Physics 438A – Lecture #3
Quantum Dynamics

Aaron Wirthwein – wirthwei@usc.edu

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1 Finite-Dimensional Energy Basis

The Schrödinger equation of quantum mechanics is analagous to Newton's second law in classical mechanics–it is formally true but physically empty without additional information. For any given physical system, you must build a model, and that includes specifying a suitable Hamiltonian[1]. Whether or not you have the *right* Hamiltonian is a serious question, and addressing it requires physical insight and sound judgment. Once you have a Hamiltonian, it is often convenient to express the state vector in the energy eigenbasis, where the Hamiltonian takes a diagonal form. We'll consider finite-dimensional quantum systems in this lecture, but many of the concepts apply equally well to infinite-dimensional systems with discrete energy spectra (such as bound particle system). Questions related to the convergence of sequences naturally arise in such contexts, but we won't be concerned with them in this class.

If we label the allowed energies as E_n, then the energy eigenvalue equation is

$$H|E_n\rangle = E_n|E_n\rangle \tag{1.1}$$

where $|E_n\rangle$ is the energy eigenstate corresponding to the eigenvalue E_n. In our present discussion, we'll assume the eigenvalues are non-degenerate and that the Hamiltonian is time-independent for simplicity. The spectral decomposition of H is

$$H = \sum_n E_n|E_n\rangle\langle E_n| \tag{1.2}$$

and the unitary time evolution operator is

$$U(t) = e^{-iHt/\hbar} = \sum_n e^{-iE_nt/\hbar}|E_n\rangle\langle E_n| \tag{1.3}$$

If the initial state vector is

$$|\psi(0)\rangle = \sum_n c_n|E_n\rangle \tag{1.4}$$

[1] In almost any scientific paper on a quantum system, the first or second equation is usually a Hamiltonian!

where the coefficients are $c_n = \langle E_n|\psi(0)\rangle$, then it follows that

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle = \sum_n c_n e^{-iE_n t/\hbar}|E_n\rangle \tag{1.5}$$

We can also expand the final state vector in the energy eigenbasis using time-dependent coefficients such that

$$|\psi(t)\rangle = \sum_n c_n(t)|E_n\rangle \tag{1.6}$$

where $c_n(0) = c_n$ are the initial coefficients defined above. The energy eigenstates are orthonormal, meaning $\langle E_k|E_n\rangle = \delta_{kn}$ where δ_{kn} is the Kronecker delta symbol. We can use this fact to solve for the coefficients of the state vector in the energy eigenbasis:

$$\langle E_k|\psi(t)\rangle = \sum_n c_n(t)\langle E_k|E_n\rangle = \sum_n c_n(t)\delta_{kn} = c_k(t) \tag{1.7}$$

From Eq. (1.5), it follows that

$$\begin{aligned}\langle E_k|\psi(t)\rangle &= \sum_n c_n e^{-iE_n t/\hbar}\langle E_k|E_n\rangle \\ &= \sum_n c_n e^{-iE_n t/\hbar}\delta_{kn} \\ &= c_k e^{-iE_k t/\hbar}\end{aligned} \tag{1.8}$$

Hence,

$$c_n(t) = c_n e^{-iE_n t/\hbar} \tag{1.9}$$

If we measure an observable A on a quantum system in the state $|\psi(t)\rangle$, there are general statements we can make regarding the probability to measure an eigenvalue a_n of the observable A that depend on depend on properties of A and $|\psi(t)\rangle$, which we will outline:

(i) If $|\psi(0)\rangle$ is an energy eigenstate, then the probability to measure a_n is time independent and is equal to the probability at the initial time. For this reason, the energy eigenstates are called **stationary states**–there is no *measurable* time evolution.

(ii) The probability to measure any particular energy of a quantum system will not change over time (assuming H is time-independent and the system is closed).

(iii) If $[H, A] = 0$, then A and H will share common eigenstates, and the probability to measure any particular eigenvalue of A will not change over time.

(iv) If $[H, A] \neq 0$, and $|\psi(0)\rangle$ is a superposition of eigenstates, then the probability to measure any particular eigenvalue of A will change over time.

Proof of (i). Let $|\psi(0)\rangle = |E_k\rangle$ such that $|\psi(t)\rangle = e^{-iE_k t/\hbar}|E_k\rangle$. The probability to measure a_n is

$$|\langle a_n|\psi(t)\rangle|^2 = |\langle a_n|e^{-iE_k t/\hbar}|E_k\rangle|^2 = |\langle a_n|E_k\rangle|^2 \tag{1.10}$$

which is independent of time. The claim is also true when a_n is degenerate.

Proof of (ii). The probability to measure E_n is

$$\begin{aligned} |\langle E_n|\psi(t)\rangle|^2 &= \Big|\sum_k c_k e^{-iE_k t/\hbar}\langle E_n|E_k\rangle\Big|^2 \\ &= |c_n|^2 \end{aligned} \tag{1.11}$$

Proof of (iii). When the observable A commutes with H, it has a spectral decomposition in terms of the energy eigenstates–it is diagonal in the energy eigenbasis. Hence,

$$A = \sum_n a_n \langle E_n|E_n\rangle \tag{1.12}$$

In other words, the probability to measure a_n is the same as the probability to measure E_n, assuming they both correspond to the same eigenvector. The probability to measure a_n is therefore $|c_n|^2$ as we found in the proof of statement (ii).

Proof of (iv). Here's where things get interesting. I'll do this in a rather technical way and leave the simpler, more illuminating examples for you to work through on your own. Since the energy eigenstates form a basis, we can expand the eigenstates of A in terms of energy eigenstates as

$$|a_n\rangle = \sum_k \alpha_{nk}|E_k\rangle$$

The probability of measuring the eigenvalue a_n is

$$\begin{aligned} |\langle a_n|\psi(t)\rangle|^2 &= \Big|\sum_{k\ell} \alpha^*_{nk} c_\ell e^{-iE_\ell t/\hbar}\langle E_k|E_\ell\rangle\Big|^2 \\ &= \Big|\sum_k \alpha^*_{nk} c_k e^{-iE_k t/\hbar}\Big|^2 \\ &= \sum_{k\ell} \alpha^*_{nk}\alpha_{n\ell} c_k c^*_\ell e^{-i(E_k - E_\ell)t/\hbar} \end{aligned}$$

$$= \sum_k |\alpha_{nk}|^2 |c_k|^2 + \sum_{k \neq \ell} \alpha_{nk}^* \alpha_{n\ell} c_k c_\ell^* e^{-i(E_k - E_\ell)t/\hbar}$$

$$= \sum_k |\alpha_{nk}|^2 |c_k|^2 + \sum_{k < \ell} 2\mathrm{Re}\left[\alpha_{nk}^* \alpha_{n\ell} c_k c_\ell^* e^{-i(E_k - E_\ell)t/\hbar}\right]$$

We see that the probability separates into a part that is time independent and a term that oscillates with a combination of **Bohr frequencies** defined as

$$\omega_{k\ell} = \frac{E_k - E_\ell}{\hbar} \tag{1.13}$$

It's reassuring that a measurable aspect of time evolution depends on *energy differences* rather than energies themselves. In classical mechanics, energy is only well defined up to an overall constant and dynamical evolution is tied to changes in energy that occur over time.

2 Spin Precession

Consider a single magnetic dipole (e.g., a silver atom) in a uniform magnetic field. From classical electromagnetism, the potential energy of interaction between the dipole and the magnetic field is

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{2.1}$$

Recall that the magnetic dipole of an electron is given by

$$\boldsymbol{\mu} = g \frac{q}{2m_e} \mathbf{S} \tag{2.2}$$

where $q = -e$ and we'll take $g = 2$, even though the g-factor of the electron famously differs slightly from 2. We'll *define* our quantum system by the Hamiltonian

$$H = \frac{e}{m_e} \mathbf{S} \cdot \mathbf{B} \tag{2.3}$$

where $\mathbf{S}$ is not a unit vector, or even an ordinary vector–it's an *operator-valued vector* with components S_x, S_y, and S_z. The magnetic field is an ordinary vector (we are treating the magnetic field as a classical vector field), so it's actually unclear what the dot product means in this context. In fact, it's just the usual dot product in terms of Cartesian coordinates:

$$\mathbf{S} \cdot \mathbf{B} = B_x S_x + B_y S_y + B_z S_z$$

While the Hamiltonian operator represents the total energy of the system, only energy differences are relevant. We may consider only energy terms that differentiate between the two possible spin states in the system.

2.1 Spin Component in a General Direction

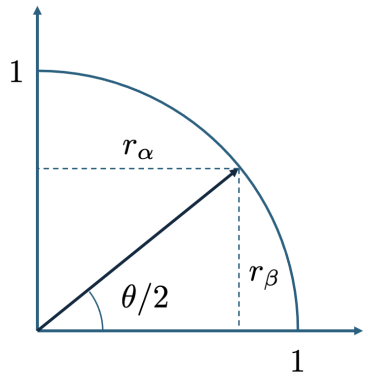
We'll see where the spin operators and their eigenstates come from in lecture #4, but for now I'd like to discuss the spin component in an arbitrary direction. Let's adopt a mathematical perspective given that state vectors are notoriously abstract and physical intuition takes time and effort to build. An arbitrary two-dimensional state vector may be written as a linear combination of $|+z\rangle$ and $|-z\rangle$ in the following manner:

$$|\psi\rangle = \alpha|+z\rangle + \beta|-z\rangle, \quad \text{where } |\alpha|^2 + |\beta|^2 = 1$$

Starting with a general spin state in the z basis, let

$$\alpha = r_\alpha e^{i\phi_\alpha}, \quad \beta = r_\beta e^{i\phi_\beta} \quad \text{(complex numbers in polar form)}$$

where $r_\alpha, r_\beta > 0$ are real numbers (amplitudes) and ϕ_α, ϕ_β are phases (also real numbers). From the condition, $|\alpha|^2 + |\beta|^2 = 1$, it follows that $r_\alpha^2 + r_\beta^2 = 1$. This is the equation for a quarter circle since $r_\alpha, r_\beta > 0$ (see diagram below).



$$r_\alpha = \cos(\theta/2), \quad r_\beta = \sin(\theta/2), \quad \theta \in [0, \pi]$$

$$|\psi\rangle = \cos(\theta/2)e^{i\phi_\alpha}|+z\rangle + \sin(\theta/2)e^{i\phi_\beta}|-z\rangle$$

$$e^{-i\phi_\alpha}|\psi\rangle = \cos(\theta/2)|+z\rangle + \sin(\theta/2)e^{i(\phi_\beta - \phi_\alpha)}|-z\rangle$$

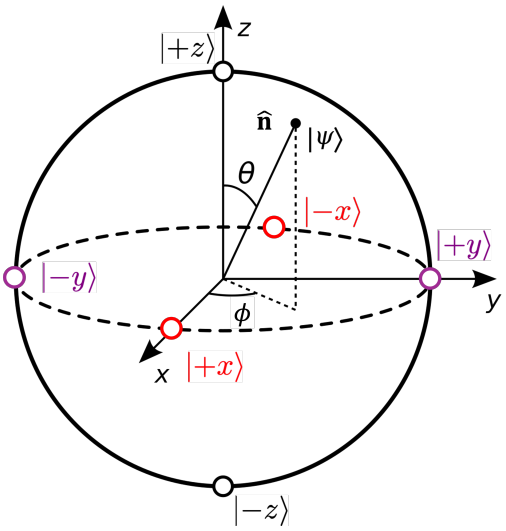


Figure 2.1: The Bloch sphere–a convenient way to visualize spin-1/2 systems.

Let $\phi = (\phi_\beta - \phi_\alpha) \in [0, 2\pi)$, and note that the state $e^{-i\phi_\alpha}|\psi\rangle$ is *physically equivalent* to $|\psi\rangle$. The most general spin-1/2 state can be written as

$$|\psi\rangle = \cos(\theta/2)|+z\rangle + \sin(\theta/2)e^{i\phi}|-z\rangle \tag{2.4}$$

where $0 \leq \theta \leq \pi$, and $0 \leq \phi < 2\pi$. Hence, any point on the surface of a unit sphere represents a valid spin-1/2 state–we call the unit sphere the **Bloch sphere** in this context.

For every spin-1/2 state, there corresponds a unit vector in 3D Euclidean space called the **Bloch vector** given by

$$\hat{\mathbf{n}} = \hat{\mathbf{x}}\sin\theta\cos\phi + \hat{\mathbf{y}}\sin\theta\sin\phi + \hat{\mathbf{z}}\cos\theta \tag{2.5}$$

The spin component along this direction is obtained by projecting the spin vector $\mathbf{S}$ onto the Bloch vector:

$$S_n = \mathbf{S}\cdot\hat{\mathbf{n}} = S_x\sin\theta\cos\phi + S_y\sin\theta\sin\phi + S_z\cos\theta$$

In matrix form,

$$S_n = \frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta\ e^{-i\phi} \\ \sin\theta\ e^{i\phi} & -\cos\theta \end{pmatrix}$$

It is relatively straightforward to show that the general spin-1/2 state given by Eq. (2.4) is an eigenvector of S_n when the parameters θ and ϕ match–that is, when the Bloch vector

is aligned with the spin component. The way I've set this up guarantees alignment... For notational convenience, let

$$|+n\rangle = \cos(\theta/2)|+z\rangle + \sin(\theta/2)e^{i\phi}|-z\rangle \tag{2.6}$$

such that

$$S_n|+n\rangle = \frac{\hbar}{2}|+n\rangle$$

To find the other eigenvector (there must be two after all), we use the guess-and-check method, informed by intuition. If $|+n\rangle$ is the eigenvector aligned with $\hat{\mathbf{n}}$, then $|-n\rangle$ must be an eigenvector aligned with $-\hat{\mathbf{n}}$. The vector $\hat{\mathbf{n}}$ is mapped to $-\hat{\mathbf{n}}$ under the transformation $(\theta, \phi) \to (\pi - \theta, \phi + \pi)$. Hence,

$$|-n\rangle = \sin(\theta/2)|+z\rangle - \cos(\theta/2)e^{i\phi}|-z\rangle \tag{2.7}$$

and indeed,

$$S_n|-n\rangle = -\frac{\hbar}{2}|-n\rangle$$

2.2 Uniform Magnetic Field

A uniform magnetic field points in some direction, so we might as well define that to be the z direction such that $\mathbf{B} = B_0\hat{\mathbf{z}}$. The Hamiltonian in Eq. (2.3) simplifies to

$$H = \frac{eB_0}{m_e}S_z = \omega_0 S_z \tag{2.8}$$

where the constant $\omega_0 = eB_0/m_e$ has units of frequency. Since the Hamiltonian commutes with S_z, it shares the same eigenstates. Let's write the Hamiltonian as a matrix in S_z representation:

$$H = \frac{\hbar\omega_0}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.9}$$

The unitary time evolution operator is therefore

$$U(t) = e^{-iHt/\hbar} = \begin{pmatrix} e^{-i\omega_0 t/2} & 0 \\ 0 & e^{i\omega_0 t/2} \end{pmatrix} = e^{-i\omega_0 t/2}\begin{pmatrix} 1 & 0 \\ 0 & e^{i\omega_0 t} \end{pmatrix} \tag{2.10}$$

We consider the most general state vector written in the Bloch sphere representation as

$$|\psi(0)\rangle = \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2)e^{i\phi} \end{pmatrix} \tag{2.11}$$

Hence, the final state vector is

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle = e^{-i\omega_0 t/2} \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2)e^{i(\phi+\omega_0 t)} \end{pmatrix} \tag{2.12}$$

The overall phase does not have a measurable effect here, so we can interpret the evolved state as a spin up eigenstate along a direction that maintains a constant polar angle θ as it revolves around the z axis with an angular frequency of ω_0.

We can test a few of the statements we made in the opening section. For instance, the probability of measuring the spin component along the z-axis is

$$|\langle +z|\psi(t)\rangle|^2 = \cos^2(\theta/2) \tag{2.13}$$

which is time independent because the S_z eigenstates are also energy eigenstates for this problem (H commutes with S_z). Alternatively, the probability for measuring spin up along the x-axis is

$$|\langle +x|\psi(t)\rangle|^2 = \tfrac{1}{2}\big[1 + \sin\theta\cos(\phi + \omega_0 t)\big] \tag{2.14}$$

This probability is time dependent because the S_x eigenstates are not energy eigenstates (H does not commute with S_x).

While it may be helpful to think of the state vector in the Bloch sphere representation as revolving around the z axis, one should be cautious when ascribing any physical picture to the state vector itself. A better approach to understanding spin precession would be to calculate the expectation values of the spin components. One may verify

$$\langle S_z\rangle = \frac{\hbar}{2}\cos\theta \tag{2.15}$$

$$\langle S_x\rangle = \frac{\hbar}{2}\sin\theta\cos(\phi + \omega_0 t) \tag{2.16}$$

$$\langle S_y\rangle = \frac{\hbar}{2}\sin\theta\sin(\phi + \omega_0 t) \tag{2.17}$$

After many measurements of the spin components performed on identical systems, we ex-

pect the average results to be consistent with the classical picture in which the spin vector precesses around the magnetic field direction with frequency ω_0. The precession of the spin vector is *Larmor precession* and the frequency of precession is the *Larmor frequency*. This precession of the spin vector suggests the system has angular momentum, rather than simply having a magnetic dipole moment. The equivalence of the classical Larmor precession and the expectation value of the quantum mechanical spin vector is one example of *Ehrenfest's theorem*, which states that quantum mechanical expectation values obey classical laws.

Example 2.1: Spin Precession

The Hamiltonian for an electron in a magnetic field $\mathbf{B} = B_0\hat{\mathbf{x}}$ is

$$H = \omega_0 S_x$$

where $\omega_0 \approx eB_0/m_e$ is the Larmor frequency. If the particle is initially in the state $|\psi(0)\rangle = |+z\rangle$, determine $|\psi(t)\rangle$, the state of the electron at time t.

Solution: The Hamiltonian is time independent, so the unitary time evolution operator is

$$U(t) = e^{-\omega_0 S_x t/\hbar} = \begin{pmatrix} \cos(\omega_0 t/2) & i\sin(\omega_0 t/2) \\ i\sin(\omega_0 t/2) & \cos(\omega_0 t/2) \end{pmatrix}$$

where this result was obtained in a previous example. The state of the electron is

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle = \begin{pmatrix} \cos(\omega_0 t/2) \\ i\sin(\omega_0 t/2) \end{pmatrix} = \cos(\omega_0 t/2)|+z\rangle + i\sin(\omega_0 t/2)|-z\rangle$$

3 Magnetic Resonance

Here we study a simple, yet rich example to understand the phenomena of *magnetic resonance*. By applying a transverse oscillating magnetic field with a frequency close to the Larmor frequency, we can induce transitions between energy (spin) states. This same model of the interaction between a two-level system and an applied time-dependent field is also used to explain how atoms absorb and emit light.

The Hamiltonian we'll consider in this example is time-dependent and given by

$$\begin{aligned} H(t) &= -\boldsymbol{\mu} \cdot \mathbf{B} \\ &= \frac{e}{m_e}\mathbf{S} \cdot \Big[B_0 \hat{\mathbf{z}} + B_1 \cos(\omega t)\hat{\mathbf{x}} + B_1 \sin(\omega t)\hat{\mathbf{y}} \Big] \\ &= \omega_0 S_z + \omega_1 \Big[\cos(\omega t) S_x + \sin(\omega t) S_y \Big] \end{aligned} \tag{3.1}$$

where ω is the "driving frequency" of the magnetic field and the two Larmor frequencies are

$$\omega_0 = \frac{eB_0}{m_e} \quad \text{and} \quad \omega_1 = \frac{eB_1}{m_e} \tag{3.2}$$

The matrix representation of the Hamiltonian in the S_z basis is

$$H(t) = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_1 e^{-i\omega t} \\ \omega_1 e^{i\omega t} & -\omega_0 \end{pmatrix} \tag{3.3}$$

We can't use Stone's theorem because the Hamiltonian is time dependent. Instead, we'll write out the components of the Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle \tag{3.4}$$

Here we'll use the S_z eigenstates as our basis, even though they aren't the energy eigenstates anymore. The state vector is

$$|\psi(t)\rangle = c_+(t)|+z\rangle + c_-(t)|-z\rangle = \begin{pmatrix} c_+(t) \\ c_-(t) \end{pmatrix} \tag{3.5}$$

and the components of the Schrödinger equation are

$$i\dot{c}_+(t) = \frac{\omega_0}{2} c_+(t) + \frac{\omega_1}{2} e^{-i\omega t} c_-(t) \tag{3.6}$$

$$i\dot{c}_-(t) = \frac{\omega_1}{2} e^{i\omega t} c_+(t) - \frac{\omega_0}{2} c_-(t) \tag{3.7}$$

where $\dot{c}_\pm(t)$ denotes the time derivative. Coupled differential equations are notoriously difficult to work with, but we can solve these with a clever *gauge transformation*.

3.1 Foldy-Wouthuysen Gauge Transformations

The Schrödinger equation and all empirical predictions of quantum mechanics are invariant under transformation by an *arbitrary time-dependent unitary operator* $V(t)$:

$$|\psi(t)\rangle \mapsto V(t)|\psi(t)\rangle$$

$$A(t) \mapsto V(t)A(t)V^\dagger(t)$$

$$H(t) \mapsto V(t)H(t)V^\dagger(t) + i\hbar\dot{V}(t)V^\dagger(t)$$

where $A(t)$ is a time-dependent observable and $\dot{V}(t)$ is the time derivative of $V(t)$. This set of transformations was discovered by Foldy and Wouthuysen in 1950 [1].

In order to establish the validity of these transformations, we must consider the *gauge invariant quantities* of quantum mechanics. These are the quantities that do not depend on our choice of $V(t)$. For instance, the expectation value of an observable should not depend on $V(t)$, and indeed

$$\langle\tilde{A}(t)\rangle = \langle\tilde{\psi}(t)|\tilde{A}(t)|\tilde{\psi}(t)\rangle = \langle\psi|V^\dagger V A V^\dagger V|\psi\rangle = \langle\psi|A|\psi\rangle = \langle A(t)\rangle$$

Probabilities generated via the Born rule will also be unaffected. Given that $V(t)$ is time-dependent, if we insist on using the Schrödinger equation for any choice of $V(t)$, then the Hamiltonian must be modified:

$$\begin{aligned}
\frac{d}{dt}|\tilde{\psi}(t)\rangle &= \dot{V}(t)|\psi(t)\rangle + V(t)\frac{d}{dt}|\psi(t)\rangle \\
&= \dot{V}(t)|\psi(t)\rangle - \frac{i}{\hbar}V(t)H(t)|\psi(t)\rangle \\
&= \dot{V}(t)V^\dagger(t)|\tilde{\psi}(t)\rangle - \frac{i}{\hbar}V(t)H(t)V^\dagger(t)|\tilde{\psi}(t)\rangle \\
i\hbar\frac{d}{dt}|\tilde{\psi}(t)\rangle &= \Big[V(t)H(t)V^\dagger(t) + i\hbar\dot{V}(t)V^\dagger(t)\Big]|\tilde{\psi}(t)\rangle = \tilde{H}(t)|\tilde{\psi}(t)\rangle
\end{aligned}$$

Hence, the Schrödinger equation is preserved under this transformation.

3.2 Rotating Frame

Recall from Section 2.2 that the unitary operator

$$U(t) = \begin{pmatrix} e^{-i\omega_0 t/2} & 0 \\ 0 & e^{i\omega_0 t/2} \end{pmatrix}$$

corresponds to continuous rotation around the z axis with constant frequency ω_0. If we transform to a frame that rotates around the z axis at the same rate as the oscillating component of the magnetic field, then that component will appear stationary and it might be easier to solve the problem.

Define the time-dependent rotation operator in the S_z representation as

$$V(t) = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \tag{3.8}$$

and the transformed state vector in the rotating frame is

$$|\tilde{\psi}(t)\rangle = V^\dagger(t)|\psi(t)\rangle \tag{3.9}$$

where the idea is that if $|\psi(t)\rangle$ appears to be rotating in the "lab frame," then $|\tilde{\psi}(t)\rangle$ is stationary in the rotating frame... Ultimately, we're simply using a gauge transformation of the type discussed in the previous section where $V \to V^\dagger$, so we won't strain ourselves to understand the physical significance of Eq. (3.9).

The transformed Hamiltonian in the rotating frame is given by

$$\tilde{H}(t) = V^\dagger(t)H(t)V(t) + i\hbar\dot{V}^\dagger(t)V(t) \tag{3.10}$$

After working through some calculations, the transformed Hamiltonian can be written as

$$\tilde{H} = \frac{\hbar}{2}\begin{pmatrix} -\Delta\omega & \omega_1 \\ \omega_1 & \Delta\omega \end{pmatrix} \tag{3.11}$$

where $\Delta\omega = \omega - \omega_0$. In the rotating frame, the Hamiltonian appears stationary! Furthermore,

$$\tilde{H} = \omega_1 S_x - \Delta\omega S_z = \frac{e}{m_e}\mathbf{S}\cdot\Big[B_1\hat{\mathbf{x}} - \Delta B\hat{\mathbf{z}}\Big] \tag{3.12}$$

where $\Delta B = m_e \Delta\omega / e$, so the magnetic field lies in the xz-plane. Let

$$\tan\theta = -\frac{B_1}{\Delta B} = -\frac{\omega_1}{\Delta\omega} \tag{3.13}$$

so that θ may be interpreted as the angle between the magnetic field vector and the z axis. Then,

$$\Delta\omega = -\cos\theta\sqrt{\Delta\omega^2 + \omega_1^2} \quad \text{and} \quad \omega_1 = \sin\theta\sqrt{\Delta\omega^2 + \omega_1^2} \tag{3.14}$$

and the Hamiltonian can be written in a more suggestive form as

$$\tilde{H} = \frac{\hbar}{2}\sqrt{\Delta\omega^2 + \omega_1^2}\begin{pmatrix}\cos\theta & \sin\theta \\ \sin\theta & -\cos\theta\end{pmatrix} = \sqrt{\Delta\omega^2 + \omega_1^2}\; S_n \tag{3.15}$$

where S_n is the spin component along a direction in the xy-plane (the azimuthal angle is zero in this case). It follows that the eigenvalues of $\tilde{H}$, denoted $E_\pm$, are

$$E_\pm = \pm\frac{\hbar}{2}\sqrt{\Delta\omega^2 + \omega_1^2} \tag{3.16}$$

and the corresponding eigenvectors are $|\pm n\rangle$ with $\phi = 0$ (on the xy-plane). The unitary time evolution operator in the rotating frame is therefore

$$\tilde{U}(t) = e^{-iE_+ t/\hbar}|+n\rangle\langle+n| + e^{-iE_- t/\hbar}|-n\rangle\langle-n| \tag{3.17}$$

3.3 Spin Flip

Let's consider a specific scenario known as a **spin flip** where we start with a spin up eigenstate of S_z and compute the probability for it to flip to a spin down state. Starting with the spin up eigenstate of S_z, the probability to measure $S_z = -\hbar/2$ after some time t is

$$\mathcal{P} = |\langle -z|\psi(t)\rangle|^2 \tag{3.18}$$

where

$$|\psi(t)\rangle = V(t)|\tilde{\psi}(t)\rangle = V(t)\tilde{U}(t)|\tilde{\psi}(0)\rangle = V(t)\tilde{U}(t)|+z\rangle$$

After some tedious calculations, it follows that

$$\mathcal{P} = \frac{\omega_1^2}{(\omega-\omega_0)^2 + \omega_1^2}\sin^2\left[\frac{\sqrt{(\omega-\omega_0)^2 + \omega_1^2}}{2}\; t\right] \tag{3.19}$$

The static magnetic field case is generally referred to as spin precession, while the rotating field case is referred to as **Rabi flopping** (or Rabi oscillations), and the equation above is a generalization of **Rabi's formula**. Rabi oscillations represent transitions between energy eigenstates; there is exchange of energy between the system and the applied field. The energy exchange occurs because the Hamiltonian is time dependent.

The probability of a Rabi spin flip oscillates with an angular frequency given by

$$\Omega = \sqrt{(\omega - \omega_0)^2 + \omega_1^2} \tag{3.20}$$

that is typically referred to as the **generalized Rabi frequency**. The term **Rabi frequency** generally refers to the frequency ω_1, which is the value of the generalized Rabi frequency when the frequency ω of the rotating field is on **resonance** (i.e., ω is set equal to the Larmor precession frequency ω_0 of the system in the presence of the magnetic field B_0 alone). For this choice of $\omega = \omega_0$, the probability of a spin flip becomes

$$\mathcal{P} = \sin^2\left(\frac{\omega_1 t}{2}\right) \tag{3.21}$$

which implies that the spin is flipped with 100% probability at an angular frequency ω_1, *even if the transverse field is weak*. For other off-resonance choices of the frequency ω, the probability of a spin flip oscillates with an amplitude smaller than one. A graph of $\mathcal{P}$ as a function of ω shows a curve called a Lorentzian with a peak at $\omega = \omega_0$ and a full width at half-maximum of $2\omega_1$.

4 Light-Matter Interactions

The same model we used to study spin flipping is used to explain how atoms absorb and emit light. In the interaction of atoms with light, the oscillating electric field of the light wave interacts with the electric dipole of the atom, and energy exchange between the field and the atom corresponds to absorption and emission of photons. Though atoms have more than two energy levels, we can reduce the problem to a two-level system if the frequency ω of the applied light field is close to just one of the Bohr frequencies of the atom. Label the lower state $|g\rangle$ (for ground state) and the upper state $|e\rangle$ (for excited state). The energy difference between the two levels is defined to be

$$E_e - E_g = \hbar\omega_0 \tag{4.1}$$

The applied light field (e.g., laser beam) has a frequency ω that is close to, but not necessarily equal to, the atomic Bohr frequency ω_0. By analogy with the spin problem, we can express the Hamiltonian for this atom-light system in two parts

$$H = \frac{\hbar}{2}\begin{pmatrix} \omega_0 & \omega_1 e^{-i\omega t} \\ \omega_1 e^{i\omega t} & -\omega_0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} \omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix} + \frac{\hbar}{2}\begin{pmatrix} 0 & \omega_1 e^{-i\omega t} \\ \omega_1 e^{i\omega t} & 0 \end{pmatrix} \tag{4.2}$$

where the first term as the atomic Hamiltonian and the second term as the interaction Hamiltonian. We can interpret the parameter ω_1 as an off-diagonal matrix element of the interaction Hamiltonian that connects the two states. The Rabi formula then gives the probability for the light field to cause transitions between the two atomic energy states. Studying induced transitions is the most powerful tool we have for discovering what the energy levels of a system are and ultimately for determining the Hamiltonian of the system. This tool is known as **spectroscopy** and has played a pivotal role in relating experiments and theory in quantum mechanics.

4.1 Atomic Clocks

Atomic clocks are among the most precise measurement devices ever created, and at their core lies the quantum physics of driven two-level systems. These clocks operate by exploiting transitions between two discrete energy levels in atoms–typically hyperfine levels of an alkali metal like cesium or rubidium. The transition frequency between the energy levels can be used to define a unit of time: one second is *defined* as a specific number of oscillations (e.g., 9,192,631,770 for cesium-133) of radiation corresponding to this transition.

Physically, the clock works by preparing the atoms in one hyperfine state and then subjecting them to an oscillating electromagnetic field (usually in the microwave or optical range) whose frequency corresponds to the energy difference between the two levels. The interaction of this field with the atom is an example of a *driven two-level system*, governed by the physics of *Rabi oscillations*. When the driving field is resonant with the energy splitting, the population of the atom oscillates between the two levels with a frequency known as the *Rabi frequency*, which depends on the strength of the field and the dipole moment of the transition.

By tuning the driving field and observing the population of the final state, experimenters can determine the frequency at which the transition is maximally excited. That is, the frequency of the field is exactly resonant with the atomic transition. This frequency becomes the reference for the clock. The narrower the transition linewidth and the more stable the oscillation, the more precise the clock. Advanced atomic clocks (like optical lattice clocks)

push this technique to its extreme, using ultra-stable lasers and atoms trapped in standing light waves to suppress motion and environmental noise, yielding timing precision at the level of 1 part in 10^{18}.

5 The Heisenberg Picture

In the "Heisenberg picture," the state vector is time-independent and the operators evolve in time. Starting from the Schrödinger picture, consider a time-independent operator A_S in a quantum system where the Hamiltonian is also time-independent. If we know the initial state of the system, we can write the expectation value of A_S at a later time as

$$\langle\psi(t)|A_S|\psi(t)\rangle = \langle\psi(0)|U^\dagger(t)A_S U(t)|\psi(0)\rangle, \tag{5.1}$$

and we define the **Heisenberg picture operator** as

$$A_H(t) \equiv U^\dagger(t)A_S U(t) \tag{5.2}$$

Evidently, the same expectation value can be obtained in either picture. Furthermore, since

$$\frac{d}{dt}U(t) = -\frac{i}{\hbar}HU(t) \tag{5.3}$$

it follows that

$$\begin{aligned}
\frac{d}{dt}A_H(t) &= \left(\frac{d}{dt}U^\dagger(t)\right)A_S U(t) + U^\dagger(t)A_S\left(\frac{d}{dt}U(t)\right) \\
&= \frac{i}{\hbar}U^\dagger(t)HA_S U(t) - \frac{i}{\hbar}U^\dagger(t)A_S HU(t) \\
&= \frac{i}{\hbar}HU^\dagger(t)A_S U(t) - \frac{i}{\hbar}U^\dagger(t)A_S U(t)H \\
&= \frac{i}{\hbar}[H, A_H(t)]
\end{aligned}$$

This is called Heisenberg's equation of motion in quantum mechanics. We get a similar equation for the expectation value of A for a quantum system in the state $|\psi\rangle$, also called Heisenberg's equation of motion, given by

$$\frac{d\langle A\rangle}{dt} = \frac{i}{\hbar}\Big\langle[H, A]\Big\rangle \tag{5.4}$$

This equation holds in both the Heisenberg picture and the Schrödinger picture.

6 Energy-Time Uncertainty Relation

Consider a time-independent observable A and a Hamiltonian H for some quantum system. The product of their uncertainties must satisfy

$$\Delta H \Delta A \geq \tfrac{1}{2}\left|\langle [H, A]\rangle\right| \tag{6.1}$$

where ΔH denotes the uncertainty in H. The Heisenberg equation of motion for A is

$$\frac{d\langle A\rangle}{dt} = \frac{i}{\hbar}\langle [H, A]\rangle \tag{6.2}$$

so it follows that

$$\Delta H \Delta A \geq \frac{\hbar}{2}\left|\frac{d\langle A\rangle}{dt}\right| \tag{6.3}$$

Define δt_A as the time for $\langle A\rangle$ to change by an amount on the order of ΔA. Informally, it is the timescale over which a "significant" change in $\langle A\rangle$ will occur. More precisely, if

$$\delta t_A = \frac{\Delta A}{|d\langle A\rangle/dt|} \tag{6.4}$$

then

$$\Delta H \ \delta t_A \geq \frac{\hbar}{2} \tag{6.5}$$

This relation **does not** say that time is uncertain in the same way that observables are uncertain. There is no time operator in quantum theory! The energy-time uncertainty relation expresses a tradeoff between the uncertainty in energy and the speed of evolution. A state with well-defined energy ($\Delta H = 0$) doesn't evolve in time, so $d\langle A\rangle/dt = 0$ for any observable A. A state that changes rapidly must involve a superposition of energy eigenstates and hence $\Delta H > 0$.

References

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