Supplementary Notes for Quantum Physics 2

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Chapter 1

Electromagnetic Transitions

Our understanding of the quantum physics of atoms relies heavily on optical spectroscopy. i) We observe the difference in energy between two states by observing the frequency (wavelength) of light that is emitted or absorbed. ii) The lifetime of an electron in a particular excited state depends on whether a transition is allowed quantum mechanically. In this section I first address optical transitions using a relatively simple classical analogy to estimate transition rate and lifetimes. I then outline a quantum mechanical approach that leads to an understanding of the origins and meaning optical selection rules.

The quantum mechanical approach uses time-dependent perturbation theory, which is above the normal expectations for this course, but worthwhile as a first exposure. You will not be expected to reproduce this theory, but rather to understand the logical argument and its consequences.

1.1   A classical analogy that works pretty well

Classical charge distributions radiate only when there is accelerating charge. (Pure eigenstates do not radiate - the charge distribution (probability density) does not change with time.) Quantum mechanically, the wave function sloshes with time (acceleration) if two states are mixed. We will address the details in the quantum mechanical part of this chapter. For now, let's just assume that sloshing occurs and that the dipole moment has the form $\overrightarrow{p} = q\,\overrightarrow{d}\,cos(\omega t)$ where d is $\approx$ size of the atom.

An oscillating electric dipole is the closest analogy to sloshing of a mixed

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[1]This chapter is intended to follow Chapter 6 and precede section 7.3 in Townsend.
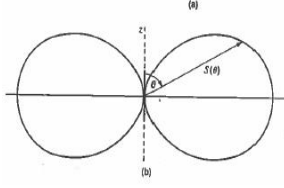
Figure 1.1: A schematic of the radiated field strength as a function of angle for an oscillating dipole oriented vertically.

state. Radiation from an oscillating dipole is treated in intermediate electromagnetics texts[2]. I provide an outline of the argument here.

Consider a large spherical shell with very small[3] charge distribution at its center. The total power passing through a spherical surface is the integral of the Poynting vector over this surface:

$$P(r) = \oint \vec{S} \cdot d\vec{a} = \frac{1}{\mu_0} \oint (\vec{E} \times \vec{B}) \cdot d\vec{a}.$$

Since the electric field from a static dipole falls off as $1/r^3$ and the magnetic field of a moving charge falls off as $1/r^2$ the power passing though a surface at very large r is negligible compared to the radiating field of the accelerating charges.

First let's consider the field from a single charge q near the origin with acceleration a. To solve for the radiating fields, one writes the potentials $V(\vec{r}, t)$ and $\vec{A}(\vec{r}, t)$ and takes appropriate derivatives, and for $d << 2\pi c/\omega << r$ the predominant electric field is transverse to the radius from the dipole and is approximately given by the relation:

$$E_{perp} = \frac{qa}{4\pi\epsilon_0 c^2 r} sin\theta$$

where a is the acceleration of the charge and θ is the angle from the axis of the dipole. The magnitude of the magnetic field is given by

$$E/c$$

and the magnetic field is perpendicular to the electric field. These electric and magnetic fields propagate radially outward at the speed of light, with

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[2]e.g.- Griffiths, Introduction to Electrodynamics, Chapter 11.

[3]This means that the distance d between the charges of the dipole is small compared to the distance r at which the observation is made and the wavelength $2\pi c/\omega$ of the emitted radiation (or $d << 2\pi c/\omega << r$), which is easy to satisfy for optical radiation from an atom.

the Poynting vector magnitude given by:

$$S = \epsilon_0 c E^2$$

. Therefore

$$S = \frac{q^2 a^2}{16\pi^2 \epsilon_0 c^3 r^2} sin^2\theta$$

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The total radiated power R is found by integrating over all angles

$$R = \frac{1}{4\pi\epsilon_0}\frac{2}{3}\frac{q^2 a^2}{c^3}$$

If we now consider the radiation from an electron wavefunction oscillating on a nearly stationary proton so that the average position of the electron charge oscillates as $x = A sin\omega t$ so that $a = -A\omega^2 sin\omega t$ and

$$R = \frac{1}{4\pi\epsilon_0}\frac{2}{3}\frac{q^2 x^2 \omega^4}{c^3}$$

and the average radiation rate is therefore:

$$\langle R \rangle = \frac{1}{6\pi\epsilon_0}\frac{q^2 \overline{x^2} \omega^4}{c^3} = \frac{1}{12\pi\epsilon_0 c^3}q^2 A^2 \omega^4. \tag{1.1}$$

If we assume that the instantaneous dipole moment of an electron wavefunction is $p = qx$ then the average power emitted is can also be written:

$$\langle R \rangle = \frac{p^2 \omega^4}{12\pi\epsilon_0 c^3}.$$

Exercise P1.01:
a) Assuming that the frequency of oscillation is due to the difference in energy between the 2p and 1s states of the H atom, and that the amplitude of oscillation is about one Bohr radius, estimate the rate at which energy is classically radiated in eV/s.
b) Estimate the classical time it takes for this atom to radiate the energy difference between these two states.[a]

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[a]Actual atomic lifetimes for allowed transitions are of order 10-100 ns.

This argument can be made slightly more "quantum mechanical" by explicitly calculating the time dependent dipole moment for an equal mixture

of two states (initial and final). (We will justify this assumption in the next section on time-dependent perturbation theory.)

Our mixed state is:

$$\Psi = \psi_1 exp(-iE_1 t/\hbar) + \psi_2 exp(-iE_1 t/\hbar)$$

. So the instantaneous expectation value of the dipole moment is:

$$\langle p \rangle = -q \int \Psi^* \overrightarrow{r} \Psi d\overrightarrow{r}.$$

$$\Psi^* \Psi = \psi_1^* \psi_1 + \psi_2^* \psi_2 + \psi_1^* \psi_2 e^{(-i(E_1 - E_2)/\hbar)} + \psi_2^* \psi_1 e^{(i(E_1 - E_2)/\hbar)}$$

and for real space wavefunctions:

$$\Psi^* \Psi = \Psi^* \Psi = \psi_1^2 + \psi_2^2 + 2\psi_1 \psi_2 cos((E_1 - E_2)t/\hbar).$$

Notice that the only remaining time dependence is in the overlap term, so that's where the "sloshing" comes from.

> Exercise P1.02: Calculate the rate of change of the dipole moment for a mixture of the n=1 and n=2 states of an electron in a one-dimensional box of length 1 nm.

1.2   Time-dependent Perturbation theory

Although the classical estimation above gives the order of magnitude of the power emitted, it does not tell us whether a transition will actually occur. It is necessary to resort to time dependent perturbation theory to do this.[4] This is a topic you will take up with more rigor in a Quantum Mechanics course. I will outline the argument here and discuss the ramifications of components of the argument.

The perturbation in this case is an oscillating electromagnetic field, which could have background blackbody radiation as its origin. We assume an electric field polarized along the x axis $E(t) = E_p cos(\omega t)$ which yields a local perturbing potential of

$$v_p(x, t) = E_0 x cos(\omega t).$$

We assume that the effect of this potential on the atomic wavefunctions is small. The key idea in perturbation theory is that we can fruitfully express

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[4]The source for my notes here is Chapter 10 of the text, Introduction to Modern Physics by McGervey.

the new solutions to the perturbed Hamiltonian $H = H_0 + v_p$ in terms of the solutions to the unperturbed Hamiltonian.[5]

The old, unperturbed eigenfunctions are found from:

$$H_0 \psi_l = E_l \psi_l$$

and where $\psi_l(x,t) = u_l(x)e^{-iE_l t/\hbar}$.

Since we are interested in time-dependent effects, let's start with the time-dependent Schrodinger equation for the perturbed Hamiltonian:[6]

$$(H_0 + v_p(x,t))\chi_n = i\hbar \frac{\partial \chi_n}{\partial t}$$

The ψ_l form a complete orthonormal set of solutions, so we can also write the new wavefunctions χ_n as the sum of the ψ_l's:

$$\chi_n = \sum_l a_{nl}(t)\psi_l.$$

And substituting this form for the perturbed states into the time-dependent Schrodinger equation:

$$(H_0 + v_p(x,t))\sum_l a_{nl}(t)\psi_l = i\hbar \frac{\partial \sum_l a_{nl}(t)\psi_l}{\partial t}$$

Taking the derivative on the right and distributing the operators on the left:

$$*H_0 \sum_l a_{nl}(t)\psi_l + v_p(x,t)\sum_l a_{nl}(t)\psi_l = i\hbar(\sum_l \psi_l \frac{\partial a_{nl}(t)}{\partial t} + a_{nl}\frac{\partial \psi_l}{\partial t}).*$$

Since the operator H_0 does not operate on time and $a_{nl}(t)$ is only a function of time, and only working on the leftmost term:

$$H_0 \sum_l a_{nl}(t)\psi_l = \sum_l a_{nl}(t)H_0\psi_l = i\hbar \sum_l a_{nl}\frac{\partial \psi_l}{\partial t}.$$

This means that the leftmost term in the asterisked equation above can be canceled with the rightmost term, leaving:

$$v_p(x,t)\sum_l a_{nl}(t)\psi_l = i\hbar(\sum_l \psi_l \frac{\partial a_{nl}(t)}{\partial t})$$

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[5]We can always express the new wavefunctions in terms of the old ones because the old ones form a complete set, but would like to be able to express the new ones in terms of just a few old ones.

[6]We'll make all of these arguments in one dimension because the logic is the same as for three, but the math is simpler.

We can eliminate the sum using a standard expansion trick: by multiplying both sides by $\psi_{n'}^*$,

$$\psi_{n'}^* v_p(x,t) \sum_l a_{nl}(t)\psi_l = i\hbar(\sum_l \psi_{n'}^* \frac{\partial a_{nl}(t)}{\partial t}\psi_l)$$

and integrating over space to select one term (remember the ψ_l are orthonormal and a_{nl} is independent of position)

$$\sum_l a_{nl}(t)[\int \psi_{n'}^* v_p(x,t)\psi_l dV] = i\hbar\frac{\partial a_{nn'}(t)}{\partial t}$$

Remember that $a_{nn'}$ is the coefficient that tells us how much of the n'^{th} original eigenfunction $\psi_{n'}$ makes up the χ_n state of the perturbed wavefunction. $a_{nn'}^2$ therefore tells us the probability that we find the system in state $\psi_{n'}$ with energy $E_{n'}$ given that it is in state χ_n. If we assume that the perturbed states are very similar to the unperturbed states, then the $\psi_{n'}$ state has nearly unity overlap with the χ_n state and if the system is in $\psi_{n'}$ immediately prior to application of the field, then it will be in $\psi_{n'}$ immediately after the field is applied. Therefore for short times $a_{nl} \approx 1$ for l=n' and all other a_{nl} terms are nearly zero, thus:

$$i\hbar\frac{\partial a_{nn'}(t)}{\partial t} = \int \psi_{n'}^* v_p(x,t)\psi_l dV. \qquad (1.2)$$

In words, the rate at which the coefficient of the ψ_n state transitions to the $\psi_{n'}$ state is proportional to an integral of the product of the two wavefunctions and the perturbing potential.

$$i\hbar\Delta a_{nn'}(t) = i\hbar\int \partial a_{nn'}(t) \approx \int_0^t \int_{space} \psi_{n'}^* v_p(x,t')\psi_l dV \partial t'.$$

We can make the integrals more physically meaningful by remembering that the original wavefunctions are products of space and time components, $\psi_l(x,t) = u_l(x)e^{-iE_l t/\hbar}$. Making this substitution yields:

$$\Delta a_{mn}(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{nn'}t}v_{mn}\partial t'$$

where $\hbar\omega_{nn'} = (E_{n'} - E_n)$ and $v_{nn'} = \int u_{n'}^* v_p(x,t)u_l dV$ is called the spatial matrix element for the transition between $u_{n'}$ and u_n with the perturbation v_p.[7]

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[7]We are almost there!

Now we can use the appropriate potential for electromagnetic wave perturbation,

$$v_p = qxE_0 cos(\omega t) = qxE_0(e^{i\omega t} + e^{-i\omega t})/2$$

which produces a "simple" expression for the probability of finding a system that was in state ψ_n at $t = 0$ in a new state ψ_m for a perturbing field along the x-direction:

$$\Delta a_{nn'} = \frac{iqE_0}{2\hbar}x_{nn'}\int_0^t [e^{i(\omega_{nn'}-\omega)t'} + e^{i(\omega_{nn'}+\omega)t'}]dt'.$$

where

$$x_{nn'} = \int u_{n'}^* x u_n dV.$$

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1.2.1   Energy-Time Relationship

First we address the consequences of the time integral. Later we will address the space integral. Integrating in time with the assumption that the pulse starts at time zero and continues for a short time t:[9]

$$\Delta a_{nn'} = \frac{iqE_0}{2\hbar}v_{nn'}\Big[\frac{1 - e^{i(\omega_{nn'}-\omega)t}}{(\omega_{nn'} - \omega)} + \frac{1 - e^{i(\omega_{nn'}+\omega)t}}{(\omega_{nn'} + \omega)}\Big]$$

The probability the a system that starts in state ψ_n' will be found in state ψ_n a short time t later is $\Delta a_{nn'}^2$, so:

$$|\Delta a_{nn'}|^2 = q^2 E_0^2 |x_{nn'}|^2 t^2 \frac{\sin^2(\beta t)}{(\beta t)^2} \tag{1.3}$$

where $\beta = (\omega_{n'} - \omega_n - \omega)/2$ for a transition in one direction and $\beta = (\omega_{n'} - \omega_n + \omega)/2$ for a transition in the other. (A perturbing EM wave can induce a transition upward (absorption of a photon) or downward (emission)).

All of this math so far leads to the following observations with respect to the time and frequency dependence of the probability of induced transition:

- A transition is most probable when the perturbing EM wave has a frequency equal to the energy difference between the initial and final states divided by $\hbar$.

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[8]For field along the y-axis the spatial integral is $x_{nn'} = \int u_{n'}^* y u_n dV.$

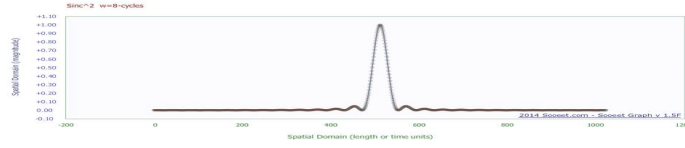[9]By short time t, we mean that the probability of transition in time t is much less than 1.

Figure 1.2: Spectral response for an atomic transition due to a pulse of frequency ω

- The probability that a transition occurs increases with field amplitude and with time.

- Transitions can be induced either upwards or downwards. The stimulation of a downwards transition by a perturbing EM wave is called *stimulated emission*

- The width of the peak in the transition probability depends on the length of time that the perturbation is applied. This relationship between the width of the peak in frequency and the time of the pulse, is another way of expressing the Heisenburg Uncertainty Principle.

- The probability of transition is proportional to the square of the spatial integral x_{nm}.

Energy-Lifetime Fourier Transform

The state $|\Psi\rangle$ can be expressed in terms of its time dependence $\Psi(t)$ or its frequency spectrum $A(\omega)$ where the two representations are related by a Fourier transform pair:

$$\Psi(t) = \frac{1}{\sqrt{2\pi}} \int A(\omega)e^{-i\omega t}d\omega$$

and

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int \Psi(t)e^{i\omega t}$$

So the time dependence of the probability that an atom is in a given state determines the probability that a photon of a particular frequency is emitted.

When we say that an atom has a particular lifetime τ in an excited state we mean that the average rate of emission of photons from a large number of atoms corresponds to an average lifetime of τ. The actual time of emission for any individual atom is not known. If the lifetime is τ and the number of excited atoms at $t = 0$ is N_0, then the number of atoms remaining after time t is
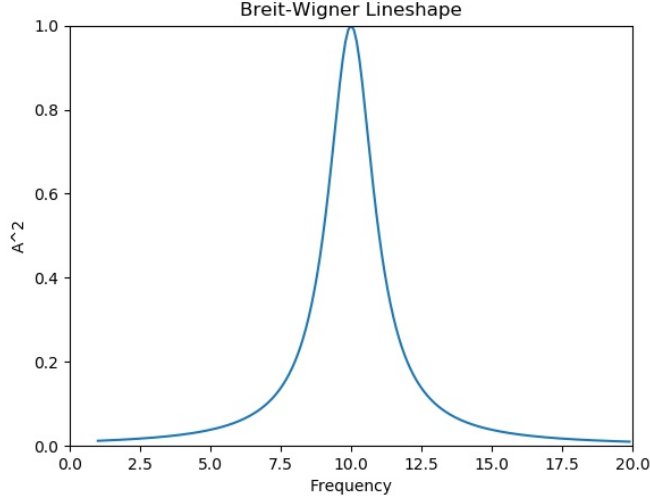
$$N(t) = N_0 e^{-t/\tau}.$$

Figure 1.3: Breit-Wigner lineshape for a center frequency of 10 units and a lifetime of 1 unit^{-1}

Figure 1.4:

This exponential decay law applies to any random decay process.

$\frac{N(t)}{N_0} = \int_t^\infty \Psi^*\Psi dt$ is the probability that an atom has survived to time t, so $\Psi^*\Psi = \frac{e^{-t/\tau}}{\tau}$. We can therefore infer that

$$|\Psi(t)| \propto e^{-t/2\tau}. \tag{1.4}$$

If the energy of the excited state is E_0, then the time-dependence of the wavefunction is given by:

$$\Psi(t) \propto e^{-t/2\tau} e^{i\omega_0 t}$$

where $\omega_0 = E_0/\hbar$. The energy spectrum $|A(\omega)|^2$ of emitted photons can be found from the Fourier transform of $\Psi(t)$ which yields the Breit-Wigner line shape:

$$|A(\omega)|^2 \propto \frac{1}{(\omega - \omega_0)^2 + (1/2\tau)^2} \tag{1.5}$$

Exercise P1.03: Show that the Fourier transform of equation 1.4 leads to the Breit-Wigner spectrum of equation 1.5.

1.2.2   The Spatial Matrix Element: Selection Rules

The transition probability above still has the

$$x_{nn'} = \int u_{n'}^* x u_n dV \tag{1.6}$$

term, which is a spatial integral. Now we will consider the ramifications of this term.

Parity

The symmetry properties of the wavefunction can frequently be used to quickly determine whether a dipole matrix element is zero or not. The parity of a wavefunction is determined by how it transforms when the sign of the spatial coordinates is changed.[10]

$$\Pi \psi(x, y, z) = \psi(-x, -y, -z)$$

with the eigenvalue equation:

$$\Pi \psi_\lambda(x, y, z) = \lambda \psi_{lambda}(x, y, z)$$

so that an eigenfunction corresponding to $\lambda = +1$ is even and corresponding to $\lambda = -1$ is odd. The dipole matrix element involves multiplication of the wavefunctions by x, y or z, which are odd functions. If the initial and final wavefunctions are both even or both odd, then the integral will be zero, because the product of two functions of the same parity is always even and integration of an odd function over symmetric limits is zero. **The conclusion is that a dipole transition is forbidden if initial and final states do not have different parity.**

Atomic transitions

The wavefunctions for atoms are usually expressed in spherical coordinates, so we'll convert the operator $x = r sin\theta cos\phi$ and $dV = r sin\theta dr d\theta d\phi$ so

$$x_{nn'} = \int_0^\pi d\phi \int_0^\infty dr \int_0^{2\pi} d\theta u_m^* u_n r^2 sin^2\theta \cos\phi.$$

If the spatial integral is zero, then the transition is said to be "forbidden". This does not actually mean that the transition can not occur, remember that we used first order perturbation approximations to get to this point. There

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[10]See Townsend section 5.1 pp. 153 ff.

are higher order corrections as well as higher order multipole electromagnetic interactions that might permit the transition, but the transition rate will be much lower.

For any spherically symmetric potential, the angular solutions to the Schrodinger equation are the spherical harmonics $Y_{l,m}(\theta, \phi) = \Phi(\phi) P_l^{|m|}(\theta)$.[11]

Magnetic Quantum Number

Consider the ϕ integral first. For spherical harmonics, $\Phi(\phi) \propto e^{im\phi}$ where m is an integer. For electric field along the x axis, we therefore want to evaluate

$$\int_0^{2\pi} e^{-im'\phi} cos\phi e^{-im\phi} d\phi = 2 \int_0^{2\pi} e^{-im'\phi}(e^{i\phi} + e^{-i\phi]})e^{im\phi}d\phi$$

This integral will only be non-zero if $m' - m = \pm 1$. This is our first "selection rule" for optical transitions. In words, the change in magnetic quantum number for electric field polarized along the x-axis, m, can only be of magnitude one.

We must also consider the possibility that the perturbing field is oriented along the z-axis. In this case $z = rcos\theta$ and therefore

$$\int_0^{2\pi} e^{-im'\phi} z e^{-im\phi} d\phi = \int_0^{2\pi} e^{-im'\phi} rcos\theta e^{-im\phi} d\phi = rcos\theta \int_0^{2\pi} e^{-im'\phi} e^{-im\phi} d\phi.$$

Which is non-zero only if $m' - m = 0$.

In summary, the transition probability can only be non-zero if $m' - m = 0$ or ± 1, depending on polarization.

Angular Momentum

The θ integral is of the form:

$$\int_0^{2\pi} u_m^* u_n sin^2\theta d\theta.$$

For spherical potentials the θ portion of the spatial matrix element involves integration of associated Legendre polynomials.[12] The math is not too bad, but the arithmetic for a general proof is more involved than I want to go into in this course. To summarize the conclusion: **If $P_l^{|m|}(cos\theta)$ represents the initial state and $P_{l'}^{|m|'}(cos\theta)$ represents the final state, then the integral on θ vanishes unless $l - l' = \pm 1$.** Note that this selection rule

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[11]See section 6.2 in Townsend, esp. p.183.
[12]See Appendix B in Townsend.

is just a special case of the parity selection rule, because the parity of an associated Legendre function is even for l=even and odd if l is odd.

Exercise P1.04: Show that the θ integral is zero for a dipole transition between a $Y_{0,0}$ state and a $Y_{2,0}$ state.