Statistical Interpretation of ψ

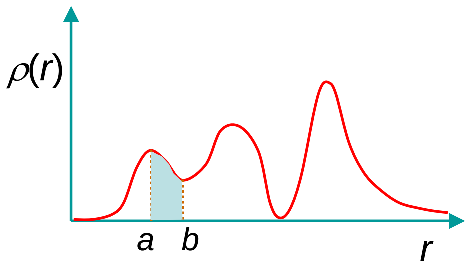
Born

The probability density of finding a particle at position *r*

$$\rho(r) = |\psi(r)|^2 = \psi^* \psi$$

The probability of finding the particle between a and b

$$P_{ab} = \int_a^b \rho(r)dr = \int_a^b |\psi(r)|^2 dr$$



N.B. The wave function may be complex, but a probability must be real and nonnegative.

The statistical interpretation implies indeterminacy: Until you measure the position you only know the probability of finding it at a particular position.

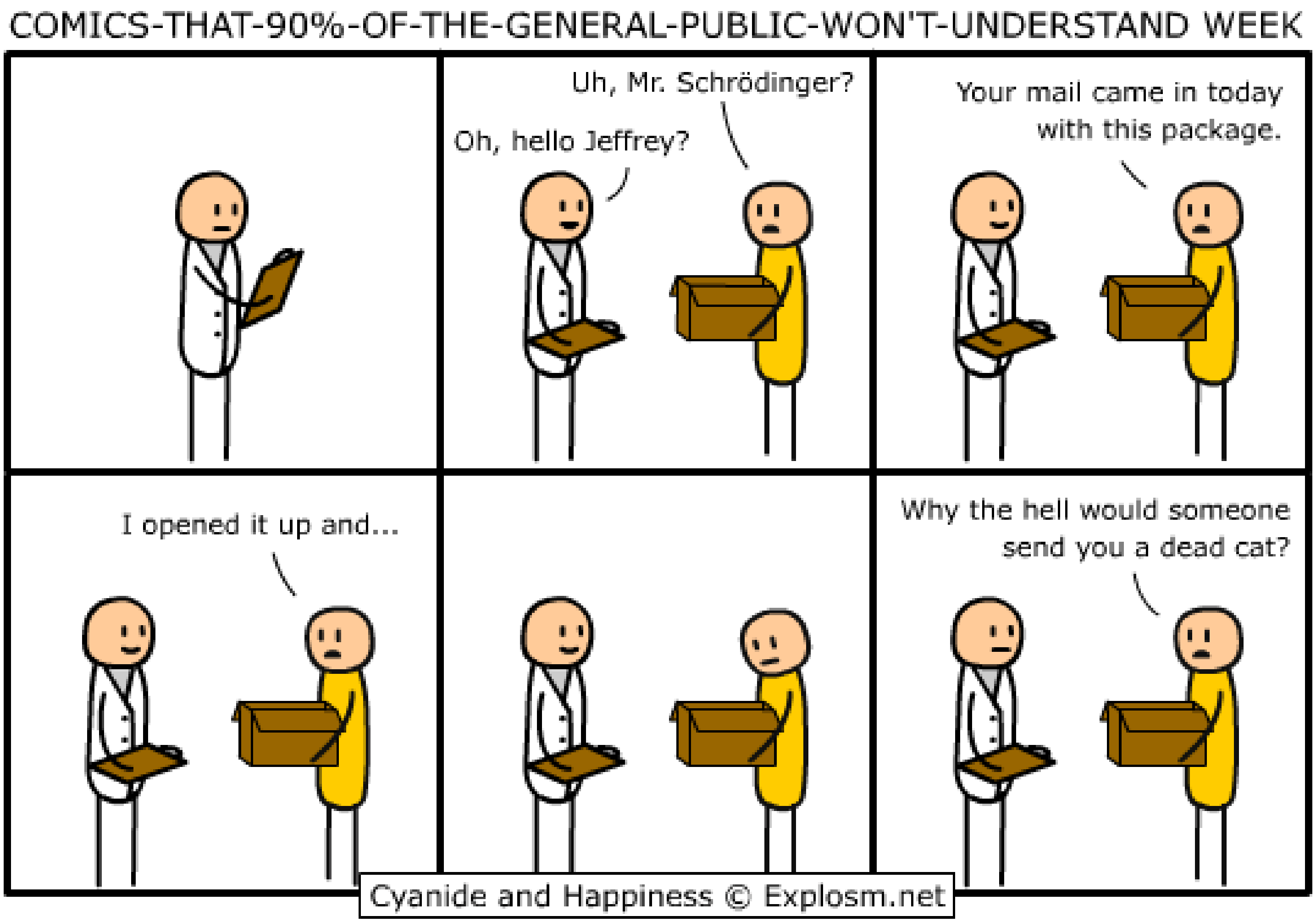
The Copenhagen interpretation says that the particle is not anywhere particular *until* we measure it. Measurement collapses the wave function.

Bohr

Measurements on a set of identical particles will generate different values (subject to the probability distribution $\psi\psi^*$.

The *average* position is the expectation value: $\langle r \rangle = \int_{-\infty}^{\infty} r|\psi(r)|^2 dr = \int_{-\infty}^{\infty} \psi^* r \psi \, dr$

Schrödinger's Cat



http://www.explosm.net/comics/949/

Schrödinger's Cat

Schrödinger

A closed box contains a small amount of radioactive material,
a Geiger counter hooked to a triggering device that can break
a vial of poison gas

…and a cat.

What is the state of the cat after a short time (during which one atom might decay)?

As long as the box is shut the cat's state is indeterminate:

$$\psi = \frac{1}{\sqrt{2}}\left(\psi_{\text{alive}} + \psi_{\text{dead}}\right)$$

Opening the box collapses the wave function to one state or the other.

Alternative (modern) explanation:

Triggering the Geiger counter is the measurement, *not* opening the box.

The Time Independence of Normalization

Schrödinger Equation $$i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial r^2}+V(r)\psi$$

In general, $\psi=\psi(r,t)$ is a function of both time and space.

By the statistical interpretation, ψ must be normalized $$\int_{-\infty}^{\infty}\rho(r)dr=\int_{-\infty}^{\infty}\left|\psi(r)\right|^2 dr=1$$

But is this true at all times?

$$\frac{\partial\left|\psi\right|^2}{\partial t}=\frac{\partial\left|\psi^*\psi\right|}{\partial t}=\psi^*\frac{\partial\psi}{\partial t}+\psi\frac{\partial\psi^*}{\partial t}$$

Substitute with S eqn and its complex conjugate

$$=\frac{i\hbar}{2m}\left(\psi^*\frac{\partial^2\psi}{\partial r^2}-\frac{\partial^2\psi^*}{\partial r^2}\psi\right)=\frac{\partial}{\partial r}\left[\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial r}-\frac{\partial\psi^*}{\partial r}\psi\right)\right]$$

$$\frac{d}{dt}\int_{-\infty}^{\infty}\left|\psi(r,t)\right|^2 dr=\int_{-\infty}^{\infty}\frac{\partial}{\partial t}\left|\psi(r,t)\right|^2 dr=\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial r}-\frac{\partial\psi^*}{\partial r}\psi\right)\Bigg|_{-\infty}^{\infty}=0$$

provided ψ goes to zero at infinity

Derivation of Momentum Operator

Since the position of an individual particle is indeterminate, so is its momentum.

We can only calculate the expectation values of position and momentum.

$$\langle x \rangle = \int_{-\infty}^{\infty} x \left| \psi(x,t) \right|^2 dx \qquad \langle p \rangle = m \frac{d\langle x \rangle}{dt} = m \int_{-\infty}^{\infty} x \frac{\partial}{\partial t} \left| \psi(x,t) \right|^2 dx$$

$$m \frac{d\langle x \rangle}{dt} = \frac{i\hbar}{2} \int x \frac{\partial}{\partial x} \left(\psi^* \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x} \psi \right) dx = -\frac{i\hbar}{2} \int \psi^* \left(\frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x} \psi \right) dx$$

integrate by parts

but since $\int \frac{\partial \psi^*}{\partial x} \psi dx = -\int \psi^* \frac{\partial \psi}{\partial x} dx + \psi \psi^* \Big|_{-\infty}^{\infty}$, $\quad m \frac{d\langle x \rangle}{dt} = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} dx$

$$\langle x \rangle = \int \psi^* (x) \psi \, dx \qquad \langle p \rangle = \int \psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \psi \, dx$$

Operators

The Postulates of Quantum Mechanics

1. The state of a system is fully described by a function $\psi(r,t)$ which is determined by a set of quantum numbers $|m,n,o,\ldots\rangle$. $\psi^*\psi \, d\tau$ is proportional to the probability of finding the particle(s) between r and $r+\delta r$ at specific time t.

2. For every observable property there exists a corresponding linear Hermitian operator whose mathematical properties can be used to infer the value of that observable.

3. (i) When ψ_m is an eigenfunction of the operator $\hat{\Omega}$ corresponding to the observable Ω, experimental measurement of Ω will always yield the same result, namely the eigenvalue ω_m.

   $$\hat{\Omega}\psi_m = \omega_m \psi_m$$

   (ii) If ψ_m is *not* an eigenfunction of $\hat{\Omega}$ experiments will yield a range of values with average

   $$\langle \Omega \rangle = \frac{\langle m|\Omega|m\rangle}{\langle m|m\rangle}$$

4. The evolution of a state function in time is given by where $\hat{H}$ is the Hamiltonian.

   $$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$$

5. ψ must be antisymmetric with respect to the exchange of fermions.

Pauli Exclusion Rule

Expansion of Wave Functions

Further to postulate 3(ii)

If the state function ψ_m is not an eigenfunction of the desired operator $\hat{\Omega}$, it can always be expanded as a linear combination of eigenfunctions ϕ_n:

$$\psi_m = \sum_n c_{mn}\phi_n \qquad \text{for} \qquad \hat{\Omega}\phi_n = \omega_n\phi_n$$

Then

$$\hat{\Omega}\psi_m = \sum_n c_{mn}\left(\hat{\Omega}\phi_n\right) = \sum_n c_{mn}\omega_n\phi_n$$

$$\langle m|\hat{\Omega}|m\rangle = \sum_k c^*_{mk}\sum_n c_{mn}\omega_n\langle k|n\rangle = \sum_n c^*_{mn}c_{mn}\omega_n$$

i.e. the expectation value of Ω is given by a weighted average of eigenvalues of $\hat{\Omega}$

A single measurement will not give $\langle\hat{\Omega}\rangle$. It will give one of the eigenvalues ω_n.

A large number of measurements will give all possible eigenvalues, weighted according to their individual probabilities $c^*_{mn}c_{mn} = |c_{mn}|^2$

Hermitian Operators – 1

Definition $$\int \psi_m^* \hat{\Omega} \psi_n \, d\tau = \int \left(\psi_n^* \hat{\Omega} \psi_m \right)^* d\tau = \int \left(\hat{\Omega} \psi_m \right)^* \psi_n \, d\tau$$

Or more succinctly $$\langle m | \hat{\Omega} | n \rangle = \langle n | \hat{\Omega} | m \rangle^*$$

Eigenvalues of Hermitian operators are real.

$$\hat{\Omega} | n \rangle = \omega_n | n \rangle$$

$$\langle n | \hat{\Omega} | n \rangle = \omega_n$$

But $$\langle n | \hat{\Omega} | n \rangle = \langle n | \hat{\Omega} | n \rangle^* = \omega_n^*$$

$$\omega_n = \omega_n^*$$

Hermitian Operators – 2

Eigenfunctions corresponding to different eigenvalues of Hermitian operators are orthogonal.

$$\text{If}\quad \langle m|\hat{\Omega}|n\rangle = \langle n|\hat{\Omega}|m\rangle^*$$

$$\text{Then}\quad \omega_n\langle \mathrm{m}|\mathrm{n}\rangle = \omega_m^*\langle \mathrm{n}|\mathrm{m}\rangle^* = \omega_m\langle \mathrm{m}|\mathrm{n}\rangle$$

$$\text{But if}\quad \omega_n \neq \omega_m,\quad \langle \mathrm{m}|\mathrm{n}\rangle = 0$$

The product of two Hermitian operators is Hermitian itself only if the two operators commute.

$$\langle n|\hat{A}\hat{B}|m\rangle = \langle n|\hat{A}|\hat{B}\psi_m\rangle = \langle \hat{B}\psi_m|\hat{A}|n\rangle^* = \langle \hat{B}\psi_m|\hat{A}\psi_n\rangle^* = \langle \hat{A}\psi_n|\hat{B}\psi_m\rangle$$

$$\langle m|\hat{B}\hat{A}|n\rangle^* = \langle m|\hat{B}|\hat{A}\psi_n\rangle^* = \langle \hat{A}\psi_n|\hat{B}|m\rangle = \langle \hat{A}\psi_n|\hat{B}\psi_m\rangle$$

$$\langle n|\hat{A}\hat{B}|m\rangle = \langle m|\hat{B}\hat{A}|n\rangle^*$$

$$= \langle m|\hat{A}\hat{B}|n\rangle^* \quad \text{only if} \quad \hat{A}\hat{B} = \hat{B}\hat{A}$$

Commutation of Operators

If observables A and B can be precisely determined simultaneously, then the operators $\hat{A}$ and $\hat{B}$ must commute.

If the state function is simultaneously an eigenfunction of $\hat{A}$ and $\hat{B}$, then $[\hat{A},\hat{B}]=0$

Proof $\quad [\hat{A},\hat{B}]|\ \rangle = \hat{A}\hat{B}|\ \rangle - \hat{B}\hat{A}|\ \rangle = b\hat{A}|\ \rangle - a\hat{B}|\ \rangle = ab|\ \rangle - ab|\ \rangle = 0$

If $\hat{A}$ and $\hat{B}$ commute, A and B can be determined simultaneously.

Proof $\quad$ Start with $\hat{A}|\ \rangle = a|\ \rangle$ and $[\hat{A},\hat{B}]=0$

$$\hat{A}\hat{B}|\ \rangle = \hat{B}\hat{A}|\ \rangle = a\hat{B}|\ \rangle,\ \text{i.e.}\ \hat{A}\left(\hat{B}|\ \rangle\right) = a\left(\hat{B}|\ \rangle\right)$$

Evidently $\left(\hat{B}|\ \rangle\right)$ is proportional to $|\ \rangle$ assuming $|\ \rangle$ is non-degenerate

Therefore $\hat{B}|\ \rangle = b|\ \rangle$

For degenerate wave functions it is necessary to prove that any linear combination is also an eigenfunction.

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

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

$$\hat{A}\left(c_m|m\rangle + c_n|n\rangle\right) = ac_m|m\rangle + ac_n|n\rangle = a\left(c_m|m\rangle + c_n|n\rangle\right)$$

and that the coefficients can always be chosen to produce mutually orthogonal linear combinations

The Uncertainty Principle

Take a pair of non-commuting operators $\hat{\mathrm{A}}$ and $\hat{\mathrm{B}}$ whose experimental observables are

$$\langle \mathrm{A} \rangle = \langle \;\; |\hat{\mathrm{A}}| \;\; \rangle, \quad \langle \mathrm{B} \rangle = \langle \;\; |\hat{\mathrm{B}}| \;\; \rangle$$

Define $\hat{\mathrm{C}} = -i\left[\hat{\mathrm{A}},\hat{\mathrm{B}}\right] \neq 0$ and error operators $\hat{\Delta}_{\mathrm{A}} = \hat{\mathrm{A}} - \langle \mathrm{A} \rangle, \quad \hat{\Delta}_{\mathrm{B}} = \hat{\mathrm{B}} - \langle \mathrm{B} \rangle$

Then
$$\left[\hat{\Delta}_{\mathrm{A}},\hat{\Delta}_{\mathrm{B}}\right] = \hat{\mathrm{A}}\hat{\mathrm{B}} - \langle \mathrm{A} \rangle \hat{\mathrm{B}} - \langle \mathrm{B} \rangle \hat{\mathrm{A}} + \langle \mathrm{A} \rangle \langle \mathrm{B} \rangle - \hat{\mathrm{B}}\hat{\mathrm{A}} + \langle \mathrm{B} \rangle \hat{\mathrm{A}} + \langle \mathrm{A} \rangle \hat{\mathrm{B}} - \langle \mathrm{A} \rangle \langle \mathrm{B} \rangle$$
$$= \left[\hat{\mathrm{A}},\hat{\mathrm{B}}\right] = i\hat{\mathrm{C}}$$

Let $I(\alpha) = \int \left| \left(\alpha \hat{\Delta}_{\mathrm{A}} - i \hat{\Delta}_{\mathrm{B}} \right) \psi \right|^2 d\tau \;\; \geq 0$ where α is an arbitrary real parameter

Then
$$I(\alpha) = \alpha^2 \left\langle \hat{\Delta}_{\mathrm{A}}^2 \right\rangle - \left\langle i\alpha\left(\hat{\Delta}_{\mathrm{A}}\hat{\Delta}_{\mathrm{B}} - \hat{\Delta}_{\mathrm{B}}\hat{\Delta}_{\mathrm{A}} \right) \right\rangle + \left\langle \hat{\Delta}_{\mathrm{B}}^2 \right\rangle = \alpha^2 \left\langle \hat{\Delta}_{\mathrm{A}}^2 \right\rangle - \alpha \langle \hat{\mathrm{C}} \rangle + \left\langle \hat{\Delta}_{\mathrm{B}}^2 \right\rangle$$

Rearranging,
$$\left\langle \hat{\Delta}_{\mathrm{A}}^2 \right\rangle \left[\alpha + \frac{1}{2} \frac{\langle \hat{\mathrm{C}} \rangle}{\left\langle \hat{\Delta}_{\mathrm{A}}^2 \right\rangle} \right]^2 - \frac{1}{4} \frac{\langle \hat{\mathrm{C}} \rangle^2}{\left\langle \hat{\Delta}_{\mathrm{A}}^2 \right\rangle} + \left\langle \hat{\Delta}_{\mathrm{B}}^2 \right\rangle \geq 0$$

which has a minimum at $\alpha = -\frac{1}{2} \frac{\langle \hat{\mathrm{C}} \rangle}{\left\langle \hat{\Delta}_{\mathrm{A}}^2 \right\rangle}$ for which $-\tfrac{1}{4} \langle \hat{\mathrm{C}} \rangle^2 + \left\langle \hat{\Delta}_{\mathrm{A}}^2 \right\rangle \left\langle \hat{\Delta}_{\mathrm{B}}^2 \right\rangle^2 \geq 0$

Taking square roots $\left\langle \hat{\Delta}_{\mathrm{A}}^2 \right\rangle^{1/2} \left\langle \hat{\Delta}_{\mathrm{B}}^2 \right\rangle^{1/2} \geq \tfrac{1}{2} \langle \hat{\mathrm{C}} \rangle$ or $\sigma_{\mathrm{A}} \sigma_{\mathrm{B}} \geq \frac{1}{2i} \left[\hat{\mathrm{A}},\hat{\mathrm{B}}\right]$