Digital Computer Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

SUBJECT: GROUP 63 SEMINAR ON MAGNETISM XXVII

To: Group 63

From: Arthur Loeb, Norman Menyuk

Date: February 4, 1953

Radiation

In quantum mechanics, the problem of radiation is treated in terms of time-dependent perturbations. Previously we dealt with time-independent perturbation theory, and we assumed a value of ϵ close to the value of one of the diagonal terms. However, if the value of the terms are varying, ϵ might be close to the value of a particular diagonal term at one time and not later. Thus this assumption is no longer useful in radiation theory and another approach is needed.

Let us consider an impinging monochromatic electric field $F^o \cos \omega t$. The potential due to the dipole interaction with the radiation is then

$$er F^o \cos \omega t = \mu F^o \cos \omega t = \mathcal{H}'$$

where e = electron charge
r = dipole displacement
μ = dipole moment

We are interested in a system having a large number of unperturbed states. However, it should be borne in mind that systems which were formerly considered perturbed are, when solved, considered unperturbed. For example, we treated the diatomic molecule by perturbation theory. When this problem is solved the radiation is considered as the only perturbation. Each of our unperturbed states, $(\Psi_1^o, \Psi_2^o, \Psi_3^o, \_ \_ \_ \_)$, represents a possible state of the system. As before, we express the perturbed system as a linear combination of the unperturbed states. Thus:

$$\Psi = \sum_n D_n \Psi_n^o = \sum_n D_n \psi_n^o e^{-i \frac{E_n^o}{\hbar} t} \qquad \text{XXVII-1}$$

Furthermore, we previously defined our C's such that

$$\Psi = \sum_n c_n \psi_n^o$$

Therefore

$$C_n = D_n \, e^{\frac{-i E_n^o}{\hbar} t} \qquad \text{XXVII - 2}$$

Since

$$i\hbar \frac{\partial C_m}{\partial t} = \sum_n H_{mn} C_n,$$

$$D_m E_m^o \, e^{\frac{-i E_m^o}{\hbar} t} + i\hbar \frac{\partial D_m}{\partial t} e^{\frac{-i E_m^o}{\hbar} t} = \sum_n H_{mn} D_n \, e^{\frac{-i E_n^o}{\hbar} t}$$

$$i\hbar \frac{\partial D_m}{\partial t} = - D_m E_m^o + \sum_n H_{mn} D_n \, e^{\frac{-i (E_n^o - E_m^o) t}{\hbar}}$$

Recall (equation XXV-2)

$$H_{mn} = E_m^o \delta_{mn} + H_{mn}'$$

Therefore

$$i\hbar \frac{\partial D_m}{\partial t} = -D_m E_m^o + D_m E_m^o + \sum_n H_{mn}' D_n \, e^{\frac{-i (E_n^o - E_m^o) t}{\hbar}}$$

$$i\hbar \frac{\partial D_m}{\partial t} = \sum_n H_{mn}' D_n \, e^{\frac{-i (E_n^o - E_m^o) t}{\hbar}} \qquad \text{XXVII - 3}$$

We are interested in determining the manner of variation of the D's immediately after the radiation impinges upon the system. Let us assume that at time t = o the system is in a particular unperturbed state; e.g. the k^{th} state. In that case, initially

$$i\hbar \frac{\partial D_{km}}{\partial t} = H_{mk}' D_{kk} \, e^{-i \frac{E_k^o - E_m^o}{\hbar} t} \qquad \text{XXVII - 4}$$

since at time t = o, only the state n = k exists.

We have previously defined the perturbed part of our Hamiltonian

$$H' = \mu F^o \cos \omega t$$

Therefore

$$H'_{mk} = \mu_{mk} \frac{F^o}{2} (e^{i\omega t} + e^{-i\omega t}) \qquad \text{XXVII - 5}$$

where $\mu_{mk} = \int \psi_m^{o*} \mu \psi_n^o \, dt$

Substituting into XXVII - 4,

$$i\hbar \frac{\partial D_{km}}{\partial t} = \frac{\mu_{mk} F^o D_{kk}}{2} \left[e^{-i\left(\frac{E_k - E_m}{\hbar} - \omega\right) t} + e^{-i\left(\frac{E_k - E_m}{\hbar} + \omega\right) t} \right] \qquad \text{XXVII-6}$$

For the particular case m = k

$$i\hbar \frac{\partial D_{kk}}{\partial t} = \mu_{kk} F^o D_{kk} \cos \omega t$$

$$\frac{d D_{kk}}{D_{kk}} = \frac{-i \mu_{kk} F^o}{\hbar} \cos \omega t \, dt$$

Integrating,

$$\ln D_{kk} = \frac{-i \mu_{kk} F^o}{\hbar \omega} \sin \omega t + \text{Constant}$$

$$D_{kk} = K e^{\frac{-i\mu_{kk} F^o}{\hbar\omega} \sin \omega t}$$

At time $t = o$, $D_{kk} = 1$

Therefore $K = 1$ and

$$D_{kk} = e^{-\frac{i\mu_{kk} F^o}{\hbar\omega} \sin \omega t} \qquad \text{XXVII - 7}$$

Substituting into XXVII - 6, we have

$$i\hbar \frac{\partial D_{km}}{\partial t} = \frac{\mu_{mk} F^o}{2} \left(e^{\frac{-i \mu_{kk} F^o}{\hbar \omega} \sin \omega t} \right) \left[e^{-i\left(\frac{E_k - E_m}{\hbar} - \omega\right) t} + e^{-i\left(\frac{E_k - E_m}{\hbar} + \omega\right) t} \right] \quad \text{XXVII - 8}$$

We are interested in integrating the above to determine the value of D_{km} shortly after radiation begins. If the time involved is short, we may make approximation $D_{kk} = 1$. In that case we set the term in parenthesis in equation XXVII - 8 equal to unity. This is justified if $\mu_{kk} F^o << E_k - E_m$ (small perturbation).

Then:

$$D_{km} = \frac{\mu_{mk} F^o}{i \hbar} \int \left[e^{-i\left(\frac{E_k - E_m}{\hbar} - \omega\right) t} + e^{-i\left(\frac{E_k - E_m}{\hbar} + \omega\right) t} \right] dt$$

$$D_{km} = \frac{\mu_{mk} F^o}{i \hbar} \left[\frac{e^{-i\left(\frac{E_k - E_m}{\hbar} - \omega\right) t}}{\left(\frac{E_k^o - E_m^o}{\hbar} - \omega \right)} + \frac{e^{-i\left(\frac{E_k - E_m}{\hbar} + \omega\right) t}}{\left(\frac{E_k^o - E_m^o}{\hbar} + \omega \right)} \right] + \text{Constant}$$

$$D_{km} = \text{Constant} - i \mu_{mk} F^o \left[\frac{e^{-i\left(\frac{E_k - E_m}{\hbar} - \omega\right) t}}{(E_k^o - E_m^o - \hbar\omega)} + \frac{e^{-i\left(\frac{E_k - E_m}{\hbar} + \omega\right) t}}{(E_k^o - E_m^o + \hbar\omega)} \right]$$

at time $t = o$, $D_{km} = 0 \quad (k \neq m)$

Therefore

$$\text{Constant} = i \mu_{mk} F^o \left[\frac{1}{(E_k^o - E_m^o - \hbar\omega)} + \frac{1}{(E_k - E_m + \hbar\omega)} \right]$$

and

$$D_{km} = i \mu_{mk} F^o \left[\frac{1 - e^{-i\left(\frac{E_k^o - E_m^o}{\hbar} - \omega\right) t}}{(E_k^o - E_m^o - \hbar\omega)} + \frac{1 - e^{-i\left(\frac{E_k^o - E_m^o}{\hbar} + \omega\right) t}}{(E_k^o - E_m^o + \hbar\omega)} \right] \quad \text{XXVII-9}$$

If $E_k^o - E_m^o = \pm \hbar\omega$, we have a resonance effect and the response is large. This is the condition assumed by Bohr and discussed at our twelfth meeting. We see from the above that this resonance occurs if the radiation frequency multiplied by Planck's constant is equal to the difference between two energy levels of the system.

To find the probability of transition between the k^{th} and m^{th} levels, we find

$$\frac{\partial |D_{km}|^2}{\partial t} \propto \left(\frac{\mu_{mk} F^o}{\hbar}\right)^2 \qquad \text{XXVII-10}$$

Thus the transition probability between any levels is proportional to the radiation intensity. A transition between states k and ℓ, where $\mu_{k\ell} = 0$, cannot occur, and this is known as a forbidden transition.

Spectroscopists have long been aware of the fact that not all conceivable transitions between energy levels do occur. Evaluation of the expression μ_{mk} has provided an explanation for the experimentally evaluated selection rules.

Signed ______________
Arthur Loeb

Signed ______________
Norman Menyuk

Approved ______________
David R. Brown

ALL/NM:jrt

cc: Group 62 (20)