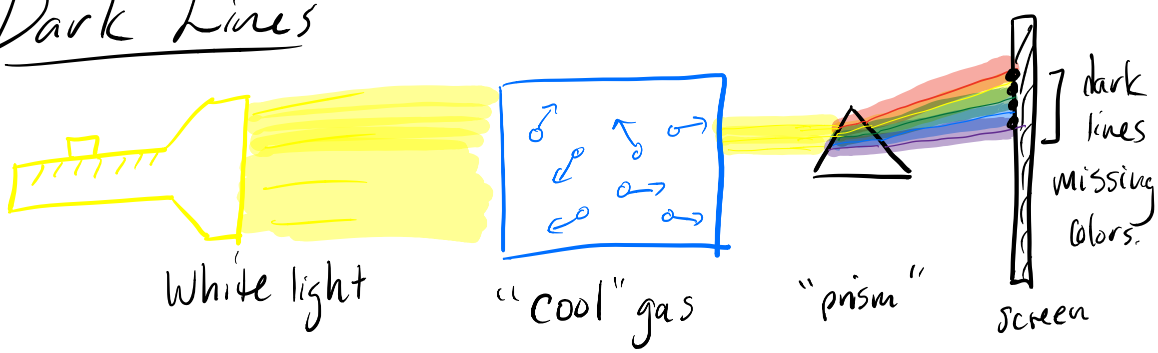
Nuclei, Atoms, & Molecules

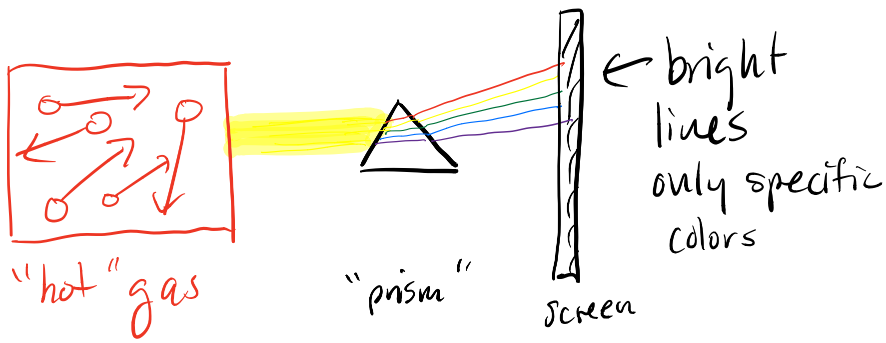
Two of the most important observations made in early 20th century physics were the observations of dark & bright lines lines in experiments with atomic gases.

Dark Lines



- When a broadband source (lots of wavelengths) is directed at a "cool" gas (low energy) and the subsequent light is separated by color, some colors are missing on the screen. ("dark lines").
- For a given atomic gas (Hydrogen, Sodium, etc), the same colors are always missing and are unique to the gas.

Bright lines



- A "hot" gas (high energy) will produce light. When that light is color separated ("prism"), the resulting light consists of specific colors only.
- For a given atomic gas, these colors are always the same and unique to the gas.

- These two experimental observations along with the photoelectric effect lead to the theoretical foundations of quantum mechanics.
- In addition, these two experiments lead to the study of spectroscopy — how

We get these dark & bright lines
in many fields of physics – atomic, molecular, nuclear, astrophysics, solid state, laser, etc.

We now know these dark lines to be absorption spectra and the bright lines to be emission spectra

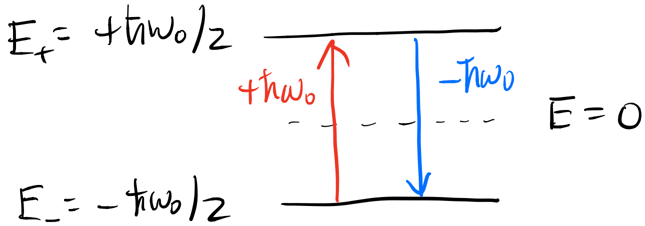
Energy Spectra Spin 1/2

As we saw with spin 1/2 systems, we can describe QM systems in terms of discrete (i.e., quantized) energies.

With $\vec{B} = B_0 \hat{z}$ & $\omega \equiv \frac{eB_0}{m_e}$,

$$H|+\rangle = +\frac{\hbar\omega}{2}|+\rangle \qquad H|-\rangle = -\frac{\hbar\omega}{2}|-\rangle$$

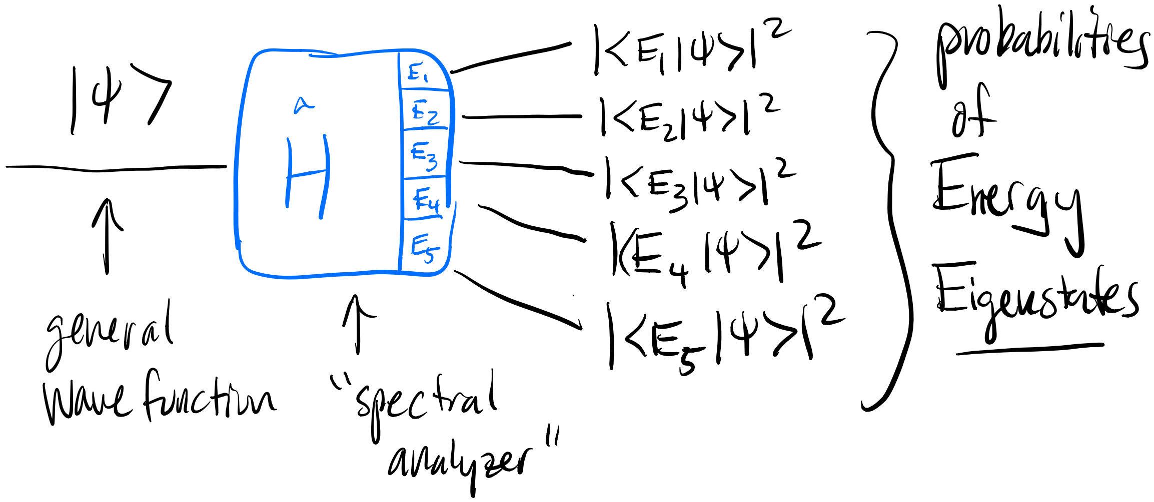
So the spectrum (allowed energies) for a spin 1/2 system is quite simple,



- So this indicates to us that if the particle were to be driven from $|-\rangle$ to $|+\rangle$ that requires exactly $\hbar\omega_0$ of energy to be <u>absorbed</u>. (red line)
- So we would expect a dark line precisely at whatever color corresponds to $E = \hbar\omega_0$ or $f = \frac{\omega_0}{\hbar}$ or $\lambda = \frac{\hbar c}{\omega_0}$
- By contrast a transition from $|+\rangle$ to $|-\rangle$ would require exactly $\hbar\omega_0$ of energy be <u>emitted</u>. (blue line)
- So we would expect a bright line of precisely the same color, $E = \hbar\omega_0$ or $f = \frac{\omega_0}{\hbar}$ or $\lambda = \frac{\hbar c}{\omega_0}$

<u>What about other QM systems?</u>

Other systems conceptually follow the same idea, but often have many more energy eigenstates. We can still use the same architecture to understand measurements, but if we start trying to do calculations we need to introduce a new representation



Energy Eigenvalues and the Position Representation

- Spin systems are really great b/c they introduce the quantum ideas with relatively low dimensional systems (2D for spin ½).
- However most QM systems have higher dimensionality b/c they have a large number of energy eigenstates.
- In fact some systems have an infinite number of energy eigenstates even though those eigenstates are discrete!

To handle these situations, we will need some new mathematical architecture and a new representation of our state vectors, <u>the wave function</u>.

To build this up, let's start with the

$$\hat{H}|E_i\rangle = E_i|E_i\rangle$$ energy eigenvalue eqn.

For now, we focus on 1D problems. The operator $\hat{H}$ is a description of the total kinetic & potential energy of a systems written as <u>operators</u>.

From classical mechanics, we know

$$H = \underbrace{T}_{\text{kinetic}} + \underbrace{V}_{\text{potential}}$$

In 1D, $H = \frac{p_x^2}{2m} + V(x)$

For QM, p_x & x become operators, so that,

$$\boxed{\hat{H} = \frac{\hat{p}_x^{\,2}}{2m} + V(\hat{x})}$$

Hamiltonian for 1D QM systems

In advanced texts (Sakurai, Shankar, etc.), they derive these operators, but we will take them as given,

$$\boxed{\hat{x} \doteq x \qquad \hat{p}_x = -i\hbar \frac{d}{dx}}$$

1D operators (position basis)

- It is not obvious yet, but by choosing this form of the operators, we have also chosen the "position representation" of the system. Also known as the position basis.
- Later we might work in the momentum basis where $\boxed{\hat{x} \doteq i\hbar \frac{d}{dp_x} \qquad \hat{p}_x = p_x}$ 1D operators (momentum basis)

With our choice of operators, we need a position representation for the state vectors $|\psi\rangle$ and $|E_i\rangle$.

Such a representation is called a wavefunction,

$$\boxed{|\psi\rangle \doteq \psi(x) \qquad |E_i\rangle \doteq \varphi_{E_i}(x)}$$

general state $\qquad\qquad$ energy eigenstate.

- A (spatial) wavefunction is a continuous representation of our state vectors in position space.
- What is nice about them is that they turn our energy eigenvalue equation $\hat{H}|E_i\rangle = E_i|E_i\rangle$ into a partial differential equation — something we have many tools to solve!

Derivation:

$$|E_i\rangle \doteq \varphi_{E_i}(x) \qquad \hat{x} \doteq x \qquad \hat{p}_x \doteq -i\hbar\frac{d}{dx}$$

with $\hat{H}|E_i\rangle = E_i|E_i\rangle$,

$$\hat{H}\varphi_{E_i}(x) = E_i\varphi_{E_i}(x)$$

$$\left(\frac{\hat{p}^2}{2m} + V(\hat{x})\right)\varphi_{E_i}(x) = E_i\varphi_{E_i}(x)$$

$$\left[\frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2 + V(x)\right]\varphi_{E_i}(x) = E_i\varphi_{E_i}(x)$$

$$\boxed{\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\varphi_{E_i}(x)=E_i\,\varphi_{E_i}(x)}$$

Differential Eq. for 1D QM systems.

Properties of Wavefunctions

the wave function is the position representation of our abstract state vectors $|\psi\rangle$. Formally,

$$\boxed{\psi(x)=\langle x|\psi\rangle}$$

This formal definition leads to various properties,

$\psi(x)$ is the position projection of $|\psi\rangle$ so

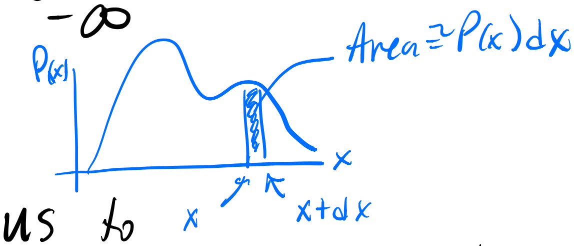
$$\boxed{P(x)=|\langle x|\psi\rangle|^2=|\psi(x)|^2}$$

That is the absolute square of the wave function is a continuous probability function, $P(x)$.

Because $P(X)$ is continuous from $[-\infty,\infty]$, the normalization condition is now,

$$\int_{-\infty}^{+\infty} \underbrace{P(x)}_{\text{probability density}}\,dx = \int_{-\infty}^{+\infty} |\psi(x)|^2 = 1$$

probability density $\Rightarrow$



This further allows us to define a probability over an interval say from x_1 to x_2,

$$\boxed{P_{x_1 < x < x_2} = \int_{x_1}^{x_2} |\psi(x)|^2 dx}$$

Probability of finding the system between x_1 & x_2

All of this relies on normalized wavefunctions,

$$\boxed{\langle\psi|\psi\rangle = 1 \implies \int_{-\infty}^{+\infty} \psi^*(x)\,\psi(x)\,dx = 1}$$

Finally, we can map all our ket notation to the position representation,

$$\boxed{\begin{array}{ll} |\psi\rangle \doteq \psi(x) & \langle\psi| \doteq \psi^*(x) \\ \langle\,|\,\rangle \doteq \int_{-\infty}^{\infty} dx & \hat{A} \doteq A(x) \end{array}}$$

What about other eigenstates?

— in spin 1/2, we could project a state vector onto another eigenstate (say $|+\rangle_x$) and find the probability we would measure a given eigenvalue (say, $+\hbar/2$ for S_x),

$$P_{S_x=+\hbar/2} = |{}_x\langle + | \psi \rangle|^2$$ for spin 1/2

— We can use the same concept for our position representation.

Assume φ_A is an eigenstate of some operator $\hat{A}$,

$$\hat{A}|\varphi_A\rangle = a|\varphi_A\rangle$$

if the system is in a state $|\psi\rangle$ then the probability we measure a is,

$$P_{\hat{A}=a} = |\langle \varphi_A | \psi \rangle|^2 \Leftarrow$$ just like with spin 1/2

All that changes is how we do this calculation in the position representation, probability of measuring a

$$\boxed{P_{A=a} = |\langle \varphi_A | \psi \rangle|^2 = \left| \int_{-\infty}^{\infty} \varphi_A^*(x)\, \psi(x)\, dx \right|^2}$$

the most common use for us will be for energy eigenstates $|E_n\rangle \doteq \varphi_n(x)$,

$$\boxed{P_{E_n} = |\langle E_n | \psi \rangle|^2 = \left| \int_{-\infty}^{+\infty} \varphi_n^*(x)\, \psi(x)\, dx \right|^2}$$

Expectation Values

- Let's finish our discussion of this formalism with average / expectation values.
- With Spin 1/2, we could make use of the linear algebra formulation,

1. $\langle S_z \rangle = \langle \psi | S_z | \psi \rangle = (a\ b)\, \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$

or the probability formulation,

2. $\langle S_z \rangle = P_{\hbar/2}\left(\frac{\hbar}{2}\right) + P_{-\hbar/2}\left(-\frac{\hbar}{2}\right)$

For our position representation, the approach is closer to method 2. In fact, for $\hat{x}$, it is very much a generalization to the continuous formulation,

$$\langle \hat{x} \rangle = \langle \psi | \hat{x} | \psi \rangle$$
$$= \int_{-\infty}^{+\infty} \psi^*(x) \, x \, \psi(x) \, dx$$
$$= \int_{-\infty}^{\infty} x \, |\psi(x)|^2 dx$$

$$\boxed{\langle \hat{x} \rangle = \int_{-\infty}^{\infty} x \, P(x) \, dx}$$

expectation of $\hat{x}$. True for all scalar operators.

All scalar operators (e.g., $\hat{x} \doteq x$) have this weighted average analogy.

For other operators (e.g., $\hat{p} \doteq -i\hbar \frac{d}{dx}$) the analogy is not applicable,

$$\langle \hat{p} \rangle = \langle \psi | \hat{p} | \psi \rangle$$
$$= \int_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{d}{dx}\right) \psi(x) \, dx$$

$$\boxed{\langle \hat{p} \rangle = -i\hbar \int_{-\infty}^{\infty} \psi^*(x) \frac{d\psi(x)}{dx}\, dx}$$

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expectation of $\hat{p}$

This is the best we can do without knowing $\psi(x)$.