APAS 5110. Internal Processes in Gases. Fall 1999.
Transition Probabilities and Selection Rules

1. Correspondence between Classical and Quantum Mechanical Transition Rates

According to the correspondence principle between classical and quantum mechanics (e.g. Landau and Lifshitz, Quantum Mechanics, §48), if A is a classically time-varying quantity, then there is a correspondence between its Fourier components A_ω and the matrix elements of the quantum mechanical operator between two energy eigenstates $\psi_L = \phi_L(\boldsymbol{x})e^{-i\omega_L t}$ and $\psi_U = \phi_U(\boldsymbol{x})e^{-i\omega_U t}$ differing in energy by $\omega = \omega_U - \omega_L$

$$A_\omega \rightarrow \langle \phi_L | A_\omega | \phi_U \rangle \ . \tag{1.1}$$

Equation (1.1) is used to obtain the quantum mechanical transition probabilities (2.11), (3.5), and (4.3) given below.

2. Electric Dipole

Start from the classical nonrelativistic formula for electric dipole radiation (e.g. Rybicki & Lightman (1979) Radiative Processes in Astrophysics, eq. (3.23b); Weinberg (1995) Quantum Theory of Fields Vol. 1, eq. (1.2.19); note Weinberg uses Heaviside rather than Gaussian units for charge e)

$$\frac{dE}{dt} = \frac{2}{3c^3}\, \ddot{\boldsymbol{d}}^2 \ , \tag{2.1}$$

where

$$\boldsymbol{d} \equiv \sum_{\text{charges } q} q\boldsymbol{r} \tag{2.2}$$

is the electric dipole moment. The Fourier expansion of the dipole moment $\boldsymbol{d}$ is

$$\boldsymbol{d} = \sum_\omega \boldsymbol{d}_\omega e^{i\omega t} \ , \tag{2.3}$$

so the Fourier expansion of $\ddot{\boldsymbol{d}}$ is

$$\ddot{\boldsymbol{d}} = \sum_\omega -\omega^2 \boldsymbol{d}_\omega e^{i\omega t} \ , \tag{2.4}$$

and the Fourier expansion of $\ddot{\boldsymbol{d}}^2$ is

$$\ddot{\boldsymbol{d}}^2 = \sum_\omega -\omega^2 \boldsymbol{d}_\omega e^{i\omega t} \cdot \sum_{\omega'} -\omega'^2 \boldsymbol{d}_{\omega'} e^{i\omega' t} \ . \tag{2.5}$$

The thing which is really of interest is the dipole radiation rate averaged over time, or averaged over a period if the motion is periodic. Averaged over time, the periodic terms in equation (2.5) disappear, leaving only the constant terms, which are those satisfying $\omega' = -\omega$:

$$\overline{\ddot{\boldsymbol{d}}^2} = \sum_\omega \omega^4 \boldsymbol{d}_\omega \cdot \boldsymbol{d}_{-\omega} = 2\sum_{\omega>0} \omega^4 \boldsymbol{d}_\omega \cdot \boldsymbol{d}_{-\omega} \ . \tag{2.6}$$

Since the dipole moment $\boldsymbol{d}$ is real, it satisfies

$$\boldsymbol{d}_{-\omega} = \boldsymbol{d}_\omega^* \ . \tag{2.7}$$

1

Hence equation (2.6) reduces to

$$\overline{\ddot{d}^2} = 2 \sum_{\omega > 0} \omega^4 |\boldsymbol{d}_\omega|^2 \ . \tag{2.8}$$

Thus equation (2.1) for the classical dipole radiation rate, averaged over time, becomes

$$\overline{\frac{dE}{dt}} = \sum_{\omega > 0} \frac{4\omega^4}{3c^3} \ |\boldsymbol{d}_\omega|^2 \ . \tag{2.9}$$

To make the transition to quantum mechanics, according to the general prescription (1.1), the Fourier coefficient $\boldsymbol{d}_\omega$ must be replaced by the matrix element $\langle \phi_L | \boldsymbol{d} | \phi_U \rangle$, where ϕ_U and ϕ_L represent initial (Upper) and final (Lower) spatial wave functions differing in energy by $\omega_U - \omega_L = \omega$. The quantum mechanical equivalent of equation (2.9) is therefore

$$\overline{\frac{dE}{dt}} = \sum_L \frac{4\omega^4}{3c^3} \ |\langle \phi_L | \boldsymbol{d} | \phi_U \rangle|^2 \ . \tag{2.10}$$

Equation (2.10) gives the mean energy loss per unit time by electric dipole transitions out of an initial state ϕ_U to a set of final states ϕ_L. The spontaneous transition probability, or Einstein A coefficient, or simply A-value, for electric dipole transitions is obtained by dividing the energy loss rate (2.10) by the transition energy $\hbar\omega$ (this is Rybicki & Lightman, eq. (10.28a)),

$$A_{UL}(\text{electric dipole}) = \sum_L \frac{4\omega^3}{3c^3\hbar} \ |\langle \phi_L | \boldsymbol{d} | \phi_U \rangle|^2 \ . \tag{2.11}$$

Note that the spontaneous transition probability is of order α^3 (the fine-structure constant $1/137$ cubed) in atomic units $e = m_e = \hbar$. The probability depends on nuclear charge Z approximately as $A_{UL} \sim Z^4$, since $\omega \sim Z^2$ and $d \sim r \sim Z^{-1}$.

For a single electron, the electric dipole moment is

$$\boldsymbol{d} = -e\boldsymbol{r} \ . \tag{2.12}$$

The radial vector operator $\boldsymbol{r}$ can be written as the product $\boldsymbol{r} = r\hat{\boldsymbol{r}}$ of the radial operator r and the dipole operator $\hat{\boldsymbol{r}}$, which is the unit vector in the $\boldsymbol{r}$ direction. The matrix elements of the dipole operator $\hat{\boldsymbol{r}}$ are given in the notes on Angular Momentum. From these matrix elements follow the electric dipole selection rules for a single electron:

(1) $\Delta L = \pm 1, \ \Delta M = 0, \pm 1$;
(2) $\Delta S = 0, \ \Delta M_S = 0$.

The second rule follows because the radial operator acts only on the spatial part of the wave function, not the spin. The first rule implies that parity must change, which is also evident from the fact that $\boldsymbol{r}$ has odd parity (it changes sign under coordinate inversion). These selection rules reflect the fact that electric dipole photons have unit angular momentum and odd parity.

For a system of electrons, which all have the same charge $-e$, the electric dipole moment is

$$\boldsymbol{d} = -e \sum_{\text{electrons}} \boldsymbol{r} \ . \tag{2.13}$$

Since the dipole operator again has odd parity, again the parity must change in an electric dipole transition. And again, since the dipole operator acts only on the spatial part of the wave function, spin is conserved. The other rules for change in the angular momentum are easiest to infer from the fact that the departing electric dipole photon has unit angular momentum. The selection rules for electric dipole radiation from many electron atoms are, then:

(1) Parity must change;
(2) $\Delta J = 0, \pm 1$;
(3) $\Delta M_J = 0, \pm 1$;
(4) $J = 0 \leftrightarrow 0$ is not allowed;
(5) Only one electron changes its nl state; $\Delta n =$ any, $\Delta l = 1$;
(6) $\Delta L = 0, \pm 1$;
(7) $L = 0 \leftrightarrow 0$ is not allowed;
(8) $\Delta S = 0$;

where $\boldsymbol{J} \equiv \boldsymbol{L} + \boldsymbol{S}$ is the total orbital plus spin angular momentum. The electric dipole selection rules 1-4 follow from the assertion that the departing photon has unit angular momentum and odd parity — it is an electric dipole photon. The rules 1-4 remain inviolate even when LS coupling is a poor approximation. The rules 5-8 are valid insofar as LS coupling is obeyed (i.e. L and S are good quantum numbers), which is true to the extent that the electrons are nonrelativistic. In heavier atoms, if terms are designated by their dominant LS components, then rules 5-8 may appear to break down because of transitions occurring through non-dominant components. In astronomy and space science, special attention attaches to transitions in which only rule 8, $\Delta S = 0$, is violated. Such transitions are called **semi-forbidden**. Otherwise, all transitions violating any of the electric dipole selection rules are called **forbidden**. Semi-forbidden transitions are electric dipole transitions, and the violation of the $\Delta S = 0$ rules occurs through configuration mixing caused by relativistic effects. For example, the C III] 1909 Å line.

3. Magnetic Dipole

Magnetic dipole and electric quadrupole transition probabilities can be derived in a similar way from the classical formulae. Generally, one only considers these transition probabilities when the electric dipole transition probability vanishes, that is, for forbidden lines. At the low density of interplanetary or interstellar space, forbidden lines arising from transitions within the ground electronic configurations of multi-electron atoms, which are all parity forbidden, are of great importance. At the high densities of laboratory vacua such lines are collisionally deexcited, but in space collisions are so infrequent that even forbidden lines have time to radiate. The classical magnetic dipole radiation rate is

$$\frac{dE}{dt} = \frac{2}{3c^5}\, \ddot{\mu}^2 \; , \tag{3.1}$$

where

$$\boldsymbol{\mu} \equiv \frac{1}{2} \sum_{\text{charges } q} q\boldsymbol{r} \times \boldsymbol{v} \tag{3.2}$$

is the magnetic dipole moment. The magnetic dipole transition probability is then

$$A_{UL}(\text{magnetic dipole}) = \sum_L \frac{4\omega^3}{3c^5\hbar} \ |\langle\phi_L|\boldsymbol{\mu}|\phi_U\rangle|^2 \ . \tag{3.3}$$

The magnetic dipole transition probability is of order $Z^6\alpha^5$ in atomic units, down by a factor $Z^2\alpha^2$ from the electric dipole probability.

For a system of nonrelativistic electrons, the magnetic moment $\boldsymbol{\mu}$ is

$$\mu = \frac{-e}{2m_e} \ (\boldsymbol{L} + 2\boldsymbol{S}) \ . \tag{3.4}$$

The minus sign in equation (3.4) is because electrons have a negative charge $-e$, and I've added in the spin contribution $\boldsymbol{S}$ to the magnetic moment. Classically the spin $\boldsymbol{S}$ is absent, but it has to be included quantum mechanically. The factor of 2 in front of $\boldsymbol{S}$ comes from the nonrelativistic limit of the Dirac equation, which is the relativistic equivalent of Schrödinger's equation for spin $\frac{1}{2}$ particles (see the notes on Spin in Atoms). Bunging (3.4) into (3.3) gives the magnetic dipole transition probability

$$A_{UL}(\text{magnetic dipole}) = \sum_L \frac{e^2\omega^3}{3m_e^2c^5\hbar} \ |\langle\phi_L|\boldsymbol{L} + 2\boldsymbol{S}|\phi_U\rangle|^2 \tag{3.5}$$

(don't confuse L for Lower with $\boldsymbol{L}$ for angular momentum).

The selection rules for magnetic dipole transitions follow from equation (3.5): only transitions between states in which the matrix elements of either $\boldsymbol{L}$ or $\boldsymbol{S}$ are nonzero are magnetic-dipole allowed. The matrix elements of $\boldsymbol{L}$, which are also those of $\boldsymbol{S}$, are given in the notes on Angular Momentum. Since $\boldsymbol{L}$ and $\boldsymbol{S}$ both have even parity (they remain unchanged under coordinate inversion), the wave functions ϕ_L and ϕ_U must have the same parity. Since $\boldsymbol{L}$ and $\boldsymbol{S}$ act only on the angular part of the wave function, not the radial part, the n quantum numbers are unchanged. Since $\boldsymbol{L}^2$ commutes with $\boldsymbol{L}$ and $\boldsymbol{S}$, the magnitude of the total orbital angular momentum is unchanged. Likewise since $\boldsymbol{S}^2$ commutes with $\boldsymbol{L}$ and $\boldsymbol{S}$, the magnitude of the total spin angular momentum is unchanged. The remaining selection rules follow most straightforwardly from the requirement that the departing photon has unit angular momentum. The magnetic dipole selection rules are, then:

(1) Parity is unchanged;
(2) $\Delta J = 0, \ \pm 1$;
(3) $\Delta M_J = 0, \ \pm 1$;
(4) $\Delta J = 0$ together with $\Delta M_J = 0$ is not allowed; in particular, $J = 0 \leftrightarrow 0$ is not allowed;
(5) No change in electronic configuration;
(6) $\Delta L = 0$;
(7) $\Delta S = 0$.

Rules 1-4 follow from the magnetic dipole nature of the photon, and are always valid. Rules 5-8 are exact for H-like ions, but can break down in heavier ions because of mixing of LS terms.

4. Electric Quadrupole

The classical electric quadrupole radiation rate is

$$\frac{dE}{dt} = \frac{1}{180c^5} \; \dddot{D}^2 \; , \tag{4.1}$$

where $\dddot{D}^2$ means $\dddot{D}_{ij}\dddot{D}_{ij}$ (implicit summation over $i,j = 1,2,3$), and

$$D_{ij} \equiv \sum_{\text{charges } q} qr^2(3\hat{r}_i\hat{r}_j - \delta_{ij}) \tag{4.2}$$

is the (3-dimensional) electric quadrupole moment tensor. The electric quadrupole transition probability is then

$$A_{UL}(\text{electric quadrupole}) = \sum_L \frac{\omega^5}{90c^5\hbar} \; |\langle\phi_L|D_{ij}|\phi_U\rangle|^2 \; . \tag{4.3}$$

which is of order $Z^6\alpha^5$ in atomic units, the same as the magnetic dipole transition probability.

You can check that, in a single electron atom, the matrix elements are nonzero only for $\Delta L = 2$, $\Delta M = 0, \pm 1, \pm 2$. Parity is conserved, since D_{ij} has even parity, and spin is conserved, because D_{ij} acts only on spatial coordinates. These rules reflect the fact that the emitted electric quadrupole photon has angular momentum 2 and even parity. The electric quadrupole selection rules are:

   (1) Parity is unchanged;
   (2) $\Delta J = 0, \pm 1, \pm 2$;
   (3) $\Delta M_J = 0, \pm 1, \pm 2$;
   (4) $J = 0 \leftrightarrow 0, \; 0 \leftrightarrow 1, \; 1/2 \leftrightarrow 1/2$ are not allowed;
   (5) Either zero or one electron changes its nl state; $\Delta n =$ any, $\Delta l = 0, \pm 2$;
   (6) $\Delta L = 0, \pm 1, \pm 2$;
   (7) $L = 0 \leftrightarrow 0, \; 0 \leftrightarrow 1$ are not allowed;
   (8) $\Delta S = 0$.

Rules 1-4 define what is meant by an electric quadrupole transition. Rules 5-8 are exact for H-like atoms, but can break down in heavier atoms because of mixing of LS terms.

5. Two-Photon Transitions

Since photons must have an angular momentum of at least one, the selection rule

$$J = 0 \leftrightarrow 0 \quad \text{is not allowed} \tag{5.1}$$

is absolute. Furthermore, in H-like ions, the selection rule

$$L = 0 \leftrightarrow 0 \quad \text{is not allowed} \tag{5.2}$$

is also absolute since there is no violation of LS coupling for single electrons. Thus for example the $1s^2 - 1s2s\,^1S_0$ transition in He-like ions, and the $1s - 2s$ transition in H-like ions, are absolutely forbidden. However, the $2s$ levels of both He-like and H-like ions can decay by the emission of two photons, and in fact two-photon emission is the dominant mode of radiative decay from these levels.
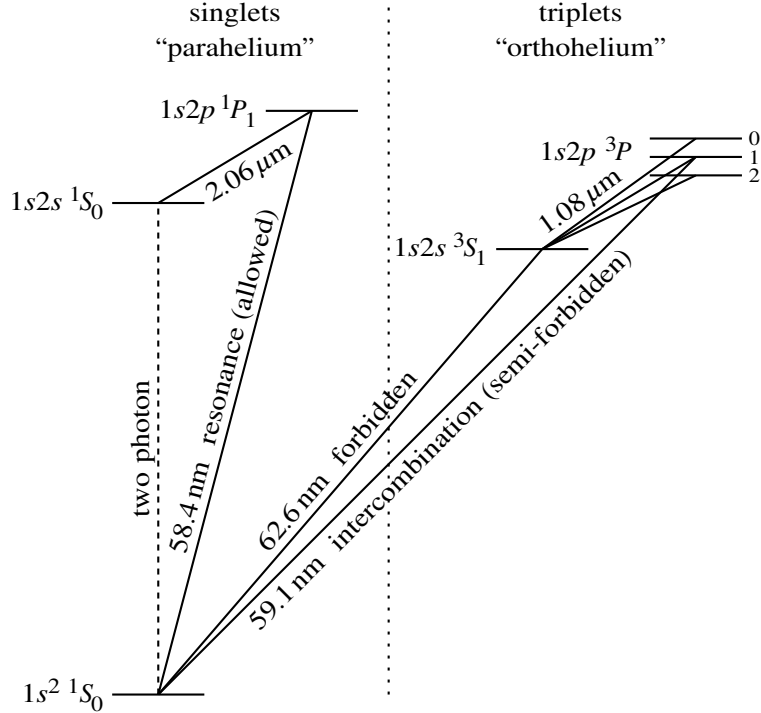
FIGURE 1. Grotrian diagram of the $n = 1$ and 2 configurations of He I. He I has two electrons, whose spins combine to yield a singlet with total spin 0, and a triplet with total spin 1. Transitions between spin singlets (left) and spin triplets (right) are sufficiently slow that the two kinds of He I behave almost as distinct species, dubbed "parahelium" and "orthohelium".

Classically, two-photon emission is represented by emission of two photons in quick succession. If P is the classical probability per unit time of emission of a photon, then the probability of emitting two photons in a time Δt is the probability of emitting a photon in a time t, times the probability of emitting a photon in a time $\Delta t - t$, integrated over all times t from zero to Δt:

$$P^2 \int_0^{\Delta t} t(\Delta t - t)\, dt = \frac{1}{6}P^2 \Delta t^2 \ . \tag{5.3}$$

The rate per unit time for two-photon emission is then $1/\Delta t$ of equation (5.1), which is

$$\frac{1}{6}P^2 \Delta t \ , \tag{5.4}$$

which tends to zero as $\Delta t \to 0$. Equation (5.1) shows that the rate for simultaneous emission of two photons vanishes in the classical limit. In quantum mechanics, however, Heisenberg's uncertainty principle prevents Δt from being specified more accurately than $\Delta t \Delta E \sim \hbar$. Thus the two-photon emission rate is finite in quantum mechanics. The most probable case is the emission of two electric dipole photons. With $\Delta t \sim \hbar/\Delta E \sim 1/\omega$, the two-photon

rate is approximately $P_{\text{dipole}}^2/\omega$. Since in atomic units $P_{\text{dipole}} \sim Z^4\alpha^3$ and $\omega \sim Z^2$, the two photon emission probability for $1s - 2s$ is of order $Z^6\alpha^6$ in atomic units, down by a factor $Z^2\alpha^3$ from single allowed electric dipole photon emission probabilities. A more detailed analysis yields, for the probability dA(2-photon) of spontaneous emission of two photons, with one photon in an angular frequency interval $d\omega_1$:

$$dA_{UL}(\text{2-photon}) \tag{5.5}$$

$$= \sum_L \left(\frac{4\omega_1^3}{3c^3\hbar}\right)\left(\frac{4\omega_2^3}{3c^3\hbar}\right)\left|\sum_I \frac{1}{\omega_{IU} + \omega_1}\langle\phi_L|\boldsymbol{d}_2|\phi_I\rangle\langle\phi_I|\boldsymbol{d}_1|\phi_U\rangle + (1 \leftrightarrow 2)\right|^2 \frac{d\omega_1}{2\pi} \ ,$$

where the summation is over all intermediate states I. If the upper state is $2s$, the intermediate states I must be p-states, by the dipole selection rules: $2p$, $3p$, ... The intermediate states include continuum as well as discrete states. Energy conservation requires that the sum of the two photon energies be equal to the transition energy $\hbar\omega$,

$$\omega_1 + \omega_2 = \omega \ . \tag{5.6}$$