

Memorandum M- 1824

Page 1 of 5

Digital Computer Laboratory
 Massachusetts Institute of Technology
 Cambridge, Massachusetts

SUBJECT: GROUP 63 SEMINAR ON MAGNETISM XXVIII

To: Group 63

From: Arthur Loeb, Norman Menyuk

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Most problems in quantum mechanics are solved using perturbation methods. The unperturbed functions are exact solutions of a physical model; since very few systems lend themselves to exact solutions, the number of models used as unperturbed systems is relatively small. Some of the unperturbed systems used are the isolated hydrogen atom, the particle in a box, and the harmonic oscillator. The solution for most of these is found in standard textbooks, and does not lie within the scope of this seminar. We will assume that the set of unperturbed wavefunctions is known.

However, before going directly into a discussion of the perturbed systems, we will indicate the importance of choosing the proper coordinate system in solving for a set of unperturbed wavefunctions.

The coordinate system used in a problem should be so chosen that the coordinates are separable. That is,

$$\mathcal{H}(q_1, \dots, q_n) = \sum_{i=1}^n \mathcal{H}_i(q_i) \quad \text{XXVII-1}$$

If the coordinates cannot be separated completely as in XXVII-1, then the portion which is not separable should be made as small as possible. This small term is then treated as a perturbation.

As illustrations of the above, let us consider the hydrogen and helium atoms. If the distance between the nucleus and electron of the hydrogen atom is r , then the potential will be

$$V = -\frac{Ze^2}{r} \quad (Z \text{ for hydrogen} = 1).$$

If we choose cartesian coordinates we have (since $r = (x^2 + y^2 + z^2)^{1/2}$).

$$\mathcal{H} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} - \frac{Ze^2}{\sqrt{x^2 + y^2 + z^2}}$$

The coordinates x , y , and z cannot be separated because of the term $\sqrt{x^2+y^2+z^2}$. However, if this problem is set up in spherical coordinates we find

$$H = \frac{p_r^2 + p_\theta^2 + p_\phi^2}{2m} - \frac{Ze^2}{r}$$

and the variables are separable.

In the helium atom, if electron 1 is a distance r_1 removed from the nucleus, electron 2 a distance r_2 away, and r_{12} the distance between electrons, then

$$H = \frac{p_{r_1}^2 + p_{\theta_1}^2 + p_{\phi_1}^2}{2m} + \frac{p_{r_2}^2 + p_{\theta_2}^2 + p_{\phi_2}^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}}$$

The coordinates of the above equation are not completely separable because of the r_{12} term. However, the term containing r_{12} is small compared to the others, and may be treated as a perturbation term. The hydrogen atom is used as the unperturbed system.

The separation of the variables simplifies the solution of a quantum mechanical problem since

$$\Psi = \prod_i \Psi_i(q_i)$$

XXVIII-2

if

$$H = \sum_i H_i(q_i).$$

We will not present a general proof of this theorem here, but we will show it is true for $\sum_i q_i = q_1 + q_2$

Then

$$H = H_1(q_1) + H_2(q_2)$$

$$(H_1 + H_2) \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

We try the solution

$$\Psi = \Psi_1(q_1) \Psi_2(q_2)$$

Substituting in the above,

$$(\mathcal{H}_1 + \mathcal{H}_2) \Psi_1 \Psi_2 = i\hbar \frac{\partial}{\partial t} (\Psi_1 \Psi_2)$$

$$\mathcal{H}_1 \Psi_1 \Psi_2 + \mathcal{H}_2 \Psi_1 \Psi_2 = i\hbar \frac{\partial}{\partial t} (\Psi_1 \Psi_2)$$

$$\Psi_2 \mathcal{H}_1 \Psi_1 + \Psi_1 \mathcal{H}_2 \Psi_2 = i\hbar \frac{\partial}{\partial t} (\Psi_1 \Psi_2)$$

Dividing by $\Psi_1 \Psi_2$

$$\begin{aligned} \frac{1}{\Psi_1} \mathcal{H}_1 \Psi_1 + \frac{1}{\Psi_2} \mathcal{H}_2 \Psi_2 &= \frac{i\hbar}{\Psi_1 \Psi_2} \frac{\partial}{\partial t} (\Psi_1 \Psi_2) \\ &= \frac{i\hbar}{\Psi_1 \Psi_2} \left(\Psi_2 \frac{\partial \Psi_1}{\partial t} + \Psi_1 \frac{\partial \Psi_2}{\partial t} \right) \end{aligned}$$

$$\frac{1}{\Psi_1} \mathcal{H}_1 \Psi_1 + \frac{1}{\Psi_2} \mathcal{H}_2 \Psi_2 = \frac{i\hbar}{\Psi_1} \frac{\partial \Psi_1}{\partial t} + \frac{i\hbar}{\Psi_2} \frac{\partial \Psi_2}{\partial t}$$

Therefore,

$$\frac{1}{\Psi_1} \mathcal{H}_1 \Psi_1 - \frac{i\hbar}{\Psi_1} \frac{\partial \Psi_1}{\partial t} = \frac{1}{\Psi_2} \mathcal{H}_2 \Psi_2 - \frac{i\hbar}{\Psi_2} \frac{\partial \Psi_2}{\partial t} \quad \text{XXVIII-3}$$

Since we have assumed that the electrons do not interact in this model, the coordinates of electron 1 can be varied without affecting the coordinates of electron 2 and vice versa. Thus we might keep electron 2 fixed, and move electron 1. This would keep the right hand side of equation XXVIII-3 constant, and may change the left hand side of this equation. However, their equality implies that if the right hand side of the equation is constant the left hand side must also be constant, so that the expression

$\frac{1}{\Psi_1} \mathcal{H}_1 \Psi_1 - \frac{i\hbar}{\Psi_1} \frac{\partial \Psi_1}{\partial t}$ must be independent of the coordinates of electron 1.

Therefore,

$$\mathcal{H}_1 \Psi_1 - i\hbar \frac{\partial \Psi_1}{\partial t} = \text{Constant} \times \Psi_1$$

and similarly

$$\mathcal{H}_2 \Psi_2 - i\hbar \frac{\partial \Psi_2}{\partial t} = \text{Constant} \times \Psi_2$$

XXVIII-4

The proof for n coordinates is completely analogous, but the complications introduced by the notation tend to obscure the general principle.

If we had solved the hydrogen atom problem using spherical coordinates we would have found that each coordinate gives rise to a quantum number. The radial terms, r , gives rise to the principal quantum number n ; the angular momentum quantum number l arises from the θ terms; and the coordinate ϕ gives rise to the quantum number m_l , which is a measure of the spatial alignment of the angular momentum with an externally imposed preferred direction. These are identical with the quantum numbers discussed at meeting 18. At that time these numbers were introduced rather artificially, but on solving the hydrogen atom problem they are found to follow directly from the boundary conditions and the single valuedness of the wave function.

For example, on obtaining the result $\psi(\phi) = Ae^{im\phi}$, the single-valuedness of $\psi(\phi)$ leads to the relationship $Ae^{im\phi} = Ae^{im(\phi + 2\pi)}$. Therefore, $\cos 2\pi m + i \sin 2\pi m = 1$, and this can be true only if m is an integer. An example in which a quantum number follows directly from the boundary conditions of the problem was given in the problem of the square well, which was solved at meeting 22.

At this point we introduce the spin coordinate, resulting from the electron spin. The spin coordinate introduces the quantum no. m_s . The concept of a spin coordinate does not follow logically from the Schroedinger equation, but is added to account for experimental data. (The spin coordinate does enter as a natural consequence of the Dirac theory, but we shall not discuss that theory in this seminar.)

The spin angular momentum of an electron can have only one value, $\frac{\hbar}{2}$, but it can be oriented either parallel (\uparrow) or anti-parallel (\downarrow) to an externally imposed preferred direction.

In order to separate the spin coordinate from the space coordinates we assume that the unperturbed Hamiltonian contains no magnetic terms effecting the energy. In that case we say

$$\Psi(q, s) = \Psi(q) \sigma(s)$$

XXVIII-5

where σ is the spin wave function.

The spin angular momentum component in the direction of the applied field must have two eigenfunctions. They will be denoted by α and β , where α corresponds to parallel spin orientation and β corresponds to anti-parallel spin orientation. This does not mean that σ is stationary since it need not be equal to either α or β . σ is, in general, a linear function of α and β . That is,

$$\sigma = c_\alpha(t)\alpha + c_\beta(t)\beta$$

XXVIII-6

An example, in which σ varies between α and β in time might be

$$\sigma = \left[\alpha \cos^2 \frac{Ht}{\hbar} + \beta \sin^2 \frac{Ht}{\hbar} \right]$$

According to equation XXVIII-5

$$\Psi(q, s) = \Psi(q) \sigma(s)$$

and the space and spin functions are independent.

Signed Arthur Loeb
Arthur Loeb

Signed Norman Menyuk
Norman Menyuk

Approved DRB
David R. Brown

ALL/NM:jrt

cc: Group 62 (20)