Digital Computer Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

SUBJECT: <u>GROUP 63 SEMINAR ON MAGNETISM, XXV</u>

To: Group 63 Staff

From: Arthur L. Loeb and Norman Menyuk

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At the previous meeting we obtained the equation

$$\sum_n C_n(t)\, H_{mn} = i\hbar \frac{\partial C_m(t)}{\partial t} \qquad \text{XXIV-5}$$

where $H_{mn} = \int \psi_m^{o*} \mathcal{H} \psi_n^{o} \, d\tau$

This represents an infinite array, as was indicated by equations XXIV-6.

Since $H = H^o + H'$, where H^o is the Hamiltonian of the unperturbed system and H' is a small corrective term, we may write

$$H_{mn} = \int \psi_m^{o*} \mathcal{H}^o \psi_n^o \, d\tau + \int \psi_m^{o*} \mathcal{H}' \psi_n^o \, d\tau \qquad \text{XXV-1}$$

But ψ^o is an eigenfunction of $\mathcal{H}^o$; therefore

$$H_{mn} = E_n^o \int \psi_m^{o*} \psi_n^o \, d\tau + H_{mn}'$$

$$H_{mn} = E_n^o \, \delta_{mn} + H_{mn}' \qquad \text{XXV-2}$$

In order to solve equation XXIV-5, we will assume

$$C_m(t) = a_m e^{-\frac{i\epsilon}{\hbar} t} \qquad \text{XXV-3}$$

This is of the general exponential form ae^{kt} since ϵ has not been defined and $-\frac{i\epsilon}{\hbar}$ is a constant. This particular form is chosen for convenience in the work to follow.

Therefore

$$i\hbar \frac{\partial C_m}{\partial t} = \epsilon C_m \qquad \text{XXV-4}$$

and equation XXIV-5 becomes

$$\sum_n C_n H_{mn} = \epsilon C_m \qquad \text{XXV-5}$$

This represents an infinite array of equations

$$\left.\begin{array}{l}
(H_{11} - \epsilon)\, C_1 + H_{12}\, C_2 + H_{13}\, C_3 + \ldots\ldots + H_{1n}\, C_n + \ldots\ldots = 0 \\
H_{21}\, C_1 + (H_{22} - \epsilon) C_2 + H_{23}\, C_3 + \ldots\ldots\ H_{2n}\, C_n + \ldots\ldots = 0 \\
H_{31}\, C_1 + H_{32}\, C_2 + (H_{33} - \epsilon)\, C_3 + \ldots\ldots\ H_{3n}\, C_n + \ldots\ldots = 0 \\
\vdots \\
H_{n1}\, C_1 + H_{n2}\, C_2 + H_{n3} C_3 + \ldots\ldots\ldots\ (H_{nn} - \epsilon) C_n + \ldots = 0 \\
\vdots
\end{array}\right\} \text{XXV-6}$$

According to Cramer's rule in algebra, a set of linear homogeneous equations like those in XXV-6 has a solution in which the unknown C_n's are not identically zero if, and only if, the determinant of the coefficients of these unknowns vanishes. That is:

$$\begin{vmatrix}
H_{11} - \epsilon & H_{12} & H_{13} & \cdots & H_{1n} & \cdots \\
H_{21} & H_{22} - \epsilon & H_{23} & \cdots & H_{2n} & \cdots \\
H_{31} & H_{32} & H_{33} - \epsilon & \cdots & H_{3n} & \cdots \\
\vdots & \vdots & \vdots & & \vdots & \\
H_{n1} & H_{n2} & H_{n3} & \cdots & H_{nn} - \epsilon & \cdots \\
\vdots & \vdots & \vdots & & \vdots &
\end{vmatrix} = 0 \qquad \text{XXV-7}$$

In dealing with the above determinant of infinite rows and columns, we will limit ourselves at first to time independent perturbations. Note that only the perturbation is assumed to be time independent; this does not mean that the system is independent of time.

Let us see how the above determinant compares with that of an inperturbed system. Since $H_{mn} = E_n^{\ o}\, \delta_{mn} + H_{mn}'$, we see that if $H_{mn}' = 0$ the only non-zero terms are the diagonal elements.

$$\begin{vmatrix}
H_{11} - \epsilon & 0 & 0 & \cdots\cdots & \\
0 & H_{22} - \epsilon & 0 & \cdots\cdots & \\
0 & 0 & H_{33} - \epsilon & \cdots\cdots & \\
\vdots & \vdots & \vdots & \ddots & H_{nn} - \epsilon \\
 & & & & \vdots
\end{vmatrix} = 0$$

We therefore have an infinite number of solutions, namely $\epsilon = H_{11}$, $\epsilon = H_{22}$, ... $\epsilon = H_{nn}$......, etc.

If we choose our unpertubed system such that the perturbation is small, then in the determinant

$$\begin{vmatrix} H_{11}-\epsilon & H_{12}' & \cdots\cdots & H_{1n}' & \cdots\cdots \\ H_{21}' & H_{22}-\epsilon & \cdots\cdots & H_{2n}' & \cdots\cdots \\ H_{31}' & H_{32}' & \cdots\cdots & H_{3n}' & \cdots\cdots \\ \vdots & \vdots & & \vdots & \\ H_{n1}' & H_{n2}' & \cdots\cdots & H_{nn}-\epsilon & \cdots\cdots \\ \vdots & \vdots & & \vdots & \end{vmatrix} = 0$$

The off-diagonal terms $(H_{k\ell})$ $k \neq \ell$ will be expected to be small.

Then, for small perturbations, the values of ϵ would not be far different from their values for the case of no perturbation. We can therefore consider a particular solution of ϵ, namely $\epsilon = \epsilon_k$, which makes $H_{kk} - \epsilon$ smaller in value than any other diagonal term.

In this case, the determinant for which we want to find the approximate solution is

$$\begin{vmatrix} H_{11}-\epsilon_k & H_{12}' & \cdots\cdots\cdots & & \cdots\cdots \\ H_{21}' & H_{22}-\epsilon_k & \cdots\cdots\cdots & & \cdots\cdots \\ \vdots & & & & \\ H'_{k1} & \cdots\cdots & H_{kk}-\epsilon_k & \cdots\cdots\; H'_{kn} & \cdots\cdots \\ \vdots & & & & \\ H'_{n1} & \cdots\cdots & H_{n}'_{k} & \cdots\cdots\; H_{nn}-\epsilon_k & \cdots \\ \vdots & & & & \end{vmatrix} = 0 \quad \text{XXV-8}$$

Let us consider the magnitude of the elements in the above determinant. We are considering the perturbation to be small; therefore, all the off diagonal terms are small. Of the diagonal elements $H_{kk} - \epsilon_k$ is smaller than all the other diagonal elements since we have chosen the particular value ϵ_k which is nearly equal to H_{kk}.

To approximate the solution of this determinant, we will consider the terms in decreasing order of magnitude. Since the off diagonal elements are small, the largest term will be the product of the diagonal term; that is,

$$(H_{11} - \epsilon_k)\ (H_{22} - \epsilon_k)\ (H_{33} - \epsilon_k)\ldots\ldots(H_{kk} - \epsilon_k)\ldots\ldots(H_{nn} - \epsilon_n). \quad \text{XXV-9}$$

This term may be said to be of first order smallness since it involves just one small term, namely, $H_{kk} - \epsilon_k$. The terms of the next largest order of magnitude will be of second order smallness, involving two small elements multiplied by all but one of the large elements. To find these terms, consider the determinant

$$\begin{vmatrix}
H_{11}-\epsilon_k & H'_{12} & \cdots & H'_{1k} & \cdots & H'_{1n} & \cdots \\
H'_{21} & H_{22}-\epsilon_k & \cdots & H'_{2k} & \cdots & H'_{2n} & \cdots \\
H'_{31} & H'_{32} & \cdots & H'_{3k} & \cdots & H'_{3n} & \cdots \\
\vdots & \vdots & & \vdots & & \vdots & \\
H'_{k1} & H'_{k2} & \cdots & H_{kk}-\epsilon_k & \cdots & H'_{kn} & \cdots \\
\vdots & \vdots & & \vdots & & \vdots & \\
H'_{n1} & H'_{n2} & \cdots & H'_{nk} & \cdots & H_{nn}-\epsilon_k & \cdots \\
\vdots & \vdots & & \vdots & & \vdots &
\end{vmatrix}$$

In reducing the above, let us multiply H'_{kn} by its minor. This has the advantage of eliminating the one small diagonal element rather than one of the large elements. Part of the above determinant then becomes

$$H'_{kn}\begin{vmatrix}
H_{11}-\epsilon_k & H'_{12} & \cdots & H'_{1k} & H'_{1,k+1} & \cdots & H'_{1,n-1} & H'_{1,n+1} & \cdots \\
H'_{21} & H_{22}-\epsilon_k & \cdots & H'_{2k} & H'_{2,k+1} & \cdots & H'_{2,n-1} & H'_{2,n+1} & \cdots \\
\vdots & & & \vdots & \vdots & & \vdots & \vdots & \\
H'_{k-1,1} & H'_{k-1,2} & & H'_{k-1,k} & H'_{k-1,k+1} & \cdots & H'_{k-1,n-1} & H'_{k-1,n+1} & \cdots \\
H'_{k+1,1} & H'_{k+1,2} & \cdots & H'_{k+1,k} & H_{k+1,k+1}-\epsilon & \cdots & H'_{k+1,n-1} & H'_{k+1,n+1} & \cdots \\
\vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots & \\
H'_{n-1,1} & H'_{n-1,2} & \cdots & H'_{n-1,k} & H'_{n-1,k+1} & \cdots & H_{n-1,n-1}-\epsilon_k & H'_{n-1,n+1} & \cdots \\
H'_{n1} & H'_{n2} & \cdots & H'_{nk} & H'_{n,k+1} & \cdots & H'_{n,n-1} & H'_{n,n+1} & \cdots \\
H'_{n+1,1} & H'_{n+1,2} & \cdots & H_{n+1,k} & H'_{n+1,k+1} & \cdots & H'_{n+1,n-1} & H_{n+1,n+1}-\epsilon_k & \cdots \\
\vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots &
\end{vmatrix}$$

The elements lying along the diagonal in the above determinant are circled. It may be noted that the a number of the large elements are no longer diagonal elements. However, if H'_{nk} is multiplied by its minor, we obtain:

$$
\begin{array}{l}
\\ \\ \\ \\
H'_{nk}\,H'_{kn}
\end{array}
\left|
\begin{array}{cccccccc}
(H_{11}-\epsilon_k) & H'_{12} & \cdots\cdots & H'_{1,k-1} & H'_{1,k+1} \cdots\cdots & H'_{1,n-1} & H'_{1,n+1} & \cdots\cdots \\
H'_{21} & (H_{22}-\epsilon_k) & \cdots\cdots & H'_{2,k-1} & H'_{2,k+1} \cdots\cdots & H'_{2,n-1} & H'_{2,n+1} & \cdots\cdots \\
\vdots & \vdots & & \vdots & \vdots & \vdots & \vdots & \\
H'_{k-1,1} & H'_{k-1,2} & \cdots & (H_{k-1,k-1}-\epsilon) & H'_{k-1,k+1} \cdots & H'_{k-1,n-1} & H'_{k-1,n+1} & \cdots\cdots \\
H'_{k+1,1} & H'_{k+1,2} & & H'_{k+1,k-1} & (H_{k+1,k+1}-\epsilon) \cdots & H'_{k+1,n-1} & H'_{k+1,n+1} & \cdots\cdots \\
\vdots & \vdots & & \vdots & \vdots & \vdots & \vdots & \\
H'_{n-1,1} & H'_{n-1,2} & \cdots & H'_{n-1,k-1} & H'_{n-1,k+1} \cdots & (H_{n-1,n-1}-\epsilon) & H'_{n-1,n+1} & \cdots \\
H'_{n+1,1} & H'_{n+1,2} & \cdots & H'_{n+1,k-1} & H'_{n+1,k+1} \cdots & H'_{n+1,n-1} & (H_{n+1,n+1}-\epsilon) & \cdots \\
\vdots & \vdots & & \vdots & \vdots & \vdots & \vdots &
\end{array}
\right|
$$

The resultant determinant, with the diagonals circled, is shown above. We see the diagonal now contains all the original terms with the single exception of $(H_{nn} - \epsilon_k)$. One term of the above determinant is:

$$(H'_{nk})\,(H'_{kn})\,(H_{11} - \epsilon_k)\,(H_{22} - \epsilon_k)\ \ldots\ldots\ldots\ldots(H_{n+1,n+1} - \epsilon_k)\ \ldots$$

and it is of second order smallness as desired. However, it is not the only term since H'_{kn} and H'_{nk} were chosen for an arbitrary value of n. We therefore sum over all values of n. Then, including the first term (equation XXV-9) we have as an approximation of the determinant XXV-8.

$$
\begin{aligned}
&(H_{11} - \epsilon_k)\,(H_{22} - \epsilon_k)\,(H_{33} - \epsilon_k)\ \ldots\ldots\ (H_{kk} - \epsilon_k)\ \ldots\ldots\ (H_{nn} - \epsilon_k) \\
&+ \sum_{\substack{n \\ n \neq k}} (H_{11} - \epsilon_k)\,(H_{22} - \epsilon_k)\ \ldots\ldots\ (H'_{nk})\ \ldots\ldots\ (H'_{kn}) = 0
\end{aligned}
\qquad \text{XXV-10}
$$

The summation represents the first order perturbation, and has two small terms. We will not consider higher order perturbations, involving more than two small terms.

We may rewrite equation XXV-10

$$\Big[(H_{11}-\epsilon_k)(H_{22}-\epsilon_k)\cdots(H_{kk}-\epsilon_k)\cdots(H_{nn}-\epsilon_k)\cdots\Big]\Big[1+\sum_{\substack{n \\ k\neq n}}\frac{H'_{kn}\,H'_{nk}}{(H_{kk}-\epsilon_k)(H_{nn}-\epsilon_n)}\Big] = 0 \qquad \text{XXV-11}$$

If none of the terms in the first bracket are zero, the second bracket must equal zero.

Therefore

$$\sum_{\substack{n \\ k \neq n}}' \frac{H'_{kn}\, H'_{nk}}{(H_{kk} - \epsilon_k)\,(H_{nn} - \epsilon_k)} = -1$$

$$\epsilon_k - H_{kk} = \sum_{\substack{n \\ k \neq n}}' \frac{H'_{kn}\, H'_{nk}}{(H_{nn} - \epsilon_k)}$$

and, since $\epsilon_k \approx H_{kk}$ we may approximate

$$\epsilon_k \approx H_{kk} + \sum_{\substack{n \\ k \neq n}}' \frac{H'_{kn}\, H'_{nk}}{(H_{nn} - H_{kk})} \qquad \text{XXV-12}$$

This enables us to obtain $C_m(t)$ for the case where ϵ has a value near H_{kk}.

From equation XXV-5 we have

$$\sum_n' H_{mn}\, C_{kn} = \epsilon_k\, C_{km} \qquad \text{XXV-13}$$

where the k in the subscripts represents the fact that we are interested in the energy region around the k^{th} level.

In order that we may determine the order of magnitude of the various elements on the left-hand side of equation XXV-13, let us consider the equation

$$\Psi = \sum_n' C_n(t)\, \psi_n^\circ$$

The above equation tells us the contribution of each unperturbed state to the wave function Ψ. Since we are in the region of the k^{th} energy level, we would expect the ψ_k° term to be the only large term. C_k should therefore be much larger than all other C_n terms. Furthermore, we know that H_{mn} is small for $m \neq n$ and large for $m = n$.

Therefore, we will approximate equation XXV-13 by eliminating all terms of second order smallness (e.g. we eliminate all terms $H_{mn}\, C_n$ where $n \neq m$ and $n \neq k$). We then have

$$H'_{mk}\, C_{kk} + H_{mm}\, C_{km} = \epsilon_k\, C_{km}$$

$$(H_{mm} - \epsilon_k)\, C_{km} = -\, H'_{mk}\, C_{kk}$$

Therefore

$$C_{km} = -\frac{C_{kk}\, H'_{mk}}{H_{mm} - \epsilon_k} \approx -\frac{C_{kk}\, H'_{mk}}{H_{mm} - H_{kk}}$$

$$C_{km} = \frac{C_{kk}\, H'_{mk}}{H_{kk} - H_{mm}} \qquad \text{XXV-14}$$

Equation XXV-14 tells us the magnitude of the admixture of unperturbed states other than the $k^{\underline{th}}$ (e.g. the $m^{\underline{th}}$) to the perturbed system which is near the $k^{\underline{th}}$ level. We see that the magnitude of C_{km} is directly proportional to be perturbation term H'_{mk} relating the $m^{\underline{th}}$ and k-$\underline{th}$ levels, and is inversely proportional to the difference between the $m^{\underline{th}}$ and k-$\underline{th}$ levels. Thus the amount of admixture is greatest between unperturbed states of small energy difference ($H_{mm} - H_{kk}$ small) and with large coupling (H'_{nk} large).

We are now able to identify the $\underline{\epsilon}$'s as physical entities. From equation XXIV-3 we have

$$\Psi_k = \sum_n c_{kn} \psi_n^{\circ}.$$

Hence equation XXV-14 gives

$$\Psi_k = c_{kk} \sum_{\substack{n \\ n \neq k}} \frac{H'_{nk}}{H_{kk} - H_{nn}} \psi_n^{\circ} + c_{kk}\, \psi_k^{\circ}$$

$$\Psi_k = c_{kk} \left[\sum_{\substack{n \\ n \neq k}} \frac{H'_{nk}}{H_{kk} - H_{nn}} \psi_n^{\circ} + \psi_k^{\circ} \right] \qquad \text{XXV-15}$$

Since we have confined ourselves to the case of time independent perturbations, the term in the brackets of the above equation is not a function of time.

Therefore,

$$\mathcal{E}\, \Psi_k = i\hbar \frac{\partial}{\partial t} \left\{ c_{kk} \left[\sum_{\substack{n \\ n \neq k}} \frac{H'_{nk}}{H_{kk} - H_{nn}} \psi_n^{\circ} + \psi_k^{\circ} \right] \right\}$$

$$= \left[\sum_{\substack{n \\ n \neq k}} \frac{H'_{nk}}{H_{kk} - H_{nn}} \psi_n^{\circ} + \psi_k^{\circ} \right] \left(i\hbar \frac{\partial C_{kk}}{\partial t} \right)$$

$$\mathcal{E}\Psi_k = \left[\sum_{\substack{n \\ n \neq k}} \frac{H'_{nk}}{H_{kk} - H_{nn}} \psi_n^{\circ} + \psi_k^{\circ}\right] (\epsilon_k \, c_{kk})$$

$$\therefore \quad \mathcal{E}\Psi_k = \epsilon_k \Psi_k \qquad \text{XXV-16}$$

ϵ_k is an eigenvalue of Ψ_k, and represents the energy of the $k^{\underline{th}}$ perturbed state.

Now let us further examine the magnitude of C_{kk}

$$\Psi_k = \sum_n C_{kn}(t)\,\psi_n^{\circ}$$

$$= (c_{kk}\psi_k^{\circ} + \sum_{\substack{n \\ n \neq k}} c_{kn}\psi_n^{\circ})$$

$$\Psi_k^{*} = (c_{kk}^{*}\psi_k^{\circ *} + \sum_{\substack{n \\ n \neq k}} c_{kn}^{*}\psi_n^{\circ *})$$

The normalization condition states:

$$\int \Psi_k^{*}\Psi_k \, d\tau = 1$$

$$\int (c_{kk}\psi_k^{\circ} + \sum_{\substack{n \\ n \neq k}} c_{kn}\psi_n^{\circ})(c_{kk}^{*}\psi_k^{\circ *} + \sum_{\substack{n \\ n \neq k}} c_{kn}^{*}\psi_n^{\circ *})\, d\tau = 1$$

Applying the orthogonality as well as the normality condition, the above becomes

$$c_{kk}\,c_{kk}^{*} + \sum_n c_{kn}\,c_{kn}^{*} = 1$$

or

$$|c_{kk}|^2 + \sum_{\substack{n \\ n \neq k}} |c_{kn}|^2 = 1$$

$$\therefore \quad |C_{kk}|^2 = 1 - \sum |C_{kn}|^2$$

Since $C_{kk} \gg C_{kn}$ for $k \neq n$

$$|C_{kk}|^2 \approx 1$$

XXV-17

Signed Norman Menyuk
Norman Menyuk

Arthur L. Loeb
Arthur L. Loeb

Approved DRB
David R. Brown

ALL/NM:jk

cc: Group 62 (20)