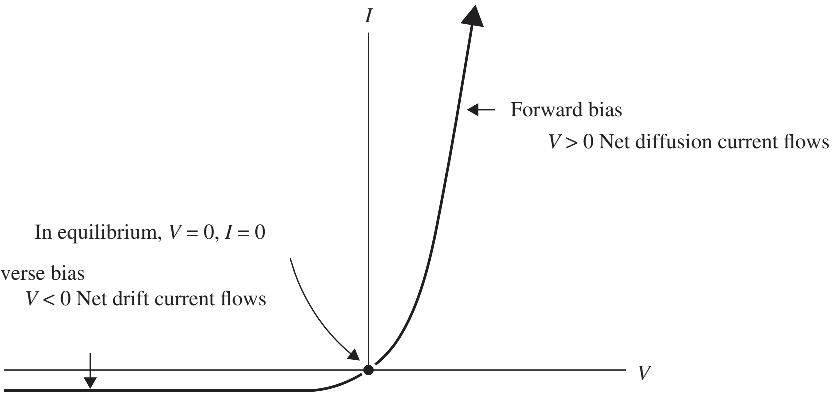


Figure 1.19 *Resulting current–voltage characteristic of a diode showing an approximately exponentially increasing forward current and a saturated reverse bias current*

n_p and p_n are the minority carrier concentrations in the p-side and n-side of the diode, respectively.

In an LED, a forward bias is applied which results in a net diffusion current. Once majority carriers diffuse across the junction into the opposite side of the diode they become minority carriers and are subject to recombination with majority carriers. This recombination process produces photons and since the 1960s, semiconductors and device structures have been developed to optimize this process resulting in today's high performance LEDs (see Chapter 7).

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