Chapter 15

Time Evolution in Quantum Mechanics

PHYSICAL systems are, in general, dynamical, i.e. they evolve in time. The dynamics of classical mechanical systems are described by Newton's laws of motion, while the dynamics of the classical electromagnetic field is determined by Maxwell's equations. Either Newton's equations or Maxwell's equations constitute laws of physics whose form is particular to the kind of system that is being described, though some unification is provided in terms of Hamilton's principle, a universal way of stating the laws of classical dynamics. What we require is a means by which the dynamical properties of quantum systems can be described, i.e. given the state $|\psi(0)\rangle$ of a quantum system at some initial time $t = 0$, what is required is a physical law that tells us what the state will be at some other time t, i.e. a quantum law of evolution. Given that a state vector is a repository of the information known about a system, what is required is a general physical law that tells us how this information evolves in time in response to the particular physical circumstances that the system of interest finds itself in. It is to be expected that the details of this law will vary from system to system, but it turns out that the law of evolution can be written in a way that holds true for *all* physical systems, in some sense similar to the way that Hamilton's principle provides a way of stating classical dynamical laws in one compact form. Of course, the quantum law of evolution is Schrödinger's equation.

15.1 Stationary States

The idea of 'stationary states' was first introduced by Bohr as a name given to those states of a hydrogen atom for which the orbits that the electron occupied were stable, i.e. the electron remained in the same orbital state for all time, in contrast to the classical physics prediction that no orbiting electron could remain in orbit forever: it would always radiate away its energy and spiral into the proton. Although Bohr's original concept is now no longer appropriate, the notion of a stationary state remains a valid one. It is a term that is now used to identify those states of a quantum system that do not change in time. This is not to say that a stationary state is one for which 'nothing happens' – there is still a rich collection of dynamical physics to be associated with such a state – but a stationary state turns out to be one for which the probabilities of outcomes of a measurement of any property of the system is the same no matter at what time the measurement is made. Our aim initial aim here is to try to learn what properties the state vector representing a stationary state might have.

The starting point is to let $|\psi(0)\rangle$ be the initial state of the system, and $|\psi(t)\rangle$ be the state at some other time t. As this state vector at time t is supposed to represent the system in the same physical state, the most that these two states can differ by is a multiplicative factor, $u(t)$ say, i.e.

$$|\psi(t)\rangle = u(t)|\psi(0)\rangle. \tag{15.1}$$

Since we would expect that if the initial state $|\psi(0)\rangle$ is normalized to unity, then so would the state $|\psi(t)\rangle$, we can write

$$\langle\psi(t)|\psi(t)\rangle = |u(t)|^2\langle\psi(0)|\psi(0)\rangle \tag{15.2}$$

and hence

$$|u(t)|^2 = 1 \tag{15.3}$$

so we must conclude that

$$u(t) = e^{-i\phi(t)} \tag{15.4}$$

where $\phi(t)$ is an as yet unknown time dependent phase. Thus we can write

$$|\psi(t)\rangle = e^{-i\phi(t)}|\psi(0)\rangle. \tag{15.5}$$

This result is very general, and perhaps not all that surprising, but it becomes more revealing if we focus on an important special case, that in which the system is assumed to be isolated i.e. that it has no interaction with any other system – the dynamics of the system are determined solely by its own internal interactions. What this means is that if, for such a system, we were initially to prepare the system in some state and allow it to evolve for, say, ten minutes, it should not matter when this 'initial' time might be. If we start the experiment at noon and allow it to run for ten minutes, or if we started it at midnight and allow it to run for ten minutes, the state of the system after the ten minutes has elapsed should be the same in either case, simply because the system is isolated: the way it behaves cannot be affected by anything external. In contrast, if the system were *open*, i.e. not isolated, then there is the prospect of time dependent external influences acting on the system – e.g. an externally produced laser pulse fired at an atom – so the evolution of the state of the atom would differ depending on the starting time. In such a situation the system might not have any stationary states at all as it is always potentially being forced to change because of these external influences.

What all this amounts to as that, for an isolated system, we can chose the initial time to be any arbitrary time t_0, and the evolution of $|\psi(t_0)\rangle$ up to the time t would be given by

$$|\psi(t)\rangle = e^{-i\phi(t-t_0)}|\psi(t_0)\rangle \tag{15.6}$$

i.e. what matters is how long the system evolves for, not what we choose as our starting time.

If we now consider the evolution of the system in a stationary state over a time interval (t, t'), then we have

$$|\psi(t')\rangle = e^{-i\phi(t'-t)}|\psi(t)\rangle = e^{-i\phi(t'-t)}e^{-i\phi(t-t_0)}|\psi(t_0)\rangle \tag{15.7}$$

but over the interval (t_0, t') we have

$$|\psi(t')\rangle = e^{-i\phi(t'-t_0)}|\psi(0)\rangle \tag{15.8}$$

so by comparing the last two equations we find that

$$e^{-i\phi(t'-t_0)} = e^{-i\phi(t'-t)}e^{-i\phi(t-t_0)} \tag{15.9}$$

or

$$\phi(t - t_0) = \phi(t' - t) + \phi(t - t_0), \tag{15.10}$$

an equation for ϕ with the solution

$$\phi(t) = \omega t \tag{15.11}$$

where ω is a constant. Thus we can conclude that

$$|\psi(t)\rangle = e^{-i\omega t}|\psi(0)\rangle \tag{15.12}$$

which is the required expression for the evolution in time of a stationary state of an isolated system.

15.2   The Schrödinger Equation – a 'Derivation'.

The expression Eq. (15.12) involves a quantity ω, a real number with the units of $(\text{time})^{-1}$, i.e. it has the units of angular frequency. In order to determine the physical meaning to be given to this quantity, we can consider this expression in the particular case of a free particle of energy E and momentum p, for which the wave function is given by

$$\Psi(x, t) = Ae^{ikx}e^{-i\omega t} \tag{15.13}$$

where, according to the de Broglie-Bohr relations, $E = \hbar\omega$ and $p = \hbar k$. In this case, we see that ω is directly related to the energy of the particle. This is a relationship that we will assume applies to any physical system, so that we will rewrite Eq. (15.12) as

$$|\psi(t)\rangle = e^{-iEt/\hbar}|\psi(0)\rangle \tag{15.14}$$

and further identify the stationary state $|\psi(0)\rangle$ as being an eigenstate of the energy observable $\hat{H}$ for the system, otherwise known as the Hamiltonian.

We now make an inductive leap, and identify a stationary state of *any* physical system as being an eigenstate of the Hamiltonian of the system, with the associated eigenvalue being the energy to be associated with the stationary state.

$$|E(t)\rangle = e^{-iEt/\hbar}|E\rangle \tag{15.15}$$

with

$$\hat{H}|E\rangle = E|E\rangle \tag{15.16}$$

from which we get

$$\hat{H}|E(t)\rangle = E|E(t)\rangle. \tag{15.17}$$

If we differentiate Eq. (15.15) we find

$$i\hbar\frac{d|E(t)\rangle}{dt} = E|E(t)\rangle = \hat{H}|E(t)\rangle \tag{15.18}$$

which we can now use to obtain the equation satisfied by an arbitrary state vector $|\psi(t)\rangle$. First, since the eigenstates of $\hat{H}$, call them $\{|E_1\rangle, |E_2\rangle, \ldots, |E_N\rangle\}$, form a complete set of basis states, we can write for the initial state

$$|\psi(0)\rangle = \sum_{n=1}^{N} |E_n\rangle\langle E_n|\psi(0)\rangle. \tag{15.19}$$

The time evolved version is then

$$|\psi(t)\rangle = \sum_{n=1}^{N} e^{-iE_n t/\hbar}|E_n\rangle\langle E_n|\psi(0)\rangle \tag{15.20}$$

which, on differentiating, becomes

$$\begin{aligned}
i\hbar\frac{d|\psi(t)\rangle}{dt} &= i\hbar \sum_{n=1}^{N} E_n e^{-iE_n t/\hbar}|E_n\rangle\langle E_n|\psi(t)\rangle \\
&= \sum_{n=1}^{N} \hat{H}e^{-iE_n t/\hbar}|E_n\rangle\langle E_n|\psi(t)\rangle \\
&= \hat{H}\sum_{n=1}^{N} e^{-iE_n t/\hbar}|E_n\rangle\langle E_n|\psi(t)\rangle \\
&= \hat{H}|\psi(t)\rangle
\end{aligned} \tag{15.21}$$

so we have

$$\hat{H}|\psi(t)\rangle = i\hbar\frac{d|\psi(t)\rangle}{dt} \tag{15.22}$$

which is the celebrated Schrödinger equation in vector form.

Determining the solution of this equation is the essential task in determining the dynamical properties of a quantum system. If the eigenvectors and eigenvalues of the Hamiltonian can be readily determined, the solution can be written down directly, i.e. it is just

$$|\psi(t)\rangle = \sum_n e^{-iE_n t/\hbar}|E_n\rangle\langle E_n|\psi(0)\rangle. \tag{15.23}$$

However, it is not necessary to follow this procedure, at least explicitly, as there are in general many ways to solving the equations. In any case, the process of obtaining the eigenvalues and eigenvectors is often very difficult, if not impossible, for any but a small handful of problems, so approximate techniques have to be employed.

Typically information about the Hamiltonian is available as its components with respect to some set of basis vectors, i.e. the Hamiltonian is given as a matrix. In the next Section, an example of solving the Schrödinger equation when the Hamiltonian matrix is given.

15.2.1   Solving the Schrödinger equation: An illustrative example

The aim here is to present an illustrative solution of the Schrödinger equation using as the example the O_2^- ion studied in the preceding Chapter. There it was shown that the Hamiltonian for the ion takes the form, Eq. (13.32), in the position representation:

$$\hat{H} \doteq \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix} \tag{15.24}$$

where A is a real number. The eigenvalues of $\hat{H}$ are

$$E_1 = E_0 + A \qquad E_2 = E_0 - A.$$

and the associated eigenstates are

$$|E_1\rangle = \frac{1}{\sqrt{2}}(|+a\rangle - |-a\rangle) \doteq \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$|E_2\rangle = \frac{1}{\sqrt{2}}(|+a\rangle + |-a\rangle) \doteq \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

Now suppose the system is prepared in some initial state $|\psi(0)\rangle$. What is the state of the system at some other time t? There are a number of ways of doing this. The first is to solve the Schrödinger equation, with the Hamiltonian as given in Eq. (15.24). The second is to make use of the known information about the eigenvalues and eigenstates of the Hamiltonian.

Direct solution of the Schrödinger equation.

It is easiest to work using the vector/matrix notation. Thus, we will write the state of the ion at time t as

$$|\psi(t)\rangle = C_+(t)|+a\rangle + C_-(t)|-a\rangle \doteq \begin{pmatrix} C_+(t) \\ C_-(t) \end{pmatrix} \tag{15.25}$$

where $C_\pm(t)$ are the probability amplitudes $\langle\pm a|\psi(t)\rangle$.

The Schrödinger equation now becomes

$$i\hbar\frac{d}{dt}\begin{pmatrix} C_+(t) \\ C_-(t) \end{pmatrix} = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}\begin{pmatrix} C_+(t) \\ C_-(t) \end{pmatrix}. \tag{15.26}$$

In the following we will use the 'dot' notation for a derivative with respect to time, i.e. $\dot{C}_+ = dC_+/dt$. So, this last equation becomes

$$i\hbar\begin{pmatrix} \dot{C}_+(t) \\ \dot{C}_-(t) \end{pmatrix} = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}\begin{pmatrix} C_+(t) \\ C_-(t) \end{pmatrix}. \tag{15.27}$$

Expanding out this matrix equation we get two coupled first-order differential equations:

$$i\hbar\dot{C}_+(t) = E_0 C_+(t) - A C_-(t) \tag{15.28}$$

$$i\hbar\dot{C}_-(t) = -A C_+(t) + E_0 C_-(t). \tag{15.29}$$

There are many different ways of solving these equations (one of them, in fact, being to work with the original matrix equation!). Here we will exploit the symmetry of these equations by defining two new quantities

$$X = C_+ + C_- \quad Y = C_+ - C_- \tag{15.30}$$

in terms of which we find

$$C_+ = \tfrac{1}{2}(X + Y) \quad C_- = \tfrac{1}{2}(X - Y). \tag{15.31}$$

So, if we add the two equations Eq. (15.28) and Eq. (15.29) we get:

$$i\hbar\dot{X} = (E_0 - A)X \tag{15.32}$$

while if we subtract them we get

$$i\hbar\dot{Y} = (E_0 + A)Y. \tag{15.33}$$

Eq. (15.32) has the immediate solution

$$X(t) = X(0)e^{-i(E_0-A)t/\hbar} \tag{15.34}$$

while Eq. (15.33) has the solution

$$Y(t) = Y(0)e^{-i(E_0+A)t/\hbar}. \tag{15.35}$$

We can now reconstruct the solutions for $C_\pm(t)$ by use of Eq. (15.31):

$$C_+(t) = \tfrac{1}{2}(X + Y) = \tfrac{1}{2}e^{-iE_0t/\hbar}\left(X(0)e^{iAt/\hbar} + Y(0)e^{-iAt/\hbar}\right) \tag{15.36}$$

$$C_-(t) = \tfrac{1}{2}(X - Y) = \tfrac{1}{2}e^{-iE_0t/\hbar}\left(X(0)e^{iAt/\hbar} - Y(0)e^{-iAt/\hbar}\right). \tag{15.37}$$

To see what these solutions are telling us, let us suppose that at $t = 0$, the electron was on the oxygen atom at $x = -a$, i.e. the initial state was

$$|\psi(0)\rangle = |-a\rangle \tag{15.38}$$

so that

$$C_-(0) = 1 \quad C_+(0) = 0 \tag{15.39}$$

and hence

$$X(0) = 1 \quad Y(0) = -1. \tag{15.40}$$

We then have

$$C_+(t) = \tfrac{1}{2} e^{-iE_0 t/\hbar} \left(e^{iAt/\hbar} - e^{-iAt/\hbar} \right)$$

$$= i e^{-iE_0 t/\hbar} \sin(At/\hbar) \tag{15.41}$$

$$\not c C_-(t) = \tfrac{1}{2} e^{-iE_0 t/\hbar} \left(e^{iAt/\hbar} + e^{-iAt/\hbar} \right)$$

$$= e^{-iE_0 t/\hbar} \cos(At/\hbar) \tag{15.42}$$

where we have used the relations

$$\cos\theta = \frac{e^{i\theta} + e^{-i\theta}}{2} \quad \sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}.$$

Consequently, the probability of finding the ion on the oxygen atom at $x = -a$, i.e. the probability of finding it in the state $|-a\rangle$ will be

$$P_-(t) = |C_-(t)|^2 = \cos^2(At/\hbar) \tag{15.43}$$

while the probability of finding the electron on the oxygen atom at $x = +a$, i.e. the probability of finding it in the state $|+a\rangle$ will be

$$P_+(t) = |C_+(t)|^2 = \sin^2(At/\hbar). \tag{15.44}$$

These two probabilities add to unity for all time, as they should:

$$P_-(t) + P_+(t) = \cos^2(At/\hbar) + \sin^2(At/\hbar) = 1. \tag{15.45}$$

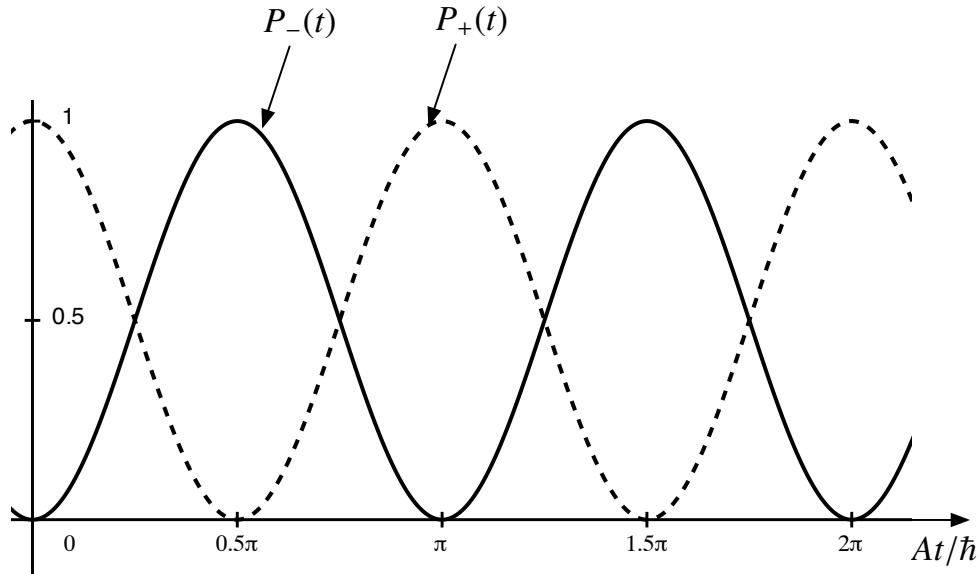We can plot these two probabilities as a function of time:

Figure 15.1: Probabilities $P_\pm(t)$ for the electron to be found on the oxygen atom at $x = \pm a$ in an O_2^- ion. The electron was initially on the atom at $x = +a$.

We can see from these curves that the probability oscillates back and forth with an angular frequency $A/\hbar$ and hence a frequency $A/\pi\hbar$, or a period $\pi\hbar/A$. Note that this oscillation is not to be interpreted as the electron being lost somewhere between the oxygen atoms between the peaks of the oscillations, rather this must be interpreted as the probability of the electron being on, say, the right hand atom, diminishing from a maximum of unity, while the probability of the atom being on the left hand atom increases from a minimum of zero, and vice versa. The electron is either more likely, or less likely, to be found at one atom or the other.

Solution using energy eigenvectors as basis vectors.

An alternate way of solving this problem is to recognize that the energy eigenstates can equally well be used as basis states for the state of the ion, i.e. we could write for the state of the ion at $t = 0$:

$$|\psi(0)\rangle = C_1|E_1\rangle + C_2|E_2\rangle \tag{15.46}$$

so that the time evolved state will be

$$|\psi(t)\rangle = C_1 e^{-i(E_0+A)t/\hbar}|E_1\rangle + C_2 e^{-i(E_0-A)t/\hbar}|E_2\rangle \tag{15.47}$$

where we have used the known energy eigenvalues $E_1 = E_0 + A$ and $E_2 = E_0 - A$ for the energy eigenstates $|E_1\rangle$ and $|E_2\rangle$ respectively. Thus, we already have the solution. But, if we want to make use of the initial condition that the electron was initially on the atom at $-a$, i.e. $|\psi(0)\rangle = |-a\rangle$, we have to use this information to determine the coefficients C_1 and C_2. Thus we have

$$|-a\rangle = C_1|E_1\rangle + C_2|E_2\rangle \tag{15.48}$$

and hence

$$C_1 = \langle E_1|-a\rangle = -\frac{1}{\sqrt{2}} \quad C_2 = \langle E_2|-a\rangle = \frac{1}{\sqrt{2}}. \tag{15.49}$$

where we have used

$$|E_1\rangle = \frac{1}{\sqrt{2}}(|+a\rangle - |-a\rangle)$$

$$|E_2\rangle = \frac{1}{\sqrt{2}}(|+a\rangle + |-a\rangle).$$

Thus, the time evolved state is

$$|\psi(t)\rangle = -\frac{1}{\sqrt{2}} e^{-iE_0t/\hbar}\left(e^{-iAt/\hbar}|E_1\rangle - e^{iA)t/\hbar}|E_2\rangle\right). \tag{15.50}$$

The probability of finding the electron on the atom at $+a$ will then be

$$P_+(t) = |\langle +a|\psi(t)\rangle|^2 = |C_+(t)|^2 \tag{15.51}$$

which requires us to calculate

$$C_+(t) = \langle +a|\psi(t)\rangle = -\frac{1}{\sqrt{2}} e^{-iE_0t/\hbar}\left(e^{-iAt/\hbar}\langle +a|E_1\rangle - e^{iA)t/\hbar}\langle +a|E_2\rangle\right) \tag{15.52}$$

$$= -\tfrac{1}{2} e^{-iE_0t/\hbar}\left(e^{-iAt/\hbar} - e^{iA)t/\hbar}\right) \tag{15.53}$$

$$= ie^{-iE_0t/\hbar}\sin(At/\hbar) \tag{15.54}$$

as before. Similarly, we can determine $\langle -a|\psi(t)\rangle$, once again yielding the result for $C_-(t)$ obtained earlier.

15.2.2   The physical interpretation of the O_2^- Hamiltonian

The results just obtained for the time evolution of the state of the O_2^- ion makes it possible to give a deeper physical interpretation to the elements appearing in the Hamiltonian matrix, in particular the off-diagonal element A.

It is important to note that evolution of the system critically depends on the off-diagonal element A having a non-zero value. If $A = 0$, then the matrix is diagonal in the position representation, which means that the states $|\pm a\rangle$ are eigenstates of $\hat{H}$, and hence are stationary states. So, if $A = 0$, once

an electron is placed on one or the other of the oxygen atoms, it stays there. Thus A is somehow connected with the internal forces responsible for the electron being able to make its way from one oxygen atom to the other. To see what this might be, we need to take a closer look at the physical makeup of the O_2^- ion.

The electron in the ion can be shown to move in a double potential well with minima at $x = \pm a$, i.e. at the positions of the two oxygen atoms. The general situation is illustrated in Fig. (15.2)
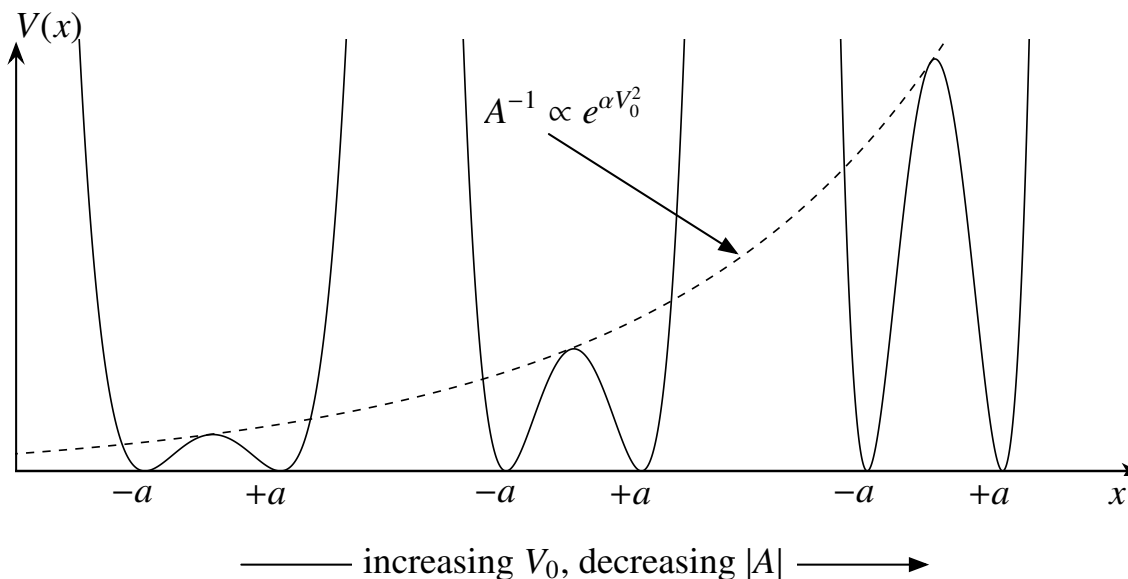

Figure 15.2: Potential experienced by electron in O_2^- ion. For increasing V_0 (the height of the barrier), the off-diagonal element of the Hamiltonian *decreases*, becoming zero when the barrier is infinitely high.

So, from a classical physics perspective, the electron would reside in the vicinity of the position of either of these two minima, unless it was provided with enough energy by some external force to cross over the intervening potential barrier of height V_0. Indeed, in the limit of $V_0 \to \infty$, the electron would never be able to cross this barrier, and so would be confined to either of the oxygen atoms to which it initially became attached. This is also true quantum mechanically – for V_0 infinitely large, the electron would remain in either of the states $\pm a$; these states would be stationary states, and hence eigenstates of the Hamiltonian. This in turn would mean that the matrix representing $\hat{H}$ would be diagonal in the position representation, which amounts to saying that $A = 0$. However, for a finite barrier height the electrons are able to 'tunnel' through the potential barrier separating the two oxygen atoms, so that the states $\pm a$ would no longer be stationary states, and the Hamiltonian would not be diagonal in the position representation, i.e. $A \neq 0$. In fact, it can be shown that the $A \propto \exp(-\alpha V_0^2)$ where α is a constant that depends on the detailed physical characteristics of the ion, so as V_0 increases, A decreases, the chances of the electron tunnelling through the barrier decreases, and the oscillation frequency of the probability will decrease.

15.3   The Time Evolution Operator