V. Semiclassical theory of light-matter interactions

Classical and quantum mechanics of the electron in a light field

Joseph John Thomson (1856-1940) performed a famous experiment in 1897, in which he showed that the "cathode rays" consist of negatively charged particles. These particles have become known as the *electrons*. They carry the elementary charge

$$e = 1.602 \times 10^{-19}\ \mathrm{C}$$

Their mass

$$m = 9.109 \times 10^{-31}\ \mathrm{kg}$$

is orders of magnitude smaller than the mass of other charged particles. As compared to other charged particles (such as e.g. protons) electrons therefore

- move fast and create high microscopic current at the expense of moderate excitation energy

and

- respond swiftly to light fields.

As a consequence, the motion of electrons is responsible for

i) the emission of optical radiation

and

ii) the response of matter to optical radiation.

Thus *electrons are key players in both the generation of light and light-matter interactions.*
Light emission from excited atoms, molecules or solids just as the polarizability of matter (expressed in terms the linear and nonlinear susceptibilities in the constitutive law) are direct consequences of the motion of electron on a sub-atomic scale. Hence the theory accounting for the generation of light (both coherent and incoherent) and the optical properties of materials (expressed in terms of the linear and nonlinear susceptibilities in the constitutive law) must address the motion of electrons in light-fields. This motion can be accounted for accurately only in the framework of quantum mechanics. The quantum mechanical motion of electrons in classical electromagnetic fields forms the basis for the description of a wide-range of light generation and propagation phenomena. This model is referred to as the *semiclassical theory of light-matter interactions*. Its postulates include those of *electromagnetic optics* and those of *the quantum theory of the electron*.

Semiclassical theory of light-matter interactions =
electromagnetic optics + quantum mechanics of the electron

Hamiltonian formulation of classical mechanics, the Poisson bracket

The transition from classical to quantum mechanics can be made most conveniently by using the Hamiltonian formulation of classical mechanics (the simplest formulation of which is based upon Newton's law).

The state of motion of a mechanical system with *f* degrees of freedom is fully characterized at any instant by 2*f* variables, by *f* coordinates

$$q_1,\ q_2,\ q_3,\ \ldots\ldots,\ q_f,$$

and by *f* generalized (so-called canonical) momenta

$$p_1,\ p_2,\ p_3,\ \ldots\ldots,\ p_f,$$

which obey Hamilton's equations of motion:

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \tag{V-1}$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} \tag{V-2}$$

where

$$H = H\,(q_i,\ p_i, t) \tag{V-3}$$

is the Hamiltonian of the mechanical system. This formalism can be extended to other fields of physics, e.g. the equations of the electromagnetic fields can also be formulated this way. Generally, finding the Hamiltonian of a physical system is not straightforward. The proper Hamiltonian is one which leads to a description of the physical system that is in agreement with experimental observations. If the equations of motion are known, the Hamiltonian can usually be constructed by guessing, so that Eqs. (V-1) and (V-2) are the proper equations of motion. If *H* does not explicitly depend on time, i.e.

$$\frac{\partial H}{\partial t} = 0 \tag{V-4}$$

as is the case for any isolated system not acted on by external forces, the Hamiltonian happens to represent the total energy of the system. In these cases the construction of the Hamiltonian is fairly straightforward.

The Poisson bracket

The concept of the Poisson bracket will be important for our discussion of quantum mechanics. Let $F(q_i,p_i,t)$ an arbitrary analytic function. Its time variation can be expressed by its total derivative with respect to time

$$\frac{dF}{dt} = \sum_{i=1}^{f} \left\{ \frac{\partial F}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial F}{\partial p_i}\frac{dp_i}{dt} \right\} + \frac{\partial F}{\partial t} \tag{V-5}$$

Using the canonical equations of motion, (V-1) and (V-2), we can write (V-5) in the form

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \sum_{i=1}^{f} \left\{ \frac{\partial F}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial F}{\partial p_i} \frac{\partial H}{\partial q_i} \right\} \tag{V-6}$$

The sum term is called a Poisson bracket and is written as

$$\{F,H\} = \sum_{i=1}^{f} \left\{ \frac{\partial F}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial F}{\partial p_i} \frac{\partial H}{\partial q_i} \right\} \tag{V-7}$$

The time derivative of *F* can now be rewritten as

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F,H\} \tag{V-8}$$

It is apparent from the definition of the Poisson bracket that

$$\{H,H\} = 0 \quad \Rightarrow \quad \frac{dH}{dt} = \frac{\partial H}{\partial t} \tag{V-9}$$

indicating that *H* is conserved during the motion if we have to do with an isolated system represented by (V-4). This supports our claim that *H* is the total energy of the system.

Another interesting case of a special Poisson bracket is

$$\{q_i, p_j\} = \delta_{ij} \tag{V-10}$$

where δ_{ij} is the Kronecker symbol and equals unity if $i=j$ and zero if $i \neq j$.
This brief derivation of the expressions of Hamiltonian mechanics includes all the formulas that we will need to develop quantum mechanics. Before doing that let's see how Hamiltonian mechanics leads to the well-known formulas of Newtonian mechanics for a point particle moving in a conservative potential and a charged particle moving in a temporally-varying electromagnetic field.

Point particle in a conservative potential

A conservative potential is a function of the spatial coordinate $V(\mathbf{r})$, defined so that the force acting on the particle is given by

$$\mathbf{F} = -\nabla V(\mathbf{r}) \tag{V-11}$$

In a Cartesian system the variables characterizing the state of motion of a point particle are the coordinates *x,y,z* and the momenta p_x, p_y, p_z. If the Hamiltonian represents the energy of the particle, it takes the form

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x,y,z) \tag{V-12}$$

Now the canonical equation (V-1) leads to

$$\frac{dx}{dt} \equiv \dot{x} = \frac{1}{m} p_x \tag{V-13a}$$

$$\dot{y} = \frac{1}{m} p_y \tag{V-13b}$$

$$\dot{z} = \frac{1}{m} p_z \tag{V-13c}$$

and the canonical equation (V-2) results in

$$\dot{p}_x = -\frac{\partial V}{\partial x} = F_x \tag{V-14a}$$

$$\dot{p}_y = -\frac{\partial V}{\partial y} = F_y \tag{V-14b}$$

$$\dot{p}_z = -\frac{\partial V}{\partial z} = F_z \tag{V-14c}$$

which are the well-known equations of motion.

Charged particle in an electromagnetic field

From (V-12) it is obvious that the Hamiltonian of a particle of charge *e* and mass *m* in a static electric field E characterized by the scalar potential Φ is given by

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + e\phi \tag{V-15}$$

We now postulate that the Hamiltonian of the same particle in a temporally-varying electromagnetic field is obtained from (V-15) by simply performing the substitution

$$p_i \rightarrow p_i - eA_i \tag{V-16}$$

where A_i is the respective Cartesian component of the vector potential of the electromagnetic field.
With this transformation we obtain

$$H = \frac{1}{2m}\left[\left(p_x - eA_x\right)^2 + \left(p_y - eA_y\right)^2 + \left(p_z - eA_z\right)^2 \right] + e\phi \tag{V-17}$$

Using (V-17), the canonical equations lead to

$$\dot{x} = \frac{1}{m}(p_x - eA_x) \tag{V-18}$$

And similar equations for the *y* and *z* components. Equation (V-2) yields for the *x* component of the canonical momentum

$$\dot{p}_x = \frac{e}{m}\left[(p_x - eA_x)\frac{\partial A_x}{\partial x} + (p_y - eA_y)\frac{\partial A_y}{\partial x} + (p_z - eA_z)\frac{\partial A_z}{\partial x} \right] - e\frac{\partial \phi}{\partial x} \tag{V-19}$$

Differentiating Eq. (V-18) with respect to time and substituting (V-19) gives

$$m\frac{d^2x}{dt^2} \equiv m\ddot{x} = \frac{dp_x}{dt} - e\frac{dA_x}{dt} =$$

$$\frac{e}{m}\left[(p_x - eA_x)\frac{\partial A_x}{\partial x} + (p_y - eA_y)\frac{\partial A_y}{\partial x} + (p_z - eA_z)\frac{\partial A_z}{\partial x} \right] - e\frac{dA_x}{dt} - e\frac{\partial \phi}{\partial x} \tag{V-20}$$

Which, by substituting *dx*/*dt* from (V-18) and using the corresponding equations for the *y* and *z* components, simplifies to

$$m\ddot{x} = e\left(\dot{x}\frac{\partial A_x}{\partial x} + \dot{y}\frac{\partial A_y}{\partial x} + \dot{z}\frac{\partial A_z}{\partial x} \right) - e\frac{dA_x}{dt} - e\frac{\partial \phi}{\partial x} \tag{V-21}$$

Expressing the total derivative of A_x with respect to time as

$$\frac{dA_x}{dt} = \frac{\partial A_x}{\partial x}\dot{x} + \frac{\partial A_x}{\partial y}\dot{y} + \frac{\partial A_x}{\partial z}\dot{z} + \frac{\partial A_x}{\partial t} \tag{V-22}$$

in (V-21), we obtain

$$m\ddot{x} = e\left[\dot{y}\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) - \dot{z}\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\right] - e\frac{\partial A_x}{\partial t} - e\frac{\partial \phi}{\partial x} \tag{V-23}$$

By using the connection between the potentials A, Φ and the fields E and B as given by (IV-23), the potentials in (V-23) can be expressed with the respective components of the electric and magnetic fields as

$$m\ddot{x} = e[E_x + (\mathbf{v}\times\mathbf{B})_x] \tag{V-24}$$

where v is the velocity of the charged particle. With the corresponding equations derived for the *y* and *z* components, so that Eq. (V-24) can be written in vector notation as

$$m\frac{d\mathbf{v}}{dt} = e(\mathbf{E} + \mathbf{v}\times\mathbf{B}) \tag{V-25}$$

Equation (V-25) represents the equation of motion of a charged particle subject to the Lorentz force. Hence the respective Hamiltonian is properly defined by (V-17), consequently the influence of an electromagnetic field on a point charge can be accounted for by replacing the momentum vector p by the vector p – eA in the Hamiltonian.

Mathematical tools of quantum mechanics in Dirac's representation

Operators and vectors

Classical mechanics uses variables, such as the position and momentum of particles, and functions of these variables to describe the state of physical systems. The variables are assumed to be measurable with any degree of accuracy. The measurement of any of these variables does not influence the measurement of any other variable.

Quantum mechanics does not permit all variables of a physical system to be measurable independently. It replaces the classical variables by operators that operate on state functions (Schrödinger's representation) or vectors (Dirac's representation) used to describe the state of a physical system.

The state vectors, on which the quantum mechanical operators operate, are written in Dirac's notation[1]

$$|a\rangle \tag{V-26}$$

and are called *ket vectors*, which constitute vectors of infinite dimension. The scalar (or inner) product of two state vectors $|a\rangle$ and $|b\rangle$ is written as

$$\langle b|a\rangle \tag{V-27}$$

The scalar product of two state vectors results in a complex number and is defined such that

[1] P. A. M. Dirac, *The Principles of Quantum Mechanics,* 4th. Ed. (New York: Oxford, 1958).

$$\langle a|b\rangle = \langle b|a\rangle^* \tag{V-28}$$

Dirac called the vectors appearing on the left hand side as *bra vectors*. His terminology derives from the fact that in his above notation the bra and the ket vectors combine to form a bracket, when they scalar product, which plays a central role in quantum mechanics, is calculated. If the operator $\hat{A}$ operates on the vector $|a\rangle$ the scalar product of the new vector $|\hat{A}a\rangle$ with vector $|b\rangle$ leads to a new complex number

$$\langle b|\hat{A}a\rangle \tag{V-29}$$

that is different from $\langle b|a\rangle$. We now define the operator $\hat{A}^\dagger$ such that

$$\langle \hat{A}^\dagger b|a\rangle = \langle b|\hat{A}a\rangle \tag{V-30}$$

which is called the *adjoint operator* of $\hat{A}$. From this definition and (V-28) it is evident (exercise) that

- $\hat{A}^{\dagger\dagger} = \hat{A}$ for any operator (V-31a)
- If $\hat{A} = c$ (that is, if $\hat{A}$ is simply a complex number) $\Rightarrow \hat{A}^\dagger = c^*$ (V-31b)
- $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$ (V-31c)
- $(c\hat{A})^\dagger = c^*\hat{A}^\dagger$ (V-31d)

If $\hat{A}^\dagger = \hat{A}$, we call the operator a *self-adjoint operator* or a *Hermitian operator*. In this case we have

$$\langle \hat{A}b|a\rangle = \langle b|\hat{A}a\rangle \tag{V-32}$$

that is the operator can be applied either to the bra or the ket vector, the scalar product of the two vectors (for an arbitrary choice of the vectors) is the same. As a consequence, we can introduce the symmetric notation

$$\langle b|\hat{A}|a\rangle \equiv \langle b|\hat{A}a\rangle = \langle \hat{A}b|a\rangle \tag{V-33}$$

because having the operator sandwiched between the bra and the ket vector operate on either of them yields the same result if $\hat{A}$ is Hermitian. A very important property of Hermitian operators is (exercise) that

$$\langle a|\hat{A}|a\rangle = \text{real number} \tag{V-34}$$

Eigenvectors and eigenvalues

The relation

$$\hat{A}|a_n\rangle = a_n|a_n\rangle \tag{V-35}$$

means that operation of $\hat{A}$ on $|a_n\rangle$ does not change the "direction" but merely the "magnitude" $|a_n\rangle$ of a state into a new vector, merely multiplies it with the number a_n called the *eigenvalue* with $|a_n\rangle$ being the respective *eigenvector* of the operator $\hat{A}$. From (V-34) and (V-35) follows that the *eigenvalues of Hermitian operators are real numbers.*

The eigenvectors of Hermitian operators are mutually orthogonal (exercise)

$$\langle a_m|a_n\rangle = 0 \tag{V-36}$$

and form a complete set, that is any state vector $|\psi\rangle$ can be expressed as a sum of the orthogonal eigenvectors

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n|a_n\rangle \tag{V-37}$$

where c_n are expansion coefficients. It is customary and convenient to normalize the eigenvectors so that $\langle a_n|a_n\rangle = 1$. The mutual orthogonality with this normalization can now be expressed as

$$\langle a_n|a_m\rangle = \delta_{nm} = \begin{cases} 1 \text{ if } & n = m \\ 0 \text{ if } & n \neq m \end{cases} \tag{V-38}$$

with δ_{nm} representing Kronecker's delta. With this normalization the expansion coefficients in (V-37) can be expressed as

$$c_n = \langle a_n|\psi\rangle \tag{V-39}$$

so that

$$|\psi\rangle = \sum_{n=0}^{\infty} |a_n\rangle\langle a_n|\psi\rangle \tag{V-40}$$

We can now formally write

$$|\psi\rangle = \left(\sum_{n=0}^{\infty} |a_n\rangle\langle a_n| \right) |\psi\rangle \tag{V-41}$$

And introduce the identity operator

$$\hat{I} = \sum_n |a_n\rangle\langle a_n| \tag{V-42}$$

which can be expressed in this manner by using any complete orthonormal set of state vectors. This form of the identity operator (which is also Hermitian) is very useful for finding series expansions for products of operators and vectors.

Postulates of quantum mechanics

In classical mechanics we dealt with functions of the coordinates q_i and momenta p_i, such as the energy H. We call these quantities collectively "observables". The term "observable" describes any quantity accessible to measurement whether actually or in principle.

- Postulate #1: Every physical observable is mathematically represented by a Hermitian operator and a measurement of this observable will – with some probability – result in one of the eigenvalues of the corresponding Hermitian operator.
- Postulate #2: The quantity $\langle\psi|\hat{A}|\psi\rangle$ represents the average value of a series of measurements on an ensemble of systems that are all described by the state vector $|\psi\rangle$.
- Postulate #3: The operator $\hat{A}$ of a physical observable is the same function of the *operators* of the coordinates q_i and momenta p_i, $\hat{A} = f(\hat{q}_i, \hat{p}_i, t)$, as the corresponding classical variable of the coordinates q_i and momenta p_i, $A = f(q_i, p_i, t)$.
- Postulate #4: The quantum-mechanical Poisson bracket is defined as

  $$\{A,B\} \to \frac{1}{i\hbar}(\hat{A}\hat{B} - \hat{B}\hat{A}) \equiv \frac{1}{i\hbar}[\hat{A},\hat{B}] \tag{V-43}$$

  and has the same physical meaning as its classical-mechanical counterpart. Here

  $$\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34}\, Js \tag{V-44}$$

is Planck's constant divided by 2π.

The immediate consequences of postulate #4 and the classical expressions (V-8) and (V-10) are that the time variation of the operator of a physical observable $\hat{F}$ is given by

$$\frac{d\hat{F}}{dt} = \frac{\partial \hat{F}}{\partial t} + \frac{1}{i\hbar}[\hat{F}, \hat{H}] \tag{V-45}$$

and the operators $\hat{q}_i$ and $\hat{p}_i$ corresponding to the classical coordinates and momenta have the commutator

$$[\hat{q}_i, \hat{p}_j] \equiv (\hat{q}_i \hat{p}_j - \hat{p}_j \hat{q}_i) = i\hbar\,\delta_{ij} \tag{V-46}$$

Unitary transformations – quantum mechanical pictures

Let $\hat{U}$ be an operator which – when operating upon all state vectors – does not change the scalar product of the vectors

$$\left\langle \hat{U}a \middle| \hat{U}b \right\rangle = \langle a | b \rangle \tag{V-47a}$$

From this requirement follows (exercise) that

$$\hat{U}^\dagger \hat{U} = \hat{U}\hat{U}^\dagger = \hat{I} \tag{V-47b}$$

The operator $\hat{U}$ is called a unitary operator. The above property of the unitary operator implies that the transformation leading to the transformed state vectors and operators

$$\hat{U}|\psi\rangle = |\psi'\rangle \tag{V-48a}$$

$$\hat{U}\,\hat{A}\,\hat{U}^\dagger = \hat{A}' \tag{V-48b}$$

leaves

$$\langle \psi | \hat{A} | \psi \rangle = \langle \psi' | \hat{A}' | \psi' \rangle \tag{V-49}$$

unchanged for any Hermitian operator $\hat{A}$. As a consequence, this transformation, which is called a *unitary transformation*, does not alter the result of a measurement. Hence, the transformed state vectors $|\psi'\rangle$ and the transformed operators $\hat{A}'$ can be equivalently used for the quantum mechanical description of a physical system. This set of state vectors and respective operators form a *quantum mechanical picture*. The unitary transformation (V-48) leads us from one quantum mechanical picture into another one. Because there are infinitely many unitary operators, there are also infinitely many possible quantum mechanical pictures.

Equation (V-45) is called the equation of motion in the *Heisenberg picture*. This particular quantum-mechanical picture assumes that the operators vary with time while the state vectors are time-independent. The Heisenberg picture is formally analogous to classical mechanics, because the equations of motion for the operators resemble the corresponding classical equations.

The Schrödinger picture, the Schrödinger equation

The most frequently used quantum mechanical picture is the *Schrödinger picture*, in which the state vectors evolve in time and the operators are constant (except for a possible explicit time dependence).

Let us now find the unitary operator that transforms the Heisenberg picture into the Schrödinger picture.
The total time derivative of the transformed operator is obtained by differentiation of (V-48b) and using (V-45) as

$$\frac{d\hat{A}'}{dt} = \frac{d\hat{U}}{dt}\hat{A}\hat{U}^\dagger + \hat{U}\frac{d\hat{A}}{dt}\hat{U}^\dagger + \hat{U}\hat{A}\frac{d\hat{U}^\dagger}{dt} =$$

$$\frac{d\hat{U}}{dt}\hat{A}\hat{U}^\dagger + \hat{U}\frac{\partial\hat{A}}{\partial t}\hat{U}^\dagger + \frac{1}{i\hbar}\hat{U}[\hat{A},\hat{H}]\hat{U}^\dagger + \hat{U}\hat{A}\frac{d\hat{U}^\dagger}{dt} \qquad \text{(V-50)}$$

and required to be zero in the case of $\partial\hat{A}/\partial t = 0$, leading to

$$\frac{d\hat{U}}{dt}\hat{A}\hat{U}^\dagger + \hat{U}\hat{A}\frac{d\hat{U}^\dagger}{dt} + \frac{1}{i\hbar}\hat{U}[\hat{A},\hat{H}]\hat{U}^\dagger = 0 \qquad \text{(V-51)}$$

which can be reformed as

$$\frac{d\hat{U}}{dt}\hat{U}^\dagger\hat{A}' + \hat{A}'\hat{U}\frac{d\hat{U}^\dagger}{dt} + \frac{1}{i\hbar}(\hat{A}'\hat{H}' - \hat{H}'\hat{A}') = 0$$

or

$$\left(\frac{d\hat{U}}{dt}\hat{U}^\dagger - \frac{1}{i\hbar}\hat{H}'\right)\hat{A}' + \hat{A}'\left(\hat{U}\frac{d\hat{U}^\dagger}{dt} + \frac{1}{i\hbar}\hat{H}'\right) = 0 \qquad \text{(V-52)}$$

by making use of (V-48b) for both $\hat{A}$ and the Hamilton operator $\hat{H}$. Since this has to hold for any $\hat{A}$, we have to require

$$\frac{d\hat{U}}{dt}\hat{U}^{\dagger} = \frac{1}{i\hbar}\hat{H}' \;\Rightarrow\; i\hbar\frac{d\hat{U}}{dt} = \hat{H}'\hat{U} \tag{V-53}$$

We have found an operator equation to determine the unitary operator $\hat{U}$ that transforms the Heisenberg picture into the Schrödinger picture. By differentiating (V-48a), using (V-53) and utilizing that $d|\psi\rangle/dt = 0$ in the Heisenberg picture, we obtain the equation of motion in the Schrödinger picture

$$i\hbar\frac{d}{dt}|\psi'\rangle = \hat{H}'|\psi'\rangle \tag{V-54}$$

which is the well-known *Schrödinger equation* for the time variation of the state vectors in the Schrödinger picture.

The Schrödinger representation: wave mechanics

Different sets of orthogonal vectors may be used for representing quantum mechanical states. In the most widely used representation, the so-called Schrödinger representation, the eigenvectors of the position operators $\hat{q}_i$ are used as basis vectors. In what follows we restrict ourselves to one dimension
By considering the continuous set of eigenvalues q of the position operator $\hat{q}$. The corresponding eigenvectors $|q\rangle$ form a complete orthogonal set, satisfying $\hat{q}\,|q\rangle = q|q\rangle$. Any arbitrary state vector can be expressed as a sum of these eigenvectors by using the expansion coefficients

$$c(q) = \langle q|\psi\rangle \tag{V-55}$$

Since the spectrum of eigenvalues is continuous, $c(q)$ is a continuous function of q and fully represent the state vector $|\psi\rangle$ in the Schrödinger representation. To establish the connection between the expansion coefficients and the state vector, we can rename the function $c(q)$ as

$$\psi(q) \equiv c(q) \tag{V-56}$$

in which we recognize the familiar *wave function* of *wave mechanics*. The scalar product of two state vectors $|\psi_1\rangle$ and $|\psi_2\rangle$ can be expressed in the Schrödinger representation as

$$\langle\psi_1|\psi_2\rangle = \int \psi_1^{*}\psi_2\, d^n q \tag{V-57}$$

where the integration is to be performed over all n coordinates of the system.

To obtain the equation of motion of wave mechanics, we need to construct the operators $\hat{q}_i$ and $\hat{p}_i$. When doing so the commutation relation (V-46) must be satisfied. A convenient choice is to define

- $\hat{q}_i$ as a real multiplicative factor q_i (V-58a)

and

- $\hat{p}_i = -i\hbar\frac{\partial}{\partial q_i}$ (V-58b)

which obey the commutation relation (V-46) and constitute the Schrödinger representation of the canonically conjugate position and momentum operators.

By dot-multiplying (V-54) with the bra vector $\langle q|$ and utilizing

$$\langle q|\frac{d}{dt}|\psi\rangle = \frac{\partial}{\partial t}\langle q|\psi\rangle = \frac{\partial}{\partial t}\psi(q) \tag{V-59}$$

(where the partial differentiation indicates that only the explicit time dependence of $|\psi(t)\rangle$ but not $\langle q|$ must be differentiated) we obtain the equation of motion of wave mechanics

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}(\hat{q}_i,\hat{p}_i)\,\psi(q_i,t) \tag{V-60}$$

Equations (V-58) and (V-60) along with postulate #3 now allow us to construct a differential equation describing the temporal evolution of the wave function of a quantum mechanical system, whereas the recipe for the practical implementation of the scalar product along with postulates #1 and #2 permit us making predictions (in form of statistics and probabilities) about the results of physical measurements.

This formalism now allows us to develop the quantum theory of the electron in the presence of light fields and using this theory for describing light-matter interactions.

Quantum mechanics of a single particle in a conservative potential, centre-of-mass motion of a particle: Ehrenfest theorem

By using the postulates of quantum mechanics we can now make some predictions for the expectation values of physical observables. To this end, we shall use the Schrödinger picture. According to Postulate #2, the rate of change of the expectation value of the physical observable represented by the Hermitian operator $\hat{A} = f(\hat{q}_i,\hat{p}_i,t)$ is given by

$$\frac{d\langle A\rangle}{dt} = \frac{d}{dt}\langle\psi|A|\psi\rangle = \left(\frac{d}{dt}\langle\psi|\right)A|\psi\rangle + \langle\psi|\frac{\partial A}{\partial t}|\psi\rangle + \langle\psi|A|\left(\frac{d}{dt}|\psi\rangle\right) \tag{V-61}$$

In the Schrödinger picture we can now express – according to (V-54) – the temporal derivative of the state vector with the Hamilton operator, yielding

$$\frac{d\langle A\rangle}{dt} = \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle + \frac{1}{i\hbar}\left\langle [\hat{A},\hat{H}] \right\rangle \tag{V-62}$$

For a particle moving in a conservative potential we obtain from the classical Hamiltonian given by (V-12) the Hamilton operator in the Schrödinger representation

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z) \tag{V-63}$$

where we have utilized that $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, $\hat{p}_y = -i\hbar\frac{\partial}{\partial y}$, and $\hat{p}_z = -i\hbar\frac{\partial}{\partial z}$.

By the use of (V-62) we can now calculate the expectation value of the rate of change of the position and the momentum can be written as (exercise)

$$\frac{d\langle x\rangle}{dt} = \frac{1}{i\hbar}\frac{\hbar^2}{2m}\left\langle \psi \middle| \nabla^2 x - x\nabla^2 \middle| \psi \right\rangle = \frac{i\hbar}{m}\int \psi^* \frac{\partial \psi}{\partial x}\, d^3r = \frac{\langle p_x \rangle}{m} \tag{V-64a}$$

and

$$\frac{d\langle p_x\rangle}{dt} = \frac{1}{i\hbar}(-i\hbar)\left\langle \psi \middle| \frac{\partial}{\partial x}V(\mathbf{r}) - V(\mathbf{r})\frac{\partial}{\partial x} \middle| \psi \right\rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle \tag{V-64b}$$

where we have utilized that x commutes with $V(x)$ and $\hat{p}_x$ commutes with $\hat{p}^2$, respectively. The centre-of-mass motion of the quantum mechanical particle obeys the classical equation of motion. This is Ehrenfest's theorem.

Quantum mechanics of the electron in an electromagnetic field, electric dipole approximation

The classical Hamiltonian of a physical system consisting of an electron (of charge e = - |e|) and an electromagnetic field is given by r

$$H_{\text{total}} = H_e + H_{\text{field}} \tag{V-65a}$$

where

$$H_e = \frac{1}{2m}(\mathbf{p} - e\mathbf{A})^2 + e\phi \tag{V-65b}$$

and

$$H_{\text{field}} = \frac{1}{2}\,\varepsilon_0 \int (\mathbf{E}^2 + c^2\,\mathbf{B}^2)\; d^3r \tag{V-65c}$$

H_{total} describes an energy-conserving system, as opposed to H_e. However, for intense fields, the field energy exceeds that of interacting electrons by many orders of magnitudes, that is the relative change of the field energy during the interaction is negligible. In this case the fields are virtually not affected by the interaction and can be considered as classical input variables in H_e. These considerations form the basis for the description of light-electron interactions in the *semiclassical approximation*. If the fields become weak, they must also be quantized and H_{total} is used.

For the time being, we assume sufficiently intense fields so that the semiclassical description remains valid so that only the particle observables need to be quantized. The Hamiltonian of the electron can be decomposed into

$$\hat{H}_e = \hat{H}_0 + \hat{H}_{\text{int}} \tag{V-66}$$

with

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \tag{V-67}$$

where the static scalar potential has been incorporated in the conservative potential $V(\mathbf{r})$ and

$$\hat{H}_{\text{int}} = -\frac{e}{m}\,\hat{\mathbf{p}}\mathbf{A}(\mathbf{r},t) + \frac{e^2}{2m}\,\mathbf{A}(\mathbf{r},t)^2 \tag{V-68}$$

In deriving (V-68) from (V-65b) we made use of the Schrödinger representation of the position operator $\mathbf{r}$ and the momentum operator $-i\hbar\nabla$ together with the operator relation $\nabla\,\mathbf{A} = \mathbf{A}\,\nabla$, which directly follows from the use of the Coulomb gauge $\nabla\,\mathbf{A} = 0$ and assuming $\frac{\partial}{\partial t}\phi = 0$.
The Coulomb gauge and the static scalar potential imply a transverse time-varying (radiation) field according to (IV-23b).

Unless the light fields become extremely strong, the second term in $\hat{H}_{\text{int}}$ is negligible with respect to the first, leading to

$$\hat{H}_{\text{int}} \approx -\frac{e}{m}\,\hat{\mathbf{p}}\mathbf{A}(\mathbf{r},t) \tag{V-69}$$

Equation (V-69) can be changed by another approximation, which turns out to be very useful. If the electron´s motion is confined to a volume small compared to the wavelength of the electromagnetic wave, the vector potential in $\hat{H}_{\text{int}}$ is – to a good approximation – constant in space:

$$\mathbf{A}(\mathbf{r},t) \approx \mathbf{A}(\mathbf{r}_0,t)$$

where $\mathbf{r}_0$ is the centre of gravity of the electron's probability distribution. This approximation is referred to as the *electric dipole approximation.*

For a harmonic field oscillating at ω, hence according to (IV-23b) (exercise)

$$\mathbf{E}(\mathbf{r}_0,t) = \omega \mathbf{A}(\mathbf{r}_0, t - \pi/2\omega) \tag{V-70}$$

The electron subjected to this field has a momentum that also varies periodically

$$\mathbf{p}(t) = m\frac{d\mathbf{r}}{dt} = m\omega\mathbf{r}(t + \pi/2\omega) \tag{V-71}$$

where we assumed $\mathbf{r}_0 = 0$. From (V-70) and (V-71) we obtain

$$\mathbf{p}(t - \pi/2\omega)\mathbf{A}(\mathbf{r}_0, t - \pi/2\omega) = m\mathbf{r}(t)\mathbf{E}(\mathbf{r}_0,t)$$

yielding

$$\hat{H}_{\text{int}} = -e\,\mathbf{E}\,\mathbf{r} \tag{V-72}$$

This expression of the interaction Hamiltonian has a simple intuitive meaning: a particle of charge e experiences a force $e\mathbf{E}$ in the electric field; if it is moved a distance $\mathbf{r}$ in the direction of the field it changes its potential energy by an amount of $-e\mathbf{E}\mathbf{r}$, explaining the name of the approximation leading to this form of $\hat{H}_{\text{int}}$.

From (V-66), (V-67) and (V-72) the Hamilton operator of an electron in an electromagnetic field in the Schrödinger representation takes the form

$$\hat{H}_e = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - e\,\mathbf{E}\,\mathbf{r} \tag{V-73}$$

Ensemble average – the density matrix

Quantum mechanics makes only predictions of probabilistic or statistic nature. There are two types of uncertainties in quantum mechanical system. The first type of uncertainty is implicit in Postulate #2 and occurs even if the state vector (possibly represented by the wave function) is precisely known. The second type of uncertainty results from insufficient information about the state of a quantum mechanical system or from our inability to put each individual system in an ensemble of identical system into the same quantum mechanical state. This second type of uncertainty is handled by the density matrix.

The state vector of a system may be expressed in terms of a complete orthonormal set of eigenvectors of some operator

$$\left|\psi\right\rangle = \sum_{n=0}^{\infty} c_n \left|\varphi_n\right\rangle \tag{V-74}$$

so that the expected value of a physical observable becomes

$$\left\langle\psi\left|\hat{A}\right|\psi\right\rangle = \sum_{m,n=0}^{\infty} c_m^* c_n \left\langle\varphi_m\left|\hat{A}\right|\varphi_n\right\rangle \tag{V-75}$$

Calculation of this expectation value assumes that the expansion coefficients c_n are precisely known. If this is not the case, Eq. (V-75) is fairly meaningless unless we interpret it as an average over the incompletely known values of c_n. The averaging can be introduced as follows. Let us prepare an ensemble of N systems (N large) so that they their quantum states

$$\left|\psi_s(t)\right\rangle = \sum_{n=0}^{\infty} c_n^{(s)}(t) \left|\varphi_n\right\rangle \tag{V-76}$$

are as nearly identical as allowed by our incomplete information. The ensemble average of $c_m^{(s)*}(t)c_n^{(s)}(t)$ is then computed according to the formula

$$\overline{c_m^*(t)c_n(t)} = \frac{1}{N}\sum_{s=1}^{N} c_m^{(s)*}(t)\, c_n^{(s)}(t) \tag{V-77}$$

It is convenient to define

$$\rho_{nm} = \overline{c_m^* c_n} \tag{V-78}$$

The matrix formed by the values of ρ_{nm} is known as the *density matrix.* Its diagonal elements ρ_{nn} gives the probability of finding any one of the systems in the ensemble in the state $\left|\varphi_n\right\rangle$. The off-diagonal term ρ_{nm} is related to the radiating dipole of the ensemble, as we shall see in the next Chapter.

With this notation, the ensemble average of the expectation value of the physical observable $\hat{A}$ can be written as

$$\overline{\left\langle A\right\rangle} = \overline{\left\langle\psi\left|\hat{A}\right|\psi\right\rangle} = \sum_{m,n} \overline{c_m^* c_n}\, \left\langle\varphi_m\left|\hat{A}\right|\varphi_n\right\rangle \tag{V-79}$$

For convenience, we can define the matrix elements

$$A_{mn} = \langle \varphi_m | \hat{A} | \varphi_n \rangle \tag{V-80}$$

Eq. (V-80) is the matrix representation of the operator $\hat{A}$ in terms of the complete orthonormal set of state vectors $|\varphi_n\rangle$. If $\hat{A}$ is a Hermitian operator, its matrix elements satisfy

$$A_{k\ell} = A^*_{\ell k} \tag{V-81}$$

ρ_{nm} may also be considered as the representation of an operator $\hat{\rho}$ called the *density operator* in the $|\varphi_n\rangle$ representation. From Eq. (V-78) and (V-81) follows that $\hat{\rho}$ is a Hermitian operator.

With (V-78) and (V-80) the ensemble average of the expectation value of the physical observable $\hat{A}$ takes the form

$$\overline{\langle A \rangle} = \sum_{m,n=0}^{\infty} \rho_{nm} A_{mn} \tag{V-82}$$

which can be rewritten as the sum of the diagonal elements of the matrix

$$M_{k\ell} = \sum_n \rho_{kn} A_{n\ell} \tag{V-83}$$

to yield

$$\overline{\langle A \rangle} = \sum_n M_{nn} = \sum_n (\hat{\rho}\hat{A})_{nn} = Tr(\hat{\rho}\hat{A}) \tag{V-84}$$

which is called the trace of the product of the matrices $\hat{\rho}$ and $\hat{A}$. Although for the calculation of the ensemble average of $\hat{A}$ we used the representations of $\hat{\rho}$ and $\hat{A}$ in the $|\varphi_n\rangle$ representation, it can be shown (exercise) that the trace of $\hat{\rho}\hat{A}$ and hence the ensemble average of the expectation value of a physical measurable is independent of the choice of the system of unit vectors $|\varphi_n\rangle$. The average given by (V-84) is an average in a double sense. It is a statistical average of quantum-mechanical average (expectation) values.

The time evolution of the density matrix

The states (V-76) of each system in the ensemble satisfy Schrödinger's equation

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H}|\psi\rangle \tag{V-85}$$

Substituting (V-74) for $|\psi\rangle$ yields

$$i\hbar \sum_n \frac{dc_n(t)}{dt}|\varphi_n\rangle = \sum_n c_n(t)\hat{H}|\varphi_n\rangle \tag{V-86}$$

Multiplying Eq. (V-86) with the bra vector $\langle\varphi_m|$ and using the orthonormality of the eigenvectors $|\varphi_n\rangle$ we obtain

$$i\hbar \frac{d}{dt}c_m(t) = \sum_n c_n(t)\, H_{mn} \tag{V-87}$$

where $H_{mn} = \langle\varphi_m|\hat{H}|\varphi_n\rangle$. From Eq. (V-78)

$$\frac{d\rho_{nm}}{dt} = \overline{c_n \frac{dc_m^*}{dt}} + \overline{c_m^* \frac{dc_n}{dt}} \tag{V-88}$$

By making use of (V-87) and the Hermiticity of $\hat{H}$, Eq. (V-88) takes the form

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}] \tag{V-89}$$

which is the *equation of motion of the density operator in the Schrödinger picture*.