CHAPTER II

MATHEMATICAL AND PHYSICAL BASIS OF MATRIX MECHANICS

2.1 Historical Review

The founding of "Quantum Mechanics" can be placed between
the years of 1923 and 1927. Two equivalent formulation were
proposed almost simultaneously :   Wave Mechanics and Matrix Mechanics.
These two theories were initiated by de Broglie in 1923 and by
Heisenberg in 1925. The theory of de Broglie was greatly improved
and extended by Schroedinger. The theories of Heisenberg and
Schroedinger won quick favor, since their fundamental postulates
are reasonable and because they are fruitful. They were developed
independently, and seem at first sight to have little in common,
but physicists proved them to be equivalent ; they are different
mathematical formulations of the same physical relations.

2.2 The Fundamentals of Matrix Mechanics

Heisenberg's Matrix Mechanics is a formulation of the
principles of quantum theory which represents a considerable advance
over the theory of multiply periodic systems (4). It completely
avoids a mechanical kinematic visualization of the motion of
electrons in the stationary states of an atom. Apart from time
averages of classical kinematic quantities, only harmonic partial
vibrations are introduced, which are associated with each transition
between two stationary states and which are directly related to the
spontaneous transition probabilities of the system.

If

$$x_m^n = a_m^n \exp\left[2\pi i \nu_m^n t\right]$$

is the partial vibration of the Cartesian coordinate x of a given electron in an atom, associated with the transition from a state n to another state m. Generally, the partial vibrations assigned to each of the transition processes are physically defined by the intensity and polarization of the emitted radiation. However, they can not be combined into definite "orbits" of the atomic electrons, since they are assigned to transition processes, and not to stationary states.

Heisenberg's formulation of the quantum theory is further extended to a consistent mathematical system, in which all relations taken from classical mechanics are replaced by analogously constructed quantum-theoretical relations between the times averages x_n^n and the partial vibrations x_m^n of the coordinates of each of the atomic particles. In order to formulate these relations, it proves convenient to assign a matrix to each classical kinematic quantity x. The diagonal terms of such a matrix are the time averages x_n^n belonging to the individual stationary states, and the (n,m) and (m, n) elements (nth row, mth column, and mth row, nth column, respectively) are complex conjugates vibrations. i.e.,

$$x_m^n = a_m^n \exp\left[2\pi i \nu_m^n t\right] \quad \text{and} \quad x_n^m = a_n^m \exp\left[2\pi i \nu_n^m t\right] \quad (2.1)$$

with a_m^n (equal to a_n^m) positive and real, and

$$\nu_n^m \quad = \quad -\nu_m^n \tag{2.2}$$

The harmonic vibration x_n^m belongs to the transition from m to n and the harmonic vibration x_m^n to the reverse transition from n to m, so that one of these transitions shows an emission, and the other an absorption.

To the time derivative $\dot{x}$ we assign the matrix whose individual elements are time derivatives of the corresponding elements of the matrix $\hat{x}$, i.e.

$$\dot{x}_m^n \quad = \quad 2\pi i \nu_m^n \, x_m^n \tag{2.3}$$

In particular, we have $\dot{x}_n^n = 0$, i.e., the diagonal terms of $\hat{\dot{x}}$ vanish. Since $\nu_n^m = -\nu_m^n$, it also follows that $\dot{x}_m^n$ and $\dot{x}_n^m$ are conjugate complex (the matrices are Hermitian in character). To the energy E we have to assign a diagonal matrix. The energy value of the quantum state characterized by the index n is given by $E_n = E_n^n$, whence follows the frequency condition,

$$h\nu_m^n \quad = \quad E_n - E_m \tag{2.4}$$

in agreement with the above prescription $\nu_n^m = -\nu_m^n$, $\nu_n^n = 0$. The essential point lies in the fact that the multiplication of two matrices $\hat{x}$ and $\hat{y}$ has now acquired a proper meaning, in view of the frequency condition. The product of the two matrices $\hat{x}$ and $\hat{y}$ is defined by

$$(xy)_m^n \quad = \quad \sum_l x_l^n y_m^l \tag{2.5}$$

From (2.4) follows the combination rule

$$\nu_1^n + \nu_m^1 = \nu_m^n \tag{2.6}$$

and therefore the quantity $(xy)_m^n$ represents a harmonic vibration of frequency ν_m^n, if x_1^n and y_m^1 are harmonic vibrations having frequencies ν_1^n and ν_m^1 respectively.

All the normal calculation rules apply to the multiplicaiton of two matrices, with the exception of the commutation law : in general $\hat{x}\hat{y}$ differs from $\hat{y}\hat{x}$. Thus, e.g., the difference $\hat{E}\hat{x} - \hat{x}\hat{E}$ where $\hat{E}$ denotes the diagonal energy matrix and prooducts are to be formed according to the general prescription (2.5), can be simply related to the matrix $\hat{\dot{x}}$, the time derivative of $\hat{x}$:

$$\hat{E}\hat{x} - \hat{x}\hat{E} = \frac{h}{2\pi i} \hat{\dot{x}} \tag{2.7}$$

using (2.3) and the frequency condition (2.4). This relation holds for and arbitrary matrix $\hat{x}$

If we denote the Cartesian coordinates and the respective momenta of the atomic particles by $\hat{q}_i$ and $\hat{p}_i$ $(i = 1,..,\ f)$ with $p_x = m\dot{x}$, etc. Then, in addition to the frequency condition (2.4) we have the quantum conditions.

$$\left[\hat{p}_\rho, \hat{p}_\sigma\right] = 0, \qquad \left[\hat{q}_\rho, \hat{q}_\sigma\right] = 0$$

$$\left[\hat{q}_\rho, \hat{p}_\sigma\right] = \begin{cases} 0 & \text{for } \rho \neq \sigma \\ -\frac{h}{2\pi i}\mathbf{1} & \text{for } \rho = \sigma \end{cases} \tag{2.8}$$

Here the symbol $\mathbf{1}$ denotes the unit matrix.

The physical significance of the above condition is that it is impossible to specify precisely and simultaneously the values of those two quantities ; the uncertainty principle. Finally, one has the energy conservation law

$$\hat{H}(\hat{p}, \hat{q}) \quad = \quad \hat{E} \text{ (diagonal matrix)} \qquad (2.9)$$

The matrix function $\hat{H}(\hat{p}, \hat{q})$ characterizes a given mechanical system, and the most obvious assumption to make is to expect this function to coincide formally with the classical function when Cartesian coordinates are used. It suffices to consider the case in which it comprises two parts, coressponding to kinetic and potential energy, of which the one depends only on $\hat{p}$ and the other only on $\hat{q}$. According to the multiplication rule (2.5), only those matrix functions are defined in the first instance which can be written in form of a power series in $\hat{p}$ and $\hat{q}$ (with positive and negative powers). In this case the basic laws (2.4), (2.8) and (2.9) lead to matrix relations that are completely analogous to the equations of motion in classical mechanics. They can be written as

$$\dot{\hat{q}} = \frac{\partial \hat{H}(\hat{p}, \hat{q})}{\partial \hat{p}} \quad , \quad \dot{\hat{p}} = -\frac{\partial \hat{H}(\hat{p}, \hat{q})}{\partial \hat{q}} \qquad (2.10)$$

Noting that the sequence in which the stationary states of the system under consideration are arranged with in the matrices is immaterial and that in the theory the concept of quantum number does not enter into the basic laws.

In the next section, we will show how this basic theroy can be applied to solve a fundamentally quantum-mechanical system, an harmonic oscillator problem. In classical mechanics, a harmonic

oscillator is a particle constrained to move along an axis and subject to a restoring force proportional to a point located on that axis. The solution of this problem is well-known.

2.3 The Harmonic Oscillator

Historically, Heisenberg was the first to solve the harmonic oscillator problem and showed that the energy of a stationary state of the oscillator is $(n + \frac{1}{2})h\nu$.

For the oscillator, the Hamiltonian function is

$$H = \frac{1}{2m_o} p^2 + \frac{1}{2} kq^2 \tag{2.11}$$

The Hamiltonian equations are $\dot{q} = \frac{p}{m_o}$, $\dot{p} = -kq$

$$\therefore \ddot{q} = -\frac{k}{m_o} q \text{ and writing } \frac{k}{m_o} = (2\pi\nu)^2,$$

Then

$$\ddot{q} + (2\pi\nu)^2 q = 0 \tag{2.12}$$

Letting $q = q_m^n \exp(2\pi i \nu_m^n t)$, we have, from (2.12) and (2.11),

$$\left[-(2\pi\nu_m^n)^2 + (2\pi\nu)^2 \right] q_m^n = 0 \tag{2.13}$$

and $H_m^n = \frac{1}{2} \sum_1 m_o \left[-(2\pi)^2 \nu_1^n \nu_m^1 q_1^n q_m^1 + (2\pi\nu)^2 q_1^n q_m^1 \right]$ (2.14)

respectively, noting that,

$$p_m^n = m_o (2\pi i \nu_m^n) q_m^n \tag{2.15}$$

The quantum condition (2.8), write down in term of the matrix form, yeilds,

$$2\pi i m_o \sum_1 \left[\nu_1^n q_1^n q_m^1 - \nu_m^1 q_1^n q_m^1 \right] \quad = \quad \frac{h}{2\pi i} \delta_m^n \tag{2.16}$$

Equations (2.13), (2.15) and (2.16) contain the solution of the problem

To obtain the required solution, consider (2.13) we have, when $\nu_m^n \neq 0$,

$$\nu_m^n \quad = \quad \pm \nu \tag{2.17}$$

and rewrite down eq. (2.16), with the help of eq. (2.2),

$$\sum_1 \nu_1^n q_1^n q_n^1 \quad = \quad - \frac{h}{8\pi^2 m_o} \tag{2.18}$$

If we assume the values of n to be constant, and let m be variable, we will get the values of m in order that q_m^n not be equal to zero,

$$m \quad = \quad \begin{cases} n-1 \\ \\ n+1 \end{cases} \tag{2.19}$$

And, similarly, if we assume the values of m to be constant, and let n be variable, we will get

$$n \quad = \quad \begin{cases} m-1 \\ \\ m+1 \end{cases} \tag{2.20}$$

Hence, equation (2.18) becomes

$$\nu_{n-1}^n q_{n-1}^n q_n^{n-1} + \nu_{n+1}^n q_{n+1}^n q_n^{n+1} \quad = \quad - \frac{h}{8\pi^2 m_o}$$

or, with the help of Eq. (2.17),

$$q^n_{n+1} \, q^{n+1}_n \;=\; q^n_{n-1} \, q^{n-1}_n \;+\; \frac{h}{8\pi^2 m_o \nu} \tag{2.21}$$

Considering Eq. (2.21), if one substitutes the values of $n = 0, 1, 2, 3\ldots$ in this equation, one finds that

$$q^n_{n-1} \, q^{n-1}_n \;=\; n \, \frac{h}{8\pi^2 m_o \nu}$$

or $\hspace{9cm}$ (2.22)

$$q^n_{n+1} \, q^{n+1}_n \;=\; (n+1) \, \frac{h}{8\pi^2 m_o \nu}$$

Now, from Eq. (2.14) and the diagonal character of the energy matrix, if we assume $n = m$, we will have,

$$\nu^n_1 \, \nu^1_n \;=\; (+\nu)(-\nu) \qquad \text{for} \quad 1 \;=\; \begin{cases} n+1 \\ n-1 \end{cases} \tag{2.23}$$

Substituting Eq. (2.23) and (2.22) into Eq. (2.14), we finally obtain

$$H^n_n \;=\; 4\pi m_o \nu^2 \left[(n+1) \, \frac{h}{8\pi m_o \nu} \;+\; n \, \frac{h}{8\pi m_o \nu} \right]$$

or

$$H^n_n \equiv E_n \;=\; (n + \tfrac{1}{2}) h\nu \tag{2.24}$$

which is the well-known result

In the Hydrogen atom problem, which will be discussed in the next chapter, is not simple as the above problem since the potential term of the Hamiltonian function of the hydrogen atom is inversely proportional to r, the distance between the nucleus and the electron of the atom. If we attempt to solve this problem in the same manner as that of the harmonic oscillator, we would find ourselves in difficulty since the linear oscillator constitutes a system having only one degree of freedom wheareas the hydrogen atom has more. In fact, the difficulty of the matrix method increases with the number of degrees of freedom. According to the basic theory, the matrix computations in the equations of motion will be relatively simple as long as the matrices are diagonal, but when this is not the case, we become involved in a maze of infinite sums. We seek, therefore, to find as many diagonal matrices as possible. In this search we are guided by the fact that such matrices are analogous to constants in ordinary algebra. Therefore, it may be expected that any dynamical quantity which is conserved, such as momentum or energy, will be represented by a diagonal matrix. Now in the case of the hydrogen atom as treated by ordinary mechanics we know that angular momentum is constant and that its components parallel to the three axes are also constant, so that we expect the matrix of angular momentum to be diagonal.

To conquer this difficulty, Pauli found that a second vector discovered by W. Lenz is also constant in magnitude and direction in this problem. This is called the "Lenz Vector" (5). We can obtain a system of matrix equations contributed by this vector that comprise only the time-independent matrices. The solutions of these matrix equations then leads to the energy spectrum of the hydrogen atom.