3.4 Why do atoms radiate light?

Eq. (3.6) already demonstrated that in a mixed state of Eigenvalues, not belonging to the same energy-Eigenvalue, the fraction of each state changes as a function of time. The consequences for this changing state shall be discussed in what follows. As an example we take a state of two Eigenfunctions with different energies:

$$\psi(t,\vec{r}) = c_1 f_1(\vec{r}) e^{i\omega_1 t} + c_2 f_2(\vec{r}) e^{i\omega_2 t} \tag{3.14}$$

For the probability density we find

$$\psi^*(t,\vec{r})\psi(t,\vec{r}) = |c_1 f_1(\vec{r})|^2 + |c_2 f_2(\vec{r})|^2 + 2c_1c_2 f_1 f_2 \cos(\omega_1 - \omega_2)t \tag{3.15}$$

The probability density of the electron will thus change harmonically with the rotation frequency $(\omega_1 - \omega_2)$. This will in generally lead to a periodic change in the charge distribution, respectively of the dipole moment of the atom. Since the charge density is defined by

$$e\psi^*(t,\vec{r})\psi(t,\vec{r})d^3r \qquad , \tag{3.16}$$

we find for the complete dipole moment

$$\langle \vec{P} \rangle = e \int \psi^*(t,\vec{r})\vec{r}\psi(t,\vec{r})d^3r \qquad . \tag{3.17}$$

Defining the matrix elements

$$\vec{M}_{ij} = e \int f_i^*(\vec{r})\vec{r} f_j(\vec{r})d^3r \qquad , \tag{3.18}$$

Eq. (3.17) can be rewritten as

$$\langle \vec{P} \rangle = |c_1|^2 \vec{M}_{11} + |c_2|^2 \vec{M}_{22} + 2c_1c_2\vec{M}_{12}\cos(\omega_2 - \omega_1)t \qquad . \tag{3.19}$$

i.e. the dipole moment of the atom will change periodically. Consequently the atom serves as a sender for electromagnetic radiation with the frequency $(\omega_2 - \omega_1)$. It will loose power in the state with the higher energy. After a short time the atom will be in the ground state which is not a mixed state.

- This is the quantum mechanical explanation for the formula

$$\Delta E = h\nu \qquad . \tag{3.20}$$

- This explains too, why atoms can be stable, although they have a rotational momentum (in the classical description they would always radiate light and thus be destroyed). This classical explanation results from the *wrong picture*, that the electron is moving through the orbital, leading to a steady change in the dipole moment.
- Each state which is not an Eigenstate of the Hamiltonian has a non infinite-lifetime, which is defined in our example by the matrix element in Eq. (3.18).
- The calculation of these matrix elements is the main task of quantum mechanics.
- Non-zero matrix elements (even if the corresponding states are not degenerate) define rules for allowed transitions; e.g. radiative transitions only occur when $\Delta l = \pm 1$ holds.
- In addition to the radiative transitions there exist a large number of different mechanisms for an excited state to loose energy. The corresponding matrix elements (cross sections) may differ extremely.
- If the probability for an excited state to loose energy is very small, the state is called metastable.