Theoretical physics V
Sheet 12

SoSe 2025 **25.06.2025**

Exercise 1 *Time-independent Perturbation Theory*

In this exercise, we consider a generic Hamiltonian of the form $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{W}$, where the eigenstates $|\Psi_{0,n}\rangle$ and eigenvalues $E_{0,n}$ of $\hat{H}_0$ are known. In particular, we assume here a non-degenerate spectrum of $\hat{H}_0$, that is, $E_{0,n} \neq E_{0,m}$ if $n \neq m$. The operator $\lambda\hat{W}$ is considered a perturbation with dimensionless parameter $\lambda \ll 1$. In the following, we derive the first (λ^1) and second order (λ^2) corrections to the eigenenergies $E_{0,n}$ arising from the perturbation. To this end, we expand the eigenstates $|\Psi_n(\lambda)\rangle$ and eigenenergies $E_n(\lambda)$ of the Hamiltonian $\hat{H}(\lambda)$ – all functions of the parameter λ – in a power series:

$$|\Psi_n(\lambda)\rangle = \sum_{j=0}^{\infty} \lambda^j |\Psi_n^{(j)}\rangle \quad \text{and} \quad E_n(\lambda) = \sum_{j=0}^{\infty} \lambda^j E_n^{(j)} \,. \tag{1}$$

a) Considering the eigenvalue equation $\hat{H}(\lambda)|\Psi_n(\lambda)\rangle = E_n(\lambda)|\Psi_n(\lambda)\rangle$, show that the zeroth-order equation (λ^0) corresponds to the eigenvalue equation of the unperturbed Hamiltonian $\hat{H}_0$. Verify by means of this that $|\Psi_n^{(0)}\rangle \equiv |\Psi_{0,n}\rangle$ and $E_n^{(0)} \equiv E_{0,n}$. *(1 point)*

b) Using the expansions (1), derive from the eigenvalue equation of $\hat{H}(\lambda)$ expressions for the correction to the energy $E_n^{(1)}$ and the state $|\Psi_n^{(1)}\rangle$ to first order in λ. *(1 point)*

c) Derive further the second-order (λ^2) correction to the energy $E_n^{(2)}$. *(2 points)*

Exercise 2 *Light-matter interaction: Rayleigh and Thomson scattering*

During the lectures, you broached the topic of light-matter interaction with a focus on light-emission by matter (spontaneous emission) and the renormalization of the mass of electrons by quantum fluctuations (Lamb shift). Here, we propose to go one step further by exploring the quantum description of the scattering of light by matter. More precisely, we will focus on the Rayleigh and Thomson regimes of light-scattering.

a) Attached to the exercise sheet, you can find an extract of the textbook "Advanced Quantum Mechanics" by J. J. Sakurai (Chapter 2 - Section 5, pages 47-53). Using the information contained in this material, prepare a short presentation to be realized at the blackboard. You are expected to present the derivation of the Kramers-Heisenberg formula before applying it to the Rayleigh regime.

(6 points)

b) Present also the case of the Thomson scattering.

(2 points)

Notes:

- In the reference, Sakurai uses a formulation of electrodynamics in terms of the Lorentz units. In this system of units, the Maxwell equations take the form

$$\boldsymbol{\nabla}\cdot\boldsymbol{E}=\rho \;\;;\;\; \boldsymbol{\nabla}\times\boldsymbol{E}=-\frac{1}{c}\frac{\partial\boldsymbol{B}}{\partial t}$$
$$\boldsymbol{\nabla}\cdot\boldsymbol{B}=0 \;\;;\;\; \boldsymbol{\nabla}\times\boldsymbol{B}=\frac{1}{c}\boldsymbol{j}+\frac{1}{c}\frac{\partial\boldsymbol{E}}{\partial t}.$$

- In this framework, the minimal coupling Hamiltonian reads

$$\hat{H}=\frac{1}{2m}\left(\boldsymbol{p}-\frac{q}{c}\boldsymbol{A}\right)^2+q\phi,$$

  where ϕ stands for the electric potential, while $\boldsymbol{A}$ is the vector potential such that $\boldsymbol{E}=-\boldsymbol{\nabla}\phi-\frac{1}{c}\partial_t\boldsymbol{A}$ and $\boldsymbol{B}=\boldsymbol{\nabla}\times\boldsymbol{A}$.

- Therefore, for an atomic electron, the interaction with light is taken into account via a perturbative term of the form

$$\hat{H}_{\text{int}}=-\frac{q}{2mc}\left(\boldsymbol{p}\cdot\boldsymbol{A}+\boldsymbol{A}\cdot\boldsymbol{p}\right)+\frac{q^2}{2mc^2}\boldsymbol{A}\cdot\boldsymbol{A}.$$

- We shall note the equivalence between the notation used by Sakurai and the one used in the lecture for

$$|1_\lambda\rangle\equiv|\boldsymbol{k},\epsilon^{(a)}\rangle$$

  where $\lambda\equiv(\boldsymbol{k},\epsilon^{(a)})$.

- In Sakurai's book, equation (2.124) gives the following relation

$$\langle B|\boldsymbol{p}|A\rangle=\frac{im}{\hbar}\langle B|[H_0,\boldsymbol{x}]|A\rangle=-\frac{im(E_B-E_A)}{\hbar}\langle B|\boldsymbol{x}|A\rangle$$

- We remind the definition of the diffraction function

$$\delta^{(T)}(E_f-E_i)=\frac{1}{2\pi\hbar}\int_{-T/2}^{T/2}\mathrm{d}\tau e^{i(E_f-E_i)\tau/\hbar}.$$

  Therefore, for a system perturbed by an interaction $\hat{V}$, up to second order in perturbation theory the elements of the scattering matrix take the form

$$S_{fi}(t)=\delta_{fi}-2\pi i\left[V_{fi}+\lim_{\eta\to0^+}\sum_k\frac{V_{fk}V_{ki}}{E_i-E_k+i\eta}\right]\delta^{(t)}(E_f-E_i),$$

  with $V_{fi}=\langle f|\hat{V}|i\rangle$.

It is instructive to compare our derivation of Planck's law with Einstein's 1917 derivation.‡ They are both based on thermal equilibrium between the atoms and the radiation field. In Einstein's derivation the principle of detailed balance is *explicitly* invoked; by contrast, in our derivation the physics of detailed balance is contained in (2.153) which is an automatic consequence of the hermiticity of the Hamiltonian used in the quantum theory of radiation. Note also that in our derivation we do not distinguish between the contributions from spontaneous emission and induced emission.

Although our attention has been focused in this section on the radiative transitions between two atomic states, the techniques we have acquired can readily be applied to a host of other phenomena. For instance, the reader may calculate the cross section for the photoelectric effect (Problem 2–4) or the lifetime of the Σ^0 hyperon (Problem 2–5):

$$\Sigma^0 \xrightarrow{\mathscr{H}'} \Lambda + \gamma.$$

2-5. RAYLEIGH SCATTERING, THOMSON SCATTERING, AND THE RAMAN EFFECT

Kramers-Heisenberg formula. Let us now examine the field-theoretic treatment of the scattering of photons by atomic electrons. Before the scattering, the atom is in state A, and the incident photon is characterized by $(\mathbf{k}, \boldsymbol{\epsilon}^{(\alpha)})$. After the scattering, the atom is left in state B, and the outgoing photon is characterized by $(\mathbf{k}', \boldsymbol{\epsilon}^{(\alpha')})$. For simplicity let us again consider a one-electron atom and neglect the spin-magnetic-moment interaction.

The interaction Hamiltonian (2.94) is made up of a linear $(\mathbf{A}\cdot\mathbf{p})$ term and a quadratic $(\mathbf{A}\cdot\mathbf{A})$ term. Since $\mathbf{A}$ changes the number of photons by one, $\mathbf{A}\cdot\mathbf{p}$ makes no contribution in first order to a scattering process in which there is no *net* change in the number of photons. On the other hand, the $\mathbf{A}\cdot\mathbf{A}$ term contains $aa^\dagger$, $a^\dagger a$, $a\,a$, and $a^\dagger a^\dagger$, the first two of which *do* give nonvanishing contributions provided that $a^\dagger$ and a, respectively, represent the creation operator for $(\mathbf{k}', \alpha')$ and the annihilation operator for $(\mathbf{k}, \alpha)$, e.g., $\langle \mathbf{k}', \alpha' | a_{\mathbf{k},\alpha} a^\dagger_{\mathbf{k}',\alpha'} | \mathbf{k}, \alpha\rangle = 1$. Hence

$$\begin{aligned}
&\langle B; \mathbf{k}', \boldsymbol{\epsilon}^{(\alpha')} | H_{\text{int}} | A; \mathbf{k}, \boldsymbol{\epsilon}^{(\alpha)}\rangle \\
&\quad = \langle B; \mathbf{k}', \boldsymbol{\epsilon}^{(\alpha')} \left| \frac{e^2}{2mc^2} \mathbf{A}(\mathbf{x}, t)\cdot\mathbf{A}(\mathbf{x}, t) \right| A; \mathbf{k}, \boldsymbol{\epsilon}^{(\alpha)}\rangle \\
&\quad = \langle B; \mathbf{k}', \boldsymbol{\epsilon}^{(\alpha')} \left| \frac{e^2}{2mc^2} (a_{\mathbf{k},\alpha} a^\dagger_{\mathbf{k}',\alpha'} + a^\dagger_{\mathbf{k}',\alpha'} a_{\mathbf{k},\alpha}) \frac{c^2\hbar}{2V\sqrt{\omega\omega'}} \boldsymbol{\epsilon}^{(\alpha)}\cdot\boldsymbol{\epsilon}^{(\alpha')} \right. \\
&\qquad\qquad \times \exp[i(\mathbf{k} - \mathbf{k}')\cdot\mathbf{x} - i(\omega - \omega')t] | A; \mathbf{k}, \boldsymbol{\epsilon}^{(\alpha)}\rangle \\
&\quad = \frac{e^2}{2mc^2} \frac{c^2\hbar}{2V\sqrt{\omega\omega'}} 2\boldsymbol{\epsilon}^{(\alpha)}\cdot\boldsymbol{\epsilon}^{(\alpha')} \exp[-i(\omega - \omega')t] \langle B | A\rangle, \qquad (2.158)
\end{aligned}$$

‡See, for example, Kittel (1958), pp. 175–176.

where we have replaced $e^{i\mathbf{k}\cdot\mathbf{x}}$ and $e^{-i\mathbf{k}'\cdot\mathbf{x}}$ by 1, since in the long-wave approximation the atomic electron may be assumed to be situated at the origin. For the first-order transition amplitude $c^{(1)}(t)$ we have

$$c^{(1)}(t) = \frac{1}{i\hbar}\frac{e^2}{2mc^2}\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}2\delta_{sH}\epsilon^{(\alpha)}\cdot\epsilon^{(\alpha')}\int_0^t \exp\left[i(\hbar\omega' + E_B - \hbar\omega - E_A)t_1/\hbar\right]dt_1, \tag{2.159}$$

with $\omega = |\mathbf{k}|c$ and $\omega' = |\mathbf{k}'|c$ as usual.

Although the $\mathbf{A}\cdot\mathbf{p}$ term makes no contribution in first order, the $\mathbf{A}\cdot\mathbf{p}$ term taken *twice* is of the same order as the $\mathbf{A}\cdot\mathbf{A}$ term, so far as powers of e are concerned. Therefore we must treat a double $\mathbf{A}\cdot\mathbf{p}$ interaction and a single $\mathbf{A}\cdot\mathbf{A}$ interaction simultaneously. The $\mathbf{A}\cdot\mathbf{p}$ interaction acting at t_1 can either annihilate the incident photon $(\mathbf{k}, \alpha)$ or create the outgoing photon $(\mathbf{k}', \alpha')$. When the $\mathbf{A}\cdot\mathbf{p}$ interaction acts again at a time t_2 which is later than t_1 it must necessarily create the outgoing photon $(\mathbf{k}', \alpha')$ if the outgoing photon has not yet been created. Otherwise we would end up with a zero matrix element. On the other hand, if the outgoing photon has already been created but the incoming photon has not yet been annihilated, the $\mathbf{A}\cdot\mathbf{p}$ interaction acting at $t_2 > t_1$ must annihilate the incoming photon $(\mathbf{k}, \alpha)$. Between t_1 and t_2 the atom is in state I which is, in general, different from A and B. To summarize, two types of intermediate states are possible. In the first type the atom is in state I and no photons are present. In the second type the atom is in state I and both the incident and the outgoing photon are present.‡

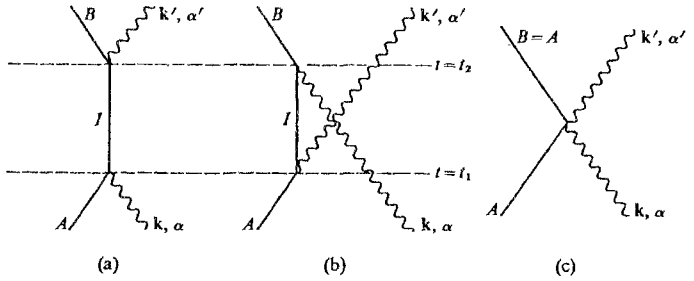

Fig. 2–2. Space-time diagram for scattering of light.

All this can best be visualized if we draw a space-time diagram (Feynman diagram) in which a solid line represents the atom, and a wavy line represents a photon. Time is assumed to run upward (Fig. 2–2). For a type 1 process, represented by Fig. 2–2(a), the atomic state A first absorbs the incident photon at t_1 and becomes state I; subsequently at t_2 the atomic state I emits the outgoing photon and changes

‡Strictly speaking, we should also consider the case where I stands for a continuum state. The relevant matrix element then corresponds to a photo-effect matrix element (cf. Problem 2–4). In practice such "distant" intermediate states are not important because the energy denominators become large (cf. Eq. 2.160 below).

into state B. For a type 2 process, represented by Fig. 2–2(b), state A first emits the outgoing photon at t_1 and changes into state I; subsequently at t_2 state I absorbs the incident photon (which has not yet been annihilated) and becomes state B. In contrast, the lowest-order $\mathbf{A}\cdot\mathbf{A}$ interaction, discussed earlier, is represented by Fig. 2–2(c) ("seagull graph").

As emphasized in the previous section, the emission and absorption of a photon by an atomic electron are equivalent to interactions of the atomic electron with the time-dependent potentials (2.102). Using this rule, we can readily write down the second-order transition amplitude $c^{(2)}(t)$ as follows:

$$\begin{aligned} c^{(2)}(t) &= \frac{1}{(i\hbar)^2}\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}\left(-\frac{e}{mc}\right)^2\int_0^t dt_2\int_0^{t_2} dt_1 \\ &\quad\times\Big[\sum_I \langle B\,|\,\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')}\,|\,I\rangle \exp\left[i(E_B - E_I + \hbar\omega')t_2/\hbar\right] \\ &\quad\times\langle I\,|\,\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)}\,|\,A\rangle \exp\left[i(E_I - E_A - \hbar\omega)t_1/\hbar\right] \\ &\quad+\sum_I \langle B\,|\,\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)}\,|\,I\rangle \exp\left[i(E_B - E_I - \hbar\omega)t_2/\hbar\right] \\ &\quad\times\langle I\,|\,\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')}\,|\,A\rangle \exp\left[i(E_I - E_A + \hbar\omega')t_1/\hbar\right] \\ &= -\frac{c^2\hbar}{i\hbar 2V\sqrt{\omega\omega'}}\left(\frac{e}{mc}\right)^2\sum_I\left(\frac{(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')})_{BI}(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)})_{IA}}{E_I - E_A - \hbar\omega} + \frac{(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)})_{BI}(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')})_{IA}}{E_I - E_A + \hbar\omega'}\right) \\ &\quad\times\int_0^t dt_2 \exp\left[i(E_B - E_A + \hbar\omega' - \hbar\omega)t_2/\hbar\right], \end{aligned} \tag{2.160}$$

where we have made the dipole approximation and ignored a term that depends on the artificial sudden turning of the perturbation (which is negligible if the energy conservation, $E_B - E_A + \hbar\omega' - \hbar\omega = 0$, is nearly satisfied). Combining $c^{(1)}(t)$ and $c^{(2)}(t)$, we have the transition probability

$$\begin{aligned} w_{d\Omega} &= \int (|c^{(1)} + c^{(2)}|^2/t)\rho_{E,d\Omega}\,dE \\ &= \frac{2\pi}{\hbar}\left(\frac{c^2\hbar}{2V\sqrt{\omega\omega'}}\right)^2\left(\frac{e^2}{mc^2}\right)^2\frac{V}{(2\pi)^3\hbar c^3}\omega'^2\,d\Omega \\ &\times\left|\delta_{AB}\boldsymbol{\epsilon}^{(\alpha)}\cdot\boldsymbol{\epsilon}^{(\alpha')} - \frac{1}{m}\sum_I\left(\frac{(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')})_{BI}(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)})_{IA}}{E_I - E_A - \hbar\omega} + \frac{(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)})_{BI}(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')})_{IA}}{E_I - E_A + \hbar\omega'}\right)\right|^2. \end{aligned} \tag{2.161}$$

To obtain the differential cross section we must divide this transition probability by the flux density which is just c/V, since initially there is one photon in the normalization box of volume V. Finally, we have for the differential cross section

$$\begin{aligned} \frac{d\sigma}{d\Omega} = r_0^2\left(\frac{\omega'}{\omega}\right)\Big|\delta_{AB}\boldsymbol{\epsilon}^{(\alpha)}\cdot\boldsymbol{\epsilon}^{(\alpha')} - \frac{1}{m}\sum_I\Big(&\frac{(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')})_{BI}(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)})_{IA}}{E_I - E_A - \hbar\omega} \\ &+ \frac{(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)})_{BI}(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')})_{IA}}{E_I - E_A + \hbar\omega'}\Big)\Big|^2, \end{aligned} \tag{2.162}$$

where r_0 stands for the classical radius of the electron, and

$$r_e = \frac{e^2}{4\pi mc^2} \simeq \frac{1}{137}\frac{\hbar}{mc} \simeq 2.82\times 10^{-13}\ \text{cm}. \tag{2.163}$$

A formula equivalent to (2.162) was first obtained by H. A. Kramers and W. Heisenberg using the correspondence principle in 1925; hence it is called the Kramers-Heisenberg formula.

Rayleigh scattering. There are certain special cases of (2.162) worth examining in detail. Let us first discuss the case in which $A = B$, $\hbar\omega = \hbar\omega'$. This situation corresponds to elastic scattering of light. It is also called Rayleigh scattering because this problem was treated classically by Lord Rayleigh. To simplify (2.162) we rewrite $\epsilon^{(\alpha)}\cdot\epsilon^{(\alpha')}$, using the commutation relation between x and $\mathbf{p}$, the completeness of the intermediate states I, and (2.124):‡

$$\begin{aligned}\epsilon^{(\alpha)}\cdot\epsilon^{(\alpha')} &= \frac{1}{i\hbar}\sum_I [(\mathbf{x}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha')})_{IA} - (\mathbf{p}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{x}\cdot\epsilon^{(\alpha')})_{IA}] \\ &= \frac{1}{m\hbar}\sum_I \frac{1}{\omega_{IA}}[(\mathbf{p}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha')})_{IA} + (\mathbf{p}\cdot\epsilon^{(\alpha')})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha)})_{IA}] \quad (2.164)\end{aligned}$$

where $\omega_{IA} = (E_I - E_A)/\hbar$. We now see that the three terms in (2.162) combine so that

$$\begin{aligned}&\delta_{AA}\epsilon^{(\alpha)}\cdot\epsilon^{(\alpha')} - \frac{1}{m\hbar}\sum_I \left[\frac{(\mathbf{p}\cdot\epsilon^{(\alpha')})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha)})_{IA}}{\omega_{IA}-\omega} + \frac{(\mathbf{p}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha')})_{IA}}{\omega_{IA}+\omega}\right] \\ &\quad = -\frac{1}{m\hbar}\sum_I \left[\frac{\omega(\mathbf{p}\cdot\epsilon^{(\alpha')})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha)})_{IA}}{\omega_{IA}(\omega_{IA}-\omega)} - \frac{\omega(\mathbf{p}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha')})_{IA}}{\omega_{IA}(\omega_{IA}+\omega)}\right]. \quad (2.165)\end{aligned}$$

Using the expansion $1/(\omega_{IA} \mp \omega) \approx [1 \pm (\omega/\omega_{IA})]/\omega_{IA}$, valid for small values of ω, and

$$\begin{aligned}&\sum_I \frac{1}{\omega_{IA}^2}[(\mathbf{p}\cdot\epsilon^{(\alpha')})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha)})_{IA} - (\mathbf{p}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha')})_{IA}] \\ &\quad = m^2\sum_I [(\mathbf{x}\cdot\epsilon^{(\alpha')})_{AI}(\mathbf{x}\cdot\epsilon^{(\alpha)})_{IA} - (\mathbf{x}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{x}\cdot\epsilon^{(\alpha')})_{IA}] \\ &\quad = m^2([\mathbf{x}\cdot\epsilon^{(\alpha')}, \mathbf{x}\cdot\epsilon^{(\alpha)}])_{AA} \\ &\quad = 0, \quad (2.166)\end{aligned}$$

we obtain the Rayleigh cross section for $\omega \ll \omega_{IA}$:

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \left(\frac{r_0}{m\hbar}\right)^2\omega^4\left|\sum_I\left(\frac{1}{\omega_{IA}}\right)^2[(\mathbf{p}\cdot\epsilon^{(\alpha')})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha)})_{IA} + (\mathbf{p}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{p}\cdot\epsilon^{(\alpha')})]_{IA}\right|^2 \\ &= \left(\frac{r_0 m}{\hbar}\right)^2\omega^4\left|\sum_I\left(\frac{1}{\omega_{IA}}\right)[(\mathbf{x}\cdot\epsilon^{(\alpha')})_{AI}(\mathbf{x}\cdot\epsilon^{(\alpha)})_{IA} + (\mathbf{x}\cdot\epsilon^{(\alpha)})_{AI}(\mathbf{x}\cdot\epsilon^{(\alpha')})_{IA}]\right|^2. \quad (2.167)\end{aligned}$$

Thus we see that *the scattering cross section at long wavelengths varies as the inverse fourth power of the wavelength* (Rayleigh's law). For atoms in ordinary colorless gases the light wave corresponding to a typical ω_{IA} is in the ultraviolet region.

‡The intermediate states I form a complete set only when we include the continuum states as well as the discrete (bound) states.

Hence the approximation $\omega \ll \omega_{I,I}$ is good for ω in the visible optical region. This theory explains why the sky is blue and the sunset is red.

Thomson scattering. Let us now consider the opposite case in which the incident photon energy is much larger than the atomic binding energy. It is then legitimate to ignore the second and third term of (2.162), since $\hbar\omega(=\hbar\omega')$ is much larger than $(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha')})_{II}(\mathbf{p}\cdot\boldsymbol{\epsilon}^{(\alpha)})_{I,I}/m$, so the scattering is due solely to the matrix element corresponding to the "seagull graph" (Fig. 2–2c). Now the $\delta_{II}\boldsymbol{\epsilon}^{(\alpha)}\cdot\boldsymbol{\epsilon}^{(\alpha')}$ term is insensitive to the nature of the binding of the atomic electron. The cross section we compute in this case coincides with the cross section for the scattering of light by a free (unbound) electron, first obtained classically by J. J. Thomson:

$$\frac{d\sigma}{d\Omega} = r_0^2 |\boldsymbol{\epsilon}^{(\alpha)}\cdot\boldsymbol{\epsilon}^{(\alpha')}|^2. \tag{2.168}$$

Note that this expression is independent of ω.

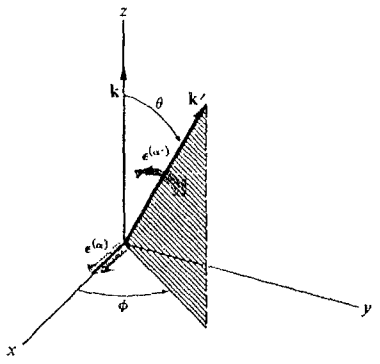

Fig. 2-3. Polarization in Thomson scattering.

To study the polarization dependence of Thomson scattering we consider a coordinate system in which $\boldsymbol{\epsilon}^{(\alpha)}$ and $\mathbf{k}$ are taken along the x-and the z-axes respectively, as shown in Fig. 2-3. The orientation of $\mathbf{k}'$ is characterized by the spherical coordinate angles θ and ϕ. The final polarization vector $\boldsymbol{\epsilon}^{(\alpha')}$ may be taken to be *normal* to the shaded plane (the plane determined by $\mathbf{k}$ and $\mathbf{k}'$) for $\alpha' = 1$; $\boldsymbol{\epsilon}^{(\alpha')}$ with $\alpha' = 2$ must then lie *in* the shaded plane. The Cartesian components of $\boldsymbol{\epsilon}^{(\alpha')}$ are given by

$$\boldsymbol{\epsilon}^{(\alpha')} = \begin{cases} (\sin\phi, -\cos\phi, 0) & \text{for } \alpha' = 1, \\ (\cos\theta\cos\phi, \cos\theta\sin\phi, -\sin\theta) & \text{for } \alpha' = 2. \end{cases} \tag{2.169}$$

Hence

$$\frac{d\sigma}{d\Omega} = r_0^2 \begin{cases} \sin^2\phi & \text{for } \alpha' = 1, \\ \cos^2\theta\cos^2\phi & \text{for } \alpha' = 2. \end{cases} \tag{2.170}$$

For initially unpolarized photons we may either integrate (2.170) over the angle ϕ and divide by 2π or evaluate

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{unpolarized}} = \frac{1}{2}\left[\frac{d\sigma}{d\Omega}(\phi = 0) + \frac{d\sigma}{d\Omega}\left(\phi = \frac{\pi}{2}\right)\right]. \tag{2.171}$$

The two procedures are completely equivalent. Note that even if the initial polarization vector is randomly oriented, the final photon emitted with $\cos\theta \neq \pm 1$ is polarized, since the differential cross section is $r_0^2/2$ for $\epsilon^{(\alpha')}$ normal to the plane determined by $\mathbf{k}$ and $\mathbf{k}'$ and $(r_0^2/2)\cos^2\theta$ for $\epsilon^{(\alpha')}$ lying in the plane. It is remarkable that the polarization of the scattered photon is complete for $\theta = \pi/2$. We find, then, that a completely unpolarized light beam, when scattered through 90°, results in a 100 % linearly polarized beam whose polarization vector is normal to the plane determined by $\mathbf{k}$ and $\mathbf{k}'$.

If the initial photon is polarized but the final photon polarization is not observed, we must sum over the two possible states of polarization. We have

$$\frac{d\sigma}{d\Omega}\bigg|_{\substack{\text{final}\\ \text{polarization}\\ \text{summed}}} = r_0^2(\sin^2\phi + \cos^2\theta\cos^2\phi). \tag{2.172}$$

If the initial photon is not polarized and the final photon polarization is not measured, we have

$$\frac{d\sigma}{d\Omega}\bigg|_{\substack{\text{unpolarized;}\\ \text{final polarization}\\ \text{summed}}} = \frac{r_0^2}{2}(1 + \cos^2\theta). \tag{2.173}$$

The total cross section for Thomson scattering is

$$\sigma_{\text{tot}} = \frac{8\pi r_0^2}{3} = 6.65 \times 10^{-25}\ \text{cm}^2. \tag{2.174}$$

As we emphasized earlier, this expression for the cross section is valid at photon energies much greater than the atomic binding energy. However, the foregoing derivation breaks down if the photon energy is so high that it actually becomes comparable to the rest energy of the electron. We must then take into account the relativistic nature of the electron, as we shall do in Section 4–4, discussing Compton scattering.

The quantum-theoretic treatment of Rayleigh and Thomson scattering can be compared to the classical counterpart. The scattering of an electromagnetic wave can be visualized in classical mechanics by the following two-step process:

a) A bound electron oscillates when it is exposed to a time-dependent electric field.
b) The oscillating charge in turn radiates an electromagnetic wave.

For a model of the electron bound by a force obeying Hooke's law, the displacement $\mathbf{x}$ of the electron in the presence of an applied electric field $\mathbf{E}_0 e^{-i\omega t}$ satisfies the differential equation

$$\ddot{\mathbf{x}} + \omega_0^2\mathbf{x} = (e/m)\mathbf{E}_0 e^{-i\omega t}, \tag{2.175}$$

where ω_0 is the characteristic angular frequency of the oscillator. Knowing that the acceleration of the electron is given by

$$\ddot{\mathbf{x}} = -\left(\frac{e}{m}\right)\left(\frac{\omega^2}{\omega_0^2 - \omega^2}\right)\mathbf{E}_0 e^{-i\omega t}, \tag{2.176}$$

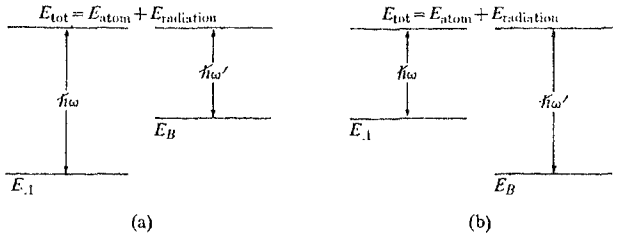

Fig. 2–4. (a) Stokes' line, (b) anti-Stokes' line.

we can readily compute the total scattering cross section in a straightforward manner.‡ We obtain

$$\sigma_{tot} = \frac{8\pi r_0^2}{3} \frac{\omega^4}{(\omega_0^2 - \omega^2)^2}. \tag{2.177}$$

For $\omega \ll \omega_0$ we have the ω^4 dependence of (2.167), whereas for $\omega \gg \omega_0$ we recover the frequency independent cross section (2.174).

The Raman effect. The Kramers-Heisenberg formula (2.162) can also be applied to inelastic scattering of light in which $\omega \neq \omega'$ and $A \neq B$. In atomic physics this phenomenon is called the *Raman effect* after C. V. Raman who observed a shift in the frequency of radiation scattered in liquid solutions, an effect predicted earlier by A. Smekal. If the initial atomic state A is the ground state, then the energy of the final photon $\hbar\omega'$ cannot be greater than the incident photon energy $\hbar\omega$ because $\hbar\omega + E_A = \hbar\omega' + E_B$ (Fig. 2–4a). This accounts for the presence of a *Stokes' line* in atomic spectra, a spectral line more reddish than that of incident radiation. On the other hand, if the atom is in an excited state, ω' can be larger than ω (Fig. 2–4b). This leads to an *anti-Stokes' line* which is more violet than the spectral line of the incident radiation.

2–6. RADIATION DAMPING AND RESONANCE FLUORESCENCE

The Kramers-Heisenberg formula we derived in the previous section is clearly inadequate if $\hbar\omega$ becomes equal to $E_I - E_A$ for some state I. The cross section according to (2.162) is then infinite, a phenomenon not observable in nature, of course. It is nevertheless true that the scattering cross section becomes very large and goes through a very sharp maximum in the neighborhood of $E_I - E_A = \hbar\omega$. This is a phenomenon known as resonance scattering of light or *resonance fluorescence.*

Where did our theory go wrong? When we use the second-order time-dependent perturbation theory, we assumed that the intermediate state I is a stationary state with an infinitely long lifetime. In other words, we did not take into account the

‡Panofsky and Phillips (1955), p. 326; Jackson (1962), pp. 602–604.