Digital Computer Laboratory
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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM XXIV

To: Group 63

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The square potential well problem is important in the study of atomic behavior because it represents a first order approximation of the potential field in which the electrons of an atom find themselves. This is shown in figure 49, in which a typical potential function is shown with the square well approximation superposed.

In figure 49, r represents the radial distance of the electron from the nucleus.

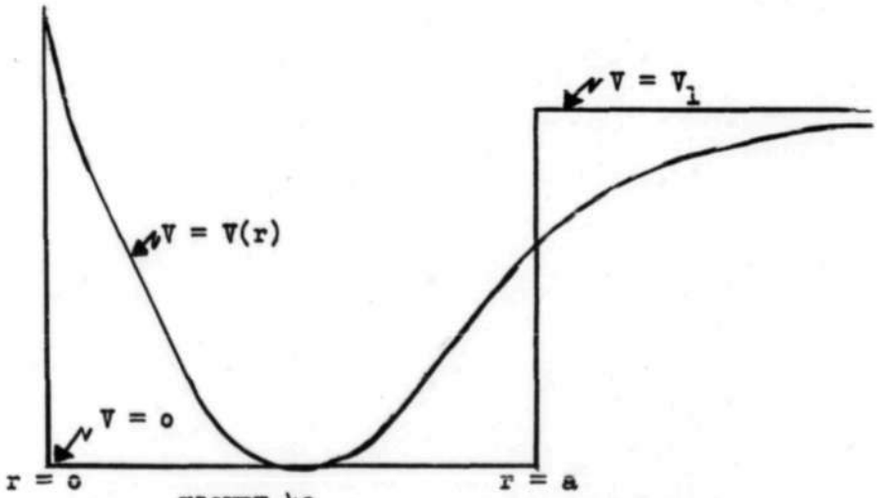
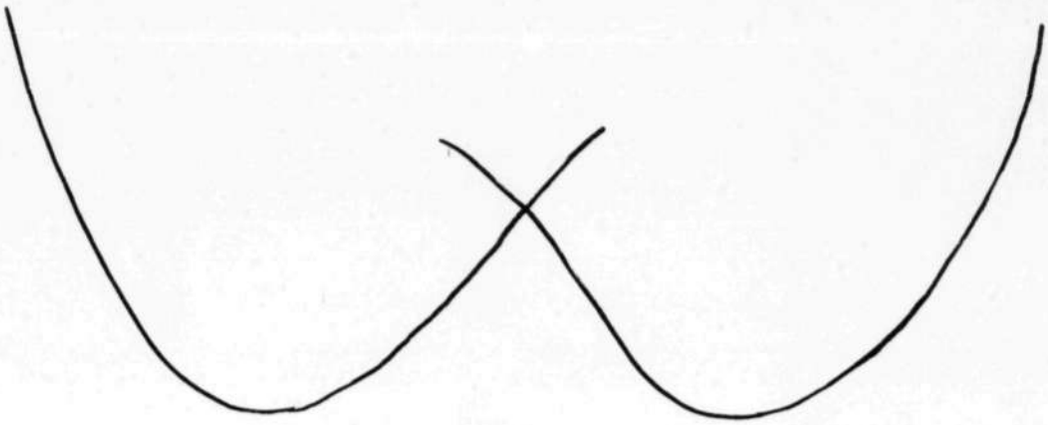
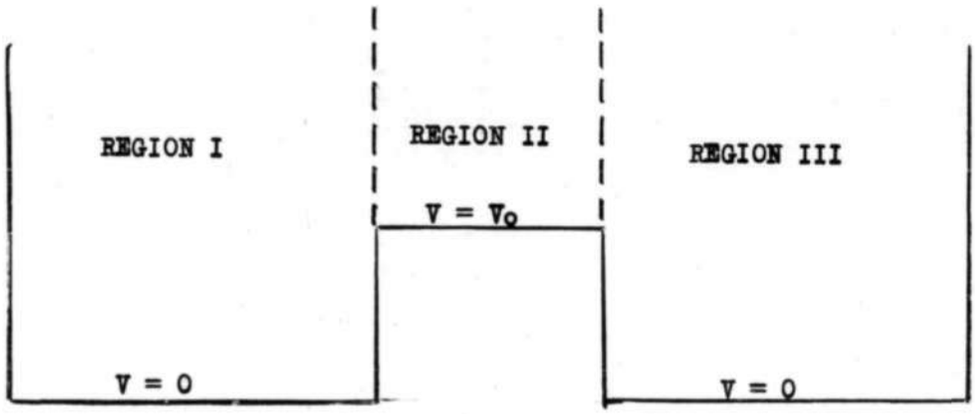


FIGURE 49

If two or more identical atoms are brought near each other, an interaction will exist between the atoms, perturbing the individual systems. This is shown in figure 50(a) with an approximation thereto shown in figure 50(b).



(a)



(b)

FIGURE 50

It may be recalled that on solving the problem of two identical coupled oscillators (meeting 14) we found there were two modes of vibration. One had a frequency above and the other was below the unperturbed frequency.

By analogy, since $\omega = \frac{E}{\hbar}$, one might expect the interaction of the two atoms to lead to energy levels which differ from the levels exhibited by the individual atoms. If the perturbed system has one or more energy levels lower than the unperturbed energy, the diatomic system is more stable than the single atoms. This reasoning can be expanded to include a large number of atoms, and one can thereby explain the stability of condensed systems.

Since these perturbed systems cannot be solved exactly, approximation methods must be used. One method of approach is to consider another system which has already been solved and which has a Hamiltonian operator H^0 which is only slightly different from the Hamiltonian H of the perturbed system in which we are interested.

The system whose solution is known will have eigenvalues E_1^0, E_2^0 — E_n^0 and corresponding stationary eigenfunctions ψ_1^0, ψ_2^0,----ψ_n^0, obeying the equation

$$\mathcal{H}^0 \psi_n^0 = E_n^0 \psi_n^0 \qquad \text{XXIV-1}$$

Since the Hamiltonian $\mathcal{H}$ of the perturbed system is not very different from $\mathcal{H}^0$, we may say

$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}'$, where $\mathcal{H}'$ is a small corrective factor.

Since $\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$, this is the same as saying $V = V^0 + V'$, where V' is a small corrective term to be added to the potential of the unperturbed system.

The wave function of the perturbed system are expressed in terms of the unperturbed wave functions. That is,

$$\psi_k = \sum_n a_{kn} \psi_n^0 \qquad \text{XXIV-2}$$

The first subscript of the a's denote the particular perturbed state to which they correspond. This must be done since the value of the a's is different for different states.

If the wave functions of the unperturbed system (ψ_n^0) are known, and the a's determined, the solution of the problem may be carried through using the six steps described at meeting 22.

However, we should look at step 5 more closely. This step was to find $\Psi(t)$. Previously, we used the relationship

$$\Psi(t) = \sum_n c_n \psi_n e^{\frac{-i E_n t}{\hbar}}$$

which implied that the Ψ is an eigenfunction of the energy. We can no longer make this assumption, so we write

$$\Psi(t) = \sum_n C_n(t)\psi_n^0 \qquad \text{XXIV-3}$$

where the C_n's are functions of the time which are unknown and must be determined.

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

Therefore

$$\sum_n C_n(t)\mathcal{H}\psi_n^0 = +i\hbar \sum_n \frac{\partial C_n(t)}{\partial t}\psi_n^0 \qquad \text{XXIV-4}$$

Let us consider the special case $\mathcal{H} = \mathcal{H}^0$ using equations XXIV-3 and XXIV-4, and see if we obtain the form of $\Psi(t)$ which we had originally.

Then
$$\sum_n C_n(t)\mathcal{H}^0\psi_n^0 = +i\hbar \sum_n \frac{\partial C_n(t)}{\partial t}\psi_n^0$$

but we know that

$$\mathcal{H}^0\psi_n^0 = E_n^0\psi_n^0 \qquad \text{XXIV-1}$$

Therefore

$$\sum_n C_n(t)E_n^0\psi_n^0 = i\hbar\sum_n \frac{\partial C_n(t)}{\partial t}\psi_n^0$$

The coefficients of the corresponding terms of ψ_n^0 in the above series in ψ_n^0 must equal each other, so

$$C_n(t)E_n^0 = i\hbar\frac{\partial C_n(t)}{\partial t}$$

Integration yields

$$C_n(t) = c_n e^{-\frac{iE_n^0}{\hbar}t}$$

Substituting this into equation XXIV-3 we find

$$\Psi(t) = \sum_n c_n e^{-\frac{iE_n^0}{\hbar}t}\psi_n^0$$

in agreement with our previous result for the unperturbed system.

Returning to the general case expressed by equation XXIV-4,

$$\sum c_n(t)\,\mathcal{H}\psi_n^0 = -i\hbar \sum_n \frac{\partial c_n(t)}{\partial t}\,\psi_n^0$$

Multiplying by ψ_m^{0*} and integrating,

$$\sum_n c_n(t)\int \psi_m^{0*}\,\mathcal{H}\psi_n^0\,d\tau = i\hbar \sum_n \frac{\partial c_n(t)}{\partial t}\int \psi_m^{0*}\psi_n^0\,d\tau$$

If we define $\int \psi_k^*\,\mathcal{H}\psi_l\,d\tau = H_{kl}$, and recalling the orthonormality of the wave functions ψ_n^0 we have

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

Thus if the $c_n(t)$'s are known at any time t, the manner in which the set changes will also be known.

Equation XXIV-5 represents n equations of the form

$$\begin{aligned}
c_1(t)H_{11} + c_2(t)H_{12} + \cdots + c_n(t)H_{1n} &= i\hbar\,\frac{\partial c_1(t)}{\partial t}\\
c_1(t)H_{21} + c_2(t)H_{22} + \cdots + c_n(t)H_{2n} &= i\hbar\,\frac{\partial c_2(t)}{\partial t}\\
&\vdots\\
c_1(t)H_{n1} + c_2(t)H_{n2} + \cdots + c_n(t)H_{nn} &= i\hbar\,\frac{\partial c_n(t)}{\partial t}
\end{aligned}$$

In order to solve the above, the C's are assumed of the form

$$c_n(t) = e^{kt}$$

and the procedure is essentially the same as the one carried out for the coupled harmonic oscillator problem. This will be done at the next meeting.

We are particularly interested in obtaining the set of C's at a particular time. Let us consider the case at time t = o. Then

$$\sum_n C_n (0) H_{mn} = i\hbar \left(\frac{\partial C_n}{\partial t}\right)_{t=0}$$

At time t = o, $\Psi(o)$ is an eigenfunction of the energy. This implies

$$\Psi(t) = \psi_k e^{-\frac{i E_k}{\hbar} t} \qquad \text{XXIV - 7}$$

$\Psi(o) = \psi_k$ (system in k^{th} perturbed state at time t = o.)

At meeting 24 we showed that if the state of a certain system is at some time described by an eigenfunction of the energy, it remains in that energy state. Yet here

$$\frac{\partial C_n}{\partial t} \neq 0,$$

indicating a non-stationary system. This seeming paradox is resolved when we remember that the C_n's relate the eigenfunction of the perturbed system to the eigenfunctions of the unperturbed system. While the system is stationary with respect to the perturbed eigenfunctions, it is not stationary with respect to the unperturbed system. Physically, this means that the whole system (e.g. a diatomic system or a system made up of matter plus radiation) has constant energy, but that any part of the system that is taken as the (originally) unperturbed system (e.g. the separate, non-interacting atoms in the diatomic system or just the matter in the matter-radiation system) exchanges energy with the rest of the system as a result of the perturbation. It is physically more interesting to us to express the effect of a perturbation with respect to the original unperturbed system as a frame of reference, and to express any changes with respect to this frame of reference in terms of the changes in C_n with time.

A striking analogy is evident with the use of coordinate systems as frames of reference in classical mechanics. This analogy is discussed in appendix V.

From equations XXIV - 7 and XXIV - 3

$$\Psi(0) = \psi_k = \sum_n C_n (0) \psi_n^o \qquad \text{XXIV - 8}$$

If, for the $k^{\underline{th}}$ state, we define

$$C_n(0) = a_{kn}$$

Then

$$\psi_k = \sum_n a_{kn} \psi_n^0 \qquad \text{XXIV - 9}$$

Equation XXIV - 9 represents the equation frequently found in the literature as the starting point of a study of time-independent perturbation theory. We see from the above that it can be derived as a special case from the more general time dependent case. We will deal with this at the next meeting.

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