V. Time Dependence

Up to this point, the systems we have dealt with have been time independent. The variable t has not appeared in any of our equations and thus the formalism we have developed is not yet able to describe any kind of motion. This is at odds with our understanding of reality, where things clearly *move*. In order to describe quantum motion, we need one additional rule of quantum mechanics: *The time evolution of any state is governed by Schrödinger's equation*

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle.$$

Note that in quantum mechanics time, t, plays a fundamentally different role than the position, $\hat{q}$, or momentum, $\hat{p}$. The latter two are represented by *operators* that act on the states, while the **time is treated as a parameter**. The state of the system depends on the parameter, t, but it makes no sense to have a state that depends on an operator like $\hat{q}$. That is to say, $|\psi(t)\rangle$ is well-defined but $|\psi(\hat{q})\rangle$ is not.

In most cases, the dependence on t is understood and we can write the short-hand version of Schrödinger's equation:

$$i\hbar|\dot{\psi}\rangle = \hat{H}|\psi\rangle.$$

Time dependent quantum systems are the primary focus of the second half of this course. However, it is appropriate at this point to at least introduce the basic principles of quantum dynamics, especially focusing on how it relates to the time independent framework we've developed.

A. Energy Eigenstates Are Stationary States

First, we want to address the very important question of how eigenstates of the Hamiltonian (i.e. energy eigenstates) evolve with time. Applying Schrödinger's equation,

$$i\hbar|\dot{\psi}_n\rangle = \hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

This is just a simple first order differential equation for $|\psi_n(t)\rangle$ and it is easily verified that the general solution is:

$$|\psi_n(t)\rangle = e^{-iE_n t/\hbar}|\psi_n(0)\rangle$$

Thus, if the system starts in an energy eigenstate, it will remain in this eigenstate. The only effect of the time evolution is to multiply the state by a time-dependent phase factor ($e^{-iE_n t/\hbar}$). Since an overall phase factor cannot influence the outcome of an observation, from an experimental perspective, **energy eigenstates do not change with time**. It is therefore termed a "stationary state". This motivates our interest in finding energy eigenstates for arbitrary Hamiltonians; any other state has the potential to change between observations, but a stationary state lives forever if we don't disturb it.

B. The Propagator Governs Time Evolution

So it is trivial to determine $|\psi(t)\rangle$ if the system begins in a stationary state. But what if the initial state is not an eigenfunction of the Hamiltonian? How do we evolve an arbitrary $|\psi(t)\rangle$? As we show below, time evolution is governed by the propagator,

$$\hat{K}(t) \equiv e^{-i\hat{H}t/\hbar}$$

in terms of which the time evolved state is given by

$$|\psi(t)\rangle = \hat{K}(t)|\psi(0)\rangle.$$

In order to prove that this is so, we merely take the derivative of the propagator ansatz and verify it satisfies Schrödinger's equation:

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle &= i\hbar\frac{\partial}{\partial t}e^{-i\hat{H}t/\hbar}|\psi(0)\rangle \\
&= i\hbar\frac{\partial}{\partial t}\left(1-\tfrac{i}{\hbar}\hat{H}t-\tfrac{1}{2\hbar^2}\hat{H}\hat{H}t^2+\tfrac{i}{\hbar}\hat{H}\hat{H}\hat{H}t^3+\ldots\right)|\psi(0)\rangle \\
&= i\hbar\left(0-\tfrac{i}{\hbar}\hat{H}-\tfrac{1}{\hbar^2}\hat{H}\hat{H}t+\tfrac{i}{2\hbar^3}\hat{H}\hat{H}\hat{H}t^2+\ldots\right)|\psi(0)\rangle \\
&= \left(\hat{H}-\tfrac{i}{\hbar}\hat{H}\hat{H}t-\tfrac{1}{2\hbar^2}\hat{H}\hat{H}\hat{H}t^2+\ldots\right)|\psi(0)\rangle \\
&= \hat{H}\left(1-\tfrac{i}{\hbar}\hat{H}t-\tfrac{1}{2\hbar^2}\hat{H}\hat{H}t^2+\ldots\right)|\psi(0)\rangle \\
&= \hat{H}\left(e^{-i\hat{H}t/\hbar}|\psi(0)\rangle\right) \\
&= \hat{H}|\psi(0)\rangle
\end{aligned}$$

Since this wavefunction satisfies Schrödinger's equation, we conclude that the propagator is, indeed, the time evolution operator. Physically, this operator performs a very impressive task: $\hat{K}(t)$ takes

any state and evolves that state forward to time t according to the Schrödinger equation.

C. Important Properties of the Propagator

There are a number of very important properties of the propagator, of which we mention only a few:

The Propagator is Unitary: $\hat{K}^{\dagger}(t)\hat{K}(t)=1$

To see this, expand each propagator in a power series:

$$\hat{K}^{\dagger}(t)\hat{K}(t)=$$

$$\left(1+\tfrac{i}{\hbar}\hat{H}t-\tfrac{1}{2\hbar^2}\hat{H}\hat{H}t^2-\tfrac{i}{\hbar}\hat{H}\hat{H}\hat{H}t^3+\ldots\right)\left(1-\tfrac{i}{\hbar}\hat{H}t-\tfrac{1}{2\hbar^2}\hat{H}\hat{H}t^2+\tfrac{i}{\hbar}\hat{H}\hat{H}\hat{H}t^3+\ldots\right)$$

Expanding the product on the right and collecting terms, one obtains:

t^0 terms: 1

t^1 terms: $\tfrac{i}{\hbar}\hat{H}t-\tfrac{i}{\hbar}\hat{H}t=0$

t^2 terms: $-\tfrac{1}{2\hbar^2}\hat{H}\hat{H}t^2-\tfrac{1}{2\hbar^2}\hat{H}\hat{H}t^2-\left(\tfrac{i}{\hbar}\hat{H}t\right)\left(\tfrac{i}{\hbar}\hat{H}t\right)=-\tfrac{1}{\hbar^2}\hat{H}\hat{H}t^2+\tfrac{1}{\hbar^2}\hat{H}\hat{H}t^2=0$

…

Thus, the only non-zero contribution is the t^0 term, and $\hat{K}^{\dagger}(t)\hat{K}(t)=1$. This point gains significance when we realize that unitary operators correspond to a **change of basis**. Thus time evolution corresponds to a change from the basis appropriate at time 0 to the basis appropriate at time t.

The Propagator obeys Time Reversal: $\hat{K}^{\dagger}(t)=\hat{K}(-t)$

Proof: $\hat{K}^{\dagger}(t)=\left(e^{-i\hat{H}t/\hbar}\right)^{\dagger}=e^{i\hat{H}t/\hbar}=e^{-i\hat{H}(-t)/\hbar}=\hat{K}(-t)$

Thus, the Hermitian conjugate of the Propagator is also a propagator, but one that evolves the system **backward in time**. This gives another physical justification for the Unitarity of the propagator, since $\hat{K}^{\dagger}(t)\hat{K}(t)=\hat{K}(-t)\hat{K}(t)$. On the right, we propagate the system forward in time by t and then immediately propagate backward by the same time interval. Clearly, this operation cannot affect the state of the system and the unitarity and time reversal qualities of the propagator are related.

The Product Rule: $\hat{K}(t_1)\hat{K}(t_2)=\hat{K}(t_1+t_2)$

First, we note that this makes perfect sense from a physical perspective: on the left we have a product of operators that evolve the system for a time t_1, followed by another evolution for a time t_2. It

is clear that this should be the same as propagating once for a combined time of $t_1 + t_2$. To verify that this is true, we expand out the propagators yet again:

$$\begin{aligned}\hat{K}(t_1)\hat{K}(t_2) &= \left(1 - \tfrac{i}{\hbar}\hat{H}t_1 - \tfrac{1}{2\hbar^2}\hat{H}\hat{H}t_1^{\,2} + \ldots\right)\left(1 - \tfrac{i}{\hbar}\hat{H}t_2 - \tfrac{1}{2\hbar^2}\hat{H}\hat{H}t_2^{\,2} + \ldots\right) \\ &= 1 - \tfrac{i}{\hbar}\left(\hat{H}t_1 + \hat{H}t_2\right) - \left(\tfrac{1}{2\hbar^2}\hat{H}\hat{H}t_1^{\,2} - \left(\tfrac{i}{\hbar}\hat{H}t_1\right)\left(\tfrac{i}{\hbar}\hat{H}t_2\right) + \tfrac{1}{2\hbar^2}\hat{H}\hat{H}t_2^{\,2}\right) + \ldots \\ &= 1 - \tfrac{i}{\hbar}\hat{H}(t_1 + t_2) - \tfrac{1}{2\hbar^2}\hat{H}\hat{H}\left(t_1^{\,2} + 2t_1t_2 + t_2^{\,2}\right) + \ldots \\ &= 1 - \tfrac{i}{\hbar}\hat{H}(t_1 + t_2) - \tfrac{1}{2\hbar^2}\hat{H}\hat{H}(t_1 + t_2)^2 + \ldots \\ &= \hat{K}(t_1 + t_2)\end{aligned}$$

D. Time Dependence of Average Values

We define the time dependent average of an operator by

$$\left\langle \hat{O}(t) \right\rangle \equiv \langle \psi(t) | \hat{O} | \psi(t) \rangle .$$

We want to obtain an equation that governs the evolution of this average value. We do this by taking the time derivative and using :

$$\begin{aligned}\frac{\partial}{\partial t}\left\langle \hat{O}(t) \right\rangle &= \frac{\partial}{\partial t}\langle \psi(t) | \hat{O} | \psi(t) \rangle = \langle \dot{\psi}(t) | \hat{O} | \psi(t) \rangle + \langle \psi(t) | \hat{O} | \dot{\psi}(t) \rangle \\ &= \langle \psi(t) | \frac{\hat{H}}{-i\hbar}\hat{O} | \psi(t) \rangle + \langle \psi(t) | \hat{O}\frac{\hat{H}}{i\hbar} | \dot{\psi}(t) \rangle\end{aligned}$$

where the second line makes use of the Schrödinger equation and its Hermitian conjugate:

$$i\hbar|\dot{\psi}\rangle = \hat{H}|\psi\rangle \qquad -i\hbar\langle\dot{\psi}| = \langle\psi|\hat{H}$$

Simplifying the above expression, we obtain a powerful equation of motion for the evolution of this average:

$$\frac{\partial}{\partial t}\left\langle \hat{O}(t) \right\rangle = -\frac{i}{\hbar}\langle \psi(t) | \hat{O}\hat{H} - \hat{H}\hat{O} | \psi(t) \rangle$$

Or, if we suppress the explicit dependence on time:

$$\left\langle \dot{\hat{O}} \right\rangle = -\frac{i}{\hbar}\left\langle \left[\hat{O}, \hat{H}\right] \right\rangle .$$

This leads to the important conclusion that **if an observable commutes with the Hamiltonian, its average value does not change with time**. This is clear, because in this case

$$\left\langle \dot{\hat{O}} \right\rangle = -\frac{i}{\hbar}\left\langle \left[\hat{O}, \hat{H}\right] \right\rangle = -\frac{i}{\hbar}\langle 0 \rangle = 0 .$$

If we consider the specific case of a Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{q})$, we obtain two important equations of motion:

$$\left\langle \dot{\hat{q}} \right\rangle = -\frac{i}{\hbar}\left\langle [\hat{q}, \hat{H}] \right\rangle = -\frac{i}{\hbar}\left(\left\langle \left[\hat{q}, \frac{\hat{p}^2}{2m} \right] \right\rangle + \left\langle [\hat{q}, V(\hat{q})] \right\rangle \right)$$

$$= -\frac{i}{2m\hbar}\left\langle \left[\hat{q}, \hat{p}^2 \right] \right\rangle = \frac{\langle \hat{p} \rangle}{m}$$

$$\left\langle \dot{\hat{p}} \right\rangle = -\frac{i}{\hbar}\left\langle [\hat{p}, \hat{H}] \right\rangle = -\frac{i}{\hbar}\left(\left\langle \left[\hat{p}, \frac{\hat{p}^2}{2m} \right] \right\rangle + \left\langle [\hat{p}, V(\hat{q})] \right\rangle \right)$$

$$= -\frac{i}{\hbar}\left\langle [\hat{p}, V(\hat{q})] \right\rangle = -\left\langle V'(\hat{q}) \right\rangle$$

where a prime indicates differentiation with respect to the argument and we have used the fact that

$$[\hat{q}, f(\hat{p})] = i\hbar f'(\hat{p}) \qquad [\hat{p}, g(\hat{q})] = -i\hbar g'(\hat{q})$$

for any functions f and g. Thus for any potential, the average values of position and momentum obey:

$$\left\langle \dot{\hat{q}} \right\rangle = \frac{\langle \hat{p} \rangle}{m} \quad \text{and} \quad \left\langle \dot{\hat{p}} \right\rangle = -\left\langle V'(\hat{q}) \right\rangle$$

These two equations are the quantum analog of Hamilton's equations; the time derivative of the average position is the average *velocity* (momentum divided by mass) and the time derivative of the average momentum is the average *force* (the derivative of the potential). What's even more amazing is that **Planck's constant $\hbar$ appears nowhere in these equations of motion**! Hence, these equations are almost entirely classical.

It is useful to work these out for a specific example. Consider a harmonic oscillator, in which case $V(\hat{q}) = \frac{1}{2} m\omega^2 \hat{q}^2$. Then the equations of motion for the average position and momentum are:

$$\left\langle \dot{\hat{q}} \right\rangle = \frac{\langle \hat{p} \rangle}{m} \quad \text{and} \quad \left\langle \dot{\hat{p}} \right\rangle = -\left\langle V'(\hat{q}) \right\rangle = -m\omega \langle \hat{q} \rangle$$

These equations should be compared with Hamilton's equations for the Harmonic oscillator:

$$\dot{q} = \frac{p}{m} \quad \text{and} \quad \dot{p} = -V'(q) = -m\omega q$$

Thus, for the harmonic oscillator, the **quantum** equations of motion for the average values of q and p are precisely the **classical** equations for the variables q and p! For example, we can immediately write down the solution to the equations of motion because they are first order in time:

$$\langle q(t)\rangle = \langle q(0)\rangle \cos\omega t + \frac{\langle p(0)\rangle}{\omega}\sin\omega t$$
$$\langle p(t)\rangle = m\langle p(0)\rangle \cos\omega t - m\omega\langle q(0)\rangle \sin\omega t .$$

These should be compared to the classical trajectory for a particle with initial position $q(0)$ and initial momentum $p(0)$:

$$q(t) = q(0)\cos\omega t + \frac{p(0)}{\omega}\sin\omega t$$
$$p(t) = mp(0)\cos\omega t - m\omega q(0)\sin\omega t .$$

Thus, if one starts the quantum system in a state with an initial average position $\langle q(0)\rangle$ and initial average momentum $\langle p(0)\rangle$ and the potential is harmonic, then the average values evolve exactly as if the system were following the classical trajectory.

Is there then no difference between quantum dynamics and classical dynamics? Quite the contrary. The equivalence above holds only for the specific case of position and momentum operators in a Harmonic potential. If we change either the operators involved or the potential, the quantum results become unique. If we change our attention to the operator $\langle q^2\rangle$, we immediately run into a problem because classically $q^2(0) = q(0)\cdot q(0)$, whereas the uncertainty principle dictates that (in general) $\langle q^2(0)\rangle \neq \langle q(0)\rangle^2$. Meanwhile if we consider evolution in an anharmonic potential (like $V(\hat{q}) = k\hat{q}^4$) then the equation of motion for $\langle \hat{p}\rangle$ will involve the average force ($-\langle V'(\hat{q})\rangle = -4k\langle \hat{q}^3\rangle$) which is not simply a function of $\langle \hat{q}\rangle$. That is to say that:

$$-\langle V'(\hat{q})\rangle = -4k\langle \hat{q}^3\rangle \neq -4k\langle \hat{q}^3\rangle = -V'(\langle \hat{q}\rangle)$$

Thus, the equations of motion for $\langle \hat{q}\rangle$ and $\langle \hat{p}\rangle$ are not even closed, except in special cases, and an analytic solution is not typically possible. However, the similarity between the quantum equations of motion and the classical counterparts is the basis for a number of **semiclassical** approximations we may discuss later in the course.

E. Matrix Representations of the Propagator

Often, one is interested in the time evolution of a particular initial wavefunction. That is, given some $|\phi(0)\rangle$ one wants to know $|\phi(t)\rangle$. Now, formally we know that the solution to this problem is given by the propagator: $|\phi(t)\rangle = \hat{K}(t)|\phi(0)\rangle$. But how does one go about computing the propagator? More specifically, how should one make a matrix representation of $\hat{K}(t)$ that is amenable to computation? There are two routes to solving this problem.

First, let us assume we know the eigenstates and eigenvalues of the Hamiltonian:

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

and let us try to work out the action of the propagator in this basis. We can re-write $|\phi(t)\rangle$ as:

$$|\phi(t)\rangle = \hat{K}(t)|\phi(0)\rangle = \sum_{n=1}^{\infty} \hat{K}(t)|\psi_n\rangle\langle\psi_n|\phi(0)\rangle = \sum_{n=1}^{\infty} e^{-iE_n t/\hbar}|\psi_n\rangle\langle\psi_n|\phi(0)\rangle$$

where in the first equality, we have inserted the identity in terms of the eigenstates of $\hat{H}$ and in the second equality we have used the fact that the eigenstates of $\hat{H}$ are stationary states. We now perform our favorite trick and multiply both sides by $\langle\psi_m|$:

$$\Rightarrow \langle\psi_m|\phi(t)\rangle = \sum_{n=1}^{\infty} e^{-iE_n t/\hbar}\langle\psi_m|\psi_n\rangle\langle\psi_n|\phi(0)\rangle = e^{-iE_m t/\hbar}\langle\psi_m|\phi(0)\rangle$$

($\langle\psi_m|\psi_n\rangle = \delta_{mn}$)

If we expand $|\phi(0)\rangle$ and $|\phi(t)\rangle$ in terms of the eigenstates of the Hamiltonian:

$$|\phi(0)\rangle = \sum_{n=1}^{\infty}|\psi_n\rangle\langle\psi_n|\phi(0)\rangle \equiv \sum_{n=1}^{\infty}|\psi_n\rangle c_n(0)$$

$$|\phi(t)\rangle = \sum_{n=1}^{\infty}|\psi_n\rangle\langle\psi_n|\phi(t)\rangle \equiv \sum_{n=1}^{\infty}|\psi_n\rangle c_n(t)$$

Then, our previous result reduces to

$$\langle\psi_m|\phi(t)\rangle = e^{-iE_m t/\hbar}\langle\psi_m|\phi(0)\rangle$$
$$\Rightarrow c_m(t) = e^{-iE_m t/\hbar}c_m(0).$$

Thus, if we expand the wavefunction in terms of the eigenfunctions of the Hamiltonian, then the expansion coefficients (the c_m) are *independent* of one another (i.e. c_m does not depend on c_n) and the

evolution of each coefficient is just a phase factor. Motion arises in this picture from the fact that each c_n has a *different* phase. Thus, at different times we can get complicated constructive or destructive interference between different contributions.

Now, if we assume that we do not know the eigenfunctions of $\hat{H}$, we can also work out the action of the propagator on $|\phi(0)\rangle$ using an arbitrary basis, $|\chi_n\rangle$. Note that in the present picture, the basis is fixed in time and all of the time dependence will be carried by the coefficients $d_n(t) = \langle \chi_n | \phi(t) \rangle$. We can re-write $|\phi(t)\rangle$ as:

$$|\phi(t)\rangle = \hat{K}(t)|\phi(0)\rangle = \sum_{n=1}^{\infty} \hat{K}(t)|\chi_n\rangle\langle\chi_n|\phi(0)\rangle = \sum_{n=1}^{\infty} \hat{K}(t)|\chi_n\rangle d_n(0)$$

Again, we multiply both sides by $\langle \chi_m |$:

$$\langle \chi_m | \phi(t) \rangle = \sum_{n=1}^{\infty} \langle \chi_m | \hat{K}(t) | \chi_n \rangle d_n(0).$$

If we then define the matrix representation of the propagator:

$$K_{mn}(t) \equiv \langle \chi_m | \hat{K}(t) | \chi_n \rangle$$

we can re-write the above equation using the convenient matrix short-hand:

$$\mathbf{d}(t) = \mathbf{K}(t)\mathbf{d}(0).$$

This expression is the natural counterpart of the Dirac expression $|\phi(t)\rangle = \hat{K}(t)|\phi(0)\rangle$. But we are still left with the difficulty of computing $\langle \chi_m | \hat{K}(t) | \chi_n \rangle$. To do this, we will first assume that we know the matrix elements of the Hamiltonian in this basis: $\langle \chi_m | \hat{H} | \chi_n \rangle$. Then, if we expand the exponential in a power series,

$$\begin{aligned}
\langle \chi_m | \hat{K}(t) | \chi_n \rangle &= \langle \chi_m | e^{-i\hat{H}t/\hbar} | \chi_n \rangle \\
&= \langle \chi_m | \left(1 - \tfrac{it}{\hbar}\hat{H} - \tfrac{t^2}{2\hbar^2}\hat{H}\hat{H} + \tfrac{it^3}{6\hbar^3}\hat{H}\hat{H}\hat{H} + \ldots\right) | \chi_n \rangle \\
&= \delta_{mn} - \tfrac{it}{\hbar}\langle \chi_m | \hat{H} | \chi_n \rangle - \tfrac{t^2}{2\hbar^2}\langle \chi_m | \hat{H}\hat{H} | \chi_n \rangle + \tfrac{it^3}{6\hbar^3}\langle \chi_m | \hat{H}\hat{H}\hat{H} | \chi_n \rangle + \ldots
\end{aligned}$$

In order to evaluate the third and fourth terms, we insert the identity (once in the third term and twice in the fourth):

$$\langle \chi_m | \hat{K}(t) | \chi_n \rangle = \delta_{mn} - \tfrac{it}{\hbar} \langle \chi_m | \hat{H} | \chi_n \rangle - \tfrac{t^2}{2\hbar^2} \sum_{k=1}^{\infty} \langle \chi_m | \hat{H} | \chi_k \rangle \langle \chi_k | \hat{H} | \chi_n \rangle$$

$$+ \tfrac{it^3}{6\hbar^3} \sum_{k,l=1}^{\infty} \langle \chi_m | \hat{H} | \chi_k \rangle \langle \chi_k | \hat{H} | \chi_l \rangle \langle \chi_l | \hat{H} | \chi_n \rangle + \ldots$$

We now recognize that in the second and third terms the products of the operators ($\hat{H}$) can be replaced by products of the associated matrix ($\mathbf{H}$). Thus, if we use matrix shorthand

$$\mathbf{K}(t) = \mathbf{1} - \tfrac{it}{\hbar} \mathbf{H} - \tfrac{t^2}{2\hbar^2} \mathbf{HH} + \tfrac{it^3}{6\hbar^3} \mathbf{HHH} + \ldots$$

However, this is just the power series expansion for the exponential of a matrix and we can therefore write

$$\mathbf{K}(t) = e^{-i\mathbf{H}t/\hbar}$$

which allows us to succinctly express the time evolution of an arbitrary state in matrix notation:

$$\mathbf{d}(t) = e^{-i\mathbf{H}t/\hbar} \mathbf{d}(0).$$

Once we have determined the time evolved states (either in the energy eigenbasis or some other basis) we can easily compute any expectation value we like. For example, the average value of an observable $\hat{O}$ at time t can be computed using the standard rules of matrix mechanics:

$$\langle \phi(t) | \hat{O} | \phi(t) \rangle \rightarrow \mathbf{d}^{\dagger}(t) \mathbf{O} \mathbf{d}(t)$$

In order to apply these equations in practice, one can follow a simple ansatz. First, pick a basis $|\chi_n\rangle$, preferably one in which the matrix elements of $\hat{H}$ can be easily computed. As shown above, the extreme example of this is the energy eigenbasis, where $\mathbf{H}$ is just a diagonal matrix. However, in practice any basis where $\mathbf{H}$ can be computed is acceptable. The second step is to build the matrix $\mathbf{K}(t) = e^{-i\mathbf{H}t/\hbar}$. This can be done in several ways. However, most precompiled programs have a utility for computing the exponential of a matrix and this is probably the easiest route to follow, in practice. Third, one applies $\mathbf{K}(t)$ to the vectors that correspond to the state(s) of interest to obtain $\mathbf{d}(t)$. Fourth, one computes the desired properties of the system, such as average values like $\langle \hat{O}(t) \rangle$. Note that these average values could also, in principle, be obtained by

integrating the equations of motion discussed in the previous section. The result is the same, but the present method is typically simpler. Finally, one is only rarely interested in the state of the system at an isolated time; rather one is interested in tracing the behavior as a *function* of time. Thus, one typically repeats this process for many times to get an idea of what the system is doing.

It is important to note that, in doing this on a computer, one immediately makes an approximation. All the matrix representations above assume a complete (infinite) basis, whereas any computation will clearly have to use a finite number of basis functions (N). As before we will need to be sure to choose N large enough that our calculations are converged.

F. Inversion of the Ammonia Molecule

Let's do a simple application of the time evolution formalism we've developed. Suppose we have an ammonia molecule where each of the hydrogens is labeled (i.e. one is a proton, the other deuterium and the other tritium). Then, the molecule is chiral and has two possible enantiomers (left-handed and right-handed). Let us represent these two states by $|L\rangle$ and $|R\rangle$, respectively. We are interested in the timescale of the "umbrella motion" that converts $|L\rangle$ into $|R\rangle$: if the system begins in $|L\rangle$ at time 0, what is the probability of finding the molecule in $|R\rangle$ at time t?

To answer this question, we follow the steps outlined above:

Build a Matrix Representation of $\hat{H}$. Since there are only two states, $\hat{H}$ will be represented by a 2x2 matrix:

$$\mathbf{H} = \begin{pmatrix} \langle L|\hat{H}|L\rangle & \langle L|\hat{H}|R\rangle \\ \langle R|\hat{H}|L\rangle & \langle R|\hat{H}|R\rangle \end{pmatrix}$$

The diagonal elements are just the average energies of the two enantiomers, which must be the same (since they are just mirror images of one another). So, we define a variable for this:

$$\langle L|\hat{H}|L\rangle = \langle R|\hat{H}|R\rangle = \varepsilon$$

We don't know what the off-diagonal term is, so we'll define another variable (which we assume is real)

$$\langle L|\hat{H}|R\rangle = \langle R|\hat{H}|L\rangle = V$$

Which allows us to write:

$$\mathbf{H} = \begin{pmatrix} \varepsilon & V \\ V & \varepsilon \end{pmatrix}.$$

Build the time evolution operator $\mathbf{K}(t)$. On a computer, this can be done in one step (by building the exponential of a matrix), but if we're doing it by hand, there's two steps: diagonalize $\mathbf{H}$ and then build the exponential in the eigenbasis. To diagonalize $\mathbf{H}$, we obtain the eigenvalues and eigenvectors:

$$0 = \det \mathbf{H} = \begin{vmatrix} \varepsilon - \lambda & V \\ V & \varepsilon - \lambda \end{vmatrix} = (\varepsilon - \lambda)^2 - V^2$$

$$\Rightarrow \varepsilon - \lambda = \pm V \Rightarrow \lambda_{\pm} = \varepsilon \pm V$$

It's easiest to guess the eigenvectors:

$$\vec{c}_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \vec{c}_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

It is easy to verify that:

$$\mathbf{H}\vec{c}_{\pm} = \frac{1}{\sqrt{2}}\begin{pmatrix} \varepsilon & V \\ V & \varepsilon \end{pmatrix}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} \varepsilon \pm V \\ V \pm \varepsilon \end{pmatrix} = \varepsilon \pm V \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} = \lambda_{\pm}\vec{c}_{\pm}$$

Further, once we have the eigenvectors, we can obtain the transformation matrix for the Hamiltonian: its columns are just the eigenvectors, so

$$\mathbf{T} \equiv \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}.$$

We can verify that we've got everything right at this point by checking that

$$\mathbf{H} \stackrel{?}{=} \mathbf{T}\begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}\mathbf{T}^{\dagger} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \lambda_+ & \lambda_+ \\ \lambda_- & -\lambda_- \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} \lambda_+ + \lambda_- & \lambda_+ - \lambda_- \\ \lambda_+ - \lambda_- & \lambda_+ + \lambda_- \end{pmatrix} = \begin{pmatrix} \varepsilon & V \\ V & \varepsilon \end{pmatrix}$$

Now that we've successfully diagonalized $\mathbf{H}$, we proceed to build the propagator:

$$\mathbf{K}(t)\overset{?}{=}\mathbf{T}\begin{pmatrix} e^{-i\lambda_+ t} & 0 \\ 0 & e^{-i\lambda_- t}\end{pmatrix}\mathbf{T}^\dagger = \frac{1}{2}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}\begin{pmatrix} e^{-i\lambda_+ t} & 0 \\ 0 & e^{-i\lambda_- t}\end{pmatrix}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}\begin{pmatrix} e^{-i\lambda_+ t} & e^{-i\lambda_+ t} \\ e^{-i\lambda_- t} & -e^{-i\lambda_- t}\end{pmatrix} = \frac{1}{2}\begin{pmatrix} e^{-i\lambda_+ t}+e^{-i\lambda_- t} & e^{-i\lambda_+ t}-e^{-i\lambda_- t} \\ e^{-i\lambda_+ t}-e^{-i\lambda_- t} & e^{-i\lambda_+ t}+e^{-i\lambda_- t}\end{pmatrix}$$

We can simplify this if we note that

$$\frac{1}{2}\left(e^{-i\lambda_+ t} \pm e^{-i\lambda_- t}\right) = \frac{1}{2}\left(e^{-i(\varepsilon+V)t} \pm e^{-i(\varepsilon-V)t}\right) = \frac{1}{2}e^{-i\varepsilon t}\left(e^{-iVt} \pm e^{-iVt}\right)$$

$$= \begin{cases} e^{-i\varepsilon t}\cos Vt & if + \\ -ie^{-i\varepsilon t}\sin Vt & if - \end{cases}$$

Thus,

$$\mathbf{K}(t) = e^{-i\varepsilon t}\begin{pmatrix} \cos Vt & -i\sin Vt \\ -i\sin Vt & \cos Vt\end{pmatrix}.$$

We can check that this is correct by checking that this matrix is unitary:

$$\mathbf{K}^\dagger(t)\mathbf{K}(t) = e^{i\varepsilon t}\begin{pmatrix} \cos Vt & i\sin Vt \\ i\sin Vt & \cos Vt\end{pmatrix}e^{-i\varepsilon t}\begin{pmatrix} \cos Vt & -i\sin Vt \\ -i\sin Vt & \cos Vt\end{pmatrix} = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

Apply the time evolution operator to the initial state. This involves significantly less algebra:

$$\mathbf{K}(t)\vec{c}(0) = e^{-i\varepsilon t}\begin{pmatrix} \cos Vt & -i\sin Vt \\ -i\sin Vt & \cos Vt\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = e^{-i\varepsilon t}\begin{pmatrix} \cos Vt \\ -i\sin Vt\end{pmatrix}$$

Hence, we see that the state oscillates with time. This is because our initial state is not a stationary state, but a *superposition* of different stationary states. The oscillation comes about because of the interference between the two states as a function of time.

Make measurements at time t. Here, we want to measure the probability of being found in state $|R\rangle$:

$$P_R(t) = |c_R|^2 = \left|-ie^{-i\varepsilon t}\sin Vt\right|^2 = \sin^2 Vt$$

Thus, the probability of the molecule being right-handed oscillates with time. In particular, for $t = \left(n+\frac{1}{2}\right)\pi/V$ there is a 100% probability of the molecule being right-handed. Thus, the timescale of the umbrella motion in ammonia is governed by the magnitude of the off-diagonal element $\langle L|\hat{H}|R\rangle = \langle R|\hat{H}|L\rangle = V$: a large value of V leads to

fast interconversion and a small value leads to slow interconversion. In ammonia the off-diagonal coupling is such that the interconversion occurs with microwave frequency and by resonantly enhancing this motion, one can create a very efficient microwave laser (or maser).