Bohr's condition (1.2.4). We will not pursue this approach here, because it was soon made obsolete by the advent of wave mechanics.

In 1916 (in his spare time while discovering the general theory of relativity), Einstein returned to the theory of black-body radiation,[7] this time combining it with the Bohr idea of quantized atomic energy states. Einstein defined a quantity A_m^n as the rate at which an atom will spontaneously make a transition from a state m to a state n of lower energy, emitting a photon of energy $E_m - E_n$. He also considered the absorption of photons from radiation (not necessarily black-body radiation) with an energy density $\rho(\nu)d\nu$ at frequencies between ν and $\nu + d\nu$. The rate at which an individual atom in such a field makes a transition from a state n to a state m of higher energy is written as $B_n^m \rho(\nu_{nm})$, where $\nu_{nm} \equiv (E_m - E_n)/h$ is the frequency of the absorbed photon. Einstein also took into account the possibility that the radiation would stimulate the emission of photons by the atom in transitions from a state m to a state n of lower energy, at a rate written as $B_m^n \rho(\nu_{nm})$. The coefficients B_n^m and B_m^n like A_m^n are assumed to depend only on the properties of the atoms, not the radiation.

Now, suppose the radiation is black-body radiation at a temperature T, with which the atoms are in equilibrium. The energy density of the radiation will be the function $\rho(\nu, T)$, given by Eq. (1.1.5). In equilibrium the rate at which atoms make a transition $m \to n$ from higher to lower energy must equal the rate at which atoms make the reverse transition $n \to m$:

$$N_m \left[A_m^n + B_m^n \rho(\nu_{nm}, T)\right] = N_n \, B_n^m \, \rho(\nu_{nm}, T) \,, \tag{1.2.13}$$

where N_n and N_m are the numbers of atoms in states n and m. According to the Boltzmann rule of classical statistical mechanics, the number of atoms in a state of energy E is proportional to $\exp(-E/k_{\mathcal{B}}T)$, so

$$N_m/N_n = \exp\left(-(E_m - E_n)/k_{\mathcal{B}}T\right) = \exp\left(-h\nu_{nm}/k_{\mathcal{B}}T\right) . \tag{1.2.14}$$

(It is important here to take the N_n as the numbers of atoms in individual states n, some of which may have precisely the same energy, rather than the numbers of atoms with energies E_n.) Putting this together, we have

$$A_m^n = \frac{8\pi h}{c^3} \frac{\nu_{nm}^3}{\exp(h\nu_{nm}/k_{\mathcal{B}}T) - 1} \Big(\exp(h\nu_{nm}/k_{\mathcal{B}}T) \, B_n^m - B_m^n \Big) . \tag{1.2.15}$$

For this to be possible at all temperatures for temperature-independent A and B coefficients, these coefficients must be related by

$$B_m^n = B_n^m \,, \qquad A_m^n = \left(\frac{8\pi h \nu_{nm}^3}{c^3}\right) B_m^n \,. \tag{1.2.16}$$

Hence, knowing the rate at which a classical light wave of a given energy density is absorbed or stimulates emission by an atom, we can calculate the rate

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[7] A. Einstein, Phys. Z. **18**, 121 (1917).

at which it spontaneously emits photons.[8] This calculation will be presented in Section 6.5.

1.3 Wave Mechanics

Ever since Maxwell, light had been understood to be a wave of electric and magnetic fields, but after Einstein and Compton, it became clear that it is also manifested in a particle, the photon. So is it possible that something like the electron, that had always been regarded as a particle, could also be manifested as some sort of wave? This was suggested in 1923 by Louis de Broglie (1892–1987),[1] a doctoral student in Paris. Any kind of wave of frequency ν and wave number $\mathbf{k}$ has a spacetime dependence $\exp(i\mathbf{k}\cdot\mathbf{x} - i\omega t)$, where $\omega = 2\pi\nu$. Lorentz invariance requires that $(\mathbf{k}, \omega)$ transform as a four-vector, just like the momentum four-vector $(\mathbf{p}, E)$. For light, according to Einstein, the energy of a photon is $E = h\nu = \hbar\omega$, and its momentum has a magnitude $|\mathbf{p}| = E/c = h\nu/c = h/\lambda = \hbar|\mathbf{k}|$, so de Broglie was led to suggest that in general a particle of any mass is associated with a wave having the four-vector $(\mathbf{k}, \omega)$ equal to $1/\hbar$ times the four-vector $(\mathbf{p}, E)$:

$$\mathbf{k} = \mathbf{p}/\hbar\,, \qquad \omega = E/\hbar\,. \tag{1.3.1}$$

This idea gained support from the fact that a wave satisfying (1.3.1) would have a group velocity equal to the ordinary velocity $c^2\mathbf{p}/E$ of a particle of momentum $\mathbf{p}$ and energy E. For a reminder about group velocity, consider a wave packet in one dimension:

$$\psi(x,t) = \int dk\; g(k)\, \exp\Big(ikx - i\omega(k)t\Big), \tag{1.3.2}$$

where $g(k)$ is some smooth function with a peak at an argument k_0. Suppose also that the wave $\int dk\;\; g(k)\exp(ikx)$ at $t = 0$ is peaked at $x = 0$. By expanding $\omega(k)$ around k_0, we have

$$\psi(x,t) \simeq \exp\Big(-it[\omega(k_0) - k_0\omega'(k_0)]\Big)\int dk\; g(k)\, \exp\Big(ik\Big[x - \omega'(k_0)t\Big]\Big),$$

and therefore

$$|\psi(x,t)| \simeq \Big|\psi\Big([x - \omega'(k_0)t], 0\Big)\Big|\;. \tag{1.3.3}$$

The wave packet that was concentrated at time $t = 0$ near $x = 0$ is evidently concentrated at time t near $x = \omega'(k_0)t$, so it moves with speed

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[8] Einstein actually used this argument, together with some thermodynamic relations, to give a new derivation of the Planck formula for $\rho(\nu, T)$.

[1] L. de Broglie, Comptes Rendus **177**, 507, 548, 630 (1923).

and the allowed energies E are those for which there is a single-valued solution $\psi(\mathbf{x}_1, \ldots \mathbf{x}_N)$, vanishing when any $|\mathbf{x}_r|$ goes to infinity, of the Schrödinger equation

$$E\,\psi(\mathbf{x}_1, \ldots \mathbf{x}_N) = \left[\sum_{r=1}^{N} \frac{-\hbar^2}{2m_r}\nabla_r^2 + V(\mathbf{x}_1, \ldots \mathbf{x}_N)\right]\psi(\mathbf{x}_1, \ldots \mathbf{x}_N)\,. \qquad (1.3.10)$$

So now it was possible at least in principle to calculate the spectrum not only of hydrogen, but of any other atom, and indeed of any non-relativistic system with a known potential.

1.4 Matrix Mechanics

A few years after de Broglie introduced the idea of wave mechanics, and a little before Schrödinger developed his version of the theory, a quite different approach to quantum mechanics was developed by Werner Heisenberg (1901–1976). Heisenberg suffered from hay fever, so in 1925 he escaped the pollen-laden air of Göttingen to go on vacation to the grassless North Sea island of Helgoland. While on vacation he wrestled with the mystery surrounding the quantum conditions of Bohr and de Broglie. When he returned to the University of Göttingen he had a new approach to the quantum conditions, which has come to be called matrix mechanics.[1]

Heisenberg's starting point was the philosophical judgment, that a physical theory should not concern itself with things like electron orbits in atoms that can never be observed. This is a risky assumption, but in this case it served Heisenberg well. He fastened on the energies E_n of atomic states, and the rates A_m^n at which atoms spontaneously make radiative transitions from one state m to another state n, as the observables on which to base a physical theory. In classical electrodynamics, a particle with charge $\pm e$ with a position vector $\mathbf{x}$ that undergoes a simple harmonic oscillation emits a radiation power

$$P = \frac{4e^2}{3c^3}|\ddot{\mathbf{x}}|^2\,. \qquad (1.4.1)$$

Heisenberg guessed that this formula gives the power emitted in a radiative transition from an atomic state with energy E_m to one with a lower energy E_n, with $\mathbf{x}$ replaced with

$$\mathbf{x} \mapsto [\mathbf{x}]_{nm} \propto \exp(-i\omega_{nm}t)\,, \qquad (1.4.2)$$

where $[\mathbf{x}]_{nm}$ is a complex vector amplitude characterizing this transition, and ω_{nm} is the circular frequency (the frequency times 2π) of the radiation emitted in the transition:

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[1] W. Heisenberg, Z. f. Physik **33**, 879 (1925).

$$\omega_{nm} = (E_m - E_n)/\hbar. \tag{1.4.3}$$

Then Eq. (1.4.1) becomes a formula for the radiation power emitted in the transition $m \to n$:

$$P(m \to n) = \frac{4e^2\omega_{nm}^4}{3c^3}\left|[\mathbf{x}]_{nm}\right|^2 . \tag{1.4.4}$$

That is, the rate of emitting photons carrying energy $\hbar\omega_{nm}$ in the transition $m \to n$ is, in Einstein's notation,

$$A_m^n = \frac{P(m \to n)}{\hbar\omega_{nm}} = \frac{4e^2\omega_{nm}^3}{3c^3\hbar}\left|[\mathbf{x}]_{nm}\right|^2 , \tag{1.4.5}$$

and, according to the Einstein relations (1.2.16), this gives the coefficients of $\rho(\nu_{nm})$ in the rates for induced emission and absorption

$$B_n^m = B_m^n = \frac{2\pi e^2}{3\hbar^2}\left|[\mathbf{x}]_{nm}\right|^2 . \tag{1.4.6}$$

In Eqs. (1.4.5) and (1.4.6), $[x]_{nm}$ appears only with $E_m > E_n$, but Heisenberg extended the definition of $[\mathbf{x}]_{nm}$ to the case where $E_n > E_m$, by the condition

$$[\mathbf{x}]_{nm} = [\mathbf{x}]_{mn}^* \propto \exp(i\omega_{nm}t) , \tag{1.4.7}$$

so that Eq. (1.4.6) holds whether $E_m > E_n$ or $E_n > E_m$.

Heisenberg limited his calculations to the example of an anharmonic oscillator in one dimension, for which the energy is given classically in terms of position and its rate of change by

$$E = \frac{m_e}{2}\dot{x}^2 + \frac{m_e\omega_0^2}{2}x^2 + \frac{m_e\lambda}{3}x^3 . \tag{1.4.8}$$

To calculate the E_n and $[x]_{nm}$, Heisenberg used two relations. The first is a quantum mechanical interpretation of Eq. (1.4.8):

$$\frac{m_e}{2}[\dot{x}^2]_{nm} + \frac{m_e\omega_0^2}{2}[x^2]_{nm} + \frac{m_e\lambda}{3}[x^3]_{nm} = \begin{cases} E_n & n = m \\ 0 & n \neq m \end{cases} , \tag{1.4.9}$$

where E_n is the energy of the quantum state labeled n. But what meaning should be attached to $[\dot{x}^2]_{nm}$, $[x^2]_{nm}$, and $[x^3]_{nm}$? Heisenberg found that the "simplest and most natural assumption" was to take

$$[x^2]_{nm} = \sum_l [x]_{nl}\,[x]_{lm} \qquad [x^3]_{nm} = \sum_{l,k}[x]_{nl}\,[x]_{lk}\,[x]_{km} \tag{1.4.10}$$

and likewise

$$[\dot{x}^2]_{nm} = \sum_k [\dot{x}]_{nk}[\dot{x}]_{km} = \sum_k \omega_{nk}\omega_{mk}[x]_{nk}\,[x]_{km} . \tag{1.4.11}$$

Note that because $[x]_{nm}$ is proportional to $\exp(i(E_m - E_n)/\hbar)$ for all n and m, each term in Eq. (1.4.9) is time-independent for $n = m$. Also, by virtue of the condition (1.4.7), the first two terms are positive for $n = m$ though the last may not be.

The second relation is a quantum condition. Here Heisenberg adopted a formula that had been published a little earlier by W. Kuhn[2] and W. Thomas[3], which Kuhn derived using a model of an electron in a bound state as an ensemble of oscillators vibrating in three dimensions at frequencies ν_{nm}. From the condition that at very high frequency the scattering of light from such an electron should be the same as if the electron were a free particle, Kuhn derived the purely classical statement[4] that, for any given state n:

$$\sum_m B_n^m (E_m - E_n) = \frac{\pi e^2}{m_e} \ . \tag{1.4.12}$$

Combining this with Eq. (1.4.6) gives

$$\hbar = \frac{2m_e}{3} \sum_m \Big|[\mathbf{x}]_{nm}\Big|^2 \omega_{nm} \ . \tag{1.4.13}$$

Since in three dimensions there are three terms in $\Big|[\mathbf{x}]_{nm}\Big|^2$, the factor 1/3 gives the average of these three terms, so in one dimension we would have

$$\hbar = 2m_e \sum_m \Big|[x]_{nm}\Big|^2 \omega_{nm} \ . \tag{1.4.14}$$

This is the quantum condition used by Heisenberg.

Heisenberg was able to find an exact solution[5] of Eqs. (1.4.9) and (1.4.14) for the case $\lambda = 0$: For any integer $n \geq 0$,

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega_0, \quad [x]^*_{n+1,n} = [x]_{n,n+1} = e^{-i\omega_0 t} \sqrt{\frac{(n+1)\hbar}{2m_e\omega_0}} \ , \tag{1.4.15}$$

with $[x]_{nm}$ vanishing unless $n - m = \pm 1$. We will see how to derive these results for $\lambda = 0$ in Section 2.5. Heisenberg was also able to calculate the corresponding results for small non-zero λ, to first order in λ.

This was all very obscure. On his return from Helgoland, Heisenberg showed his work to Max Born (1882–1970). Born recognized that the formulas in Eq. (1.4.10) were just special cases of a well-known mathematical procedure,

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[2] W. Kuhn, Z. Phys. **33**, 408 (1925).

[3] W. Thomas, Naturwiss. **13**, 627 (1925).

[4] Kuhn actually gave this condition only where n is the ground state, the state of lowest energy, but the argument applies to any state. Where n is not the ground state, the terms in the sum over m are positive if m has higher energy than n, but negative if m has lower energy.

[5] Somewhat inconsistently, Heisenberg took the time-dependence factor in $[x]_{nm}$ to be $\cos(\omega_{nm}t)$ rather than $\exp(-i\omega_{nm}t)$. The results here apply to the case where $[x]_{nm} \propto \exp(-i\omega_{nm}t)$; $[x]_{nm}$ is the term in Heisenberg's solution proportional to $\exp(-i\omega_{nm}t)$.

known as *matrix multiplication.* A matrix denoted $[A]_{nm}$ or just A is a square array of numbers (real or complex), with $[A]_{nm}$ the number in the nth row and mth column. In general, for any two matrices $[A]_{nm}$ and $[B]_{nm}$, the matrix AB is the square array

$$[AB]_{nm} \equiv \sum_l [A]_{nl}[B]_{lm} \; . \tag{1.4.16}$$

We also note for further use that the sum of two matrices is defined so that

$$[A+B]_{nm} \equiv [A]_{nm} + [B]_{nm} \; , \tag{1.4.17}$$

and the product of a matrix and a numerical factor is defined as

$$[\lambda A]_{nm} \equiv \lambda \, [A]_{nm} \; . \tag{1.4.18}$$

Matrix multiplication is thus associative $[A(BC) = (AB)C]$ and distributive $[A(\lambda_1 B_1 + \lambda_2 B_2) = \lambda_1 AB_1 + \lambda_2 AB_2$ and $(\lambda_1 B_1 + \lambda_2 B_2)A = \lambda_1 B_1 A + \lambda_2 B_2 A]$, but in general it is not commutative [AB and BA are not necessarily equal]. As defined by Eq. (1.4.10), $[x^2]$ is the square of the matrix $[x]$, $[x^3]$ is the cube of the matrix $[x]$, and so on.

The quantum condition (1.4.14) can also be given a pretty formulation as a matrix equation. Note that according to Eq. (1.4.7), the matrix for momentum is

$$[p]_{nm} = m_e[\dot{x}]_{nm} = -im_e\omega_{nm}[x]_{nm} \; ,$$

so the matrix products $[px]$ and $[xp]$ have the diagonal components

$$[px]_{nn} = \sum_m [p]_{nm}[x]_{mn} = -im_e \sum_m \omega_{nm}\Big|[x]_{mn}\Big|^2 ,$$

$$[xp]_{nn} = \sum_m [x]_{nm}[p]_{mn} = -im_e \sum_m \omega_{mn}\Big|[x]_{mn}\Big|^2 .$$

(In both formulas, we have used the relation (1.4.7), which says that $[x]_{mn}$ is what is called an *Hermitian* matrix.) Since $\omega_{nm} = -\omega_{mn}$, the quantum condition (1.4.14) can be written in two ways

$$i\hbar = -2[px]_{nn} = +2[xp]_{nn} \; . \tag{1.4.19}$$

Of course, the relation can then also be written

$$i\hbar = [xp]_{nn} - [px]_{nn} = [xp - px]_{nn} \; , \tag{1.4.20}$$

where we have used the definitions (1.4.17) and (1.4.18).

Shortly after the publication of Heisenberg's paper, there appeared two papers that extended Eq. (1.4.20) to a general formula for all elements of the matrix $xp - px$:

$$xp - px = i\hbar \times 1 \; , \tag{1.4.21}$$

where here 1 is the matrix

$$[1]_{nm} \equiv \delta_{nm} \equiv \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases} . \tag{1.4.22}$$

That is, in addition to Eq. (1.4.20), we have $[xp - px]_{nm} = 0$ for $n \neq m$. Born and his assistant Pascual Jordan[6] (1902–1984) gave a mathematically fallacious derivation of this fact, on the basis of the Hamiltonian equations of motion. Paul Dirac[7] (1902–1984) simply assumed Eq. (1.4.21), from an analogy with the Poisson brackets of classical mechanics, described in Section 9.4.

Matrix mechanics was now a general scheme for calculating the spectrum of any system described classically by a Hamiltonian $H(q, p)$, given as a function of a number of coordinates q_r and the corresponding "momenta" p_r. One looks for some representation of the qs and ps as matrices satisfying the matrix equation

$$q_r p_s - p_s q_r = i\hbar\delta_{rs} \times 1 , \tag{1.4.23}$$

and such that the matrix $H(q, p)$ is diagonal

$$[H(q, p)]_{nm} = E_n \delta_{nm} . \tag{1.4.24}$$

The diagonal elements E_n are the energies of the system, and the matrix elements $[x]_{nm}$ can be used with Eqs. (1.4.5) and (1.4.6) to calculate the rates for spontaneous and stimulated emission and absorption of radiation.

Unfortunately, there are very few physical systems for which this sort of calculation is practicable. One is the harmonic oscillator, already solved by Heisenberg. Another is the hydrogen atom, whose spectrum was obtained using matrix mechanics in a display of mathematical brilliance by Wolfgang Pauli[8] (1900–1958), a student of Sommerfeld. (Pauli's calculation is presented in Section 4.8.) These two problems were soluble because of special features of the Hamiltonians, the same features that make the classical orbits of particles closed curves. It was hopeless to use matrix mechanics to solve more complicated problems, like the hydrogen molecule, so wave mechanics largely superseded matrix mechanics among the tools of theoretical physics.

But it must not be thought that wave mechanics and matrix mechanics are different physical theories. In 1926, Schrödinger showed how the principles of matrix mechanics can be derived from those of wave mechanics.[9] To see how this works, note first that the Hamiltonian is what is called an Hermitian operator, meaning that for any functions f and g that satisfy the conditions

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[6] P. Jordan, Z. f. Physik **34**, 858 (1925).

[7] P. A. M. Dirac, Proc. Roy. Soc. Lond. A **109**, 642 (1926).

[8] W. Pauli, Z. Physik **36**, 336 (1926).

[9] E. Schrödinger, Ann. d. Physik **79**, 734 (1926).

of single-valuedness and vanishing at infinity imposed on wave functions, we have

$$\int f^*(Hg) = \int (Hf)^* g\ , \qquad (1.4.25)$$

the integrals being taken over all coordinates. This is trivial for the term V in Eq. (1.3.7), and it is also true for the Laplacian operator, as can be seen by integrating the identity

$$(\nabla^2 f)^* g - f^*(\nabla^2 g) = \nabla \cdot [(\nabla f)^* g - f^* \nabla g]\ .$$

It follows that for solutions ψ_n of the Schrödinger equation with energy E_n, we have

$$E_n \int \psi_m^* \psi_n = \int \psi_m^*(H\psi_n) = \int (H\psi_m)^* \psi_n = E_m^* \int \psi_m^* \psi_n\ . \qquad (1.4.26)$$

Taking $m = n$, we see that E_n is real, and then taking $m \neq n$, we see that $\int \psi_m^* \psi_n = 0$ for $E_n \neq E_m$. It can be shown that if there is more than one solution of the Schrödinger equation with the same energy, the solutions can always be chosen so that $\int \psi_m^* \psi_n = 0$ for $n \neq m$. (This is shown in footnote 3 of Section 3.1 in cases where there are a finite number of solutions of the Schrödinger equation with a given energy.) By multiplying the ψ_n with suitable factors we can also arrange that $\int \psi_n^* \psi_n = 1$, so the ψ_n are *orthonormal*, in the sense that

$$\int \psi_m^* \psi_n = \delta_{nm}\ . \qquad (1.4.27)$$

Now consider any operators A, B, etc., defined by their action on wave functions. For instance, for a single particle, the momentum operator $\mathbf{P}$ and position operators $\mathbf{X}$ are defined by

$$[\mathbf{P}\psi](\mathbf{x}) \equiv -i\hbar\nabla\psi(x), \qquad [\mathbf{X}\psi](\mathbf{x}) \equiv \mathbf{x}\psi(\mathbf{x})\ . \qquad (1.4.28)$$

For any such operator, we define a matrix

$$[A]_{nm} \equiv \int \psi_n^*[A\psi_m]\ . \qquad (1.4.29)$$

Note as a consequence of Eq. (1.3.6), this has the time-dependence (1.4.7) assumed by Heisenberg

$$[A]_{nm} \propto \exp\Big(- i(E_m - E_n)t/\hbar\Big)\ .$$

With the definition (1.4.29), we can show that the matrix of a product of operators is the product of the matrices:

$$\int \psi_n^*\Big[A[B\psi_m]\Big] = \sum_l [A]_{nl}[B]_{lm}\ . \qquad (1.4.30)$$

To prove this, we assume that the function $B\psi_m$ can be written as an expansion in the wave functions:

$$B\psi_m = \sum_r b_r(m)\psi_r \ ,$$

with some coefficients $b_r(m)$. (To make this literally true, it may be necessary to put the system in a box, like that used in Section 1.1, so that the solutions of the Schrödinger equation form a discrete set, including those corresponding to unbound electrons.) We can find these coefficients by multiplying both sides of the expansion with ψ_l^* and integrating over all coordinates, using the orthonormality property (1.4.27):

$$[B]_{lm} = \int \psi_l^*[B\psi_m] = \sum_r b_r(m)\delta_{rl} = b_l(m) \ .$$

It follows that

$$B\psi_m = \sum_l [B]_{lm}\psi_l \ . \tag{1.4.31}$$

Repeating the same reasoning, we have

$$A[B\psi_m] = \sum_{l,s} [B]_{lm}[A]_{sl}\psi_s \ . \tag{1.4.32}$$

Multiplying with ψ_n^*, integrating over all coordinates, and again using the orthonormality property (1.4.27) then gives Eq. (1.4.30).

We can now derive the Heisenberg quantization conditions. First, note that the matrix $[H]_{nm}$ is simply

$$[H]_{nm} \equiv \int \psi_n^*[H\psi_m] = E_m \int \psi_n^*\psi_m = E_m\delta_{nm} \tag{1.4.33}$$

which is the same as Eq. (1.4.24). Next, we can verify the condition (1.4.14) in the generalized form (1.4.21). Note that

$$\frac{\partial}{\partial x}(x\psi) = \psi + x\frac{\partial}{\partial x}\psi$$

so the operators P and X defined by (1.4.28) satisfy

$$\Big[P[X\psi]\Big] = -i\hbar\psi + \Big[X[P\psi]\Big] \ .$$

Applying the general formula (1.4.30), we have then

$$[xp - px]_{nm} = i\hbar\delta_{nm} \ , \tag{1.4.34}$$

which is the same as (1.4.21). The same argument can evidently be applied to give the more general condition (1.4.23).

The approach that will be adopted when we come to the general principles of quantum mechanics in Chapter 3 will be neither matrix mechanics nor wave mechanics, but a more abstract formulation, that Dirac called *transformation theory*,[10] from which matrix mechanics and wave mechanics can both be derived.

Although we will not be going into quantum electrodynamics until Chapter 11, I should mention here that in 1926 Born, Heisenberg, and Jordan[11] applied the ideas of matrix mechanics to the electromagnetic field. They showed that the free field in a cubical box with edges of length L can be written as a sum of terms with wave numbers given by (1.1.1), that is, $\mathbf{q}_\mathbf{n} = 2\pi\mathbf{n}/L$ with $\mathbf{n}$ a vector with integer components, each term described by a harmonic oscillator Hamiltonian $H_\mathbf{n} = [\dot{\mathbf{a}}_\mathbf{n}^2 + \omega_\mathbf{n}^2\mathbf{a}_\mathbf{n}^2]/2$ (with $\mathbf{a}_\mathbf{n}$ replacing $\sqrt{m}\mathbf{x}$) where $\omega_\mathbf{n} = c|\mathbf{q}_\mathbf{n}|$. The energy of this field in which the $\mathbf{n}$th oscillator is in the $\mathcal{N}_\mathbf{n}$th excited state is the sum of the harmonic oscillator energies (1.4.15)

$$E = \sum_\mathbf{n}\left[\mathcal{N}_\mathbf{n} + \frac{1}{2}\right]\hbar\omega_\mathbf{n} \,. \tag{1.4.35}$$

Such a state is interpreted as one containing $\mathcal{N}_\mathbf{n}$ photons of wave number $\mathbf{q}_\mathbf{n} = 2\pi\mathbf{n}/L$, thus justifying the Einstein assumption that light comes in quanta with energy $h\nu = \hbar\omega$. (The additional "zero-point" energy $\sum\hbar\omega_\mathbf{n}/2$ is the energy of quantum fluctuations in the vacuum, which has no effect, except on the gravitational field. This is one contribution to the "dark energy," that is currently a major concern of physicists and astronomers.) In 1927 Dirac[12] was able to use this quantum theory of radiation to give a completely quantum mechanical derivation of the formula (1.4.5) for the rate of spontaneous emission of photons, without having to rely on analogies with classical radiation theory. This derivation is presented and generalized in Section 11.7.

1.5 Probabilistic Interpretation

At first, Schrödinger and others thought that wave functions represent particles that are spread out, like pressure disturbances in a fluid — most of the particle is where the wave function is large. This interpretation became untenable with the analysis of scattering in quantum mechanics by Max Born[1] (1882–1970).

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[10] P. A. M. Dirac, Proc. Roy. Soc. Lond. A **113**, 621 (1927). This approach is the basis of Dirac's treatise, *The Principles of Quantum Mechanics*, 4th edn. (rev.) (Oxford University Press, 1976).

[11] M. Born, W. Heisenberg, and P. Jordan, Z. f. Physik **35**, 557 (1926). They ignored the polarization of light, and treated the problem in one dimension, rather than as in the three-dimensional version described here.

[12] P. A. M. Dirac, Proc. Roy. Soc. Lond. A **114**, 710 (1927).

[1] M. Born, Z. f. Physik **37**, 863 (1926); 38, 803 (1926).