Atomic transition and radiation

Note Title

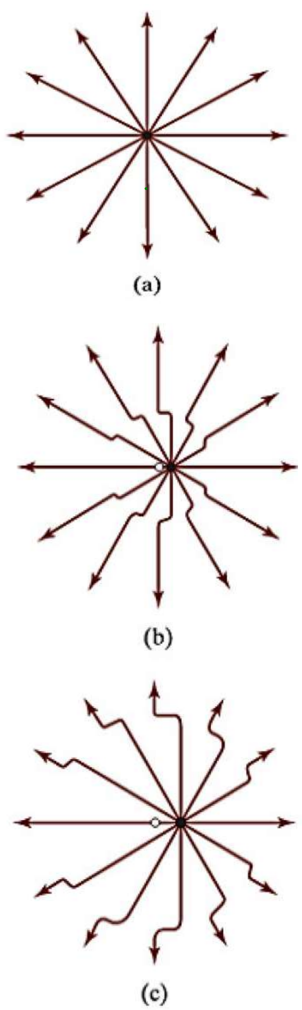
Faraday's law of induction: a changing B field induces E field

Maxwell: a changing E field induces a B field

$\Rightarrow$ an accelerating charge cause changing E & B fields

to continually induce one another

$\Rightarrow$ radiation from charge



(a)

(b)

(c)

* Radial component of E field $\sim \frac{1}{r^2}$

transverse " $\sim \frac{1}{r}$ $\Rightarrow$ dominates at large distance

Total power P radiated by single charge q (non-relativistic)

$$P = \frac{2kq^2a^2}{3c^3}$$

e.g. bremsstrahlung (braking radiation) $\rightarrow$ X-ray

classical theory: all frequencies can be produced

quantum: $hf \leq$ kinetic energy of incident e^-

Example 11.1

Find the power that would be radiated by a classical electron in the $n = 1$ Bohr orbit of a hydrogen atom.

Use Bohr theory & Newton's law ($n=1 \Rightarrow r = a_B$)

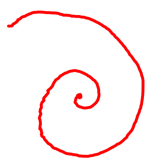
$$a = \frac{v^2}{r} = \frac{F}{m} = \frac{ke^2}{mr^2}$$

$$P = \frac{2ke^2}{3c^3}\left(\frac{ke^2}{mr^2}\right)^2 = \frac{2(ke^2)^3\, c}{3(mc^2)^2 r^4} = \frac{2\cdot(1.44\ \mathrm{eV}\cdot \underbrace{\mathrm{nm}}_{10^{-9}\,\mathrm{m}})^3\cdot 3\times 10^{8}\ \mathrm{m/s}}{3\left(5.1\times10^{5}\ \mathrm{eV}\right)^2\cdot\left(0.53\times10^{-10}\ \mathrm{m}\right)^4}$$

$$= \frac{2}{3}\,\frac{1.44^3}{5.1^2}\,\frac{3}{(0.53)^4}\,\frac{(10^{-9})^3\cdot 10^{8}}{10^{5\cdot 2}\cdot 10^{-40}}\,\frac{\mathrm{eV}}{s} = 2.9\cdot 10^{11}\ \mathrm{eV/s}$$

$\Rightarrow$ large energy loss per second

[problem 11.15]



$\Rightarrow$ e^- would collapse with proton in $\tau \sim 1.6\times10^{-11}$ sec

- Stationary states and Transitions

Levels in hydrogen atom : stationary states $\Psi_{nlm}(\vec{r},t) = \psi_{nlm}(\vec{r})\, e^{-iE_n t/\hbar}$

(pure Coulomb potential)

"stationary" probability

$\rightarrow P(r,t) = |\Psi_{nlm}(\vec{r},t)|^2$

$= |\psi_{nlm}(\vec{r})|^2$

$\Rightarrow$ e^- in stationary states does not radiate !

✱ But simple Schrödinger equation predicts all states of definite energy ψ_{nlm} are perfectly stable.

$\hookrightarrow$ but in reality, transitions occur !

2p —

1s —

$\rightsquigarrow$ Transition to occur : requires an E e.g. to induce

e.g. $W = e\mathcal{E}x$ $\Rightarrow$ perturbation

even w/o external fields, there are vacuum fluctuations

$\Rightarrow$ tiny E & B fields

$\psi_n \longleftrightarrow U$, $\psi_n + \Delta\psi_n \longleftrightarrow U + W$

We need time-dependent perturbation theory to deal with transitions

e.g. at $t=0$, $\Psi(r,t) = \psi_n(r)$ subjected to perturbation W

$\Rightarrow$ a definite probability $P(n \to m)$ to make a transition from n to m $(\psi_m(r))$

Hamiltonian operator

(1d) $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)$ $\qquad \hat{H}\psi(x) = E\psi(x)$ TISE

e.g. $\psi(x) = e^{ikx}$

$$\hat{H}\psi(x) = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U\right)e^{ikx} = \left(\underbrace{\frac{\hbar^2 k^2}{2m}}_{=K} + U\right)e^{ikx}$$

(3d) $\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U(x,y,z)$

TDSE : $i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\Psi(x,t) = \hat{H}\Psi(x,t)$

Approximation $\qquad$ (suppress spatial coordinate)

$$\Psi(t+\Delta t) \approx \Psi(t) + \Delta t\frac{\partial\Psi}{\partial t} = \Psi(t) + \frac{\Delta t}{i\hbar}\hat{H}\Psi(t)$$

Suppose $t=0$. $\Psi(0) = \psi_n$ with E_n $\qquad \hat{H}\psi_n = E_n\psi_n$

$$\Psi(\Delta t) = \Psi(0) + \frac{\Delta t}{i\hbar}H\psi_n$$

$$= \underbrace{\psi_n - \frac{i\Delta t}{\hbar}E_n\psi_n}$$

$$(\Psi(t) = e^{-iE_n t/\hbar}\psi_n \approx \Big(\overbrace{1 - \frac{iE_n t}{\hbar}} - \frac{E_n^2 t^2}{2\hbar^2} + \cdots\Big)\psi_n$$

(1) Completeness of stationary wave functions

$\hat{H}\psi_n = E_n \psi_n$

$\Rightarrow \psi(x) = \sum_n A_n \psi_n$ — complete set of functions, a basis set

$\sum_n |A_n|^2 = 1$

$|A_n|^2$: probability that a measurement of energy will give E_n

Example 11.2

Recall the stationary-state wave functions for a particle of mass m in a one-dimensional rigid box (the infinite square well) of width a, and write down the expansion of an arbitrary wave function $\psi(x)$ in terms of these stationary-state functions. What are the expansion coefficients A_n if $\psi(x)$ is in fact the ground-state wave function? What if $\psi(x)$ is the first excited state? What if $\psi(x)$ is a 50–50 mixture of the lowest two states?

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}$$

$$\psi(x) = \sum_{n=1}^{\infty} A_n \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} \quad \Rightarrow \quad \sum_n |A_n|^2 = 1$$

(a) ground state, $n=1$: $\psi(x) = \sqrt{\frac{2}{a}} \sin\frac{1\pi x}{a}$

$A_1 = 1, \quad A_2 = A_3 = \cdots = 0$

(b) 1st excited state, $n=2$. $A_1 = 0, \ A_2 = 1, \ A_3 = 0 \cdots$

$\psi(x) = \sqrt{\frac{2}{a}} \sin\frac{2\pi x}{a}$

(c) 50–50 mixture e.g. $A_1 = A_2 = \frac{1}{\sqrt{2}}, \quad A_3 = A_4 = \cdots = 0$

as $\sum_n |A_n| = 1$

another possibility $A_1 = \frac{1}{\sqrt{2}}, \quad A_2 = -\frac{1}{\sqrt{2}}, \quad A_3 = A_4 = \cdots = 0$

(2) orthogonality of stationary states

$$\int_{-\infty}^{\infty} \psi_m^*(x)\,\psi_n(x)\,dx = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases}$$

$$\langle \psi_m | \psi_n \rangle = \delta_{mn}$$

$$\vec{a}^{\,*} \cdot \vec{b}$$

(3) Expansion

$$\psi(x) = \sum_n A_n \psi_n(x)$$

$$\int_{-\infty}^{\infty} dx\, \psi_m^*(x)\, \psi(x) = \sum_n A_n \int_{-\infty}^{\infty} dx\, \underbrace{\psi_m^*(x)\,\psi_n(x)}_{\delta_{mn}} = A_m$$

Transitions & Time-Dependent Perturbation theory

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \qquad \hat{H}_0 \psi_n = E_n \psi_n$$

ψ_n's are stationary states of $\hat{H}_0$

but not of $\hat{H} = \hat{H}_0 + \hat{W}$ $\qquad \hat{W} = e\mathcal{E}x$

$$\Psi(\Delta t) \approx \Psi(0) + \frac{\Delta t}{i\hbar} \hat{H}\, \Psi(0)$$

assume $t=0$, $\Psi(0) = \psi_n$

$$= \psi_n + \frac{\Delta t}{i\hbar}(\hat{H}_0 + \hat{W})\psi_n$$

$$\approx \left(1 - \frac{i E_n \Delta t}{\hbar}\right)\psi_n - \frac{i\Delta t}{\hbar}\hat{W}\psi_n$$

Example 11.3

An electron is initially in the ground state ψ_1 of a one-dimensional rigid box. At time $t = 0$ we switch on an electric field $\mathcal{E}$ in the x direction, giving the electron an additional potential energy $W = e\mathcal{E}x$. Describe the form of the electron's wave function a short time Δt later when we switch the perturbation off.

$$\Psi(\Delta t) \approx \underbrace{\left(1 - \frac{iE_1 \Delta t}{\hbar}\right)}_{A} \psi_1 \underbrace{- \frac{ie\mathcal{E}\Delta t}{\hbar}\, x\psi_1}_{\text{extra term}}$$

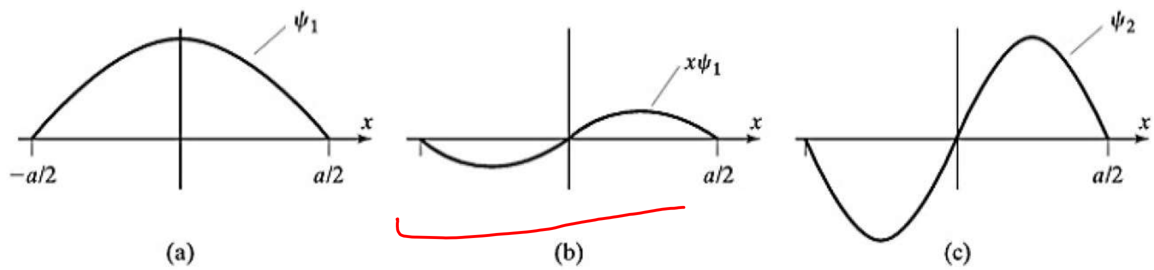


FIGURE 11.2

(a) The ground-state wave function ψ_1 for an electron in an infinite square well of width a, centered on the origin. **(b)** An electric field $\mathcal{E}$ switched on briefly adds to the wave function of part (a) a small term proportional to $x\psi_1$. **(c)** The extra term shown in part (b) has almost exactly the shape of the excited-state wave function ψ_2.

shape similar to ψ_2

$$\Psi(\Delta t) \approx A\psi_1 + B\psi_2$$

But formally we can expand the extra term

$$-\frac{i\Delta t}{\hbar} W\psi_n = \sum_m A_m \psi_m$$

$$A_m = -\frac{i\Delta t}{\hbar}\int_{-\infty}^{\infty} \psi_m^* W \psi_n \, dx$$

The transition probability

$$P(n \to m) = \left(\frac{\Delta t}{\hbar}\right)^2 \left| \underbrace{\int_{-\infty}^{\infty} \psi_m^* W \psi_n \, dx}_{\text{matrix element } W_{mn}} \right|^2$$

Example 11.4

Consider again the electron of Example 11.3, which is initially in the ground state of the infinite square well and is exposed to an electric field $\mathscr{E}$ for a short time Δt. Find the probabilities $P(1 \to m)$ that it will subsequently be found in the level m for $m = 2, 3$, and 4.

$$P(n \to m) = \left(\frac{e\mathcal{E}\Delta t}{\hbar}\right)^2 \left| \int_{-\infty}^{\infty} \psi_m^* \, x \, \psi_n \, dx \right|^2$$

Use the new origin at $x = 0$

$n=4$

$n=3$ odd $\quad \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} \rightarrow \sqrt{\frac{2}{a}} \cos\frac{n\pi x}{a}$ (n odd)

$n=2$

"$n=1$" $\quad \sqrt{\frac{2}{a}} \sin\frac{\pi x}{a} \rightarrow \sqrt{\frac{2}{a}} \cos\frac{\pi x}{a}$

even case becomes

$$\psi_{n\,\text{even}}(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}$$

$$x_{mn} \equiv \int_{-\infty}^{\infty} dx \, \psi_m^* \, x \, \psi_n$$

odd odd even

$$x_{2\leftarrow 1} = \int_{-\infty}^{\infty} dx \, \psi_2^* \, x \, \psi_1 = \frac{2}{a} \int_{-a/2}^{a/2} \sin\frac{2\pi x}{a} \cdot x \cdot \cos\frac{\pi x}{a}$$

(Prob 11.21) $= \dfrac{16a}{9\pi^2}$

$$P(1 \to 2) = \left(\frac{e\mathcal{E}\Delta t}{\hbar} \frac{16a}{9\pi^2}\right)^2 \quad ; \quad P(1 \to 4) = \left(\frac{e\mathcal{E}\Delta t}{\hbar} \frac{32a}{225\pi^2}\right)^2$$

odd odd odd

$$x_{3\leftarrow 1} = \int_{-\infty}^{\infty} dx \, \psi_3 \cdot x \cdot \psi_1 = 0$$

$\sin(\,)$ $\quad$ $\sin(\,)$

odd $\not\leftrightarrow$ odd

even $\not\leftrightarrow$ even

Selection rule

odd $\leftrightarrow$ even

Selection Rules

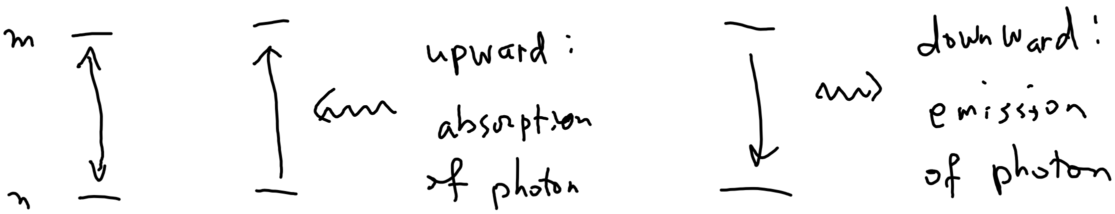
eg $P\left(\begin{matrix} odd \to odd \\ even \to odd \end{matrix}\right) = 0$ forbidden transition

Note within approximation to order $\mathcal{O}(\delta t)$ in wavefcn

Probability of forbidden transitions is small compared to nonforbidden ones!

Selection rule : odd $\leftrightarrow$ even

Upward or Downward



$$P(n \to m) \propto \left| \int_{-\infty}^{\infty} dx\, \psi_m^* W \psi_n \right|^2$$

stimulated

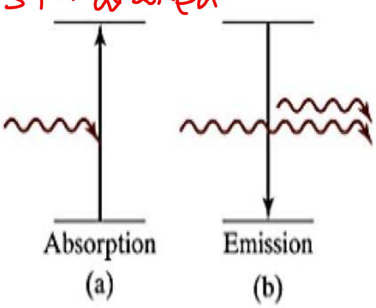


FIGURE 11.3

Schematic diagram of absorption and stimulated emission. **(a)** An incident photon is absorbed by the atom, which makes an upward transition. **(b)** In stimulated emission one photon striking the excited atom stimulates the emission of a second photon, causing the atom to make a downward transition.

EXample

$\hat{W} = W(r) \cos \omega t$

$\omega = |E_m - E_n| / \hbar$

In order to induce substantial transition

* Spontaneous emission

emission w/o an external field

$\Longrightarrow$ vacuum fluctuations

$\Rightarrow$ Need quantum electrodynamics (QED) to explain it fully

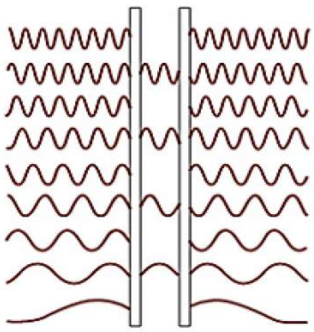


FIGURE 11.4

In the Casimir effect, zero-point radiation exerts forces on two uncharged parallel metal plates. Outside the plates, all wavelengths of radiation are allowed; between the plates, only certain discrete wavelengths are allowed (just as only certain discrete wavelengths are allowed on a stretched string). If the plates are close enough together, this difference produces a measurable inward force, due to the unequal radiation on opposite sides of either plate.

Casimir effect

$\Rightarrow$ a manifestation of vacuum fluctuations

zero-point energy

atom inside cavity can change their spontaneous emission.

Atomic selection rules

TABLE 11.1

Some of the selection rules that apply to transitions of electrons in an atom. Each rule is stated in the form of a condition that must be met if a transition is to be allowed (that is, occur with significant probability). For example, the first rule, $\Delta l = \pm 1$, means that only transitions for which $\Delta l = l_f - l_i = \pm 1$ are allowed. The quantum number s_{tot} identifies the magnitude of the total spin of all the electrons; similarly j_{tot} gives the magnitude of the total angular momentum $\sum(\mathbf{L} + \mathbf{S})$.

Quantum Number	Selection Rule	Reference
l (magnitude of **L**)	$\Delta l = \pm 1$	Eq. (11.46)
m (z component of **L**)	$\Delta m = 0$ or ± 1	Problem 11.30
s_{tot} (total spin $\sum \mathbf{S}$)	$\Delta s_{tot} = 0$	Problem 11.25
j_{tot} [total spin + orbital $\sum(\mathbf{L} + \mathbf{S})$]	$\Delta j_{tot} = 0$ or ± 1	Problem 11.27

For atomic transition (emitting or absorbing light) is mostly cause by an electric field (either externally applied or zero-point fields)

$\mathcal{E} = \mathcal{E}_0 \cos\omega t \Rightarrow -e\mathcal{E}x = -e\mathcal{E}_0 x \cos\omega t$ [assume in x direction]

The probability of transition

$$P(n \to m) \propto \mathcal{E}_0^2 \left| \int \psi_m^* x \psi_n \, dV \right|^2$$

↳ replacing it by y or z (if $\vec{\mathcal{E}}$ is in y or z direction)

(averaging over x, y, z if field is unpolarized)

The consequence is atomic selection rules.

suppose ψ_n is $l_n = 0$ (s orbital) and ψ_m is another $l_m = 0$ orbital

Thus $\psi_n(-x,y,z) = \psi_n(x,y,z)$ $\quad \psi_m(-x,y,z) = \psi_m(x,y,z)$

but $\int \psi_m^*(x,y,z)\, x\, \psi_n(x,y,z)\, dV = \int \psi_m^*(-x,y,z)\,(-x)\,\psi_n(-x,y,z)\, dV$

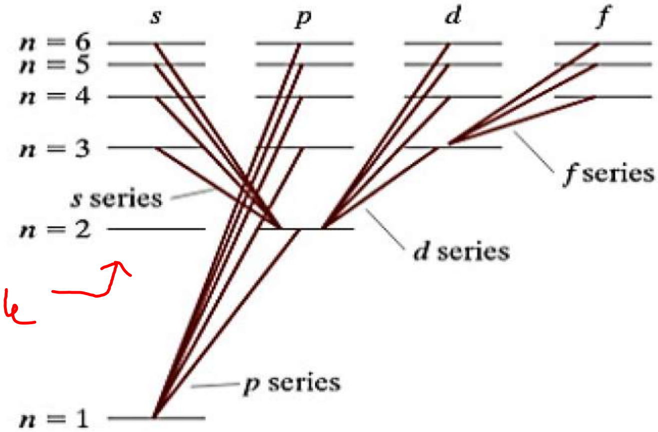
$= -\int \psi_m^*(x,y,z)\, x\, \psi_m(x,y,z)\, dV$

⇓

$P(n \to m) = 0$ transition is forbidden

unless $\boxed{l_m - l_n = \pm 1}$ see Problems $\underbrace{11.26,\ 11.30}_{\text{HW}}$ & 11.31

Intuitive explanation: photon has spin 1, absorbing or emitting it changes $|l|$ by one.



metastable state

FIGURE 11.5

Some of the allowed transitions observed in the hydrogen atom. Note that each involves a change of l by one unit, as is found to be the case for *all* allowed transitions. Note also that the traditional labels s (sharp), p (principal), d (diffuse), and f (fundamental) were originally applied to transitions, not levels.

make transitions only to adjacent columns

This leads to the transitions allowed shown in the Figure.

- We won't have time to discuss lasers, which is an important invention that enables many modern technologies.