

Chapter 16

Scattering of Photons by Atoms

16.1 Introduction

Scattering of photons by free and bound electrons takes place through the latter's interaction with the photon field. The relevant Hamiltonian is given by

$$\begin{aligned} H &= \frac{1}{2m}(\vec{p} - e\vec{A})^2 + V_a = \frac{p^2}{2m} + V_a - \frac{e}{m}\vec{A} \cdot \vec{p} + \frac{e^2 A^2}{2m} \\ &= H_a - \frac{e\vec{A} \cdot \vec{p}}{m} + \frac{e^2 A^2}{2m} \end{aligned} \quad (16.1)$$

where $H_a = \frac{p^2}{2m} + V_a$ describes the atom and as already mentioned in the previous chapter the two terms containing vector potential cause scattering of photon by the atom. Scattering is a two step process-incident photon causes electrons to get excited which on de-excitation emits photons with either the same energy but different momentum or with both different energy and momentum. The former is called elastic scattering and the latter inelastic scattering. This process is caused by the term $\frac{e\vec{A} \cdot \vec{p}}{m}$ containing both photon field \vec{A} and electron momentum \vec{p} . One uses time dependant perturbation

theory which is second order in this term. The term $\frac{e^2 A^2}{2m}$ also gives rise to scattering for which first order perturbation theory is of the same order of smallness as the second order theory for $\frac{e\vec{A}\vec{p}}{m}$ term.

Scattering of photon by a recoil-less heavy unbound charged particle will be treated in Section 2 using first order perturbation in $\frac{e^2 A^2}{2m}$ term. This will give rise to well known the Thomson scattering. Scattering by electron bound in atoms will be treated in Section 3 using second order perturbation in the $\frac{\vec{A}\vec{p}}{m}$ term. This will result in the Kramers-Heisenberg dispersion formula from which the inelastic Raman scattering will follow and will be taken up in Section 3. Scattering can be considered as absorption of the incident photon followed by emission of the scattered photon. If one considers the related process whereby the atom emits a virtual photon ($\omega^2 - k^2 \neq 0$) which is subsequently absorbed, one obtains the line shift (Lamb shift) and line width as its real and imaginary parts. Details of this will be given in the next chapter.

16.2 Scattering of Photon by Free Electron

In this section we consider scattering of photon by free electron considered as recoilless. The initial and final states in the scattering of photon by an infinitely heavy recoil-less electron are

$$|i\rangle = |\vec{k}, \vec{\epsilon}_{\vec{k}}\rangle, \quad |f\rangle = |\vec{k}', \vec{\epsilon}_{\vec{k}'}\rangle, \quad (16.2)$$

where \vec{k} and \vec{k}' are incident and scattered photon and $\vec{\epsilon}$ and $\vec{\epsilon}_{k'}$ are their polarization vectors. Since the electron does not recoil $\omega_k = \omega_{k'}$. The perturbing potential that causes the scattering is

$$V^{(s)} = \frac{e^2 \vec{A} \cdot \vec{A}}{2m} \quad c = 1 \quad (16.3)$$

The matrix element of this potential between initial and final states is

$$V_{fi}^{(s)} = \frac{e^2}{2m\omega_k} \vec{\epsilon}_{\vec{k}'} \cdot \vec{\epsilon}_{\vec{k}} e^{i(\vec{k}-\vec{k}')\vec{x}}, \quad (16.4)$$

where we have taken

$$\vec{A}_{\vec{k}}(x) = \frac{\epsilon_{\vec{k}} e^{i\vec{k}\cdot\vec{x}-i\omega t}}{\sqrt{2\omega_k}} + c.c. \quad (16.5)$$

Making use of Fermi Golden rule, we have, for the transition probability per unit time

$$dW_{fi} = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f = \frac{2\pi}{\hbar} |V_{fi}|^2 \frac{\vec{k}'^2 d\Omega_{\vec{k}'}}{(2\pi)^3}. \quad (16.6)$$

We have to sum over all final states to get cross-section for which we make use of the identity

$$\sum_{\vec{\epsilon}_{\vec{k}'}} \vec{\epsilon}_{\vec{k}} \cdot \vec{\epsilon}_{\vec{k}'} = 1 - \frac{(\vec{k}' \cdot \epsilon_{\vec{k}})^2}{(\vec{k}')^2}, \quad (16.7)$$

so that

$$\sum_{\vec{\epsilon}_{\vec{k}}} \sum_{\vec{\epsilon}_{\vec{k}'}} \vec{\epsilon}_{\vec{k}'} \cdot \vec{\epsilon}_{\vec{k}} = \frac{1}{2}(1 + \cos^2 \theta). \quad (16.8)$$

The differential and total cross-sections so obtained are

$$\frac{d\sigma}{d\Omega} = \frac{r_o^2}{2}(1 + \cos^2 \theta) \quad , \quad \sigma = \frac{8\pi}{3} r_o^2 = 6.65 \times 10^{-25} \text{cm}^2, \quad (16.9)$$

where

$$r_o = \frac{e^2}{4\pi m}, \quad (16.10)$$

is the classical radius of the electron. Formula (16.9) was obtained by J.J. Thomson

16.3 Scattering of Photon by Bound Electron

In the previous section the interaction term giving rise to scattering of photon by free electron did not contain any electron operators and was suited to the

problem where the electron, which was considered infinitely heavy, did not change its energy; the photon momentum changed its direction only. For the case of an electron bound to the nucleus, both its energy and momentum can change. Therefore the interaction term $e\vec{A} \cdot \vec{p}/m$ has to be used in second order of perturbation, matrix element V_{fi} for which is,

$$\begin{aligned}
 V_{fi} &= \frac{e^2}{m^2} \sum_n \frac{A_j(\vec{k}') \langle f | p'_j | n \rangle \langle n | p_l | i \rangle A_l(\vec{k})}{E_i + \omega_k - E_n} \\
 &+ \frac{e^2}{m^2} \sum_n \frac{A_j(\vec{k}) \langle f | p_j | n \rangle \langle n | p'_l | i \rangle A_l(\vec{k}')}{E_i + \omega_k - E_n} \\
 &= \frac{e^2}{2m^2} \frac{1}{\sqrt{\omega_k \omega_{k'}}} \sum_n \left[\frac{(\vec{\epsilon}(\vec{k}') \cdot \vec{p}'_{fn})(\vec{\epsilon}(\vec{k}) \cdot \vec{p}_{ni})}{E_i + \omega_k - E_n} + \frac{(\vec{\epsilon}(\vec{k}) \cdot \vec{p}_{fn})(\vec{\epsilon}(\vec{k}') \cdot \vec{p}'_{ni})}{E_i - \omega'_k - E_n} \right].
 \end{aligned} \tag{16.11}$$

This identity can be brought to a convenient form by employing the following kinematics

$$\begin{aligned}
 \vec{p} &= m\vec{x} = im[H, \vec{x}], \\
 \vec{p}_{fn} &= im\omega_{fn}\vec{x}_{fn}.
 \end{aligned} \tag{16.12}$$

Further, using

$$[x_i, p_j] = i\delta_{ij} \quad , \quad [x_i, x_j] = 0, \tag{16.13}$$

we have

$$\begin{aligned}
 (\vec{\epsilon}(\vec{k}') \cdot \vec{x}) (\vec{\epsilon}(\vec{k}) \cdot \vec{p}) - (\vec{\epsilon}(\vec{k}) \cdot \vec{p}) (\vec{\epsilon}(\vec{k}') \cdot \vec{x}) &= i\vec{\epsilon}_{k'} \cdot \vec{\epsilon}_k, \\
 (\vec{\epsilon}(\vec{k}') \cdot \vec{x}) (\vec{\epsilon}(\vec{k}) \cdot \vec{x}) - (\vec{\epsilon}(\vec{k}) \cdot \vec{x}) (\vec{\epsilon}(\vec{k}') \cdot \vec{x}) &= 0.
 \end{aligned} \tag{16.14}$$

$$E_f - E_i = \omega_k - \omega_{k'} \tag{16.15}$$

using (16.12), (16.13), (16.14) and (16.15) we finally get

$$V_{fi} = \frac{e^2}{2} \sqrt{\omega_k \omega_{k'}} \sum_n \frac{(\vec{\epsilon}(\vec{k}') \cdot \vec{x}_{fn}) (\vec{\epsilon}(\vec{k}) \cdot \vec{x}_{ni})}{E_i + \omega_k - E_n} + \frac{(\vec{\epsilon}(\vec{k}) \cdot \vec{x}_{fn}) (\vec{\epsilon}(\vec{k}') \cdot \vec{x}_{ni})}{E_i - \omega'_k - E_n} \tag{16.16}$$

and

$$\begin{aligned} \frac{dW_{fi}}{d\Omega} = & \left(\frac{e^2}{4\pi} \right)^2 \omega_k \omega_{k'}^3 \left| \sum_n \frac{(\vec{\epsilon}(\vec{k}') \cdot \vec{x}_{fn}) (\vec{\epsilon}(\vec{k}) \cdot \vec{x}_{ni})}{E_i + \omega_k - E_n} \right. \\ & \left. + \frac{(\vec{\epsilon}(\vec{k}) \cdot \vec{x}_{fn}) (\vec{\epsilon}(\vec{k}') \cdot \vec{x}_{ni})}{E_i - \omega_k - E_n} \right| \end{aligned} \quad (16.17)$$

This is the Kramer's-Heisenberg (dispersion) formula. It is to be noted that the energy denominators in both the terms in this formula can be written as $(E_f - E_n)$ where in the first term $E_f = E_i + \omega_k$ and in the second term $E_f = E_i - \omega_{k'}$. Therefore when $\omega_k = \omega_{k'}$, $E_f = E_i$ i.e., the initial and final states of the atom are same. This elastic scattering is called Rayleigh scattering. When $\omega_k \neq \omega_{k'}$, there arise two cases, (a) when $\omega_{k'} > \omega_k$ and (b) when $\omega_k > \omega_{k'}$. In the former, the scattered photon has greater energy than incident photon which means the photon has gained energy of amount $(\omega_{k'} - \omega_k) > 0$ which in turn means $E_f < E_i$ because total energy of the atom and photon must be conserved in the scattering process. This is called Raman scattering. In the latter case when $E_f > E_i$ the atom has gained energy and is called Stokes scattering which happens normally. The former unusual case was observed for the first time by C.V. Raman in liquids and Landsberg and Mandelshtam in crystals.

References and Sources

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2. J.J. Thomson, "Conduction of Electricity through Gases", 3rd edition, (Cambridge University Press, 1933) Vol. II p. 256.

3. C.V. Raman, *ind. Journ. Phys.* **2**, 387 (1928); G.S. Landsberg and L.I. Mandelshtam, *Naturwiss* **16**, 557 (1928).