

Digital Computer Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XXVI
To: Group 63 Staff
From: Arthur L. Loeb and Norman Menyuk
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In the previous lecture we found (equation XXXV-13)

$$\Psi_K = C_{KK} \left[\sum_{n \neq k} \frac{H_{nK}}{H_{KK} - H_{nn}} \psi_n^0 + \psi_K^0 \right] \quad \text{XXV-13}$$

wherein the factor $\frac{H_{nK}}{H_{KK} - H_{nn}}$ represents the amount of admixture of ψ_n^0 in Ψ_K .

This equation leads to difficulties if two or more diagonal terms are equal or differ by less than the off-diagonal terms. This difficulty arises from the summation term, since it will not converge for the case $H_{nn} \approx H_{KK}$.

Before continuing with the general discussion of the problem, a special example will be studied. We will consider the diatomic molecule consisting of two protons and one electron. The potential V of the molecule is shown by the solid line of Figure 51. This curve is approximated by $V_0 + V'$ where V_0 is essentially the same as V everywhere except at the center of the molecule. Here, $V_0 > V$, as indicated by the heavy dashed line of Figure 51. The difference between the potentials $V - V_0 = V'$. Therefore, V' is negative and is indicated by the shaded region of Figure 51. Hence H' will be negative in this problem.

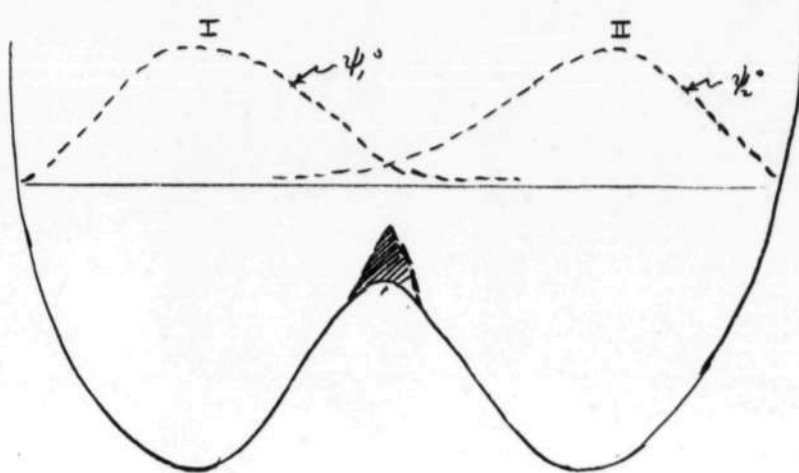


Figure 51

The levels will be doubly degenerate throughout the range of energy levels since the energy term due to proton I and the electron will have its counterpart due to proton II and the electron. All the energy levels of I will interact with all the levels of II, but since the amplitude of the interaction term varies inversely with the energy difference, we will first ignore all terms but the one between corresponding levels.

If the electron is associated with proton I we have

$$\Psi_1^0 = \psi_1^0 e^{-\frac{E^0}{\hbar} t}$$

as indicated by dotted line of Figure 51.

If electron is associated with proton II we have

$$\Psi_2^0 = \psi_2^0 e^{-\frac{E^0}{\hbar} t}$$

as indicated by dashed line of Figure 51.

These functions correspond to the same energy E^0 .

In the general case, for perturbed functions, we must write

$$\Psi(t) = \sum_n C_n(t) \psi_n^0$$

XXIV-3

Therefore, for our case

$$\Psi = C_1 \psi_1^0 + C_2 \psi_2^0$$

XXVI-1

We only consider two terms, since we know that the admixture of the other states is much smaller.

From XXIV-5,

$$\left. \begin{aligned} i\hbar \frac{\partial C_1}{\partial t} &= H_{11} C_1 + H_{12} C_2 \\ i\hbar \frac{\partial C_2}{\partial t} &= H_{21} C_1 + H_{22} C_2 \end{aligned} \right\} \text{XXVI-2}$$

We have defined

$$H_{11} = \int \psi_1^* \mathcal{H} \psi_1 d\tau$$

$$H_{22} = \int \psi_2^* \mathcal{H} \psi_2 d\tau$$

We saw in Figure 51 that the only difference between ψ_1^0 and ψ_2^0 is that the integrands are displaced with respect to each other in space. Therefore, since we are integrating over all space to obtain H_{11} and H_{22} , we can say

$$H_{11} = H_{22} = H$$

Similarly

$$H_{12} = H_{21} = H'$$

From (XXVI-3), (XXVI-2), and (XXV-3)

$$(H - \epsilon) C_1 + H' C_2 = 0$$

$$H' C_1 + (H - \epsilon) C_2 = 0$$

Therefore

$$(H - \epsilon)^2 = H'^2$$

$$H - \epsilon = \pm H'$$

$$\epsilon = H \mp H'$$

XXVI-4

This is completely analogous to the resultant frequencies we obtained on solving the two-identical-coupled-oscillator problem. (See Lecture 14).

In order to solve for C_1 and C_2 , we first consider the case $E = H - H'$.

Then

$$H' C_1 + H' C_2 = 0$$

$$C_1 = -C_2 = C_A$$

and

$$\Psi_A = C_A (\psi_1^0 - \psi_2^0)$$

XXVI-5a

On the other hand, for $E = H + H'$,

$$H'c_1 - H'c_2 = 0$$

$$c_1 = c_2 = c_2$$

and

$$\Psi_s = C_s (\psi_1^0 + \psi_2^0)$$

XXVI-5b

In equation XXVI-5a interchanging the atoms changes the sign of Ψ_A . Therefore, Ψ_A is called an antisymmetric wave function.

On the other hand, in equation XXVI-5b, changing the atoms leaves Ψ_s unchanged. Ψ_s is therefore a symmetric wave function.

From equation XXV-3, we have

$$C_m(t) = a_m e^{-\frac{E}{\hbar} t}$$

If we assume that ψ_1^0 , ψ_2^0 , Ψ_A , and Ψ_s in equations XXVI-5 are normalized, we have

$$|c| = \frac{1}{\sqrt{2}} e^{-\frac{E}{\hbar} t}$$

$$\left. \begin{aligned} \Psi_A &= \frac{1}{\sqrt{2}} (\psi_1^0 - \psi_2^0) e^{-i \frac{(H-H')}{\hbar} t} \\ \Psi_s &= \frac{1}{\sqrt{2}} (\psi_1^0 + \psi_2^0) e^{-i \frac{(H+H')}{\hbar} t} \end{aligned} \right\} \text{XXVI-6}$$

Both functions correspond to stationary states of different energy. Ψ_s is the state of lower energy because $H' < 0$.

Since Ψ_A and Ψ_s are satisfactory solutions, their sum and difference are too.

$$\Psi_1 = \frac{1}{\sqrt{2}} (\Psi_s + \Psi_A) = e^{-i \frac{H}{\hbar} t} \left[\psi_1^0 \cos \frac{H' t}{\hbar} - i \psi_2^0 \sin \frac{H' t}{\hbar} \right]$$

$$\Psi_2 = \frac{1}{\sqrt{2}} (\Psi_s - \Psi_A) = e^{-i \frac{H}{\hbar} t} \left[\psi_2^0 \cos \frac{H' t}{\hbar} - i \psi_1^0 \sin \frac{H' t}{\hbar} \right]$$

On considering the probability functions we see

$$\Psi_1^* \Psi_1 = |\psi_1^0|^2 \cos^2 \frac{H't}{\hbar} + |\psi_2^0|^2 \sin^2 \frac{H't}{\hbar}$$

$$\Psi_2^* \Psi_2 = |\psi_2^0|^2 \cos^2 \frac{H't}{\hbar} + |\psi_1^0|^2 \sin^2 \frac{H't}{\hbar}$$

Thus at time $t = 0$, the probability distribution of the Ψ_1 function is the same as that of ψ_1^0 , while the Ψ_2 function has the same probability distribution as ψ_2^0 . However, the functions Ψ_1 and Ψ_2 are not stationary, and at time $t = \pi/2H'$ the probability distribution of the Ψ_1 function is the same as that of ψ_2^0 , and Ψ_2 leads to the same probability distribution as ψ_1^0 . At time $t = \pi/H'$ the probability distribution is the same as at time $t = 0$. Thus $|\Psi_1|^2$ and $|\Psi_2|^2$ are fluctuating between the probability distribution of the individual wells. This indicates that if a particle in one well is approached by another well, the particle will be in the other well after a while and will oscillate between the wells.

If a particle in a well is approached by many wells (e. g., a condensed system), the particle will initially be in the first well and then will migrate amongst all the wells.

The initial, unperturbed wave functions would then form a set $\psi_1^0, \psi_2^0, \dots, \psi_l^0$, each function representing the particle in one of the l wells. Solving the perturbation problem results in a wave function Ψ which at $t > 0$ is very unlikely to return to its original value. This is analogous to multiple periodic motions (Lissajous figures) in classical mechanics. The larger the values of l , the smaller the probability of the system's returning to its original state. When l is very large, the problem is treated statistically. As more terms ψ_n become admixed in Ψ , the randomness of the system increases, or, in statistical language, the entropy increases. The latter result is well-known.

Physical Relationships

Let us consider the one-dimensional case, with the protons located to the left and right of the ordinate axis of Figure 52, as indicated by the asterisks. The various wave functions will then appear as shown.

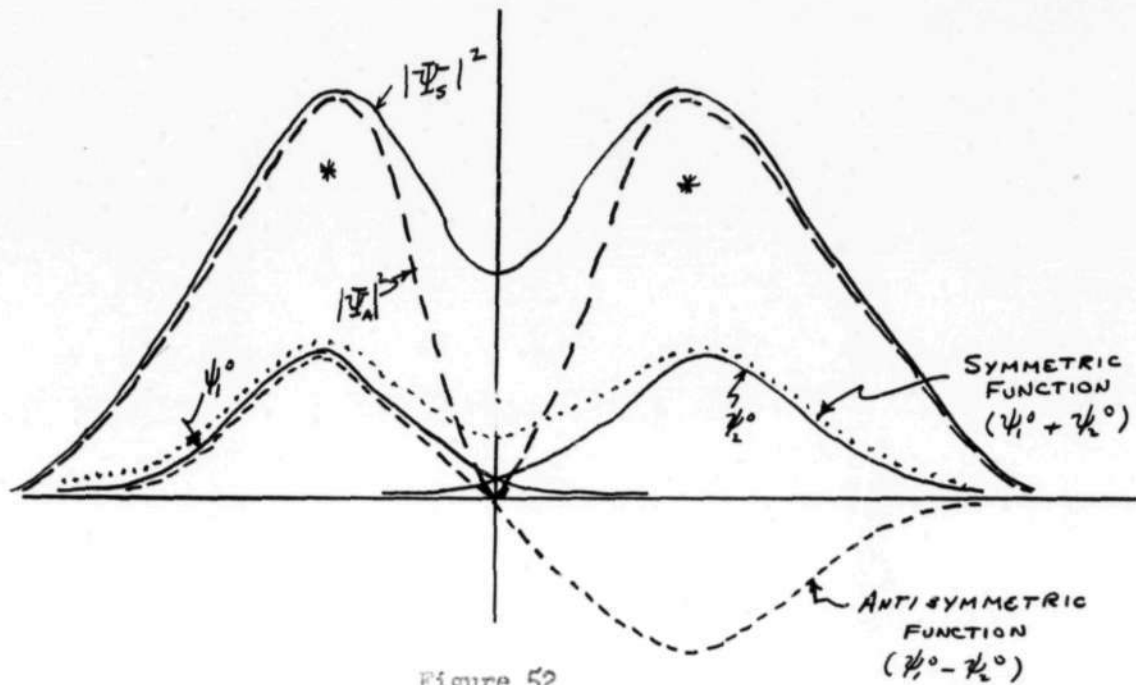


Figure 52

When the wave function is in the symmetrical state, the electron spends a good deal of time between the protons (as shown by dotted line in Figure 52). In the asymmetrical case, the electron spends little time between the protons. For the symmetrical case, there is therefore more probability of the electron's shielding one proton from the other than for the asymmetrical case.

An additional property of the symmetrical and antisymmetrical wave functions is that

$$\int \Psi_A^* H' \Psi_S d\tau = 0$$

XXVI-7

and there is no transition between a symmetrical and an antisymmetrical system.

Thus, in a matrix, both the row and the column of any non-zero element will correspond to a symmetrical or an asymmetrical wave function. If the row corresponds to a symmetrical wave function and the column to an asymmetrical function (or vice versa), the element will be zero. This is illustrated by the matrix below:

	Ψ_A	Ψ_A	Ψ_A	Ψ_S	Ψ_S	Ψ_S
Ψ_A	—	—	—	0	0	0
Ψ_A	—	—	—	0	0	0
Ψ_A	—	—	—	0	0	0
Ψ_S	0	0	0	—	—	—
Ψ_S	0	0	0	—	—	—
Ψ_S	0	0	0	—	—	—

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Let us return to the more general degeneracy problem, where we had a large number of degenerate levels. We have the set of degenerate levels contained in a sub-matrix. Then we can treat the degenerate unperturbed states by perturbation theory if we first diagonalize the sub-matrix. This, in effect, removes the degeneracy.


Thus in the case of the system of the two protons and one electron we effectively diagonalized the 2×2 matrix by dealing with Ψ_A and Ψ_B instead of Ψ_1^0 and Ψ_2^0 .

If the off-diagonal terms are zero,

$$\sum \frac{H_{nk}'}{H_{kk} - H_{nn}} = \frac{0}{\sim 0} = 0.$$

Thus the troublesome terms are removed from the summation.

Signed



 Arthur C. Leab

Signed



 Norman Menyuk

Approved



 David R. Brown

ALL:NM/bs

Group 62 (20)