Notes on the interaction between electrons and the radiation field

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1. Interaction hamiltonian

As the photon number operator commutes with the hamiltonian of the radiation field, the occupation numbers $n_{\mathbf{k}r}$, specifying the number of photons in the mode with wave vector $\mathbf{k}$ and polarization vector $\boldsymbol{\epsilon}_{\mathbf{k}r}$, are constant of the motion of the free field. However, this is no longer the case as soon as the radiation field interacts with electric charges and currents. These interactions may in fact lead to photon absorption and emission.

We will now discuss emission and absorption of photons by atomic electrons, which will be described using *nonrelativistic* quantum mechanics.

First, we need to obtain the hamiltonian of a charged particle in presence of an electromagnetic field. The classical equation of motion of a particle of mass m, charge q and position $\mathbf{x}(t)$ in presence of an electric field $\mathbf{E}$ and a magnetic field $\mathbf{B}$ is

$$m\ddot{\mathbf{x}}(t) = q\mathbf{E} + \mathbf{j} \times \mathbf{B} \ , \tag{1}$$

where the current $\mathbf{j}$ is defined as

$$\mathbf{j} = q\dot{\mathbf{x}}(t) = q\mathbf{v} \ , \tag{2}$$

$\mathbf{v}$ being the particle velocity. Eq.(1) can be rewritten in terms of the scalar and vector potentials according to

$$m\ddot{\mathbf{x}}(t) = q\left[-\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t} + \mathbf{v} \times (\boldsymbol{\nabla} \times \mathbf{A})\right] \tag{3}$$

From the Lagrangian leading to the above equation of motion*,

$$\mathcal{L} = \frac{1}{2}m\mathbf{v}^2 - q\phi + q(\mathbf{A} \cdot \mathbf{v}) \ , \tag{4}$$

we can readily obtain the classical variable conjugate to $\mathbf{x}$,

$$\boldsymbol{\pi} = m\mathbf{v} + q\mathbf{A} \ , \tag{5}$$

and the classical hamiltonian

$$H = \boldsymbol{\pi}\dot{\mathbf{x}} - \mathcal{L} = \frac{1}{2m}(\boldsymbol{\pi} - q\mathbf{A})^2 + q\phi \ . \tag{6}$$

The hamiltonian of a collection of atomic electrons interactig with an electromagnetic field can be obtained using the quantum mechanical generalization of eq.(6) and the results discussed in the notes on quantization of the electromagnetic field. The conjugate variable $\boldsymbol{\pi}$ has now to be interpreted as the quantum mechanical operator satisfying the canonical commutation rule

$$[\mathbf{x}, \boldsymbol{\pi}] = i \ . \tag{7}$$

Hence, we replace $\boldsymbol{\pi} \to -i\boldsymbol{\nabla}$ and rewrite the first contribution to the right hand side of eq.(6) according to

$$\frac{1}{2m}(\boldsymbol{\pi} - q\mathbf{A})^2 \to \frac{1}{2m}\left[-\nabla^2 + iq(\boldsymbol{\nabla} \cdot \mathbf{A} + \mathbf{A} \cdot \boldsymbol{\nabla}) + q^2\mathbf{A}^2\right] \ . \tag{8}$$

Exploiting the Coulomb gauge condition $\boldsymbol{\nabla} \cdot \mathbf{A} = 0$, implying $\boldsymbol{\nabla} \cdot \mathbf{A} = \mathbf{A} \cdot \boldsymbol{\nabla}$, we can finally rewrite the quantum mechanical hamiltonian

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*a detailed derivation of this result can be found in: J.D. Jackson, *Classical Electrodynamics* (John Wiley & Sons, New York, 1962), chapt. 12.

$$H = \frac{\mathbf{p}^2}{2m} - \frac{q}{m}(\mathbf{p}\cdot\mathbf{A}) + \frac{q^2}{2m}\mathbf{A}^2 + q\phi \ , \tag{9}$$

$\mathbf{p}$ being the usual quantum mechanical momentum operator.

Collecting all things together we can cast the full hamiltonian of the electrons in presence of the electromagnetic field in the form

$$H = H_{el} + H_{field} + H_{int} \ , \tag{10}$$

where H_{el} and H_{field} only depend upon the dynamical variables of the electrons and the radiation field, respsctively, whereas H_{int} describes the electron-field interactions.

Recalling that in the Coulomb gauge the scalar potential satisfies Poisson's equation

$$\nabla^2\phi = -\rho \ , \tag{11}$$

and using the charge distribution appropriate for a collection of pointlike particles

$$\rho(\mathbf{x},t) = \sum_i \ q_i\delta(\mathbf{x} - \mathbf{x}_i(t)) \ , \tag{12}$$

we can write the electron hamiltonian in the familiar form including a kinetic energy term and the potential energy associated with electrostatic interactions

$$H_{el} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} \frac{q_i q_j}{|\mathbf{x}_i - \mathbf{x}_j|} \ . \tag{13}$$

The hamiltonian of the radiation field is

$$H_{field} = \sum_{\mathbf{k}r} \ \omega_k N_{\mathbf{k}r} \ , \tag{14}$$

where $\omega_k = |\mathbf{k}|$ and $N_{\mathbf{k}r} = a^\dagger_{\mathbf{k}r}a_{\mathbf{k}r}$ $a^\dagger_{\mathbf{k}r}$ and $a_{\mathbf{k}r}$ being photon creation and annihilation operators, respectively. Finally, the interaction hamiltomnian reads

$$H_{int} = \sum_i \ \left[-\frac{q_i}{m}(\mathbf{p}_i\cdot\mathbf{A}) + \frac{q_i^2}{2m}\mathbf{A}^2 \right] \ . \tag{15}$$

Note that, in principle, H_{int} should also include the interaction of the electron spin with the magnetic field, that we will neglect.

2. Photon absorption and emission

Let us first consider absorption of a photon, characterized by $\mathbf{k}$ and $\boldsymbol{\epsilon}_{\mathbf{k}r}$, associated with the transition of an atom from the initial state $|A\rangle$ to the final state $|B\rangle$. The radiation field makes a transition from the state $|n_{\mathbf{k}r}\rangle$ to the state $|n_{\mathbf{k}r} - 1\rangle$ (to simplify the notation, the occupation numbers of the modes not affected by the transition are not listed).

As the vector potential $\mathbf{A}$ is linear in the photon creation and annihilation operators $a^\dagger_{\mathbf{k}r}$ and $a_{\mathbf{k}r}$, only the terms linear in $\mathbf{A}$ in eq.(15) contribute to the one-photon absorption process. The term quadratic in $\mathbf{A}$ would in fact change the number of photons by 0 or ± 2.

In first order perturbation theory, we can write the transition matrix element as ($q_i = -e$)

$$\begin{aligned} M_{if} &= \langle f|\ H_{int}\ |i\rangle = \langle B,\ n_{\mathbf{k}r} - 1|\ H_{int}\ |A,\ n_{\mathbf{k}r}\rangle \\ &= \frac{e}{m}\ \langle B,\ n_{\mathbf{k}r} - 1|\ \sqrt{\frac{1}{2V\omega_k}} \sum_i a_{\mathbf{k}r}\mathrm{e}^{-i(\omega_k t - \mathbf{k}\cdot\mathbf{x}_i)}(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_{\mathbf{k}r})\ |A,\ n_{\mathbf{k}r}\rangle \\ &= \frac{e}{m}\ \sqrt{\frac{n_{\mathbf{k}r}}{2V\omega_k}} \sum_i \langle B|\ \mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}_i}(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_{\mathbf{k}r})\ |A\rangle\ \mathrm{e}^{-i\omega_k t} \ . \end{aligned} \tag{16}$$

The corresponding matrix element for the case of photon emission reads

$$
\begin{aligned}
M_{if} &= \langle f|\ H_{int}\ |i\rangle = \langle B,\ n_{\mathbf{k}r}+1|\ H_{int}\ |A,\ n_{\mathbf{k}r}\rangle \\
&= \frac{e}{m}\sqrt{\frac{n_{\mathbf{k}r}+1}{2V\omega_k}}\sum_i \langle B|\ \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{x}_i}(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_{\mathbf{k}r})\ |A\rangle\ \mathrm{e}^{i\omega_k t}\ .
\end{aligned}
\tag{17}
$$

A remarkable feature of the above result is that $M_{if} \neq 0$ for $n_{\mathbf{k}r} = 0$, implying the possibile occurrence of *spontaneous photon emission*. This prediction is a consequence of the quantum mechanical treatment of the radiation field, having no classical analogue.

We will now evaluate the matrix element of eq.(17) in the so called *dipole approximation*. This procedure can be applied when the spacial variation of the radiation field over the atomic size is negligible, so that we can replace its values at the points $\mathbf{x}_i$ with the value at $\mathbf{x} = 0$. This amounts to replacing

$$
\mathrm{e}^{i\mathbf{k}\cdot\mathbf{x}_i} \to 1 \tag{18}
$$

when the wavelength of the radiation field λ is such that $\lambda = |\mathbf{k}|^{-1} \gg R$, R being the typical atomic size. Substitution into eq.(17) yields

$$
M_{if} = \frac{e}{m}\sqrt{\frac{n_{\mathbf{k}r}+1}{2V\omega_k}}\ \langle B|\ \sum_i(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_{\mathbf{k}r})\ |A\rangle\ \mathrm{e}^{i\omega_k t}\ . \tag{19}
$$

The transition probability per unit time, w_{if}, can be readily obtained from the above amplitude using Fermi's golden rule of time dependent perturbation theory:

$$
w_{if} = 2\pi\ \delta(E_A - E_B - \omega_k)\ |M_{if}|^2\ , \tag{20}
$$

where E_A and E_B denote the energies of the initial and final atomic state, respectively. The δ-function can be eliminated integrating over the final states available to the emitted photon. Using

$$
\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3}\int d^3k\ , \tag{21}
$$

implying that the phase-space available to a photon emitted in the solid angle $d\Omega_k$ with magnitude of the wave vector between $|\mathbf{k}|$ and $|\mathbf{k}| + d|\mathbf{k}|$ is $[V/(2\pi)^3]d\Omega_k|\mathbf{k}|^2d|\mathbf{k}|$, we can rewrite the differential transition probability

$$
\begin{aligned}
\frac{dw_{if}}{d\Omega_k} &= \frac{e^2}{m^2}\ \frac{V}{(2\pi)^2}\int |\mathbf{k}|^2 d|\mathbf{k}|\ \frac{n_{\mathbf{k}r}+1}{2V\omega_k}|\langle B|\ \sum_i(\mathbf{p}_i\cdot\boldsymbol{\epsilon}_{\mathbf{k}r})\ |A\rangle|^2\ \delta(E_A - E_B - \omega_k) \\
&= \frac{1}{8\pi^2}\ \frac{e^2\omega_k}{m^2}\ (n_{\mathbf{k}r}+1)|\mathbf{P}_{AB}\cdot\boldsymbol{\epsilon}_{\mathbf{k}r}|^2\ ,
\end{aligned}
\tag{22}
$$

with

$$
\omega_k = |\mathbf{k}| = E_A - E_B \tag{23}
$$

and

$$
\mathbf{P}_{AB} = \langle B|\ \sum_i \mathbf{p}_i\ |A\rangle\ . \tag{24}
$$

Eqs.(22)-(24) yield the probability of emitting a photon with energy given by (23) and polarization vector $\boldsymbol{\epsilon}_{\mathbf{k}r}$ within the solid angle $d\Omega_k$. The matrix element of eq.(24) can be rewritten in a more familiar form, making it clear why the approximation of eq.(18) goes under the name of dipole approximation. In Heisenberg's picture we can rewrite $\mathbf{P}_{AB}$ as

$$\begin{aligned}\mathbf{P}_{AB} &= \langle B|\ \sum_i \mathbf{p}_i\ |A\rangle\ =\ m\ \langle B|\sum_i \dot{\mathbf{x}}_i\ |A\rangle\ =\ -im\ \langle B|\ [\ \sum_i \mathbf{x}_i, H_{el}\ ]\ |A\rangle \\ &= -im\ (E_A - E_B)\langle B|\ \sum_i \mathbf{x}_i\ |A\rangle\ =\ -im\ \omega_k\ \mathbf{X}_{AB}\ ,\end{aligned} \tag{25}$$

where

$$\mathbf{X}_{AB}\ =\ \langle B|\ \sum_i \mathbf{x}_i\ |A\rangle\ =\ -\frac{1}{e}\ \langle B|\ \mathbf{D}\ |A\rangle\ =\ -\frac{1}{e}\ \mathbf{D}_{AB}\ , \tag{26}$$

$\mathbf{D}$ being the electric dipole moment associated with the distribution of atomic electrons.

Substitution of eqs.(25) and (26) into eq.(22) leads to

$$\frac{dw_{if}}{d\Omega_k} = \frac{1}{8\pi^2}\ \omega_k^3\ (n_{\mathbf{k}r}+1)|\mathbf{D}_{AB}\cdot\boldsymbol{\epsilon}_{\mathbf{k}r}|^2\ . \tag{27}$$

We are now left with the problem of carrying out the sum over possible photon polarizations. From $\boldsymbol{\epsilon}_r\cdot\boldsymbol{\epsilon}_{r'} = \delta_{rr'}$ and $\boldsymbol{\epsilon}_r\cdot\mathbf{k} = 0$ it follows that ($\widehat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$)

$$\sum_{r=1}^{2}\ \boldsymbol{\epsilon}^i_{\mathbf{k}r}\boldsymbol{\epsilon}^j_{\mathbf{k}r} = \delta^{ij} - \widehat{\mathbf{k}}^i\widehat{\mathbf{k}}^j\ , \tag{28}$$

implying

$$\sum_r |\mathbf{D}_{AB}\cdot\boldsymbol{\epsilon}_{\mathbf{k}r}|^2 = |\mathbf{D}_{AB}|^2 - (\mathbf{D}_{AB}\cdot\widehat{\mathbf{k}})(\mathbf{D}^*_{AB}\cdot\widehat{\mathbf{k}}) = |\mathbf{D}_{AB}|^2(1-\cos^2\theta)\ , \tag{29}$$

θ being the angle between $\mathbf{D}_{AB}$ and $\widehat{\mathbf{k}}$.

In conclusion, the probability per unit time of spontaneous (i.e. $n_{\mathbf{k}r} = 0$) photon emission in the atomic transition $A \to B$ is

$$\begin{aligned}w_{A\to B} = \int d\Omega_k\left(\frac{dw_{if}}{d\Omega_k}\right) &= \frac{1}{8\pi^2}\ \omega_k^3\ |\mathbf{D}_{AB}|^2\ 2\pi\int_{-1}^{+1}(1-\cos^2\theta)d\cos\theta \\ &= \frac{\omega_k^3}{3\pi}\ |\mathbf{D}_{AB}|^2\ .\end{aligned} \tag{30}$$

Note that the same result might have been obtained using the dipole approximation from the very beginnig, i.e. writing the interaction hamiltonian in the form

$$H_{int} = -\mathbf{D}\cdot\mathbf{E}(\mathbf{x}=0,t)\ , \tag{31}$$

with the dipole moment $\mathbf{D}$ given bt eq.(26) and $\mathbf{E}(\mathbf{x}=0,t) = -(\partial\mathbf{A}/\partial t)_{\mathbf{x}=0}$.

The lifetime of the quantum state A, denoted by τ, is defined through

$$\frac{1}{\tau} = \sum_n w_{A\to B_n} \tag{32}$$

where the sum includes all possible atomic final states B_n, i.e. all states compatible with the appropriate selection rules.

First of all, the initial and final atomic states, $|A\rangle$ and $|B_n\rangle$, are required to have opposite parity. The parity of the states $|A\rangle$ and $|B_n\rangle$ is specified by the eigenvalues of the equations

$$P|A\rangle = P_A|A\rangle \qquad , \qquad P|B_n\rangle = P_{B_n}|B_n\rangle \ , \tag{33}$$

where P_A, $P_{B_n} = \pm\ 1$ and the parity operator P satisfies the relations $P^{-1} = P^\dagger = P$. As under parity transformation $\mathbf{x}$ goes into $P^\dagger\ \mathbf{x}\ P = -\mathbf{x}$, we can write

$$\langle B_n|\mathbf{x}|A\rangle = -\langle B_n|P^\dagger \mathbf{x} P|A\rangle = -P_{B_n} P_A \langle B_n|\mathbf{x}|A\rangle \ , \tag{34}$$

implying $P_{B_n} P_A = -1$.

The total angular momenta of the states $|A\rangle$ and $|B_n\rangle$, J_A and J_{B_n}, and their projections along the quantization axis, J^3_A and $J^3_{B_n}$, must be such that $\Delta J = J_A - J_{B_n} = 0, \pm 1$ and $\Delta J^3 = J^3_A - J^3_{B_n} = 0, \pm 1$. In addition, as the projection of the photon angular momentum cannot take the value $J^3 = 0$, transitions between states with $J^3_A = J^3_{B_n} = 0$ are forbidden.