18.3: Hamiltonian in Quantum Theory

Heisenberg's Matrix-Mechanics Representation

The algebraic Heisenberg representation of quantum theory is analogous to the algebraic Hamiltonian representation of classical mechanics, and shows best how quantum theory evolved from, and is related to, classical mechanics. Heisenberg decided to ignore the prevailing conceptual theories, such as classical mechanics, and based his quantum theory on observables. This approach was influenced by the success of Bohr's older quantum theory and Einstein's theory of relativity. He abandoned the classical notions that the canonical variables p_k, q_k can be measured directly and simultaneously. Secondly he wished to absorb the correspondence principle directly into the theory instead of it being an ad hoc procedure tailored to each application. Heisenberg considered the Fourier decomposition of transition amplitudes between discrete states and found that the product of the conjugate variables do not commute. Heisenberg derived, for the first time, the correct energy levels of the one-dimensional harmonic oscillator as $E_n = \hbar\omega(n+\frac{1}{2})$ which was a significant achievement. Born recognized that Heisenberg's strange multiplication and commutation rules for two variables, corresponded to matrix algebra. Prior to 1925, matrix algebra was an obscure branch of pure mathematics not known or used by the physics community. Heisenberg, Born, and the young mathematician Jordan, developed the commutation rules of matrix mechanics. Heisenberg's approach represents the classical position and momentum coordinates q, p by matrices $\mathbf{q}$ and $\mathbf{p}$, with corresponding matrix elements $q_{mn}e^{i\omega_{mn}t}$ and $p_{mn}e^{i\omega_{mn}t}$. Born showed that the trace of the matrix

$$H(\mathbf{pq}) = \mathbf{p}\dot{\mathbf{q}} - L \tag{18.3.1}$$

gives the Hamiltonian function $H(\mathbf{p},\mathbf{q})$ of the matrices $\mathbf{q}$ and $\mathbf{p}$ which leads to Hamilton's canonical equations

$$\dot{\mathbf{q}} = \frac{\partial H}{\partial \mathbf{p}} \quad \dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}} \tag{18.3.2}$$

Heisenberg and Born also showed that the commutator of $\mathbf{q}, \mathbf{p}$ equals

$$\begin{gathered} q_k p_l - p_l q_k = i\hbar\delta_{kl} \\ q_k q_l - q_l q_k = 0 \\ p_k p_l - p_l p_k = 0 \end{gathered} \tag{18.3.3}$$

Born realized that Equation 18.3.3 is the only fundamental equation for introducing $\hbar$ into the theory in a logical and consistent way.

Chapter $15.2.4$ discussed the formal correspondence between the Poisson bracket, defined in chapter 15.3, and the commutator in classical mechanics. It was shown that the commutator of two functions equals a constant multiplicative factor λ times the corresponding Poisson Bracket. That is

$$(F_j G_k - G_k F_j) = \lambda\{F_j, G_k\} \tag{18.3.4}$$

where the multiplicative factor λ is a number independent of F_j, G_k, and the commutator.

In 1925, Paul Dirac, a 23-year old graduate student at Bristol, recognized the crucial importance of the above correspondence between the commutator and the Poisson Bracket of two functions, to relating classical mechanics and quantum mechanics. Dirac noted that if the constant λ is assigned the value $\lambda = i\hbar$, then Equation 18.3.4 directly relates Heisenberg's commutation relations between the fundamental canonical variables (q_j, p_k) to the corresponding classical Poisson Bracket $\{q_j, p_k\}$. That is,

$$q_k p_l - p_l q_k = i\hbar\{q_k, p_l\} = i\hbar\delta_{kl} \tag{18.3.5}$$

$$q_k q_l - q_l q_k = i\hbar\{q_k, q_l\} = 0 \tag{18.3.6}$$

$$p_k p_l - p_l p_k = i\hbar\{p_k, p_l\} = 0 \tag{18.3.7}$$

Dirac recognized that the correspondence between the classical Poisson bracket, and quantum commutator, given by Equation 18.3.4, provides a logical and consistent way that builds quantization directly into the theory, rather than using an ad-hoc, case-dependent, hypothesis as used by the older quantum theory of Bohr. The basis of Dirac's quantization principle, involves replacing the classical Poisson Bracket, $\{F_j, G_k\}$ by the commutator, $\frac{1}{i\hbar}(F_j, G_k - G_k F_j)$. That is,

$$\{F_j, G_k\} \Longrightarrow \frac{1}{i\hbar}(F_j G_k - G_k F_j) \tag{18.3.8}$$

Hamilton's canonical equations, as introduced in chapter 15, are only applicable to classical mechanics since they assume that the exact position and conjugate momentum can be specified both exactly and simultaneously which contradicts the Heisenberg's Uncertainty Principle. In contrast, the Poisson bracket generalization of Hamilton's equations allows for non-commuting variables plus the corresponding uncertainty principle. That is, the transformation from classical mechanics to quantum mechanics can be accomplished simply by replacing the classical Poisson Bracket by the quantum commutator, as proposed by Dirac. The formal analogy between classical Hamiltonian mechanics, and the Heisenberg representation of quantum mechanics is strikingly apparent using the correspondence between the Poisson Bracket representation of Hamiltonian mechanics and Heisenberg's matrix mechanics.

The direct relation between the quantum commutator, and the corresponding classical Poisson Bracket, applies to many observables. For example, the quantum analogs of Hamilton's equations of motion are given by use of Hamilton's equations of motion, $(15.2.42)$, $(15.2.45)$, and replacing each Poisson Bracket by the corresponding commutator. That is

$$\frac{dq_k}{dt} = \frac{\partial H}{\partial p_k} = \{q_k, H\} = \frac{1}{i\hbar}(q_k H - H q_k) \tag{18.3.9}$$

$$\frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k} = \{p_k, H\} = \frac{1}{i\hbar}(p_k H - H p_k) \tag{18.3.10}$$

Chapter $15.2.5$ discussed the time dependence of observables in Hamiltonian mechanics. Equation $(15.2.34)$ gave the total time derivative of any observable G to be

$$\frac{dG}{dt} = \frac{\partial G}{\partial t} + \{G, H\} \tag{18.3.11}$$

Equation 18.3.8 can be used to replace the Poisson Bracket by the quantum commutator, which gives the corresponding time dependence of observables in quantum physics.

$$\frac{dG}{dt} = \frac{\partial G}{\partial t} + \frac{1}{i\hbar}(GH - HG) \tag{18.3.12}$$

In quantum mechanics, Equation 18.3.12 is called the *Heisenberg equation*. Note that if the observable G is chosen to be a fundamental canonical variable, then $\frac{\partial q_k}{\partial t} = 0 = \frac{\partial p_k}{\partial t}$ and equation $(15.2.9)$ reduces to Hamilton's equations 18.3.9 and 18.3.10.

The analogies between classical mechanics and quantum mechanics extend further. For example, if G is a constant of motion, that is $\frac{dG}{dt} = 0$, then Heisenberg's equation of motion gives

$$\frac{\partial G}{\partial t} + \frac{1}{i\hbar}(GH - HG) = 0 \tag{18.3.13}$$

Moreover, if G is not an explicit function of time, then

$$0 = \frac{1}{i\hbar}(GH - HG) \tag{18.3.14}$$

That is, the transition to quantum physics shows that, if G is a constant of motion, and is not explicitly time dependent, then G commutes with the Hamiltonian H.

The above discussion has illustrated the close and beautiful correspondence between the Poisson Bracket representation of classical Hamiltonian mechanics, and the Heisenberg representation of quantum mechanics. Dirac provided the elegant and simple correspondence principle connecting the Poisson bracket representation of classical Hamiltonian mechanics, to the Heisenberg representation of quantum mechanics.

Schrödinger's Wave-Mechanics Representation

The wave mechanics formulation of quantum mechanics, by the Austrian theorist Schrödinger, was built on the wave-particle duality concept that was proposed in 1924 by Louis de Broglie. Schrödinger developed his wave mechanics representation of quantum physics a year after the development of matrix mechanics by Heisenberg and Born. The Schrödinger wave equation is based on the non-relativistic Hamilton-Jacobi representation of a wave equation, melded with the operator formalism of Born and Wiener. The 39-year old Schrödinger was an expert in classical mechanics and wave theory, which was invaluable when he developed the important Schrödinger equation. As mentioned in chapter $15.4.4$, the Hamilton-Jacobi theory is a formalism of classical mechanics that allows the motion of a particle to be represented by a wave. That is, the wavefronts are surfaces of constant action S, and the particle momenta are normal to these constant-action surfaces, that is, $\mathbf{p} = \boldsymbol{\nabla} S$. The wave-particle duality of Hamilton-Jacobi theory is a natural way to handle the wave-particle duality proposed by de Broglie.

Consider the classical Hamilton-Jacobi equation for one body, given by 18.3.11.

$$\frac{\partial S}{\partial t} + H(\mathbf{q}, \boldsymbol{\nabla} S, t) = 0 \tag{18.3.15}$$

If the Hamiltonian is time independent, then equation $(15.4.2)$ gives that

$$\frac{\partial S}{\partial t} = -H(\mathbf{q}, \mathbf{p}, t) = -E(\boldsymbol{\alpha}) \tag{18.3.16}$$

The integration of the time dependence is trivial, and thus the action integral for a time-independent Hamiltonian is

$$S(\mathbf{q}, \boldsymbol{\alpha}, t) = W(\mathbf{q}, \boldsymbol{\alpha}) - E(\boldsymbol{\alpha})t \tag{18.3.17}$$

A formal transformation gives

$$E = -\frac{\partial S}{\partial t} \qquad \mathbf{p} = \boldsymbol{\nabla} S \tag{18.3.18}$$

Consider that the classical time-independent Hamiltonian, for motion of a single particle, is represented by the Hamilton-Jacobi equation.

$$H = \frac{\mathbf{p}^2}{2\mu} + U(q) = -\frac{\partial S}{\partial t} \tag{18.3.19}$$

Substitute for $\mathbf{p}$ leads to the classical Hamilton-Jacobi relation in terms of the action S

$$\frac{1}{2\mu}(\boldsymbol{\nabla} S \cdot \boldsymbol{\nabla} S) + U(q) = -\frac{\partial S}{\partial t} \tag{18.3.20}$$

By analogy with the Hamilton-Jacobi equation, Schrödinger proposed the quantum operator equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \tag{18.3.21}$$

where $\hat{H}$ is an operator given by

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + U(r) \tag{18.3.22}$$

In 1926, Max Born and Norbert Wiener introduced the operator formalism into matrix mechanics for prediction of observables and this has become an integral part of quantum theory. In the operator formalism, the observables are represented by operators that project the corresponding observable from the wavefunction. That is, the quantum operator formalism for the assumed momentum and energy operators, that operate on the wavefunction ψ, are

$$p_j = \frac{\hbar}{i}\frac{\partial}{\partial q_j} \qquad E = -\frac{\hbar}{i}\frac{\partial}{\partial t} \tag{18.3.23}$$

Formal transformations of $\mathbf{p}$ and E in the Hamiltonian 18.3.17 leads to the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 \psi}{\partial q^2} + U(q)\psi = E\psi \tag{18.3.24}$$

Assume that the wavefunction is of the form

$$\psi = Ae^{\frac{iS}{\hbar}} \tag{18.3.25}$$

where the action S gives the phase of the wavefront, and A the amplitude of the wave, as described in chapter $15.4.4$ The time dependence, that characterizes the motion of the wavefront, is contained in the time dependence of S. This form for the wavefunction has the advantage that the wavefunction frequently factors into a product of terms, e.g. $\psi = R(r)\Theta(\theta)\Phi(\phi)$ which corresponds to a summation of the exponents $S = W_r + W_\theta + W_\phi - Et$. This summation form is exploited by separation of the variables, as discussed in chapter $15.4.3$.

Insert ψ defined by 18.3.25 into Equation 18.3.24, plus using the fact that

$$\frac{\partial^2 \psi}{\partial q^2} = \frac{\partial}{\partial q}\left(\frac{\partial \psi}{\partial S}\frac{\partial S}{\partial q}\right) = \frac{\partial}{\partial q}\left(\frac{i}{\hbar}\psi\frac{\partial S}{\partial q}\right) = -\frac{1}{\hbar^2}\psi\left(\frac{\partial S}{\partial q}\right)^2 + \frac{i}{\hbar}\psi\frac{\partial^2 S}{\partial q^2} \tag{18.3.26}$$

leads to

$$-\frac{\partial S}{\partial t} = \frac{1}{2\mu}(\boldsymbol{\nabla} S \cdot \boldsymbol{\nabla} S) + U(q) - \frac{i\hbar}{2\mu}\nabla^2 S = E \tag{18.3.27}$$

Note that if Planck's constant $\hbar = 0$, then the imaginary term in Equation 18.3.27 is zero, leading to 18.3.27 being real, and identical to the Hamilton-Jacobi result, Equation 18.3.20. The fact that Equation 18.3.26 equals the Hamilton-Jacobi equation in the limit $\hbar \to 0$, illustrates the close analogy between the waveparticle duality of the classical Hamilton-Jacobi theory, and de Broglie's wave-particle duality in Schrödinger's quantum wave-mechanics representation.

The Schrödinger approach was accepted in 1925 and exploited extensively with tremendous success, since it is much easier to grasp conceptually than is the algebraic approach of Heisenberg. Initially there was much conflict between the proponents of these two contradictory approaches, but this was resolved by Schrödinger who showed in 1926 that there is a formal mathematical identity between wave mechanics and matrix mechanics. That is, these two quantal representations of Hamiltonian mechanics are equivalent, even though they are built on either the Poisson bracket representation, or the Hamilton-Jacobi representation. Wave mechanics is based intimately on the quantization rule of the action variable. Heisenberg's Uncertainty Principle is automatically satisfied by Schrödinger's wave mechanics since the uncertainty principle is a feature of all wave motion, as described in chapter 3.

In 1928 Dirac developed a relativistic wave equation which includes spin as an integral part. This Dirac equation remains the fundamental wave equation of quantum mechanics. Unfortunately it is difficult to apply.

Today the powerful and efficient Heisenberg representation is the dominant approach used in the field of physics, whereas chemists tend to prefer the more intuitive Schrödinger wave mechanics approach. In either case, the important role of Hamiltonian mechanics in quantum theory is undeniable.