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Time-Dependent Perturbation Theory

10.1 Introduction

We have dealt so far with Hamiltonians that do not depend explicitly on time. In nature, however, most quantum phenomena are governed by time-dependent Hamiltonians. In this chapter we are going to consider approximation methods treating Hamiltonians that depend explicitly on time.

To study the structure of molecular and atomic systems, we need to know how electromagnetic radiation interacts with these systems. Molecular and atomic spectroscopy deals in essence with the absorption and emission of electromagnetic radiation by molecules and atoms. As a system absorbs or emits radiation, it undergoes transitions from one state to another.

Time-dependent perturbation theory is most useful for studying processes of absorption and emission of radiation by atoms or, more generally, for treating the transitions of quantum systems from one energy level to another.

10.2 The Pictures of Quantum Mechanics

As seen in Chapter 2, there are many representations of wave functions and operators in quantum mechanics. The connection between the various representations is provided by unitary transformations. Each class of representation, also called a *picture*, differs from others in the way it treats the time evolution of the system.

In this section we look at the pictures encountered most frequently in quantum mechanics: the Schrödinger picture, the Heisenberg picture and the interaction picture. The Schrödinger picture is useful when describing phenomena with time-independent Hamiltonians, whereas the interaction and Heisenberg pictures are useful when describing phenomena with time-dependent Hamiltonians.

10.2.1 The Schrödinger Picture

In describing quantum dynamics, we have been using so far the Schrödinger picture in which *state vectors depend explicitly on time, but operators do not*:

$$\boxed{i\hbar \frac{d}{dt} \mid \psi(t)\rangle = \hat{H} \mid \psi(t)\rangle,} \tag{10.1}$$

where $\mid \psi(t)\rangle$ denotes the state of the system in the Schrödinger picture. We have seen in Chapter 3 that the time evolution of a state $\mid \psi(t)\rangle$ can be expressed by means of the propagator, or time-evolution operator, $\hat{U}(t, t_0)$ as follows:

$$\boxed{\mid \psi(t)\rangle = \hat{U}(t, t_0) \mid \psi(t_0)\rangle,} \tag{10.2}$$

with

$$\hat{U}(t, t_0) = e^{i(t-t_0)\hat{H}/\hbar}. \tag{10.3}$$

The operator $\hat{U}(t, t_0)$ is unitary,

$$\hat{U}^{\dagger}(t, t_0)\hat{U}(t, t_0) = I, \tag{10.4}$$

and satisfies these properties:

$$\hat{U}(t, t) = I, \tag{10.5}$$

$$\hat{U}^{\dagger}(t, t_0) = \hat{U}^{-1}(t, t_0) = \hat{U}(t_0, t), \tag{10.6}$$

$$\hat{U}(t_1, t_2)\hat{U}(t_2, t_3) = \hat{U}(t_1, t_3). \tag{10.7}$$

10.2.2 The Heisenberg Picture

In this picture the time dependence of the state vectors is completely frozen. The Heisenberg picture is obtained from the Schrödinger picture by applying $\hat{U}$ on $\mid \psi(t)\rangle_H$:

$$\mid \psi(t)\rangle_H = \hat{U}^{\dagger}(t) \mid \psi(t)\rangle = \mid \psi(0)\rangle, \tag{10.8}$$

where $\mid \psi(t)\rangle$ and $\hat{U}^{\dagger}(t)$ can be obtained from (10.2) and (10.3), respectively, by setting $t_0 = 0$: $\hat{U}^{\dagger}(t) = \hat{U}^{\dagger}(t, t_0 = 0) = e^{i\hat{H}t/\hbar}$ and $\mid \psi(t)\rangle = \hat{U}(t) \mid \psi(0)\rangle$, $\hat{U}(t) = e^{i\hat{H}t/\hbar}$. Thus, we can rewrite (10.8) as

$$\boxed{\mid \psi(t)\rangle_H = e^{it\hat{H}/\hbar} \mid \psi(t)\rangle.} \tag{10.9}$$

As $\mid \psi\rangle_H$ is frozen in time we have: $d \mid \psi\rangle_H/dt = 0$. Let us see how the expectation value of an operator $\hat{A}$ in the state $\mid \psi(t)\rangle$ evolves in time

$$\langle \psi(t)|\hat{A}|\psi(t)\rangle = \langle \psi(0)|e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}|\psi(0)\rangle = \langle \psi(0)|\hat{A}_H(t)|\psi(0)\rangle = \langle \psi|\hat{A}_H(t)|\psi\rangle_H, \tag{10.10}$$

where $\hat{A}_H(t)$ is given by

$$\boxed{\hat{A}_H(t) = \hat{U}^{\dagger}(t)\hat{A}\hat{U}(t) = e^{-it\hat{H}/\hbar}\hat{A}e^{it\hat{H}/\hbar}.} \tag{10.11}$$

Equation (10.10) shows that the expectation value of an operator is the same in both the Schrödinger and the Heisenberg pictures. From (10.10) and (10.11) we see that both the Schrödinger and the Heisenberg pictures coincide at $t = 0$, since $\mid \psi(0)\rangle_H = \mid \psi(0)\rangle$ and $\hat{A}_H(0) = \hat{A}$.

10.2.2.1 The Heisenberg Equation of Motion

Let us now derive the equation of motion that regulates the time evolution of operators within the Heisenberg picture. Assuming that $\hat{A}$ does not depend explicitly on time (i.e., $\partial\hat{A}/\partial t = 0$), and since $\hat{U}(t)$ is unitary we have

$$\begin{aligned}\frac{d\hat{A}_H(t)}{dt} &= \frac{\partial\hat{U}^\dagger(t)}{dt}\hat{A}\hat{U}_{(t)} + \hat{U}^\dagger(t)\hat{A}\frac{\partial\hat{U}(t)}{\partial t} = -\frac{1}{i\hbar}\hat{U}^\dagger\hat{H}\hat{U}\hat{U}^\dagger\hat{A}\hat{U} + \frac{1}{i\hbar}\hat{U}^\dagger\hat{A}\hat{U}\hat{U}^\dagger\hat{H}\hat{U} \\ &= \frac{1}{i\hbar}\left[\hat{A}_H, \hat{U}^\dagger\hat{H}\hat{U}\right], \end{aligned} \tag{10.12}$$

where we have used (10.3) to write $\partial\hat{U}(t)/\partial t = \hat{H}\hat{U}/i\hbar$ and $\partial\hat{U}^\dagger(t)/\partial t = -\hat{U}^\dagger\hat{H}/i\hbar$. Since $\hat{U}(t)$ and $\hat{H}$ commute, we have $\hat{U}^\dagger(t)\hat{H}\hat{U}(t) = H$, hence we can rewrite (10.12) as

$$\boxed{\frac{d\hat{A}_H}{dt} = \frac{1}{i\hbar}\left[\hat{A}_H, \hat{H}\right].} \tag{10.13}$$

This is the *Heisenberg equation of motion*. It plays the role of the Schrödinger equation within the Heisenberg picture. Since the Schrödinger and Heisenberg pictures are equivalent, we can use either picture to describe the quantum system under consideration. The Heisenberg equation (10.13), however, is in general difficult to solve.

Note that the structure of the Heisenberg equation (10.13) is similar to the classical equation of motion of a variable A that does not depend explicitly on time $dA/dt = \{A, H\}$ where $\{A, H\}$ is the Poisson bracket between A and H (see Chapter 3).

10.2.3 The Interaction Picture

The interaction picture, also called the *Dirac picture*, is useful to describe quantum phenomena with Hamiltonians that depend explicitly on time. In this picture *both state vectors and operators evolve in time*. We need, therefore, to find the equation of motion for the state vectors and for the operators.

10.2.3.1 Equation of Motion for the State Vectors

State vectors in the interaction picture are defined in terms of the Schrödinger states $|\,\psi(t)\rangle$by

$$\boxed{|\,\psi(t)\rangle_I = e^{i\hat{H}_0 t/\hbar}\,|\,\psi(t)\rangle.} \tag{10.14}$$

If $t = 0$ we have $|\,\psi(0)\rangle_I = |\,\psi(0)\rangle$. The time evolution of $|\,\psi(t)\rangle$ is governed by the Schrödinger equation (10.1) with $\hat{H} = \hat{H}_0 + \hat{V}$ where $\hat{H}_0$ is time independent, but $\hat{V}$ may depend on time.

To find the time evolution of $|\,\psi(t)\rangle_I$, we need the time derivative of (10.14):

$$\begin{aligned} i\hbar\frac{d\,|\,\psi(t)\rangle_I}{dt} &= -\hat{H}_0 e^{i\hat{H}_0 t/\hbar}\,|\,\psi(t)\rangle + e^{i\hat{H}_0 t/\hbar}\left(i\hbar\frac{d\,|\,\psi(t)\rangle}{dt}\right) \\ &= -\hat{H}_0\,|\,\psi(t)\rangle_I + e^{i\hat{H}_0 t/\hbar}\hat{H}\,|\,\psi(t)\rangle, \end{aligned} \tag{10.15}$$

where we have used (10.1). Since $\hat{H} = \hat{H}_0 + \hat{V}$, and

$$e^{iH_0t/\hbar}\hat{V} = \left(e^{i\hat{H}_0t/\hbar}\hat{V}e^{-i\hat{H}_0t/\hbar}\right)e^{i\hat{H}_0t/\hbar} = \hat{V}_I(t)e^{i\hat{H}_0t/\hbar}, \tag{10.16}$$

with

$$\hat{V}_I(t) = e^{i\hat{H}_0t/\hbar}\hat{V}e^{-i\hat{H}_0t/\hbar}, \tag{10.17}$$

we can rewrite (10.15) as

$$i\hbar\frac{d \mid \psi(t)\rangle_I}{dt} = -\hat{H}_0 \mid \psi(t)\rangle_I + \hat{H}_0 e^{i\hat{H}_0t/\hbar} \mid \psi(t)\rangle + \hat{V}_I(t)e^{i\hat{H}_0t/\hbar} \mid \psi(t)\rangle, \tag{10.18}$$

or

$$\boxed{i\hbar\frac{d \mid \psi(t)\rangle_I}{dt} = \hat{V}_I(t) \mid \psi(t)\rangle_I.} \tag{10.19}$$

This is the Schrödinger equation in the interaction picture. It shows that the time evolution of the state vector is governed by the interaction $\hat{V}_I(t)$.

10.2.3.2 Equation of Motion for the Operators

The interaction representation of an operator $\hat{A}_I(t)$ is given, as shown in (10.17), in terms of its Schrödinger representation by

$$\boxed{\hat{A}_I(t) = e^{i\hat{H}_0t/\hbar}\hat{A}e^{-i\hat{H}_0t/\hbar}.} \tag{10.20}$$

Calculating the time derivative of $\hat{A}_I(t)$ and since $\partial\hat{A}/\partial t = 0$, we can show the time evolution of $\hat{A}_I(t)$ is governed by $\hat{H}_0$:

$$\boxed{\frac{d\hat{A}_I(t)}{dt} = \frac{1}{i\hbar}\left[\hat{A}_I(t),\ \hat{H}_0\right].} \tag{10.21}$$

This equation is similar to the Heisenberg equation of motion (10.13), save that $\hat{H}$ is replaced by $\hat{H}_0$. The basic difference between the Heisenberg and interaction pictures can be inferred from a comparison of (10.9) with (10.14), and (10.11) with (10.20): in the Heisenberg picture it is $\hat{H}$ that appears in the exponents, whereas in the interaction picture it is $\hat{H}_0$ that appears.

In conclusion we have seen that, within the Schrödinger picture, the states depend on time but not the operators; in the Heisenberg picture, only operators depend explicitly on time, state vectors are frozen in time. The interaction picture, however, is intermediate between the Schrödinger and the Heisenberg pictures, since both state vectors and operators evolve with time.

10.3 Time-Dependent Perturbation Theory

We consider here only those phenomena that are described by Hamiltonians which can be split into two parts, a time-independent part $\hat{H}_0$ and a time-dependent part $\hat{V}(t)$ that is small compared to $\hat{H}_0$:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t), \tag{10.22}$$