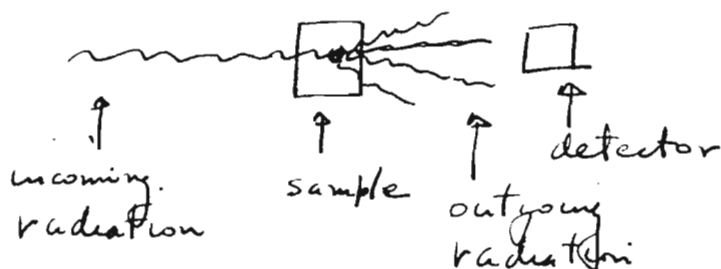


R. Cutler

Spectroscopy

Study molecular structure via the interaction of radiation with matter. Schematically



Usually, the molecules are considered to be independent of each other. That is, the radiation interacts with individual molecules.

The molecular energy levels are quantized; there is a finite energy difference between any two levels.

The incoming radiation's energy matches that of a molecular energy difference. The radiation "gives" this energy to the molecule. The detector notes this dip in the outgoing radiation.

Corresponding to different radiation energies, we probe different molecular energy levels.

Energy (or energy level differences) are expressed in terms of frequency or wave number in spectroscopy. We have that

$$\Delta E = h\nu$$

ΔE = energy difference between molecular energy states.

$h\nu$ = Planck's constant \times frequency corresponding to this energy.

Radiation is usually described in terms of frequency ν and wavelength λ . These are related by

$$\lambda\nu = c$$

where c is velocity of light in vacuum.

Combining, we have

$$\Delta E = hc(1/\lambda) = hc\sigma$$

Thus $\Delta E \sim \sigma$, the reciprocal wavelength is proportional to the energy difference.
 $\sigma = 1/\lambda =$ reciprocal wavelength (usually cm^{-1}).

We also recall that $\omega = 2\pi\nu$ (frequency in circular units)

Collecting results:

$$\Delta E = h\nu = hc\sigma$$

Representative frequencies of molecular transitions and information obtained

- 1) Rotational levels: $\nu \sim 10^{10} - 10^{13}$ cps (cycles per second) ✓
 Microwave spectroscopy: interatomic distances, dipole moments
- 2) Nuclear spin levels: $\nu \sim 10^6 - 10^8$ cps
 NMR: structure, electronic distribution
- 3) Vibrational levels: $\nu \sim 10^{12} - 10^{15}$ cps
 IR, Raman: bond force constants, bond distances.

There are 3 factors which we must consider in order to properly describe any spectroscopy experiment. Once these are understood spectroscopy is a "plug in" problem.

I) FERMI GOLDEN RULE - we must show that, in order to obtain a measurable signal in spectroscopy, we must satisfy the condition

$$h\nu = \Delta E$$

where ν is frequency of radiation and ΔE is the difference between two molecular energy eigenstates.

II) SELECTION RULES - even though $h\nu = \Delta E$ we may have no signal. This will depend on nature of interaction

between matter and radiation, and the symmetry of the eigenstates under examination.

III) THE INTERACTIONS - different spectroscopic techniques have different molecule-radiation interaction.

Once we establish these three rules, spectroscopy (whether it be IR, or NMR, or Microwave) is just an application of these rules.

I) FERMI GOLDEN RULE

We want to find differences in energy eigenstates of a molecule. To do this we induce transitions between these eigenstates with radiation. To describe this inherently time dependent process we use time dependent Schrodinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}_T \psi(t)$$

what is \hat{H}_T ? There are two parts

1) \hat{H} = hamiltonian of molecule in absence of radiation. We assume that eigenfunctions ψ_k eigenvalues E_k are known. As we saw in 461, this may be very difficult except for very simple systems, but we assume that ψ_k and E_k are known. We have

$$\hat{H} \psi_k(x) = E_k \psi_k(x)$$

2) $\hat{V}(t)$ = effect of external disturbance; the interaction between the molecule and the radiation. $\hat{V}(t)$ is time dependent because the external radiation oscillates in time.

$$\hat{H}_T = \hat{H} + \hat{V}(t)$$

Recall that if $\hat{V}(t) = 0$, the time dependent Schrodinger equation's solution is simply found from time independent Schrodinger equation's solution. [SHOW IT]

How do we work with the time dependent Schrodinger eq? If $V(t) \ll H$, then we could still use $\varphi_k(x)$ as a basis in which to expand $\Psi(x, t)$. Thus, write

$$\Psi(x, t) = \sum_k a_k(t) \varphi_k(x)$$

Insert above in time dependent Schrodinger equation to obtain equations for $a_k(t)$:

$$\sum_k \left\{ i\hbar \frac{\partial a_k(t)}{\partial t} \varphi_k(x) = [H + V(t)] a_k(t) \varphi_k(x) \right\}$$

left multiply by $\varphi_j^*(x)$ and integrate over x .

$$\sum_k \left\{ \left[\int dx \varphi_j^*(x) \varphi_k(x) \right] i\hbar \frac{\partial a_k}{\partial t} = \left[\int dx \varphi_j^*(x) H \varphi_k(x) \right] a_k(t) + \left[\int dx \varphi_j^*(x) V(t) \varphi_k(x) \right] a_k(t) \right\}$$

Note that

a) $\int dx \varphi_j^*(x) \varphi_k(x) = \delta_{jk}$; assuming orthonormal eigenfunctions.

b) $H \varphi_k(x) = E_k \varphi_k(x)$

such that

Time dep. eq. for expansion coeff.

$$i\hbar \frac{\partial a_j(t)}{\partial t} = E_j a_j(t) + \sum_k V_{jk} a_k(t)$$

where $V_{jk} = \int dx \varphi_j^*(x) V(x, t) \varphi_k(x)$

If $V(t) = 0$, we have $V_{jk} = 0$ all j, k and

$$i\hbar \frac{\partial a_j(t)}{\partial t} = E_j a_j(t)$$

or, defining new time dependent expansion coefficients,

$$U_j(t) = e^{-iE_j t/\hbar}$$

$$\hbar \frac{\partial U_j}{\partial t} = i\hbar \left(-\frac{i}{\hbar} E_j\right) U_j(t) = E_j U_j(t)$$

(5)

$$c_j(t) \equiv e^{iE_j t/\hbar} a_j(t) = E_j U_j(t)$$

[SHOW THAT, FOR $V=0$, $c_j(t) = a_j(0)$: i.e., if we use the c_j 's, then, in the absence of V , the c_j 's are constant in time. Thus, the transformation to the c_j 's extracts the harmonic oscillation of the expansion coefficients]

Using the c_j 's in the equation for the time dependence of the $a_k(t)$:

$$i\hbar \frac{\partial}{\partial t} [U_j(t) c_j(t)] = E_j U_j(t) c_j(t) + \sum_K U_K(t) V_{jK} c_K(t)$$

or, doing derivatives on l.h.s.

$$i\hbar U_j(t) \frac{\partial c_j(t)}{\partial t} + E_j U_j(t) c_j(t) = E_j U_j(t) c_j(t) + \sum_K U_K(t) V_{jK} c_K(t)$$

where $U_j(t) \equiv e^{-iE_j t/\hbar}$

left mult by $1/U_j(t)$ yields

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_K e^{i(E_j - E_K)t/\hbar} V_{jK}(t) c_K(t)$$

or, defining the frequency ω_{jK} which corresponds to difference in energy between the energy eigenstates ψ_j and ψ_K ,

$$\omega_{jK} = (E_j - E_K)/\hbar$$

we have

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_K e^{i\omega_{jK} t} V_{jK}(t) c_K(t) \quad 4$$

The above result is EXACT. It's the time dependent Schrodinger equation for the expansion coefficients $c_j(t)$.

WHAT DO WE WANT?

Want rate of transition $R_{n \rightarrow j}$ between two molecular states described by wavefunctions ψ_n and ψ_j . But a rate is probability per unit time. And, in QM, probability goes with square of expansion coefficients. That is, probability of being in

some state, say state k , is given by

$$|a_k(t)|^2 = |c_k(t)|^2$$

[SHOW that second part of above is true].

But we want transition between two states. To do this set

$$c_k(0) = \delta_{nk}$$

That is, initially have only n 'th state occupied. Then, at time t , $|c_j(t)|^2$ gives probability of transition between state n and state j in time interval t . And rate is

$$R_{n \rightarrow j} = |c_j(t)|^2 / t$$

To find this rate we make first approximation

Interaction does not cause much change. i.e. we can take

$$c_k(t) = \delta_{nk} \text{ for times of interest}$$

(this approximation can be understood precisely)

Then
$$i\hbar \frac{\partial c_j}{\partial t} = e^{i\omega_j n t} V_{jn}(t)$$

and solving

$$c_j(t) = -\frac{i}{\hbar} \int_0^t e^{i\omega_j n t'} V_{jn}(t') dt' \quad j \neq n \quad \checkmark$$

and

$$R_{n \rightarrow j} = |c_j(t)|^2 / t = \frac{1}{\hbar^2 t} \left| \int_0^t e^{i\omega_j n t'} V_{jn}(t') dt' \right|^2$$

Let us consider radiation of the form $\cos \omega t$ so that

$$\hat{V}(t) = 2\hat{V} \cos \omega t = \hat{V} (e^{i\omega t} + e^{-i\omega t}) \quad \checkmark$$

where \hat{V} = time independent interaction between radiation and molecule.

$$R_{n \rightarrow j} = \frac{1}{\hbar^2 t} V_{jn}^2 \left| \int_0^t (e^{i(\omega_{jn} + \omega)t'} + e^{i(\omega_{jn} - \omega)t'}) dt' \right|^2$$

and integrating

$$R_{n \rightarrow j} = \frac{1}{\hbar^2 t} V_{jn}^2 \left| \frac{e^{i(\omega_{jn} + \omega)t} - 1}{i(\omega_{jn} + \omega)} + \frac{e^{i(\omega_{jn} - \omega)t} - 1}{i(\omega_{jn} - \omega)} \right|^2$$

When is term in absolute value sign important? When $\omega \sim \omega_{jn}$, i.e. when energy is absorbed. If $\omega \sim \omega_{jn}$

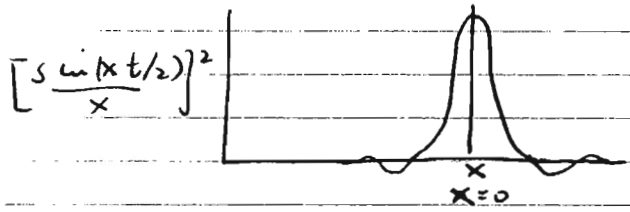
$$R_{n \rightarrow j} \sim \frac{1}{\hbar^2 t} V_{jn}^2 \left| 0(1/\omega) + \frac{e^{ixt} - 1}{ix} \right|^2$$

where $x = \omega_{jn} - \omega$ and first term is small as $x \rightarrow 0$. Thus

$$R_{n \rightarrow j} = \frac{1}{\hbar^2 t} V_{jn}^2 4 \left[\frac{\sin(xt/2)}{x} \right]^2 \quad [\text{SHOW IT}]$$

If we plot $\left[\frac{\sin(xt/2)}{x} \right]^2$ vs. x , for $t \gg 1/x$ (recall $x \rightarrow 0$)

then we have



So that for $t \gg 1/x$ predominant contribution to $R_{n \rightarrow j}$ comes from $x \sim 0$, i.e. from $\omega \approx \omega_{jn}$.

Since all radiation is never quite monochromatic (i.e. has different frequencies in it) we integrate $R_{n \rightarrow j}$ over a small range of frequency. But since only $x \sim 0$ term contributes we can integrate over all x with no appreciable error. Thus

$$R_{n \rightarrow j} = \frac{1}{\hbar^2} V_{jn}^2 \left[\frac{4}{t} \int_{-\infty}^{+\infty} dx \left[\frac{\sin(xt/2)}{x} \right]^2 \right] = \frac{2\pi}{\hbar^2} V_{jn}^2$$

Put t 's in to get t -ind. interval. But t is still then \hbar finite limit intervals

The result

$$R_{n \rightarrow j} = \frac{2\pi V_{jn}^2}{\hbar^2}$$

FERMI GOLDEN RULE ✓

is Fermi's Golden Rule. NOTE THAT $R_{n \rightarrow j}$ is time INDEPENDENT. The rate of transition between energy levels of the molecule induced by the external radiation

1) occurs at $\hbar\omega = \hbar\omega_{jn}$ (resonance condition) that is

$$\hbar\omega = \hbar\omega_{jn} = E_j - E_n$$

we have our first condition for spectroscopy.

2) The rate is independent of time.

II) SELECTION RULES Tell which transitions are allowed

$R_{n \rightarrow j}$ is proportional to V_{jn}

$$V_{jn} = \int dx \psi_j^*(x) V(x) \psi_n(x)$$

here "x" stands for all the pertinent molecular coordinates. There are two aspects which are important:

1) If $V_{jn} = 0$ for some reason, no signal will be obtained. This can arise by some symmetry.

Examples: Selection rules for HYDROGEN ATOM

a) Assume V is spin independent (usual case).

Then if

$$\psi_j^* = \alpha(m_s) X_j^* ; \psi_n = \beta(m_s) X_n$$

where α, β are spin functions.

and where X 's are spatial orbitals, then clearly

$$V_{jn} = 0 \text{ since } \langle \alpha | \beta \rangle = 0.$$

Thus, for the hydrogen atom, (with one electron) we obtain the selection rule

$$\Delta m_s = 0$$

That is, m_s must be the same, or the change Δm_s in m_s must be zero for the two states of interest if a spectroscopic signal is to be observed.

b) The selection rule depends on V of course. Lets consider, in addition to the above spin independence, that

$$V \sim \underline{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

Here, \underline{r} is a vector from nucleus to electron. This is the DIPOLE OPERATOR

We must evaluate $\langle \Psi_{NJM} | \underline{r} | \Psi_{N'J'M'} \rangle$

where the hydrogen wavefunctions Ψ are products of radial and spherical harmonic wavefunctions.

$$\Psi(r, \theta, \phi) = R_{NJ}(r) Y_J^M(\theta, \phi)$$

$$Y_J^M(\theta, \phi) = N_{JM} P_J^M(\cos \theta) \Phi_M(\phi)$$

where N_{JM} is normalization constant

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

Express \underline{r} in spherical polar coordinates

$$I = \left[\int_0^r r R_{NJ}(r) R_{N'J'}(r) r^2 dr \right]$$

$$\begin{aligned} \times & \left[\int_0^{2\pi} \cos \phi e^{i(M'-M)\phi} d\phi \int_0^\pi P_J^{|M|}(\cos \theta) P_{J'}^{|M'|}(\cos \theta) \sin^2 \theta d\theta \right] I_x \\ & + \int_0^{2\pi} \sin \phi e^{i(M'-M)\phi} d\phi \int_0^\pi P_J^{|M|}(\cos \theta) P_{J'}^{|M'|}(\cos \theta) \sin^2 \theta d\theta \quad I_y \\ & + \int_0^{2\pi} e^{i(M'-M)\phi} d\phi \int_0^\pi P_J^{|M|}(\cos \theta) P_{J'}^{|M'|}(\cos \theta) \cos \theta \sin \theta d\theta \quad I_z \end{aligned}$$

The r integral is non-zero for all combinations of Q, N, N' , so selection rule

$$\Delta N = 0, \pm 1, \pm 2, \dots$$

Let's examine the integrals I_x , I_y and I_z ;
 we know that

$$\cos\theta P_J^{|M|} = \frac{(J+|M|)}{2J+1} P_{J-1}^{|M|}(\cos\theta) + \frac{(J-|M|+1)}{2J+1} P_{J+1}^{|M|}(\cos\theta) \quad (1)$$

and

$$\sin\theta P_J^{|M|}(\cos\theta) = \frac{1}{2J+1} [P_{J+1}^{|M|+1} - P_{J-1}^{|M|+1}] = \quad (2)$$

$$= \frac{1}{2J+1} [(J+|M|+1)(J+|M|)P_{J-1}^{|M|-1} - (J-|M|+2)(J-|M|+1)P_{J+1}^{|M|-1}]$$

From now on we are going to suppress all the constants;

So

$$\cos\theta P_J^{|M|} \rightarrow P_{J-1}^{|M|}(\cos\theta) + P_{J+1}^{|M|}(\cos\theta) \quad (1)$$

$$\sin\theta P_J^{|M|} \rightarrow P_{J+1}^{|M|+1} - P_{J-1}^{|M|+1} \rightarrow P_{J-1}^{|M|-1} - P_{J+1}^{|M|-1} \quad (2)$$

$$\begin{aligned} I_x &= \int_0^{2\pi} \frac{e^{i\varphi} + e^{-i\varphi}}{2} e^{i(M-M')\varphi} d\varphi \int_0^\pi (P_{J+1}^{|M|+1} - P_{J-1}^{|M|+1}) P_J^{|M|} \sin\theta d\theta \\ &= \int_0^{2\pi} \frac{1}{2} [e^{i\varphi(1+M-M')} + e^{-i\varphi(1+M-M')}] d\varphi \left[\int_0^\pi P_{J+1}^{|M|+1} P_J^{|M|} \sin\theta d\theta - \int_0^\pi P_{J-1}^{|M|+1} P_J^{|M|} \sin\theta d\theta \right] \\ &= \frac{1}{2} \left[\frac{1}{i(1+M-M')} e^{i\varphi(1+M-M')} - \frac{1}{i(1+M-M')} e^{-i\varphi(1+M-M')} \right] \int_0^{2\pi} \left[\delta_{(J+1), J'} - \delta_{(J-1), J'} \right] \end{aligned}$$

in order to use this orthonormality in the associated Legendre polynomials $|M+1| = |M'| \Rightarrow \Delta M = \pm 1$

Also we have $J+1 = J' \Rightarrow \Delta J = -1$

$J-1 = J' \Rightarrow \Delta J = +1$

now from the first part of the I_x we get

Parity plays an important role in determining selection rules.

Recall that $[\hat{P}, \hat{H}] = 0$

for most hamiltonians. Thus the eigenfunctions of \hat{H} are either even or odd under coordinate inversion. [SEE HOMEWORK FOR EXAMPLES].

III) THE INTERACTIONS

The spectroscopic method will be determined, in part, by the nature of the interaction between the external radiation and the molecular system.

The force \underline{F} exerted on a point charge q with velocity \underline{v} is

$$\underline{F} = q\underline{E} + \frac{q}{c} \underline{v} \times \underline{B}, \quad \text{Lorentz}$$

where \underline{E} is the electric and \underline{B} the magnetic field at the charge.

For an electron in the first Bohr orbit, $\frac{\langle v^2 \rangle^{1/2}}{c} = 1/137$, so that

$\underline{v}_{jn} \sim q\underline{E} + (\frac{1}{137}) q \underline{B}$ and magnetic effects are smaller than electric effects.

Of course, if electric effect is zero (by a selection rule), we may see the magnetic effect.

It is more convenient (no new ideas) to work with the vector potential \underline{A} and the scalar potential ϕ , rather than \underline{E} and

Maxwell's equations for E.M. give

$$\underline{B} = \nabla \times \underline{A} \quad \underline{E} = -\frac{1}{c} \frac{\partial \underline{A}}{\partial t} - \nabla \phi$$

The program is to take the equation of motion,

Go TO GOLDSTEIN pg 19

$$\mathbf{F} = q \left\{ -\nabla\phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} + \frac{1}{c} \mathbf{v} \times \nabla \times \mathbf{A} \right\}$$

or. expand $\mathbf{v} \times \nabla \times \mathbf{A}$ and fiddle - see Goldstein 20, 11.

$$\mathbf{F}_x = -\frac{\partial U}{\partial x} + \frac{d}{dt} \frac{\partial U}{\partial v_x}$$

$$U = q\phi - \frac{q}{c} \mathbf{A} \cdot \mathbf{v}$$

Then

$$L = T - U = T - q\phi + \frac{q}{c} \mathbf{A} \cdot \mathbf{v} \quad \leftarrow$$

[see Goldstein, pg 20-21] $v_x = \dot{x}$

$$p_x = \frac{\partial L}{\partial \dot{x}} = m\dot{x} + \frac{q}{c} A_x$$

$H = p_x \dot{x} - L$ use p_x , eliminate \dot{x} in form of p_x

$$H = \frac{1}{2m} (p_x - (q/c) A_x)^2 + q\phi$$

quantize i.e. let $p_x \rightarrow \hat{p}_x = -i\hbar d/dx$

$$H\psi = E\psi.$$

$$H = p_x \dot{x} - L = (m\dot{x} + \frac{q}{c} A_x) \dot{x} - \frac{1}{2} m \dot{x}^2 + q\phi - \frac{q}{c} A_x \dot{x}$$

$$H = m\dot{x}^2 - \frac{1}{2} m \dot{x}^2 + q\phi = \frac{1}{2} m \dot{x}^2 + q\phi$$

sub $\dot{x} = \frac{1}{m} (p_x - \frac{q}{c} A_x)$ to get

$$H = \frac{1}{2m} (p_x - q/c A_x)^2 + (q) + (2) + q\phi$$

$$H = \frac{1}{2m} \left(\underline{p} - \frac{q}{c} \underline{A} \right)^2 + q\phi$$

DO NEWTON \rightarrow LAB \rightarrow HAMILTON HERE

$$m \frac{d^2 \underline{r}}{dt^2} = \underline{F} = q \underline{E} + q \frac{\underline{v}}{c} \times \underline{B}$$

eliminate \underline{E} and \underline{B} in favor of \underline{A} and ϕ . Then find the Lagrangian which corresponds to the above equations of motion.

Defining the generalized momenta $\underline{p}_i = \partial L / \partial \dot{\underline{x}}_i$ etc., one obtains the hamiltonian (classical). Quantizing yields, for N particles

Particle in Hamiltonian

$$V(t) = \sum_{i=1}^N \left\{ \frac{1}{2m_i} \left[-\hbar^2 \nabla_i^2 + 2i\hbar \nabla_i \cdot \underline{A}_i + 2i\hbar \frac{q_i}{c} \underline{A}_i \cdot \nabla_i + \frac{q_i^2}{2c^2} |\underline{A}_i|^2 \right] + q_i \phi \right\}$$

where $i\hbar \nabla_i = -\hat{p}_i$

For light waves (transverse radiation)

$$\nabla \cdot \underline{A} = 0$$
$$\phi = 0$$

also, unless there are strong magnetic fields, $\frac{q^2}{c^2} |\underline{A}|^2$ is small.

Thus, we have

$$\hat{V}(t) = \sum_j \frac{q_j^2}{m_j c} i\hbar \underline{A}_j \cdot \nabla_j$$

$$H = H^{(0)} + \hat{V}(t)$$

For simplicity assume \underline{A} to be $\hat{i} A_x$, a light wave propagating in the z direction with amplitude A_x :

$$A_x = A_x^0 \cos[2\pi \nu (t - \frac{z}{c})]$$

[SHOW THAT \underline{E} and \underline{B} have equal amplitudes, are at right angles to each other, and propagate along the z -axis.]

$$\underline{E} = -\frac{1}{c} \frac{\partial \underline{A}}{\partial t} \quad \underline{B} = \nabla \times \underline{A} = \hat{j} \frac{2\pi \nu}{c} A_x^0 \sin 2\pi \nu (t - \frac{z}{c}) \quad \omega = \frac{c}{\lambda} \quad \lambda \nu = c$$

Thus

$$V(t) = \sum_j \frac{q_j^2}{m_j c} A_x^0 \cos[2\pi \nu (t - \frac{z_j}{c})] \frac{\partial}{\partial x_j}$$

$$\frac{\omega \lambda}{c} = \frac{2\pi}{\lambda} \ll 1$$

For radiation wavelengths $\lambda \sim 10^3$ or longer, which is appropriate to molecular electronic states, we can take

$$\cos[2\pi \nu (t - \frac{z_j}{c})] \sim \cos 2\pi \nu t \quad \frac{c}{\lambda} \sim \frac{3 \times 10^{10} \text{ cm/sec}}{1000} = 3 \times 10^7 \text{ sec}^{-1}$$
$$c = 2\pi \nu \sim 10^{14} \text{ sec}^{-1} \text{ electron}$$

[SHOW IT by considering typical molecular dimensions and these radiation wavelengths]

Then only

As shown in Messiah, App. G, the matrix element

$$\langle j | \frac{\partial}{\partial x_i} | n \rangle = -\frac{\pi m_i}{\hbar} v_{jn} \langle j | x_i | n \rangle$$

ps 4.3
other 5.8

with $v_{jn} = (E_j - E_n)/\hbar$

Defining the dipole moment operator

$$\hat{\mu} = \sum_i q_i \hat{r}_i$$

with components $\hat{\mu}_x = \sum_i q_i \hat{x}_i$ etc

we have, for radiation polarized in the x direction

$$\langle j | \hat{V} | n \rangle = -\frac{2\pi i}{c} A_x^0 v_{jn} (\hat{\mu}_x)_{jn} \quad (\text{time ind part})$$

For radiation with no specific polarization, $\langle V^2(t) \rangle$ the phases of the waves will, for the cross terms, cancel. Thus

$$\hat{V}_{jn}^2 = \frac{4\pi^2}{c^2} v_{jn}^2 \left[(A_x^0)^2 (\hat{\mu}_x)_{jn}^2 + (A_y^0)^2 (\hat{\mu}_y)_{jn}^2 + (A_z^0)^2 (\hat{\mu}_z)_{jn}^2 \right]$$

For isotropic radiation

$$(A_x^0)^2 = (A_y^0)^2 = (A_z^0)^2 = \frac{1}{3} (A^0)^2$$

Combining with $R_{n \rightarrow j} = \frac{2\pi}{\hbar^2} \overline{\hat{V}_{jn}^2} \cos^2(2\pi\nu t)$ over period $\frac{1}{2\pi} \int_0^{2\pi} \cos^2(2\pi\nu t) dt = 1/2$

gives.

$$R_{n \rightarrow j} = \frac{2\pi}{3\hbar^2} (\langle j | \hat{\mu} | n \rangle)^2 \rho(\nu_{jn}) \quad \text{sec}^{-2}$$

where the radiation density $\rho(\nu)d\nu$ is defined by $E = \int \rho(\nu) d\nu$

$$\rho(\nu)d\nu = \frac{\pi\nu^2}{2c^2} (A^0)^2 d\nu \quad E^2 = \frac{2\pi\nu^2}{c^2} |A^0(\nu)|^2$$

[SHOW THAT $\rho(\nu)d\nu$ has the dimensions of an energy density]

$$\rho(\nu) = \frac{1}{4\pi} \overline{E^2(\nu)} = \frac{\pi\nu^2}{2c^2} (A^0)^2$$

Define Einstein transition probability coefficient for absorption:

$$B_{n \rightarrow j} = \frac{2\pi}{3\hbar^2} (\mu_{jn})^2$$

This is an absorption term since $E_n < E_j$ (examine why we only kept term $\omega \sim \omega_{jn}$ in our derivation).

For converse process; $R_{j \rightarrow n}$, can follow derivation again. Obtain

$R_{j \rightarrow n} = R_{n \rightarrow j}$
[Follow our derivation again for emission to verify above].
 $B_{j \rightarrow n} \equiv$ Einstein transition probability coefficient for emission.

Both absorption and emission are INDUCED by external field.

Now $B_{j \rightarrow n} = B_{n \rightarrow j}$

But if these transition rates are the same how do we ever see net signal? What if populations of the states are initially different; then until equalized will see a signal. But this won't work either. Proof:

Let N_i be population of state i . Then, according to detailed balance,

but if B 's are equal
 $N_j B_{j \rightarrow n} (\rho_{jn}) = N_n B_{n \rightarrow j} (\rho_{jn})$
 $N_j = N_n$

Thus, the populations of the two levels are the same, at equilibrium!

Resolution of Problem
Boltzmann distribution

$$\frac{N_j}{N_n} = e^{-h\nu_{jn}/kT} \quad \leftarrow \text{NOTE } \nu_{jn} \text{ reversed}$$

and populations can't be equal at any finite T .

A PARADOX: Einstein resolved it by postulating another

mechanism for transitions

Spontaneous emission; independent of radiation density

$$R_{j \rightarrow n} \equiv A_{j \rightarrow n}$$

$A_{j \rightarrow n}$ = Einstein transition probability for spontaneous emission

Balancing numbers now gives

$$N_j [B_{j \rightarrow n} \rho(\nu_{jn}) + A_{j \rightarrow n}] = N_n B_{n \rightarrow j} \rho(\nu_{jn})$$

If we use Planck's expression for radiation density

$$\rho(\nu) d\nu = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

we can find

$$A_{j \rightarrow n} = \frac{32\pi^3 \nu_{jn}^3}{3c^3 h} (\mu_{jn})^2$$

[SHOW THAT $A_{j \rightarrow n}$ follows from the above expressions]

Why didn't our development predict spontaneous emission? We treated the E.M. field classically. If we quantized the field, spontaneous emission would have come out of the theory.

We now have an expression which gives the rate of transitions between molecular states with the features

- I) $\omega = \omega_{jn}$; the radiation is "tuned" to an energy level difference, Fermi Golden Rule
- II) The allowed transitions are determined by selection rules
- III) The type of spectroscopy is governed by the interaction responsible for the molecular transitions

1-5 Velocity-dependent potentials and the dissipation function. Lagrange's equations can be put in the form (1-53) even if the system is not conservative in the usual sense, providing the generalized forces are obtained from a function $U(q_i, \dot{q}_i)$ by the prescription

$$Q_i = -\frac{\partial U}{\partial q_i} + \frac{d}{dt} \left(\frac{\partial U}{\partial \dot{q}_i} \right). \quad (1-54)$$

In such case Eqs. (1-53) still follow from Eqs. (1-50) with the Lagrangian given by

$$L = T - U. \quad (1-52')$$

U may be called a "generalized potential," or "velocity-dependent potential."* The possibility of using such a "potential" is not academic; it applies to one very important type of force field, namely, the electromagnetic forces on moving charges. Considering its importance, a diversion on this subject is well worthwhile.

In Gaussian units the Maxwell equations are:

$$\begin{aligned} \nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} &= 0, & \nabla \cdot \mathbf{D} &= 4\pi\rho, \\ \nabla \times \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} &= \frac{4\pi\mathbf{j}}{c}, & \nabla \cdot \mathbf{B} &= 0. \end{aligned} \quad (1-55)$$

The force on a charge q is not given entirely by the electric force

$$\mathbf{F} = q\mathbf{E} = -q\nabla\phi,$$

so that the system is not conservative in this sense. Instead, the complete force is

$$\mathbf{F} = q \left\{ \mathbf{E} + \frac{1}{c} (\mathbf{v} \times \mathbf{B}) \right\}. \quad (1-56)$$

* The history of the designation given to such a potential is curious. Apparently spurred by Weber's early (and erroneous) classical electrodynamics, which postulated velocity-dependent forces, the German mathematician E. Schering seems to have been the first to attempt seriously to include such forces in the framework of mechanics, cf. *Gött. Abh.* 18, 3 (1873). The first edition of Whittaker's *Analytical Dynamics* (1904) thus refers to the potential as "Schering's potential function," but the name apparently did not stick, for the title was dropped in later editions. We shall preferably use the name "generalized potential," including within this designation also the ordinary potential energy, a function of position only.

\mathbf{E} is not the gradient of a scalar function since $\nabla \times \mathbf{E} \neq 0$, but from $\nabla \cdot \mathbf{B} = 0$ it follows that \mathbf{B} can be represented as the curl of a vector:

$$\mathbf{B} = \nabla \times \mathbf{A}, \tag{1-57}$$

where \mathbf{A} is called the magnetic vector potential. Then the curl \mathbf{E} equation becomes

$$\nabla \times \mathbf{E} + \frac{1}{c} \frac{\partial}{\partial t} (\nabla \times \mathbf{A}) = \nabla \times \left(\mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \right) = 0.$$

Hence we can set

$$\mathbf{E} + \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = -\nabla \phi$$

or

$$\mathbf{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}. \tag{1-58}$$

go to here

In terms of the potentials ϕ and \mathbf{A} , the so-called Lorentz force (1-56) becomes

$$\mathbf{F} = q \left\{ -\nabla \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} + \frac{1}{c} (\mathbf{v} \times \nabla \times \mathbf{A}) \right\}. \tag{1-59}$$

The terms of Eq. (1-59) can be rewritten in a more convenient form. As an example consider the x component

$$(\nabla \phi)_x = \frac{\partial \phi}{\partial x}$$

and

$$\begin{aligned} (\mathbf{v} \times \nabla \times \mathbf{A})_x &= v_y \left(\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z} \right) - v_z \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) \\ &= v_y \frac{\partial A_z}{\partial x} + v_z \frac{\partial A_x}{\partial x} + v_x \frac{\partial A_x}{\partial x} - v_y \frac{\partial A_x}{\partial y} - v_z \frac{\partial A_x}{\partial z} - v_x \frac{\partial A_x}{\partial x} \end{aligned}$$

where we have added and subtracted the term

$$v_x \frac{\partial A_x}{\partial x} \quad \frac{d}{dx} (\mathbf{v} \cdot \mathbf{A})$$

Now, the total time derivative of A_x is

$$\frac{dA_x}{dt} = \frac{\partial A_x}{\partial t} + \left(v_x \frac{\partial A_x}{\partial x} + v_y \frac{\partial A_x}{\partial y} + v_z \frac{\partial A_x}{\partial z} \right),$$

where the first term arises from the explicit variation of A_x with time, and the second term results from the motion of the particle with time, which

$$\begin{aligned} f(x, y, z, t) \quad \frac{df}{dt} &= \frac{\partial f}{\partial t} \Big|_{x, y, z} + \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial y} \frac{dy}{dt} + \frac{\partial f}{\partial z} \frac{dz}{dt} \\ &= \left(\frac{df}{dt} \right)_{x, y, z} + v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} \end{aligned}$$

$$A_x = \frac{\partial}{\partial v_x} (A_x v_x + A_y v_y + A_z v_z) \\ = \frac{\partial}{\partial v_x} A_x v_x = A_x$$

1-5]

VELOCITY-DEPENDENT POTENTIALS

21

changes the spatial point at which A_x is evaluated. The x component of $\mathbf{v} \times \nabla \times \mathbf{A}$ can therefore be written as:

$$(\mathbf{v} \times \nabla \times \mathbf{A})_x = \frac{\partial}{\partial x} (\mathbf{v} \cdot \mathbf{A}) - \frac{dA_x}{dt} + \frac{\partial A_x}{\partial t}$$

With these substitutions (1-59) becomes

$$F_x = q \left\{ -\frac{\partial}{\partial x} \left(\phi - \frac{1}{c} \mathbf{v} \cdot \mathbf{A} \right) - \frac{1}{c} \frac{d}{dt} \left(\frac{\partial}{\partial v_x} (\mathbf{A} \cdot \mathbf{v}) \right) \right\}$$

$$A_x = \frac{\partial}{\partial v_x} (\mathbf{A} \cdot \mathbf{v}) ?$$

Since the scalar potential is independent of velocity this expression is equivalent to:

$$F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt} \frac{\partial U}{\partial v_x}$$

where

$$U = q\phi - \frac{q}{c} \mathbf{A} \cdot \mathbf{v} \quad (1-60)$$

$U = U(x, v)$
velocity dependent potential.

U is a generalized potential in the sense of Eq. (1-54), and the Lagrangian for a charged particle in an electromagnetic field can be written

$$L = T - q\phi + \frac{q}{c} \mathbf{A} \cdot \mathbf{v} \quad (1-61)$$

It should be noted that if only some of the forces acting on the system are derivable from a potential then Lagrange's equations can always be written in the form

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = Q_j,$$

where L contains the potential of the conservative forces as before, and Q_j represents the forces *not* arising from a potential. Such a situation often occurs when there are frictional forces present. It frequently happens that the frictional force is proportional to the velocity of the particle, so that its x component has the form:

$$F_{fx} = -k_x v_x.$$

Frictional forces of this type may be derived in terms of a function \mathcal{F} , known as *Rayleigh's dissipation function*, and defined as

$$\mathcal{F} = \frac{1}{2} \sum_i (k_x v_{ix}^2 + k_y v_{iy}^2 + k_z v_{iz}^2).$$

CHAPTER VIII

TIME-DEPENDENT PERTURBATIONS: RADIATION THEORY

8a. **Time-Dependent Perturbations.** In the previous chapter we discussed the problem of determining the new energy levels and wave functions for a system subjected to a perturbation which depended only on the space coordinates of the system. For certain problems, particularly those dealing with the emission and absorption of radiation, we need to calculate the effects produced by a perturbation which is a function of the time; therefore, we shall now develop the time-dependent perturbation theory.

The wave equation, in the form which expresses the manner in which the complete wave function Ψ changes with time, is

$$H\Psi = -\frac{h}{2\pi i} \frac{\partial \Psi}{\partial t} = i\hbar \frac{\partial \Psi}{\partial t} \quad 8.1$$

where $\hbar = \frac{h}{2\pi}$. Let us now write the Hamiltonian operator as $H = H_0 + H'$, where H_0 is independent of time and H' is a time-dependent perturbation. The unperturbed eigenfunctions Ψ^0 satisfy the equation

$$H_0\Psi^0 = i\hbar \frac{\partial \Psi^0}{\partial t} \quad 8.2$$

and are of the form $\Psi_n^0(q, t) = \Psi_n^0(q) e^{-i\frac{E_n}{\hbar}t}$. In order to obtain a solution of 8.1 we expand the function Ψ in terms of the unperturbed eigenfunctions Ψ_n^0 , with coefficients which are functions of the time; that is, we write

$$\Psi(q, t) = \sum_n c_n(t) \Psi_n^0(q, t) \quad 8.3$$

Substituting this expression for Ψ in equation 8.1 gives

$$\sum_n c_n H_0 \Psi_n^0 + \sum_n c_n H' \Psi_n^0 = i\hbar \sum_n \frac{dc_n}{dt} \Psi_n^0 + i\hbar \sum_n c_n \frac{\partial \Psi_n^0}{\partial t} \quad 8.4$$

Since the unperturbed eigenfunctions Ψ_n^0 satisfy equation 8.2, the above

equation immediately reduces to

$$\sum_n c_n \mathbf{H}' \Psi_n^0 = i\hbar \sum_n \frac{dc_n}{dt} \Psi_n^0 \quad 8.5$$

Let us now multiply both sides of this equation by Ψ_m^{0*} and integrate over coordinate space. Then

$$\sum_n c_n \int \Psi_m^{0*} \mathbf{H}' \Psi_n^0 d\tau = i\hbar \sum_n \frac{dc_n}{dt} \int \Psi_m^{0*} \Psi_n^0 d\tau = i\hbar \frac{dc_m}{dt} \quad 8.6$$

or

$$\frac{dc_m}{dt} = -\frac{i}{\hbar} \sum_n c_n \int \Psi_m^{0*} \mathbf{H}' \Psi_n^0 d\tau \quad 8.7$$

In any particular problem we will thus have a set of simultaneous differential equations which can be solved to give explicit expressions for the c_n 's.

8b. The Wave Equation for a System of Charged Particles under the Influence of an External Electric or Magnetic Field. The most important problem to which the time-dependent perturbation theory will be applied is that of radiation. In order to discuss radiation theory we need the Hamiltonian operator for a charged particle in an electromagnetic field. In deriving the classical Hamiltonian function it is more convenient to use the vector potential \mathbf{A} and the scalar potential φ rather than the electric and magnetic field strengths \mathbf{E} and \mathbf{H} . The relations between these quantities are given by the equations

$$\mathbf{H} = \nabla \times \mathbf{A}; \quad \mathbf{E} = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{A} - \nabla \varphi \quad 8.8$$

where c is the velocity of light.

A particle of mass m and charge e moving with a velocity \mathbf{v} in an electromagnetic field is subjected to a force

$$\mathbf{F} = e(\mathbf{E} + \frac{1}{c} [\mathbf{v} \times \mathbf{H}])$$

The equations of motion are therefore

$$m \frac{d^2 x}{dt^2} = -e \frac{\partial \varphi}{\partial x} - \frac{e}{c} \frac{\partial A_x}{\partial t} + \frac{e}{c} \left(\frac{dy}{dt} H_z - \frac{dz}{dt} H_y \right) \quad 8.9$$

with similar expressions for $\frac{d^2 y}{dt^2}$ and $\frac{d^2 z}{dt^2}$. Using the relation $\mathbf{H} = \nabla \times \mathbf{A}$, these equations become

$$m \frac{d^2 x}{dt^2} = -e \frac{\partial \varphi}{\partial x} - \frac{e}{c} \frac{\partial A_x}{\partial t} + \frac{e}{c} \left[\frac{dy}{dt} \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) + \frac{dz}{dt} \left(\frac{\partial A_z}{\partial x} - \frac{\partial A_x}{\partial z} \right) \right] \quad 8.10$$

etc. It is not difficult to demonstrate that these equations of motion are derivable from the Lagrangian function

$$L = \frac{m}{2} \left[\left(\frac{dx}{dt} \right)^2 + \left(\frac{dy}{dt} \right)^2 + \left(\frac{dz}{dt} \right)^2 \right] + \frac{e}{c} \left(\frac{dx}{dt} A_x + \frac{dy}{dt} A_y + \frac{dz}{dt} A_z \right) - e\varphi \quad 8.11$$

pg 126
of our
notes

From the definition of generalized momentum, $p_i = \frac{\partial L}{\partial \dot{q}_i}$, we see that

$p_x = m \frac{dx}{dt} + \frac{e}{c} A_x$, with analogous values for p_y and p_z . The Hamiltonian function is therefore

$$H = p_x \frac{dx}{dt} + p_y \frac{dy}{dt} + p_z \frac{dz}{dt} - L = \left(m \dot{x} + \frac{e}{c} A_x \right) \dot{x} - \frac{m}{2} \dot{x}^2 - \frac{e}{c} \dot{x} A_x + e\varphi$$

$$= \frac{m}{2} \left[\left(\frac{dx}{dt} \right)^2 + \left(\frac{dy}{dt} \right)^2 + \left(\frac{dz}{dt} \right)^2 \right] + e\varphi \quad 8.12$$

$$m \dot{x} = p_x - \frac{e}{c} A_x$$

or, in terms of coordinates and momenta,

$$H = \frac{1}{2m} \left[\left(p_x - \frac{e}{c} A_x \right)^2 + \left(p_y - \frac{e}{c} A_y \right)^2 + \left(p_z - \frac{e}{c} A_z \right)^2 \right] + e\varphi \quad 8.13$$

The procedure for constructing the Hamiltonian operator is identical with that followed before; in the classical Hamiltonian function the momentum p_x is replaced by $\frac{h}{2\pi i} \frac{\partial}{\partial x} = -i\hbar \frac{\partial}{\partial x}$, etc. Operating on a wave function Ψ , the first term in the Hamiltonian gives

$$\frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} - \frac{e}{c} A_x \right)^2 \Psi$$

$$= \frac{1}{2m} \left(-\hbar^2 \frac{\partial^2}{\partial x^2} + i\hbar \frac{e}{c} \frac{\partial}{\partial x} A_x + i\hbar \frac{e}{c} A_x \frac{\partial}{\partial x} + \frac{e^2}{c^2} |A_x|^2 \right) \Psi$$

$$= \frac{1}{2m} \left(-\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} + i\hbar \frac{e}{c} \frac{\partial A_x}{\partial x} \Psi \right.$$

$$\left. + i\hbar \frac{e}{c} A_x \frac{\partial \Psi}{\partial x} + i\hbar \frac{e}{c} A_x \frac{\partial \Psi}{\partial x} + \frac{e^2}{c^2} |A_x|^2 \Psi \right) \quad 8.14$$

After collecting terms, and expressing our results in vector notation, we see that the Hamiltonian operator is

$$\mathbf{H} = \frac{1}{2m} \left(-\hbar^2 \nabla^2 + i\hbar \frac{e}{c} \nabla \cdot \mathbf{A} + 2i\hbar \frac{e}{c} \mathbf{A} \cdot \nabla + \frac{e^2}{c^2} |\mathbf{A}|^2 \right) + e\varphi \quad 8.15$$

For an electromagnetic field such as that associated with a light wave, $\nabla \cdot \mathbf{A} = 0$ and $\varphi = 0$. Since the perturbation of a system by a light wave will be a small perturbation, the term $\frac{e^2}{c^2} |\mathbf{A}|^2$ may be neglected in discussing radiation, although it must be retained when discussing perturbations due to strong magnetic fields. For a system of charged particles, with an internal potential energy V , we will therefore have the Hamiltonian operator $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}'$, where

$$\mathbf{H}_0 = -\sum_j \frac{\hbar^2}{2m_j} \nabla_j^2 + V; \quad \mathbf{H}' = \sum_j \frac{e}{m_j c} i\hbar \mathbf{A}_j \cdot \nabla_j \quad 8.16$$

The operator \mathbf{H}^0 is just the operator for the system in the absence of an electromagnetic field; the perturbation \mathbf{H}' may equally well be written as $\mathbf{H}' = -\sum_j \frac{e}{m_j c} \mathbf{A}_j \cdot \mathbf{p}_j$.

8c. Induced Emission and Absorption of Radiation. Let us consider an atomic or molecular system subjected to the perturbation \mathbf{H}' of an electromagnetic field. For simplicity, we first will assume that the field is that of a plane-polarized light wave with A_y and A_z equal to zero.* We shall need to calculate the values of such matrix elements as

$$\int \Psi_m^{0*} \mathbf{H}' \Psi_n^0 d\tau = (\Psi_m^{0*} | \mathbf{H}' | \Psi_n^0) = \left(\Psi_m^{0*} \left| -\sum_j \frac{e}{m_j c} A_{xj} p_{xj} \right| \Psi_n^0 \right) \quad 8.17$$

Since molecular dimensions are of the order of 1/1000 the wavelengths of visible light, a sufficiently good approximation for our present purposes will be to take \mathbf{A} as constant over the molecule. The matrix elements

* That this situation represents a plane-polarized wave may be seen as follows: We take $\mathbf{A} = iA_x$ with

$$A_x = A_x^0 \cos 2\pi\nu \left(t - \frac{z}{c} \right)$$

This represents a wave moving in the z direction with a velocity equal to c . The associated electric and magnetic fields are then

$$\mathbf{E} = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{A} = i \frac{2\pi\nu}{c} A_x^0 \sin 2\pi\nu \left(t - \frac{z}{c} \right)$$

$$\mathbf{H} = \nabla \times \mathbf{A} = \mathbf{j} \frac{2\pi\nu}{c} A_x^0 \sin 2\pi\nu \left(t - \frac{z}{c} \right)$$

The electric and magnetic fields therefore have equal amplitudes and are at right angles to each other as well as to the direction of propagation, and hence represent a plane-polarized light wave moving along the z axis with a velocity c .

can then be written as

$$\begin{aligned} -\frac{e}{c} A_x \sum_j \frac{1}{m_j} (\Psi_m^{0*} | p_{xj} | \Psi_n^0) &\equiv -\frac{e \hbar}{c i} A_x \sum_j \frac{1}{m_j} \left(\Psi_m^{0*} \left| \frac{\partial}{\partial x_j} \right| \Psi_n^0 \right) \\ &= -\frac{e \hbar}{c i} A_x e^{i \frac{E_m - E_n}{\hbar} t} \sum_j \frac{1}{m_j} \left(\psi_m^{0*} \left| \frac{\partial}{\partial x_j} \right| \psi_n^0 \right) \end{aligned} \quad 8.18$$

In order to obtain usable results, we wish to express the matrix elements of $\frac{\partial}{\partial x_j}$ in terms of those of x_j . Let us for the moment consider that the ψ 's are functions only of one coordinate x . Then ψ_m^{0*} and ψ_n^0 satisfy the equations

$$\frac{d^2 \psi_m^{0*}}{dx^2} + \frac{2m}{\hbar^2} [E_m - V(x)] \psi_m^{0*} = 0 \quad 8.18a$$

$$\frac{d^2 \psi_n^0}{dx^2} + \frac{2m}{\hbar^2} [E_n - V(x)] \psi_n^0 = 0 \quad 8.18b$$

If we multiply the first of these equations by $x\psi_n^0$ and the second by $x\psi_m^{0*}$ and subtract, we obtain, upon integrating the resulting equation,

$$\int_{-\infty}^{\infty} \left(x\psi_n^0 \frac{d^2 \psi_m^{0*}}{dx^2} - x\psi_m^{0*} \frac{d^2 \psi_n^0}{dx^2} \right) dx = \frac{2m}{\hbar^2} (E_n - E_m) \int_{-\infty}^{\infty} \psi_m^{0*} x \psi_n^0 dx \quad 8.18c$$

The first two terms may now be integrated by parts; since the wave functions vanish at infinity, we have

$$\begin{aligned} \int_{-\infty}^{\infty} \left[\frac{d}{dx} (x\psi_n^0) \frac{d\psi_m^{0*}}{dx} - \frac{d}{dx} (x\psi_m^{0*}) \frac{d\psi_n^0}{dx} \right] dx \\ = \frac{2m}{\hbar^2} (E_m - E_n) \int_{-\infty}^{\infty} \psi_m^{0*} x \psi_n^0 dx \end{aligned} \quad 8.18d$$

or

$$\int_{-\infty}^{\infty} \left(\psi_n^0 \frac{d\psi_m^{0*}}{dx} - \psi_m^{0*} \frac{d\psi_n^0}{dx} \right) dx = \frac{2m}{\hbar^2} (E_m - E_n) \int_{-\infty}^{\infty} \psi_m^{0*} x \psi_n^0 dx \quad 8.18e$$

of we integrate the first term by parts, we see that it is equal to the second. For this one-dimensional example, we have thus obtained the result

$$\left(\psi_m^{0*} \left| \frac{\partial}{\partial x} \right| \psi_n^0 \right) = -\frac{m}{\hbar^2} (E_m - E_n) (\psi_m^{0*} | x | \psi_n^0) \quad 8.18f$$

This result can be generalized. The matrix element $(\Psi_m^{0*} | \mathbf{H}' | \Psi_n^0)$ may therefore be written as

$$(\Psi_m^{0*} | \mathbf{H}' | \Psi_n^0) = -\frac{1}{c} A_x \frac{i}{\hbar} (E_m - E_n) X_{mn} e^{i \frac{E_m - E_n}{\hbar} t} \quad 8.18g$$

where $X_{mn} = (\psi_m^{0*} | e \sum_j x_j | \psi_n^0)$ is the matrix element for the x component of the dipole moment.

If we now assume that the system was originally in the state n , so that $c_n = 1$ and all the other c 's are zero at the time $t = 0$, we have, for times sufficiently small so that all the c 's are negligible except c_n :

$$\frac{dc_m}{dt} = -\frac{1}{c\hbar^2} A_x X_{mn} (E_m - E_n) e^{\frac{i(E_m - E_n)t}{\hbar}} \quad 8.19$$

If the light has the frequency ν , the time dependence of A_x may be expressed as

$$A_x = A_x^0 \cos 2\pi\nu t = \frac{1}{2} A_x^0 (e^{2\pi i\nu t} + e^{-2\pi i\nu t})$$

Then

$$\frac{dc_m}{dt} = -\frac{1}{2c\hbar^2} A_x^0 X_{mn} (E_m - E_n) \left\{ e^{\frac{i(E_m - E_n + h\nu)t}{\hbar}} + e^{\frac{i(E_m - E_n - h\nu)t}{\hbar}} \right\} \quad 8.20$$

Integrating, and choosing the constant of integration so that c_m equal zero when $t = 0$, we have

$$c_m = \frac{i}{2c\hbar} A_x^0 X_{mn} (E_m - E_n) \left\{ \frac{e^{\frac{i(E_m - E_n + h\nu)t}{\hbar}} - 1}{(E_m - E_n + h\nu)} + \frac{e^{\frac{i(E_m - E_n - h\nu)t}{\hbar}} - 1}{(E_m - E_n - h\nu)} \right\} \quad 8.21$$

Let us consider that $E_m > E_n$, so that the transition corresponds to absorption. c_m will be large only when the denominator of the second term in brackets is nearly zero, that is, when $E_m - E_n \cong h\nu$. The probability that the system will be in the state m at time t will be the value of the product $c_m^* c_m$. The first term in brackets being neglected, this product is

$$c_m^* c_m = \frac{t^2}{4c^2\hbar^4} |A_x^0|^2 |X_{mn}|^2 (E_m - E_n)^2 \frac{\sin^2 \left\{ \frac{E_m - E_n - h\nu}{2\hbar} t \right\}}{\left\{ \frac{E_m - E_n - h\nu}{2\hbar} t \right\}^2} \quad 8.22$$

So far we have considered only a single frequency ν . To obtain the correct value of $c_m^* c_m$ we will have to integrate over a range of frequencies. Since $c_m^* c_m$ is very small except for frequencies such that $E_m - E_n \cong h\nu$, it will be satisfactory to integrate from $-\infty$ to $+\infty$ and regard A_x^0 as constant and equal to $A_x^0(\nu_{mn})$. This integration gives

$$c_m^* c_m = \frac{\pi^2 \nu_{mn}^2}{c^2 \hbar^2} |A_x^0(\nu_{mn})|^2 |X_{mn}|^2 t \quad \text{see -1} \quad 8.23$$

where $E_m - E_n$ has been replaced by $h\nu_{mn}$.

Equation 8.23 has been derived upon the assumption that the light was plane polarized. In the general case in which A_y and A_z are not zero, equation 8.23 will, of course, contain additional terms in A_y and A_z . In calculating $c_m^*c_m$ the cross terms will vanish because of the randomness of the phase differences between the various components of A ; the final expression for $c_m^*c_m$ will therefore be

$$c_m^*c_m = \frac{\pi^2\nu_{mn}^2}{c^2\hbar^2} \{ |A_x^0(\nu_{mn})|^2 |X_{mn}|^2 + |A_y^0(\nu_{mn})|^2 |Y_{mn}|^2 + |A_z^0(\nu_{mn})|^2 |Z_{mn}|^2 \} t \quad 8.24$$

If the radiation is isotropic, then

$$|A_x^0(\nu_{mn})|^2 = |A_y^0(\nu_{mn})|^2 = |A_z^0(\nu_{mn})|^2 = \frac{1}{3} |A^0(\nu_{mn})|^2 \quad 8.25$$

We may express $|A^0(\nu_{mn})|^2$ in terms of the radiation density $\rho(\nu_{mn})$. From Equation 8.8,

$$E(\nu_{mn}) = \frac{2\pi\nu_{mn}}{c} A^0(\nu_{mn}) \sin 2\pi\nu t$$

Then

$$\overline{E^2(\nu_{mn})} = \frac{2\pi^2\nu_{mn}^2}{c^2} |A^0(\nu_{mn})|^2$$

since the average value of $\sin^2 2\pi\nu t$ is $\frac{1}{2}$. In electromagnetic theory, it is shown that $\rho(\nu_{mn}) = \frac{1}{4\pi} \overline{E^2(\nu_{mn})}$, so that $|A_x^0(\nu_{mn})|^2 = \frac{2}{3} \frac{c^2}{\pi\nu_{mn}^2} \rho(\nu_{mn})$.

The product $c_m^*c_m$ may now be written in terms of the radiation density as

$$c_m^*c_m = \frac{2\pi}{3\hbar^2} \{ |X_{mn}|^2 + |Y_{mn}|^2 + |Z_{mn}|^2 \} \rho(\nu_{mn}) t \quad 8.26$$

Since the probability that the system will be in the state m is zero at time $t = 0$, and is the value given by 8.26 at time t , the probability that a transition from the state n to the state m will take place in unit time, resulting in absorption of energy from the electromagnetic field, is

$$B_{n \rightarrow m} \rho(\nu_{mn}) = \frac{2\pi}{3\hbar^2} |R_{mn}|^2 \rho(\nu_{mn}) \quad 8.27$$

where

$$|R_{mn}|^2 = |X_{mn}|^2 + |Y_{mn}|^2 + |Z_{mn}|^2 \quad 8.28$$

If the system is originally in the state m , then the same treatment shows that the probability of transition to the state n , resulting in the emission of energy, due to the perturbing effect of the electromagnetic

field, is

$$B_{m \rightarrow n} \rho(\nu_{mn}) = B_{n \rightarrow m} \rho(\nu_{mn}) \quad 8\cdot29$$

8d. **The Einstein Transition Probabilities.** The coefficients $B_{m \rightarrow n}$ and $B_{n \rightarrow m}$ are known as the Einstein transition probability coefficients for induced emission and absorption, respectively. Since a system in an excited state can emit radiation even in the absence of an electromagnetic field, the completion of the theory of radiation requires the calculation of the transition probability coefficient $A_{m \rightarrow n}$ for spontaneous emission. The direct quantum-mechanical calculation of this quantity is a problem of great difficulty, but its value has been determined by Einstein¹ by a consideration of the equilibrium between two states of different energy. If the number of systems in the state with energy E_m is N_m , and the number in the state with energy E_n is N_n , then the Boltzmann distribution law states that at equilibrium

$$\frac{N_m}{N_n} = \frac{e^{-\frac{E_m}{kT}}}{e^{-\frac{E_n}{kT}}} = e^{-\frac{h\nu_{mn}}{kT}} \quad 8\cdot30$$

where T is the absolute temperature and k is the Boltzmann constant. Expressed in terms of the transition probability coefficients discussed above, the number of systems making the transition from m to n in unit time is

$$N_m \{A_{m \rightarrow n} + B_{m \rightarrow n} \rho(\nu_{mn})\}$$

Similarly, the number of systems making the reverse transition is

$$N_n B_{n \rightarrow m} \rho(\nu_{mn})$$

Since at equilibrium these two numbers are equal, we have, after eliminating the ratio $\frac{N_m}{N_n}$ by means of equation 8·30,

$$e^{-\frac{h\nu_{mn}}{kT}} = \frac{B_{n \rightarrow m} \rho(\nu_{mn})}{A_{m \rightarrow n} + B_{m \rightarrow n} \rho(\nu_{mn})}$$

$$\text{or} \quad \rho(\nu_{mn}) = \frac{A_{m \rightarrow n} e^{-\frac{h\nu_{mn}}{kT}}}{-B_{m \rightarrow n} e^{-\frac{h\nu_{mn}}{kT}} + B_{n \rightarrow m}} \quad 8\cdot31$$

Using relation 8·29, the energy density may therefore be written as

$$\rho(\nu_{mn}) = \frac{\frac{A_{m \rightarrow n}}{B_{m \rightarrow n}}}{e^{\frac{h\nu_{mn}}{kT}} - 1} \quad 8\cdot32$$

¹ A. Einstein, *Physik. Z.*, 18, 121 (1917).

The energy density in a radiation field in equilibrium with a black body at a temperature T may be calculated by the methods of quantum statistical mechanics (Chapter XV) and, as mentioned in Chapter I, is given by Planck's radiation distribution law as

$$\rho(\nu_{mn}) = \frac{8\pi h\nu_{mn}^3}{c^3} \frac{1}{e^{\frac{h\nu_{mn}}{kT}} - 1} \quad 8.33$$

Comparing 8.32 and 8.33, we see that

$$A_{m \rightarrow n} = \frac{8\pi h\nu_{mn}^3}{c^3} B_{m \rightarrow n}$$

or

$$A_{m \rightarrow n} = \frac{32\pi^3 \nu_{mn}^3}{3c^3 \hbar} |R_{mn}|^2 \quad 8.34$$

To the degree of approximation used above, the coefficient for spontaneous emission depends only on the matrix element for the electric dipole moment between the two states. If the variation of the field over the molecule is not neglected, there will be additional terms in the expression for $A_{m \rightarrow n}$, the first two additional terms being those corresponding to magnetic dipole and electric quadrupole radiation. Including these terms gives²

$$A_{m \rightarrow n} = \frac{32\pi^3 \nu_{mn}^3}{3c^3 \hbar} \left\{ |(m|er|n)|^2 + \left| \left(m \left| \frac{e}{2mc} \mathbf{r} \times \mathbf{p} \right| n \right) \right|^2 + \frac{3}{10} \pi^3 \frac{\nu_{mn}^2}{c^2} |(m|err|n)|^2 \right\} \quad 8.35$$

We may estimate the relative orders of magnitude of these terms as follows. Disregarding the constant term, we have

$$|(m|er|n)|^2 \sim (ea_0)^2 \sim 6.5 \times 10^{-36} \text{ c.g.s.}$$

$$\left| \left(m \left| \frac{e}{2mc} \mathbf{r} \times \mathbf{p} \right| n \right) \right|^2 \sim \left(\frac{e\hbar}{2mc} \right)^2 \sim 8.7 \times 10^{-41} \text{ c.g.s.}$$

$$\frac{3}{10} \pi^3 \frac{\nu_{mn}^2}{c^2} |(m|err|n)|^2 \sim 6.8 \times 10^{-43} \text{ c.g.s.} \quad (\lambda = 5000 \text{ \AA})$$

We thus see that the probability of transition due to magnetic dipole or electric quadrupole radiation will be negligible in comparison to the probability of transition due to electric dipole radiation. The higher terms in 8.35 will therefore be of importance only in those cases in which

²E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, p. 96, Cambridge University Press, 1935.

the electric dipole matrix element $(m|er|n)$ vanishes because of the symmetry properties of the states m and n .

The actual intensity of radiation of frequency ν_{mn} due to spontaneous emission will, of course, be

$$I(\nu_{mn}) = N_m(h\nu_{mn})A_{m \rightarrow n} \quad 8.36$$

8e. **Selection Rules for the Hydrogen Atom.** According to the results derived above, the only transitions of importance in the hydrogen atom will be between those states a and b for which

$$(a|er|b) = e\{i(a|x|b) + j(a|y|b) + k(a|z|b)\}$$

is different from zero. The eigenfunctions for the hydrogen atom may be written as

$$\psi_{n, l, m} = f(r)P_l^{|m|}(\cos \theta) e^{im\varphi}$$

so that we must investigate the values of such integrals as

$$\int \psi_{n, l, m} z \psi_{n', l', m'}^* d\tau = \int \psi_{n, l, m}(r \cos \theta) \psi_{n', l', m'}^* d\tau$$

This integral may be written as the product of integrals in r , θ , and φ . The integrals in r will be non-vanishing, so that we may concentrate our attention on the integrals over the angular coordinates. For the z component of the electric dipole moment we must therefore investigate the integral

$$\int P_l^{|m|} \cos \theta P_{l'}^{|m'|} \sin \theta d\theta \int e^{i(m-m')\varphi} d\varphi \quad 8.37$$

From the recursion formulas for the associated Legendre polynomials (equation 4.85), we have

$$\cos \theta P_l^{|m'|} = \frac{l' - |m'| + 1}{2l' + 1} P_{l'+1}^{|m'|} + \frac{l' + |m'|}{2l' + 1} P_{l'-1}^{|m'|} \quad 8.38$$

The integral 8.37 is therefore non-vanishing only if

$$m = m'; \quad l = l' \pm 1 \quad 8.39$$

These relations are the selection rules for the emission of light polarized in the z direction. Rather than calculate the matrix components for x and y separately it is more convenient to calculate those for the combinations $(x + iy) = r \sin \theta e^{i\varphi}$ and $(x - iy) = r \sin \theta e^{-i\varphi}$. For the combination $(x - iy)$ we have the integrals

$$\int P_l^{|m|} \sin \theta P_{l'}^{|m'|} \sin \theta d\theta \int e^{i(m-m'-1)\varphi} d\varphi \quad 8.40$$

The integral over φ is non-vanishing only if $m = m' + 1$. From the recursion formula 4.86

$$\sin \theta P_l^{m'} = \frac{1}{2l+1} \{P_{l+1}^{m'+1} - P_{l-1}^{m'+1}\} \quad 8.41$$

we see that the integral over θ is non-vanishing only if $l = l' \pm 1$. Similarly for the combination $(x + iy)$ we have the selection rules $m = m' - 1$, $l = l' \pm 1$. The selection rules for the hydrogen atom may therefore be written as

$$\Delta l = \pm 1; \quad \Delta m = 0, \pm 1 \quad 8.42$$

The selection rules for the different types of polarization are, of course, significant only when there is a unique z direction, due, for example, to the presence of a uniform magnetic field. This subject will be discussed more fully in the following chapter, where the Zeeman effect is considered. It is apparent from the derivation of the above selection rules that they are not limited to the hydrogen atom but are valid for any central field problem where the angular portion of the wave function is identical with that of the hydrogen atom.

8f. Selection Rules for the Harmonic Oscillator. Let us now consider the system consisting of a particle moving along the x axis with a harmonic motion. Let the charge on the particle be $+e$, and let the charge at the position of equilibrium be $-e$. The instantaneous value of the electric dipole moment will then be ex . The wave functions for the system will be the eigenfunctions of the harmonic oscillator (section 5e). A transition between the states n and m will be possible only if the integral

$$(n|ex|m) = e \int \psi_n x \psi_m dx \quad 8.43$$

is different from zero. From the recursion formula (equation 4.99)

$$xH_m = mH_{m-1} + \frac{1}{2}H_{m+1} \quad 8.44$$

we see immediately that the integral 8.43 will be zero unless $m = n \pm 1$. This is the selection rule for the harmonic oscillator; only the fundamental frequency ν can be emitted or absorbed by this system. We shall later require the exact values of the integrals in 8.43. The wave functions are

$$\psi_n(x) = N_n e^{-\frac{\xi^2}{2}} H_n(\xi) \quad 8.45$$

where

$$\xi = \sqrt{\alpha} x \quad N_n = \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^n n!}\right)^{1/2}$$

so that

$$(n|ex|n+1) = N_n N_{n+1} \frac{e}{\sqrt{\alpha}} \int e^{-\xi^2} H_n(\xi) \xi H_{n+1}(\xi) dx \quad 8.46$$

By the use of the recursion formula 8.44, this reduces to

$$\begin{aligned} (n|ex|n+1) &= N_n N_{n+1} \frac{e}{\sqrt{\alpha}} \int e^{-\xi^2} H_n(\xi) (n+1) H_n(\xi) dx \\ &= \frac{e}{\sqrt{\alpha}} (n+1) \frac{N_{n+1}}{N_n} \int [\psi_n(x)]^2 dx = \frac{e}{\sqrt{\alpha}} (n+1) \frac{N_{n+1}}{N_n} \end{aligned} \quad 8.47$$

Introducing the explicit expressions for the normalizing factors, we obtain

$$(n|ex|n+1) = e \sqrt{\frac{n+1}{2\alpha}} \quad 8.48$$

Similarly,

$$\begin{aligned} (n|ex|n-1) &= N_n N_{n-1} \frac{e}{\sqrt{\alpha}} \int e^{-\xi^2} H_n(\xi) \xi H_{n-1}(\xi) dx \\ &= \frac{e}{2\sqrt{\alpha}} \frac{N_{n-1}}{N_n} = e \sqrt{\frac{n}{2\alpha}} \end{aligned} \quad 8.49$$

8g. Polarizability; Rayleigh and Raman Scattering. If α is the polarizability of an atomic system, then an electric field \mathbf{E} induces a dipole moment $\mathbf{R} = \alpha\mathbf{E}$ in the system. Let us consider classically a system in which an electron of charge $-e$ is bound elastically to an equilibrium position at which there is a charge $+e$. If the system is subjected to an alternating electric field of strength $\mathbf{E} = \mathbf{E}_0 \cos \omega t$, the classical equation of motion is

$$m \frac{d^2 \mathbf{r}}{dt^2} + k\mathbf{r} = -e\mathbf{E}_0 \cos \omega t \quad 8.50$$

where \mathbf{r} is the displacement of the electron from the origin and k is the force constant of the forces binding the electron to the equilibrium position. The steady-state solution of this equation is

$$\mathbf{r} = \frac{-e\mathbf{E}_0 \cos \omega t}{k - m\omega^2} = \frac{-\frac{e}{m} \mathbf{E}_0 \cos \omega t}{\omega_0^2 - \omega^2} \quad 8.51$$

where $\omega_0 = \sqrt{\frac{k}{m}}$. The dipole moment of the system is $\mathbf{R} = -e\mathbf{r}$;

NOTATION

$$q^{3N} = (q_1, q_2, q_3, \dots, q_{3N}) : \text{Use } \boxed{q^N \Rightarrow q^{3N}}$$

$$q^{3N} \cdot p^{3N} \equiv q_1 p_1 + q_2 p_2 + \dots + q_{3N} p_{3N} = \sum_{i=1}^{3N} q_i p_i$$

$$dp^{3N} = dp_1 dp_2 \dots dp_{3N}$$

Holonomic system – described by a minimum set of independent quantities

NUMBER OF DEGREES OF FREEDOM – minimum number of independent coordinates required to define mechanical state.

Holonomic constraints, $f(q_1 \dots q_k) = 0$, each such equation reduces the number of degrees of freedom by one.

Example: two particles tied together $\Rightarrow x = a \quad y - b = 0 \quad z - c = 0$.

Non-holonomic constraints, given by inequalities – harder – example. friction

Statistical mechanics only has holonomic constraints.

HOW COORDINATES EVOLVE IN TIME.

Newton's Equations of Motion

$$\begin{aligned} \text{Cartesian coordinate} \quad m_i \dot{x}_i &= F_{x_i} = -\partial V / \partial x_i \\ (i=1, 2, \dots, N) & \quad \quad \quad (\text{conservative systems in SM}) \\ & \quad \quad \quad = V \text{ time independent} \Rightarrow F = -\nabla V \end{aligned}$$

Two other useful formulations: *Lagrange* and *Hamilton*

Lagrange Equations of Motion

$$\text{Take Newton} \quad m_i \ddot{x}_i = -\partial V / \partial x_i \quad V = V(x_1, x_2, \dots, x_{3N})$$

define kinetic energy,

$$T = \frac{1}{2} \sum_{k=1}^N m_k (\dot{x}_k^2 + \dot{y}_k^2 + \dot{z}_k^2)$$

$$\frac{\partial T}{\partial \dot{x}_i} = m_i \dot{x}_i$$

Define *Lagrangian* $L = T - V$

Then, from Newton's equations of motion

$$\frac{d}{dt}(m_i \dot{x}_i) = \frac{d}{dt} \left(\frac{\partial T}{\partial \dot{x}_i} \right) = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}_i} \right) = + \frac{\partial L}{\partial x_i}.$$

So,

$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}_i} \right) = \frac{\partial L}{\partial x_i}$	LAGRANGE EQS. of MOTION	3N equations
---	----------------------------	--------------

$$L = L(x_1, \dots, z_{3N}, \dot{x}_1, \dots, \dot{z}_{3N}) \quad \text{i. e., positions and velocities.}$$

Important property: Lagrange's equations have same form in *any* coordinate system [YOU PROVE IN PROBLEM SET].

- Advantages:*
- 1) easy to generalize to non-conservative, non holonomic,
 - 2) scalar equations (not vector as Newton),
 - 3) natural field equations,
 - 4) easy to quantize.

Hamiltonian equations of motion

Note that Lagrange is 3N 2nd order in time.

Want to replace them by 6N 1st order in time. (More convenient for SM.)

Use new coordinate system.

General Momentum: $p_i = \frac{\partial L}{\partial \dot{q}_i}$ Defines p_i .

Example: Cartesian coordinates

$$p_{x_i} = \frac{\partial L}{\partial \dot{x}_i} = m_i \dot{x}_i$$

so, p_{x_i} is ordinary linear momentum.

If q_i is angle, p_i is angular momentum.

We want the equations of motion in terms of q^N, p^N , not q^N, \dot{q}^N . Recall the *Legendre transformation*. We have $L(q^N, \dot{q}^N, t)$ and want to go to some other function, say $H = H(q^N, p^N, t)$. Define, in anticipation,

$$-H = L - p^N \cdot \dot{q}^N = L - \sum_{k=1}^{3N} p_k \dot{q}_k$$

Now, $dH = \frac{\partial H}{\partial q^N} \cdot dq^N + \frac{\partial H}{\partial p^N} \cdot dp^N + \frac{\partial H}{\partial t} dt$. (Note—see below for expansion of any function F as a total derivative)

But, we also have

$$dH = \underbrace{-\frac{\partial L}{\partial q^N} \cdot dq^N}_{(1)} - \underbrace{\frac{\partial L}{\partial \dot{q}^N} \cdot d\dot{q}^N}_{(2)} - \underbrace{\frac{\partial L}{\partial t} dt}_{(3)} + \underbrace{\dot{q}^N \cdot dp^N}_{(4)} + \underbrace{p^N \cdot d\dot{q}^N}_{(5)}$$

but recall that $p^N = \frac{\partial L}{\partial \dot{q}^N}$ $\frac{d}{dt} \frac{\partial L}{\partial \dot{q}^N} = \frac{d}{dt} p^N = \dot{p}^N = \frac{\partial L}{\partial q^N}$ (1)
 --Lagrange Equation--

Thus, $dH = -\dot{p}^N \cdot dq^N + \dot{q}^N \cdot dp^N - \frac{\partial L}{\partial t} dt$
 (2) + (5) = 0

Comparing yields

$$\dot{p}^N = -\frac{\partial H}{\partial q^N} \quad \dot{q}^N = \frac{\partial H}{\partial p^N} \quad \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$$

HAMILTON'S EQS. OF MOTION

We all know that $H = T + V$; can we recover this? Sure

$$H = -L + p^N \cdot \dot{q}^N = \dot{q}^N \cdot \frac{\partial L}{\partial \dot{q}^N} - L = \dot{q}^N \cdot \frac{\partial T}{\partial \dot{q}^N} - L,$$

but $\dot{q}^N \cdot \frac{\partial T}{\partial \dot{q}^N} = 2T$ i.e., $\dot{x}_i \frac{\partial T}{\partial \dot{x}_i} = \dot{x}_i \frac{2m_i \dot{x}_i}{2} = 2T_{x_i}$

$$H = 2T - L = 2T - (T - V) = T + V \quad \checkmark \quad (\text{for conservative systems}).$$

We have 2N 1st order in time differential equations; i. e., given $q(t=0)p(t=0)$ have $q(t)$, $p(t)$ for all time from Hamilton's equations of motion.