From the quantum form of equation (7.9) and equation (8.14), taking the Gaunt factors as unity,

$$\frac{\mathcal{P}_m^{\text{ph}}}{\mathcal{P}_m} \approx \frac{2e_2}{m kT_e}. \quad (8.15)$$

This result indicates that at lower temperatures the continuum radiation associated with free electrons tends to be dominated by free-bound radiation.

**Exercise 8.1.** Using the principle of detailed balancing, derive the expression (II 9.21) for the photoionization cross section.

### 9. LINE RADIATION (BOUND-BOUND EMISSION)

Bohr's interpretation of the structure of line spectra in terms of transitions between discrete energy levels in atoms, as described in Sec. II 4, represented a milestone in the development of modern quantum theory. The emission by atomic systems of radiation energy at sharply defined frequencies is inherently quantum mechanical in nature, and we can expect classical theory to
provide only a qualitative description, at best. From the classical point of view, we would be led to interpret the appearance of radiation at discrete frequencies as associated with the harmonics of a periodic system. If the period of the system is $\tau = 2\pi \omega_0^{-1}$, then the average power radiated by the system during a period is

$$P = \frac{1}{\tau} \int_0^\tau P(t) \, dt = \frac{1}{6\pi \epsilon_0 c^2} \frac{1}{\tau} \int_0^\tau |d(t)|^2 \, dt,$$  

(9.1)

where $P(t)$, the instantaneous power, is given by equation (6.11). We must proceed next to identify how this radiation is distributed among the harmonic frequencies of the system.

For a periodic system, the dipole moment of the system can be expanded in a Fourier series

$$d(t) = \sum_{l=-\infty}^{\infty} d_l e^{-i\omega_0 lt}, \quad \omega_0 = 2\pi \omega_0 \quad \text{for} \quad l = 1, 2, 3, \ldots,$$

(9.2)

and therefore

$$d(t) = \sum_{l=-\infty}^{\infty} -\omega_l^2 d_l e^{-i\omega_0 lt},$$  

(9.3)

where $\omega_l = l\omega_0$ is the frequency of the $l$th harmonic. Because $d(t)$ is real, the complex conjugate $d_l^*$ of the Fourier coefficient $d_l$ must equal $d_{-l}^*$. Multiplying equation (9.2) by itself, we obtain the double series

$$|d(t)|^2 = \sum_{l=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \omega_l^2 \omega_k^2 d_l^* d_k e^{-i\omega_0 (l+k)t}.$$  

Using the relation

$$\frac{1}{\tau} \int_0^\tau e^{-i\omega_0 (l+k)t} \, dt = \delta_{k,-l},$$

we have

$$\frac{1}{\tau} \int_0^\tau |d(t)|^2 \, dt = \sum_{l=-\infty}^{\infty} \omega_l^2 \omega_{-l}^2 d_l^* d_{-l} = 2 \sum_{l=1}^{\infty} \omega_l^2 |d_l|^2,$$

and thus equation (9.1) may be written

$$\bar{P} = \sum_{l=1}^{\infty} P_l.$$  

(9.4)

*The quantity $\delta_{k,-l}$ is the Kronecker delta; it is equal to unity for $k = -l$, and to zero otherwise.*
According to classical theory, we are therefore led to interpret the expression
\[ P_l = \frac{\omega_l}{3\pi \epsilon_0 c^3} \cdot \frac{16\pi^3 \nu_l^2}{3\epsilon_0 c^3} \]  
(9.5)
as the power radiated at the frequency \( \nu_l \).

According to quantum theory, line emission results when an atomic particle experiences a spontaneous transition from an upper energy level \( \epsilon_l \) to a lower level \( \epsilon_k \). The frequency of the emitted radiation is \( \nu_{lk} = (\epsilon_l - \epsilon_k)/\hbar \).

The emission process is statistical in nature and is described in terms of a quantity \( A_{lk} \), the Einstein A coefficient, defined such that
\[ A_{lk} \, dt \]is the probability that the particle will decay spontaneously in a time \( dt \) from level \( l \) to \( k \) [see equation (II 9.15c)]. Since the energy expected to be emitted in the time \( dt \) is \( h\nu_{lk} A_{lk} \, dt \) the quantum theory expression for the power radiated at the frequency \( \nu_{lk} \) is
\[ P(l \rightarrow k) = h\nu_{lk} A_{lk}. \]  
(9.7)

By identifying the two expressions (9.5) and (9.7), we may expect to obtain an approximate estimate of \( A_{lk} \). It is clear that in equation (9.5) we should replace \( \nu_l \) with \( \nu_{lk} \). We should also replace \( d_l \) with a quantity \( d_{lk} \) that depends on the two levels involved in the transition. On the basis of the present argument there is no way of knowing what \( d_{lk} \) is in detail, but for an atomic system it is reasonable to estimate the order of magnitude of \( |d_{lk}| \) as
\[ |d_{lk}| \sim e\alpha, \]  
(9.8)
where \( \alpha \) is the radius of the first Bohr orbit [see equation (II 4.7)]. From equations (9.5) and (9.7), we obtain
\[ A_{lk} = \frac{16\pi^3 \nu_{lk}^2}{3\epsilon_0 c^3 \hbar}, \]  
(9.9)
and using (9.8),
\[ A_{lk} \sim \frac{32\pi^3 e^2}{3} \frac{4\pi \epsilon_0}{\hbar c} \left( \frac{a_0}{c} \right)^2 \nu_{lk}^2 \]
\[ \sim 7.50 \times 10^{-38} \nu_{lk}^2 \, \text{sec}^{-1}. \]  
(9.10)
For a typical optical frequency \( \nu_{lk} \sim 0.6 \times 10^{15} \, \text{sec}^{-1}, \)
\[ A_{lk} \sim 2 \times 10^7 \, \text{sec}^{-1}. \]  
(9.11)

The accurate calculation of the quantity \( d_{lk} \) appearing in equation (9.9) must be done using quantum theory. It turns out, somewhat surprisingly,
that the form of the quantum theory result is identical to equation (9.9). The quantity $d'_{l k}$ can be written as $e x_{l k}$, where $x_{l k}$ is a so-called matrix element for the transition and depends on an integral involving the wave functions of the $l$ and $k$ levels.

**Exercise 9.1.** Derive a relation connecting the frequency of electromagnetic radiation emitted in a transition between two adjacent levels of a Bohr atom and the orbital frequency of the electron in one of these levels. Study this relation in the limit of large quantum numbers and comment on its correspondence with the predictions of classical physics.

**Exercise 9.2.** Determine the ratio of the power emitted in a transition between two adjacent high-lying levels of a Bohr atom to the power radiated classically by an electron in an orbit corresponding to one of these levels. Express your answer in the simplest possible terms. (Suggestion: Employ the result of the previous exercise and Exercise II 9.2.)

**Exercise 9.3.** The ratio of the emitted intensities from two Balmer lines in hydrogen (i.e., lines terminating in the level with principal quantum number 2) originating from levels with principal quantum numbers 5 and 3, respectively, is measured and is found to be 0.088. Assuming the gas is optically thin for these lines and that the gas is in thermodynamic equilibrium, determine the gas temperature.

**Exercise 9.4.** Consider a potassium-seeded plasma at 2500 K containing $10^{17}$ unexcited K atoms/cm$^3$. The Einstein $A$ coefficient for a spontaneous transition from the $3D_{3/2}$ level to the $4P_{1/2}$ level is $2.1 \times 10^7$ sec$^{-1}$. Assuming absorption and induced emission are negligible and that the gas is in thermodynamic equilibrium calculate, the power emitted per cm$^3$ in the line radiation corresponding to this transition. The following additional information may be required for this calculation: The energies above the ground level ($4S_{1/2}$) for the $3D_{3/2}$ and $4P_{1/2}$ levels are 2.68 and 1.61 eV, respectively. The statistical weights for the $3D_{3/2}$, $4P_{1/2}$, and $4S_{1/2}$ levels are 4, 2, and 2, respectively.

### 10. LINE SHAPE

With optical instruments of sufficiently high resolving power, line radiation is observed to be not strictly monochromatic, as the name might suggest, but to exhibit a variation of intensity with frequency over a relatively narrow frequency interval. The mechanisms which contribute to this variation with frequency, or line shape, are discussed in Sec. II 9 in the context of absorption, but they apply as well to emission. In this section we