

Prerequisites

These notes assume familiarity with the mathematics of introductory quantum mechanics as taught in an undergraduate chemistry course.

Wavefunctions

Every quantum state ψ can be thought of as a normalized square-integrable function, $\psi(\vec{x}, t)$, unique up to multiplication by a nonzero complex scalar. Because wavefunctions may be freely added to each other or scaled, they form a vector space – specifically, an infinite-dimensional complex projective Hilbert space. A *Hilbert space* is a vector space that admits some notion of distance, which we can obtain from the *overlap integral*:

$$\int \psi_a(\vec{x}, t)^* \psi_b(\vec{x}, t) d\vec{x}$$

This integral serves the same purpose as the dot product, and describes the degree of similarity between ψ_a and ψ_b . The star represents complex conjugation, critical for obtaining real-valued dot products from complex-valued functions.

In many cases, we will be interested in a restricted subset of functions in this space. We can express a state ψ in terms of basis functions ϕ :

$$\psi = \sum_n c_n \phi_n$$

The choice of basis is arbitrary, as long as all ψ_n are linearly independent. Now that the basis is known, we can describe ϕ as a column vector:

$$\psi = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \dots \end{bmatrix}$$

In a vector representation, the complex conjugate is insufficient to calculate the overlap integral. Instead, we use the *adjoint*, which combines complex conjugation with transposition:

$$\psi^\dagger = [c_1^* \quad c_2^* \quad c_3^* \quad \dots]$$

This allows us to represent the dot product as a matrix multiplication.

The final form of notation we will use is the Dirac bra-ket notation. A wavefunction is described by a *ket*, $|\psi\rangle$, and its adjoint is the corresponding *bra*, $\langle\psi|$. The dot product of two wavefunctions is neatly described with this notation:

$$\langle\psi_a|\psi_b\rangle = \int \psi_a(\vec{x}, t)^* \psi_b(\vec{x}, t) d\vec{x}$$

The *bra-ket* expression implicitly includes the integral.

Operators

If functions can be thought of as vectors, operators are matrices which act on those vectors. By convention, an operator will be given a hat : for example, the momentum operator is $\hat{p} = -i\hbar \frac{d}{dx}$.

Operators corresponding to observable quantities are Hermitian, meaning they are equal to their adjoint. However, not all operators are Hermitian: for instance, the propagator, as well as the creation and annihilation operators. For an operator \hat{A} which corresponds to an observable quantity A , we can calculate its *expectation value*, the approximate value of that observable for a wavefunction ψ , with an integral:

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \int \psi(\vec{x}, t)^* \hat{A} \psi(\vec{x}, t) d\vec{x}$$

1 Perturbation theory of quantum state evolving in time

1.1 Time evolution of quantum states

A quantum system can be described in terms of a wavefunction ψ that contains all of the observable information associated with the system. These observables are encoded by Hermitian linear operators that act on ψ . Of particular note is the Hamiltonian operator \hat{H} , which describes the time evolution of ψ . This defines the *time-dependent Schrödinger equation*:

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \hat{H} \psi(x, t) \quad (1)$$

The wavefunction ψ can be described as a normalized square-integrable function. If we describe ψ as a function from a spatial coordinate and time to a complex scalar, multiplying ψ by a unit complex number (phase factor) does not affect the values of observable quantities associated with ψ , so they describe the same state.

To describe the evolution of $\psi(\vec{x}, t)$, we define the *propagator* as an exponentiation of the Hamiltonian which acts upon the state at a known time t to generate the state at a different time $t + \Delta t$:

$$\psi(\vec{x}, t + \Delta t) = \psi(\vec{x}, t) e^{\frac{-i\hat{H}\Delta t}{\hbar}} \quad (2)$$

We can derive this by describing the wavefunction at a $t + \Delta t$ as a Taylor expansion of $\psi(\vec{x}, t)$:

$$\psi(\vec{x}, t + \Delta t) = \sum_{n=0}^{\infty} \left[\frac{\Delta t^n}{n!} \frac{\partial^n}{\partial t^n} \psi(\vec{x}, t) \right]$$

Now we can use the time-dependent Schrödinger equation to substitute the wavefunction derivatives in terms of applying the Hamiltonian operator to the wavefunction, starting by introducing factors of $i\hbar$ to the derivative:

$$\begin{aligned}
\psi(\vec{x}, t + \Delta t) &= \sum_{n=0}^{\infty} \left[\frac{1}{n!} \left(\frac{\Delta t}{i\hbar} \right)^n (i\hbar)^n \frac{\partial^n}{\partial t^n} \psi(\vec{x}, t) \right] \\
&= \sum_{n=0}^{\infty} \left[\frac{1}{n!} \left(\frac{\Delta t}{i\hbar} \right)^n \left(i\hbar \frac{\partial}{\partial t} \right)^n \psi(\vec{x}, t) \right] \\
&= \sum_{n=0}^{\infty} \left[\frac{1}{n!} \left(\frac{\Delta t}{i\hbar} \right)^n \hat{H}^n \psi(\vec{x}, t) \right] \\
&= \sum_{n=0}^{\infty} \left[\frac{1}{n!} \left(\frac{\hat{H} \Delta t}{i\hbar} \right)^n \psi(\vec{x}, t) \right] \\
&= \sum_{n=0}^{\infty} \left[\frac{1}{n!} \left(-\frac{i\hat{H} \Delta t}{\hbar} \right)^n \psi(\vec{x}, t) \right]
\end{aligned}$$

Because the Hamiltonian is a linear operator, we can use its additive property to pull the $\psi(\vec{x}, t)$ terms out of the sum:

$$\sum_{n=0}^{\infty} \left[\frac{1}{n!} \left(-\frac{i\hat{H} \Delta t}{\hbar} \right)^n \psi(\vec{x}, t) \right] = \sum_{n=0}^{\infty} \left[\frac{1}{n!} \left(-\frac{i\hat{H} \Delta t}{\hbar} \right)^n \right] \psi(\vec{x}, t)$$

What we find is that the sum of operators is actually an exponentiation of $-\frac{i\hat{H} \Delta t}{\hbar}$, using the definition of the Taylor series of the exponential:

$$\sum_{n=0}^{\infty} \left[\frac{1}{n!} \left(-\frac{i\hat{H} \Delta t}{\hbar} \right)^n \right] \psi(\vec{x}, t) = e^{-\frac{i\hat{H} \Delta t}{\hbar}} \psi(\vec{x}, t)$$

The new operator we derive is the *propagator*. Any state subject to a Hamiltonian will evolve in time according to the action of the propagator upon the wavefunction.

Some Hamiltonians admit *stationary states* whose observables do not change over time. The time evolution operator applied to a stationary state $\varphi(\vec{x}, t)$ will be equal to multiplication by a unit complex scalar, generated by exponentiating a real scalar:

$$\varphi(\vec{x}, t + \Delta t) = e^{-\frac{i\hat{H} \Delta t}{\hbar}} \varphi(\vec{x}, t) = e^{-\frac{iE \Delta t}{\hbar}} \varphi(\vec{x}, t) \quad (3)$$

The real scalar $E = \hbar\omega$ is the energy of the system. This allows us to write an equation that relates the Hamiltonian operator and the energy scalar for the stationary states. This equation is the *time-independent Schrödinger equation*:

$$\hat{H} \varphi(\vec{x}, t) = E \varphi(\vec{x}, t) \quad (4)$$

Because this is an eigenvalue equation, the stationary states of \hat{H} are also known as *eigenstates*, which correspond to eigenvectors of \hat{H} , with the eigenvalues being the energies of the states.

If the Hamiltonian contains an infinitely deep potential well and an infinite number of eigenstates, any wavefunction ψ can be expressed as a linear combination of eigenstates:

$$\psi(\vec{x}, t) = \sum_{n=0}^{\infty} c_n \varphi_n(\vec{x}, t) \quad (5)$$

The time evolution of a linear combination of eigenstates can be calculated by propagating each component of the eigenbasis using the associated energies or frequencies of each state:

$$\psi(\vec{x}, t + \Delta t) = \sum_{n=0}^{\infty} e^{-\frac{iE_n \Delta t}{\hbar}} c_n \varphi_n(\vec{x}, t) = \sum_{n=0}^{\infty} e^{-i\omega_n \Delta t} c_n \varphi_n(\vec{x}, t) \quad (6)$$

Note that the eigenstates all undergo rotations at their own frequencies ω_n . Although a global shift of phase induced by multiplying ψ by a complex scalar does not change the observable state, shifting the phases of each individual component by different amounts *does* change the state over time.

One last point to remember is that Hamiltonian operators \hat{H} may be shifted by some constant energy E_0 , and that value does not affect the dynamics of the system:

$$\begin{aligned} \psi(\vec{x}, t + \Delta t) &= e^{-\frac{i(\hat{H} + E_0)\Delta t}{\hbar}} \psi(\vec{x}, t) \\ &= e^{-\frac{i\hat{H}\Delta t}{\hbar}} e^{-\frac{iE_0\Delta t}{\hbar}} \psi(\vec{x}, t) \end{aligned}$$

Because E_0 is a constant, the second exponential is a complex constant, and it only serves to change the rate of phase rotation of the wavefunction, which has no observable consequences. However, shifting the Hamiltonian so that the energy of an eigenstate of interest is zero allows for the propagation of that state to be described with an identity operator:

$$\begin{aligned} \varphi_n(\vec{x}, t + \Delta t) &= e^{-\frac{i(\hat{H} - E_n)\Delta t}{\hbar}} \varphi_n(\vec{x}, t) \\ &= e^{-\frac{i\hat{H}\Delta t}{\hbar}} e^{\frac{iE_n\Delta t}{\hbar}} \varphi_n(\vec{x}, t) \\ &= e^{-\frac{iE_n\Delta t}{\hbar}} e^{\frac{iE_n\Delta t}{\hbar}} \varphi_n(\vec{x}, t) \\ &= \varphi_n(\vec{x}, t) \end{aligned}$$

This allows us to describe the relative differences in energy or frequency between a reference eigenstate and another eigenstate of interest. Only the relative differences in frequencies between states have physically observable consequences.

1.2 The Heisenberg picture

The time-dependent Schrödinger equation describes the evolution of a quantum state over time. Although the observables associated with the state are fixed, the operators that act upon the state to generate the observable are not. But this choice is arbitrary: it is entirely possible to develop a quantum theory of fixed states and operators which propagate over time to generate the changes in observables. This formulation is known as the *Heisenberg picture*.

To derive this picture, we start with the calculation of expectation values from quantum state $\psi(\vec{x}, t)$. For some observable \hat{O} , the expectation value is

$$\langle \hat{O} \rangle(t) = \int \psi(\vec{x}, t)^\dagger \hat{O} \psi(\vec{x}, t) d\vec{x} \quad (7)$$

But we can describe the wavefunctions at time t in terms of $\psi(\vec{x}, 0)$ (shortened to $\psi(\vec{x})$) and the propagator:

$$\langle \hat{O} \rangle(t) = \int \left(e^{-\frac{i\hat{H}t}{\hbar}} \psi(\vec{x}) \right)^\dagger \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} \psi(\vec{x}) d\vec{x} \quad (8)$$

When we apply the adjoint to the application of an operator to a wavefunction, we get the reverse product of the adjoints of the operator and the wavefunction:

$$\langle \hat{O} \rangle(t) = \int \psi(\vec{x})^\dagger \left(e^{-\frac{i\hat{H}t}{\hbar}} \right)^\dagger \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} \psi(\vec{x}) d\vec{x} \quad (9)$$

We've managed to transfer the action of the propagator from the wavefunction to the operator. In general, operators evolve according to the following equation:

$$\hat{O}(t) = \left(e^{-\frac{i\hat{H}t}{\hbar}} \right)^\dagger \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} \quad (10)$$

The propagator, being the exponential of a Hermitian operator, is *unitary*, meaning that it preserves dot products. This also means its adjoint is equal to its inverse, so we can rewrite the equation:

$$\hat{O}(t) = e^{\frac{i\hat{H}t}{\hbar}} \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} \quad (11)$$

In many cases, we are interested in the changes in observable quantities, such as position or momentum, over time. What happens if we take derivatives of the operators with respect to time?

$$\begin{aligned} \frac{d}{dt} \hat{O}(t) &= \frac{d}{dt} \left(e^{\frac{i\hat{H}t}{\hbar}} \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} \right) \\ &= \frac{d}{dt} \left(e^{\frac{i\hat{H}t}{\hbar}} \right) \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} + e^{\frac{i\hat{H}t}{\hbar}} \hat{O} \frac{d}{dt} \left(e^{-\frac{i\hat{H}t}{\hbar}} \right) \\ &= \frac{i}{\hbar} \left(e^{\frac{i\hat{H}t}{\hbar}} \hat{H}^\dagger \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} - e^{\frac{i\hat{H}t}{\hbar}} \hat{O} \hat{H} e^{-\frac{i\hat{H}t}{\hbar}} \right) \end{aligned}$$

We use the fact that \hat{H} is a Hermitian operator, meaning that it is equal to its adjoint:

$$\begin{aligned}\frac{d}{dt}\hat{O}(t) &= \frac{i}{\hbar} \left(e^{\frac{i\hat{H}t}{\hbar}} \hat{H} \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} - e^{\frac{i\hat{H}t}{\hbar}} \hat{O} \hat{H} e^{-\frac{i\hat{H}t}{\hbar}} \right) \\ &= \frac{i}{\hbar} \left(e^{\frac{i\hat{H}t}{\hbar}} \hat{H} e^{-\frac{i\hat{H}t}{\hbar}} e^{\frac{i\hat{H}t}{\hbar}} \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} - e^{\frac{i\hat{H}t}{\hbar}} \hat{O} e^{-\frac{i\hat{H}t}{\hbar}} e^{\frac{i\hat{H}t}{\hbar}} \hat{H} e^{-\frac{i\hat{H}t}{\hbar}} \right) \\ &= \frac{i}{\hbar} \left(\hat{H}(t) \hat{O}(t) - \hat{O}(t) \hat{H}(t) \right)\end{aligned}$$

It should now be apparent that the quantity in parentheses is the commutator of \hat{H} and \hat{O} :

$$\frac{d}{dt}\hat{O}(t) = \frac{i}{\hbar} [\hat{H}(t), \hat{O}(t)] = \frac{1}{i\hbar} [\hat{O}(t), \hat{H}(t)] \quad (12)$$

This is the *Heisenberg equation*. Note that the Hamiltonian itself may be propagated over time: this will be important for the next portion.

1.3 The interaction picture

As hinted by the derivation of the Heisenberg picture, there are not just two different perspectives of a quantum system, but an infinite number of possible perspectives that depend on the choice of unitary operator. This is useful in perturbation theory, where we break up the Hamiltonian into an analytically solvable term and a small perturbation.

Consider a Hamiltonian that consists of two terms: a base term \hat{H}_0 , and an interaction term \hat{H}_I , which in the cases we consider in the future may be time dependent. The associated propagator can be naturally divided:

$$\hat{U} = e^{-\frac{i}{\hbar}(\hat{H}_0 + \hat{H}_I)t} \quad (13)$$

$$= e^{-\frac{i}{\hbar}\hat{H}_0 t} e^{-\frac{i}{\hbar}\hat{H}_I t} \quad (14)$$

$$= \hat{U}_0 \hat{U}_I = \hat{U}_I \hat{U}_0 \quad (15)$$

We can assign each component of the propagator to different duties: \hat{U}_0 transforms the operators and \hat{U}_I transforms the states:

$$\psi(\vec{x}, t) = e^{-\frac{i}{\hbar}\hat{H}_I t} \psi(\vec{x}, 0) \quad (16)$$

$$\hat{O}(t) = e^{\frac{i}{\hbar}\hat{H}_0 t} \hat{O}(0) e^{-\frac{i}{\hbar}\hat{H}_0 t} \quad (17)$$

This gives us the equations of motion for both the states and operators:

$$i\hbar \frac{d}{dt} \psi(\vec{x}, t) = \hat{H}_I \psi(\vec{x}, t) \quad (18)$$

$$\frac{d}{dt} \hat{O}(t) = \frac{1}{i\hbar} [\hat{O}(t), \hat{H}_0(t)] \quad (19)$$

Because \hat{H}_0 is constant over time, we have a simpler expression for the time propagation of an operator, and the propagation of the wavefunction is given only in terms of the interaction Hamiltonian \hat{H}_I . We could also reverse this to obtain a complementary picture. This division of the propagator generates the *interaction picture*.

1.4 Incorporating perturbation theory

The generic Hamiltonian we discussed previously is amenable to treatment with perturbation theory. The idea behind perturbation theory is that we can describe a Hamiltonian \hat{H} that would be difficult or impossible to solve analytically as the sum of an analytically solvable Hamiltonian \hat{H}_0 and a small perturbation \hat{H}_I . The solutions to \hat{H} will resemble those of \hat{H}_0 , but with correction terms that can be calculated by \hat{H}_I . Provided that \hat{H}_I is sufficiently small, the corrections can be written in terms of a converging power series.

Consider an atom with Hamiltonian \hat{H}_0 subject to a perturbation \hat{H}_I – in the context of quantum optics, \hat{H}_I can be thought of as an electromagnetic wave. At some time t , the wavefunction $\psi(\vec{x}, t)$ can be represented in terms of the eigenstates of \hat{H}_0 , $\phi_n^{(0)}$:

$$\psi(\vec{x}, t) = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \quad (20)$$

Although we used the eigenstates of \hat{H}_0 as a basis for the wavefunction, its time evolution is subject to the full Hamiltonian, and therefore, the coefficients c_n are not fixed, but vary over time in a way that depends on the perturbation. To understand exactly how they vary, we can insert the wavefunction into the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \sum_n \left[c_n(t) e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] = \left(\hat{H}_0 + \hat{H}_I \right) \sum_n \left[c_n(t) e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] \quad (21)$$

We'll use the product rule to split the derivative on the left into portions that depend on the coefficients c_n and the propagated eigenstate of \hat{H}_0 . Linearity allows us to omit the summation for these steps:

$$i\hbar \frac{\partial}{\partial t} \left[c_n(t) e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] = i\hbar \frac{\partial c_n}{\partial t} e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} + i\hbar c_n(t) \frac{\partial}{\partial t} \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] \quad (22)$$

We'll apply the Hamiltonian in a similar manner. Because $c_n(t)$ only scales the basis wavefunctions, it can be pulled out of the Hamiltonian operator.

$$\hat{H} \left[c_n(t) e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] = c_n(t) \hat{H} \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] \quad (23)$$

$$= c_n(t) \left(\hat{H}_0 + \hat{H}_I \right) \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] \quad (24)$$

$$= c_n(t) \hat{H}_0 \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] + c_n(t) \hat{H}_I \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] \quad (25)$$

What we find is that we have terms originating from the time-dependent Schrödinger equation of \hat{H}_0 :

$$i\hbar c_n(t) \sum_n \frac{\partial}{\partial t} \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] = \sum_n c_n(t) \hat{H}_0 \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] \quad (26)$$

We can therefore remove these terms from the time-dependent Schrödinger equation of \hat{H} and only deal with the ones arising from the perturbation:

$$\sum_n i\hbar \frac{\partial c_n}{\partial t} e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} = \sum_n c_n(t) \hat{H}_I \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] \quad (27)$$

If we want to express the evolution of a single coefficient c_k , we can project this equation onto $\phi_k^{(0)}$. Because the eigenstates form an orthonormal basis, we know that terms where $k \neq n$ become zero, allowing us to remove a sum on the left:

$$\sum_n \int \phi_k^{(0)*} i\hbar \frac{\partial c_n}{\partial t} e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} d\vec{x} = \sum_n \int c_n(t) \phi_k^{(0)*} \hat{H}_I \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] d\vec{x} \quad (28)$$

$$i\hbar \frac{\partial c_k}{\partial t} e^{-\frac{i}{\hbar} E_k t} = \sum_n c_n(t) \int \phi_k^{(0)*} \hat{H}_I \left[e^{-\frac{i}{\hbar} E_n t} \phi_n^{(0)} \right] d\vec{x} \quad (29)$$

Because the propagator behaves like a scalar for the eigenstates, we can remove the propagator from the Hamiltonian operator and combine it with $c_n(t)$. This allows us to simplify the left side:

$$i\hbar \frac{\partial c_k}{\partial t} e^{-\frac{i}{\hbar} E_k t} = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n t} \int \phi_k^{(0)*} \hat{H}_I \phi_n^{(0)} d\vec{x} \quad (30)$$

$$i\hbar \frac{\partial c_k}{\partial t} = \sum_n c_n(t) e^{-\frac{i}{\hbar} (E_n - E_k) t} \int \phi_k^{(0)*} \hat{H}_I \phi_n^{(0)} d\vec{x} \quad (31)$$

Consider a real system with an atom whose Hamiltonian is \hat{H}_0 and a perturbation introduced by an electromagnetic wave, contributing the \hat{H}_I term. The wave can cause the electrons to move from the atomic ground state ϕ_1 to some other state ϕ_k . To understand what happens here, let's treat the perturbation explicitly. An electromagnetic wave can be described by an expression of the form

$$\gamma(\vec{x}, t) = \cos(\vec{k} \cdot \vec{x} - \omega t + \varphi) \quad (32)$$

The vector \vec{k} is the wavevector, which represents the direction in which the wave propagates through space. We know that $|\vec{k}|$ is proportional to ω – the conversion factor is the speed of light:

$$\omega = c|\vec{k}| \quad (33)$$

Also recall that the energy is proportional to the frequency:

$$E = \hbar\omega \quad (34)$$

However, we can make a simplifying assumption: for a real atom interacting with photons in the visible spectrum, the wavelength is far larger than the atom. Therefore, we can ignore the spatial component and treat it as a purely temporal wave. As one last simplification, we can remove the phase factor φ and express the wave in terms of a complex exponential:

$$\hat{H}_I(t) = \hat{H}_I e^{-i\omega t} = \hat{H}_I e^{-\frac{iEt}{\hbar}} \quad (35)$$

Now we can apply this to our time evolution expression to understand how the electromagnetic wave changes the probability of the atom being found in some other state ϕ_k starting with the ground state $\phi_1^{(0)}$ at $t = 0$:

$$i\hbar \frac{\partial}{\partial t} c_k(t) = \sum_n c_n(t) e^{-\frac{i}{\hbar}(E_n - E_k)t} \int \phi_k^{(0)*} \hat{H}_I(t) \phi_n^{(0)} d\vec{x} \quad (36)$$

$$= e^{-\frac{i}{\hbar}(E_1 - E_k)t} \int \phi_k^{(0)*} \left[\hat{H}_I e^{-\frac{iEt}{\hbar}} \right] \phi_1^{(0)} d\vec{x} \quad (37)$$

$$= e^{-i(\omega_1 - \omega_k)t} \int \phi_k^{(0)*} \left[\hat{H}_I e^{-i\omega t} \right] \phi_1^{(0)} d\vec{x} \quad (38)$$

$$= e^{-i(\omega_1 - \omega_k)t} e^{-i\omega t} \int \phi_k^{(0)*} \hat{H}_I \phi_1^{(0)} d\vec{x} \quad (39)$$

We define $\Delta\omega = \omega - (\omega_k - \omega_1)$ as the *detuning*, the frequency mismatch between the electromagnetic wave and the frequency associated with the energy difference between $\phi_1^{(0)}$ and $\phi_k^{(0)}$, and simplify:

$$i\hbar \frac{\partial}{\partial t} c_k(t) = e^{-i\Delta\omega t} \int \phi_k^{(0)*} \hat{H}_I \phi_1^{(0)} d\vec{x} \quad (40)$$

Now that we have a simple expression for the change in $c_n(t)$, we can just integrate this to get the probability amplitude of finding the atom in state $\psi_k^{(0)}$ at time t .

$$c_n(t) = \int_0^t \frac{\partial}{\partial t} c_k(t') dt' = \frac{1}{i\hbar} \int_0^t e^{-i\Delta\omega t'} \int \phi_k^{(0)*} \hat{H}_I \phi_1^{(0)} d\vec{x} dt' \quad (41)$$

$$= \frac{1}{i\hbar} \int_0^t e^{-i\Delta\omega t'} \langle \phi_k^{(0)} | \hat{H}_I | \phi_1^{(0)} \rangle dt' \quad (42)$$

This looks similar to a Fourier transform, but instead of integrating over all time, the integral only takes place between times 0 and t . This is equivalent to multiplying by the boxcar function defined such that it is equal to 1 inside the interval and 0 outside of it. We can also pull out the $\langle \phi_k^{(0)} | \hat{H}_I | \phi_1^{(0)} \rangle$ term, as we have removed the time dependence from \hat{H}_I :

$$c_n(t) = \frac{1}{i\hbar} \langle \phi_k^{(0)} | \hat{H}_I | \phi_1^{(0)} \rangle \int_{-\infty}^{\infty} \text{boxcar}(0, t) e^{-i\Delta\omega t'} dt' \quad (43)$$

The Fourier transform of the boxcar function is a sinc function multiplied by a shift factor:

$$c_n(t) = \frac{1}{i\hbar} \langle \phi_k^{(0)} | \hat{H}_I | \phi_1^{(0)} \rangle e^{-\pi i \Delta \omega t} \frac{\sin\left(\frac{1}{2} \Delta \omega t\right)}{\frac{1}{2} \Delta \omega} \quad (44)$$

To get the probability, we use the modulus as per the Born rule:

$$|c_n(t)|^2 = c_n(t)^* c_n(t) = \frac{1}{\hbar^2} |\langle \phi_k^{(0)} | \hat{H}_I | \phi_1^{(0)} \rangle|^2 \left(\frac{\sin\left(\frac{1}{2} \Delta \omega t\right)}{\frac{1}{2} \Delta \omega} \right)^2 \quad (45)$$

The Fourier transform allows us to make a statement about the pulse size and the frequency mismatch. An increasing pulse duration will decrease the width of its Fourier transform, meaning that very short pulses have a higher probability of exciting states far from the frequency of the electromagnetic wave. This is an expression of the uncertainty principle, which holds not just for quantum systems, but any system that admits wavelike behavior. With a longer pulse, the mismatch tolerance is reduced, but we are more likely to only excite the system to a state whose energy difference matches that frequency.

1.5 A continuum of states

A real system will likely consist of many state that are accessible by a short excitation. If we have a near-continuum of possible final states, we may want to determine the probability of the final state being within the continuum.

The number of states N within some energy interval $[E_{\min}, E_{\max}]$ is given by the integral of the density of states (DOS) function:

$$N = \int_{E_{\min}}^{E_{\max}} \rho(E) dE \quad (46)$$

2 The two-level atom

The two-level atom is a simple model system that can be used to explore the interactions produced by electromagnetic waves. As before, we can use a perturbative approach to explore this system. The Hamiltonian of the atom, \hat{H}_0 , admits two energy eigenstates, ϕ_1 and ϕ_2 , with corresponding energies E_1 and E_2 . If required, we will assume $E_1 < E_2$. In Dirac notation, we can label these states $|1\rangle$ and $|2\rangle$. The energies of these states differ by $\Delta E = \hbar \Delta \omega$. The perturbation Hamiltonian \hat{H}_I originates from the electric dipole operator, which is the position operator scaled by the charge: $\hat{d} = q\hat{x}$. The energy of a dipole is given by the dot product $-\hat{d} \cdot \vec{E}$. The electric field generated by an electromagnetic wave can be expressed in terms of a cosine function scaled by the magnitude of the oscillation and the direction of polarization:

$$\hat{H} = \hat{H}_0 - \hat{d} \cdot \vec{\epsilon} E_0 \cos \omega t \quad (47)$$

As we have seen already, the evolution of a wavefunction of the two-level atom perturbed by an electromagnetic wave can be expressed in terms of time-dependent coefficients that contribute to the expected time evolution of each eigenstate:

$$\psi(\vec{x}, t) = c_1(t) e^{-\frac{i}{\hbar} E_1 t} \phi_1 + c_2(t) e^{-\frac{i}{\hbar} E_2 t} \phi_2 \quad (48)$$

From the previous derivation for the time evolution of the coefficients, we can find expressions for the evolution of $c_1(t)$ and $c_2(t)$:

$$\frac{\partial}{\partial t} c_1(t) = \frac{1}{i\hbar} \sum_{n=1}^2 c_n(t) e^{-\frac{i}{\hbar} (E_n - E_1)t} \langle \phi_1 | -\hat{d} \cdot \vec{\varepsilon} E_0 \cos \omega t | \phi_n \rangle \quad (49)$$

$$\frac{\partial}{\partial t} c_2(t) = \frac{1}{i\hbar} \sum_{n=1}^2 c_n(t) e^{-\frac{i}{\hbar} (E_n - E_2)t} \langle \phi_2 | -\hat{d} \cdot \vec{\varepsilon} E_0 \cos \omega t | \phi_n \rangle \quad (50)$$

To shorten this expression, we define the *dipole matrix*, a matrix representation of the dipole operator in terms of our eigenbasis and the electric field. The dot product with the polarization vector $\vec{\varepsilon}$ may be pulled out of the expression.

$$d_{ab}^{\varepsilon} = \langle \phi_a | -\hat{d} \cdot \vec{\varepsilon} | \phi_b \rangle \quad (51)$$

$$= -\vec{\varepsilon} \cdot \langle \phi_a | \hat{d} | \phi_b \rangle \quad (52)$$

$$= -q\vec{\varepsilon} \cdot \langle \phi_a | \hat{x} | \phi_b \rangle \quad (53)$$

Because the position operator \hat{x} is Hermitian, the dipole moment operator is also Hermitian, corresponding to the fact that the dipole moment is an observable quantity. This also means that $d_{ab}^{\varepsilon} = d_{ba}^{\varepsilon*}$.

Now we can rephrase our equation in terms of a matrix and vector in the eigenbasis given by the unperturbed Hamiltonian \hat{H}_0 . This allows us to write the unperturbed Hamiltonian as a diagonal matrix with the entries being the energies of each state. The Schrödinger equation then looks like:

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} c_1(t) e^{-\frac{i}{\hbar} E_1 t} \\ c_2(t) e^{-\frac{i}{\hbar} E_2 t} \end{bmatrix} = \left(\begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + E_0 \cos(\omega t) \begin{bmatrix} d_{11}^{\varepsilon} & d_{12}^{\varepsilon} \\ d_{21}^{\varepsilon} & d_{22}^{\varepsilon} \end{bmatrix} \right) \begin{bmatrix} c_1(t) e^{-\frac{i}{\hbar} E_1 t} \\ c_2(t) e^{-\frac{i}{\hbar} E_2 t} \end{bmatrix} \quad (54)$$

However, we can absorb the diagonal components of the perturbation matrix into the energies of the eigenstates, making the substitutions $E_1 \rightarrow E_1 + d_{11}^{\varepsilon}$ and $E_2 \rightarrow E_2 + d_{22}^{\varepsilon}$. We can then define $D = d_{12}^{\varepsilon}$, and use the Hermitian property to simplify even further:

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} c_1(t) e^{-\frac{i}{\hbar} E_1 t} \\ c_2(t) e^{-\frac{i}{\hbar} E_2 t} \end{bmatrix} = \left(\begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + E_0 \cos(\omega t) \begin{bmatrix} 0 & D \\ D^* & 0 \end{bmatrix} \right) \begin{bmatrix} c_1(t) e^{-\frac{i}{\hbar} E_1 t} \\ c_2(t) e^{-\frac{i}{\hbar} E_2 t} \end{bmatrix} \quad (55)$$

We can substitute this simplification back into our original equations, exploiting the fact that our perturbation is zero along the diagonal. This means that the

time evolution of one coefficient depends only on the other coefficient:

$$\frac{\partial}{\partial t} c_1(t) = \frac{1}{i\hbar} c_2(t) e^{-\frac{i}{\hbar}(E_2-E_1)t} E_0 \cos(\omega t) D \quad (56)$$

$$\frac{\partial}{\partial t} c_2(t) = \frac{1}{i\hbar} c_1(t) e^{-\frac{i}{\hbar}(E_1-E_2)t} E_0 \cos(\omega t) D^* \quad (57)$$

We can perform one more simplification with the identification of $\Delta E = E_2 - E_1$ and using a frequency representation instead, $\Delta\omega$:

$$\frac{\partial}{\partial t} c_1(t) = \frac{D^* E_0}{i\hbar} \cos(\omega t) e^{-i\Delta\omega t} c_2(t) \quad (58)$$

$$\frac{\partial}{\partial t} c_2(t) = \frac{D E_0}{i\hbar} \cos(\omega t) e^{i\Delta\omega t} c_1(t) \quad (59)$$

If we assume that D is real, the quantity $\frac{D E_0}{\hbar}$ is the *Rabi frequency*, which we represent with Ω_0 . We can also describe the cosines in terms of imaginary exponentials:

$$\frac{\partial}{\partial t} c_1(t) = -i\Omega_0 \frac{e^{i\omega t} + e^{-i\omega t}}{2} e^{-i\Delta\omega t} c_2(t) \quad (60)$$

$$\frac{\partial}{\partial t} c_2(t) = -i\Omega_0 \frac{e^{i\omega t} + e^{-i\omega t}}{2} e^{i\Delta\omega t} c_1(t) \quad (61)$$

By combining the exponential terms, we get

$$\frac{\partial}{\partial t} c_1(t) = -\frac{i\Omega_0}{2} \left(e^{i(\omega-\Delta\omega)t} + e^{-i(\omega+\Delta\omega)t} \right) c_2(t) \quad (62)$$

$$\frac{\partial}{\partial t} c_2(t) = -\frac{i\Omega_0}{2} \left(e^{-i(\omega-\Delta\omega)t} + e^{i(\omega+\Delta\omega)t} \right) c_1(t) \quad (63)$$

The term $\omega - \Delta\omega$ is the detuning that we identified earlier. the detuning parameter corresponds to a slow oscillation, but the other parameter $\omega + \Delta\omega$ corresponds to a very fast oscillation that can be averaged out. Therefore, we can neglect the exponential term that contains the sum of frequencies when our detuning parameter is small: this is the *rotating wave approximation*.

$$\frac{\partial}{\partial t} c_1(t) = -\frac{i\Omega_0}{2} e^{i(\omega-\Delta\omega)t} c_2(t) \quad (64)$$

$$\frac{\partial}{\partial t} c_2(t) = -\frac{i\Omega_0}{2} e^{-i(\omega-\Delta\omega)t} c_1(t) \quad (65)$$

If the detuning parameter is large, we cannot ignore this parameter, so the approximation becomes invalid.

2.1 The Bloch sphere

The wavefunction of a two-level atom can be written in terms of its eigenstates:

$$\psi(\vec{x}, t) = c_1 \phi_1(\vec{x}, t) + c_2 \phi_2(\vec{x}, t) \quad (66)$$

Because we know that c_1 and c_2 are complex, this gives our system four degrees of freedom – at least, to start. However, we know that wavefunctions are identical up to multiplication by a complex constant, which removes two degrees of freedom from the system.

It would be convenient to come up with alternate description of the state space of the two-level atom that did not include the redundancies associated with complex coefficients. We can come up with such a formulation by expressing the normalization condition for the wavefunction:

$$\int (c_1 \phi_1(\vec{x}, t) + c_2 \phi_2(\vec{x}, t))^\dagger (c_1 \phi_1(\vec{x}, t) + c_2 \phi_2(\vec{x}, t)) d\vec{x} = 1 \quad (67)$$

We know that the eigenstates form an orthonormal basis, so we can simplify this drastically:

$$c_1^\dagger c_1 + c_2^\dagger c_2 = 1 \quad (68)$$

To split this into two factors, we can express c_1 and c_2 in terms of two angular parameters, θ and φ , which satisfy the relation:

$$(\cos \theta)^2 + e^{-i\varphi} e^{i\varphi} (\sin \theta)^2 = 1 \quad (69)$$

and thus gives us a new expression for the wavefunction involving only two real parameters:

$$\psi = \phi_1 \cos \theta + \phi_2 e^{i\varphi} \sin \theta \quad (70)$$

There is a convenient geometric interpretation of the angular parameters: they represent coordinates on the surface of a sphere. This representation is the *Bloch sphere*. Its surface represents all possible pure states of the system. Mixed states, which will come up later, correspond to points in the interior of the sphere.

2.2 The density operator

Consider a two-level atom that has been prepared in some state $\psi(\vec{x}, 0)$. We know it was prepared in one of two states, $\phi_1(\vec{x}, 0)$ or $\phi_2(\vec{x}, 0)$, with equal probability. How can we describe this state? Our first instinct may be to describe the state as a superposition of the two states:

$$\psi = \frac{1}{\sqrt{2}} (\phi_1 + \phi_2) \quad (71)$$

But this raises a problem: this tells us that the system was prepared in exactly the superposition of states, not in a probabilistic mixture of the two pure states. An experimentalist will not know with certainty that a system is prepared in exactly in one state over the other, but superpositions do not convey this ideay. The uncertainty in state preparation requires its own treatment separate from the quantum mechanical probability amplitudes.

The solution to this problem is to define the density operator $\hat{\rho}$. Our knowledge of the state of the system can be described by this operator instead of a

wavefunction. However, we use wavefunctions to construct the operator. In the system we want to model, we know that the system is certainly in either ϕ_1 or ϕ_2 , but certainly not in any superposition state.

A *pure state* is a state that can be represented as the product of a state vector with itself. For instance, if we managed to generate exactly the state $c_1\phi_1 + c_2\phi_2$, we could describe it in terms of the eigenbasis:

$$\hat{\rho}_{ab} = \begin{bmatrix} c_1^*c_1 & c_1^*c_2 \\ c_2^*c_1 & c_2^*c_2 \end{bmatrix} \quad (72)$$