Linearity of Schrödinger's $\leftrightarrow$ Superposition Principle.

General Properties of the QM System's Hamiltonian $\mathcal{H}$.

1) On p. Sch. 20, in Schrodinger's Eq. $i\hbar\,\partial\psi/\partial t = \mathcal{H}\psi$, we have identified the (operator) $\mathcal{H}$ as the total system energy or "Hamiltonian", in an expectation value sense. This followed from the Correspondence Principle, in effect -- the imposition that for a QM "particle" of mass m, the momentum should be defined by: $\langle p\rangle = m\,(d/dt)\langle x\rangle$, and the particle should move according to Newton II : $\langle F\rangle = (d/dt)\langle p\rangle$... all in an expectation value sense. BUT, some general properties of $\mathcal{H}$ can be deduced just from the claim that Schrödinger's Eq. is of the form: $i\hbar\,\partial\psi/\partial t = \mathcal{H}\psi$, and that we require certain behavior from the QM wavefcn ψ.

For example, we can readily show that $\mathcal{H}$ must be a linear operator...

(A) $\mathcal{H}$ is a linear operator: $\mathcal{H}(c\psi) = c(\mathcal{H}\psi)$, for c = any cnst, indpt of $\mathbf{r}$ & t.

PROOF: Consider the time evolution of ψ...

$$\rightarrow d\psi = (\partial\psi/\partial t)\,dt = -\frac{i}{\hbar}(\mathcal{H}\psi)\,dt.$$

By the rules of differentiation, for c = cnst : $d(c\psi) = c(d\psi)$.

$$\text{so}/\!/ \quad -\frac{i}{\hbar}\mathcal{H}(c\psi)\,dt = -c\,\frac{i}{\hbar}(\mathcal{H}\psi)\,dt \Rightarrow \mathcal{H}(c\psi) = c(\mathcal{H}\psi). \quad \text{QED} \tag{2}$$

From this result, it is easy to see that a principle-of-superposition holds for solutions to Schrodinger's Eqtn (this is of critical importance to the theory!)...

(B) A superposition principle holds for solutions to Schrodinger's Eqtn: if ψ_1 & ψ_2 are separate solutions, then so is: $\Psi = c_1\psi_1 + c_2\psi_2$, c_1 & c_2 = arbitrary cnsts.

PROOF: Since, by (A), $\mathcal{H}$ is a linear operator, then...

$$\rightarrow \mathcal{H}\Psi = \mathcal{H}(c_1\psi_1) + \mathcal{H}(c_2\psi_2) = c_1(\mathcal{H}\psi_1) + c_2(\mathcal{H}\psi_2)$$

$$= c_1\left(i\hbar\frac{\partial\psi_1}{\partial t}\right) + c_2\left(i\hbar\frac{\partial\psi_2}{\partial t}\right) = i\hbar\frac{\partial}{\partial t}(c_1\psi_1 + c_2\psi_2) = i\hbar\frac{\partial\Psi}{\partial t}. \quad \text{QED} \tag{3}$$

In fact, linearity of $\mathcal{H}$ (per defn in Ⓐ) is true if and only if a superposition principle holds. Superposition is essential to us in constructing a theory capable of describing the diffraction of (matter) waves [Davisson-Germer].

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2) Another important property of $\mathcal{H}$ follows from imposing the notion that we want conservation of probability for the wavefcn ψ (a purely QM imposition), viz.

Ⓒ $\mathcal{H}$ is a Hermitian operator: $\int_\infty (\mathcal{H}\psi)^* \psi \, d^3r = \int_\infty \psi^* (\mathcal{H}\psi)\, d^3r$, for any wavefcn ψ that is a solution to Schrödinger's Eqtn: $i\hbar\,\partial\psi/\partial t = \mathcal{H}\psi$.

PROOF: Consider the total probability: $\mathcal{P} = \int_\infty \psi^*\psi\, d^3r$, of finding the m associated with ψ. Must have $\dot{\mathcal{P}} = 0$ for particle conservation (p. Sch. 8)...

so// $\rightarrow \dot{\mathcal{P}} = \int_\infty \underbrace{(\partial\psi^*/\partial t)}_{= +(i/\hbar)(\mathcal{H}\psi)^*} \psi\, d^3r + \int_\infty \psi^* \underbrace{(\partial\psi/\partial t)}_{= -(i/\hbar)(\mathcal{H}\psi)} d^3r = 0,$

or// $$\frac{i}{\hbar}\left[\int_\infty (\mathcal{H}\psi)^*\psi\, d^3r - \int_\infty \psi^*(\mathcal{H}\psi)\, d^3r\right] = 0. \quad \textbf{QED.} \qquad (4)$$

The significance of this relation is that it implies the expectation values of $\mathcal{H}$ must be real. This is essential for us if we are considering $\langle\mathcal{H}\rangle$ to represent the QM system's total energy, by definition real. We claim...

Ⓓ By virtue of Ⓒ, the expectation value $\langle\mathcal{H}\rangle$ is real: $\langle\mathcal{H}\rangle^* = \langle\mathcal{H}\rangle$.

PROOF: By definition, the expectation value: $\langle\mathcal{H}\rangle = \int_\infty \psi^*(\mathcal{H}\psi)\, d^3r$, so...

$\rightarrow \langle\mathcal{H}\rangle^* = \left[\int_\infty \psi^*(\mathcal{H}\psi)\, d^3r\right]^* = \int_\infty \psi(\mathcal{H}\psi)^* d^3r = \int_\infty (\mathcal{H}\psi)^*\psi\, d^3r$ ← use Eq. (4)

i.e.// $\langle\mathcal{H}\rangle^* = \int_\infty \psi^*(\mathcal{H}\psi)\, d^3r = \langle\mathcal{H}\rangle$, so// $\langle\mathcal{H}\rangle$ is real. **QED.** (5)

An intrinsic property of Hermitian operators, such as above $\mathcal{H}$, is they have real expectation values w.r.t. the distributions they define (here, ψ). As an exercise, you can show that $p_{op} = -i\hbar\frac{\partial}{\partial x}$ and $E_{op} = i\hbar\frac{\partial}{\partial t}$ are Hermitian.

Some features of Dirac's bra-ket notation.

ASIDE Dirac's bra-ket notation.

1. Dirac invented a shorthand notation to avoid writing down all the integrals $\int_\infty (\ \ ) d^3r$ we have been using. It is, for general fcns f & g...

$$\boxed{\langle f|g\rangle \equiv \int_\infty f^*(\mathbf{r},t)\, g(\mathbf{r},t)\, d^3r.} \tag{6}$$

It is called "bra" $\langle f|$ - "ket $|g\rangle$" notation, after the word "bracket"; mathematicians would call $\langle f|g\rangle$ an "inner-product"... we shall see why, later. Several properties of $\langle f|g\rangle$ that should be obvious are:

$$\left[\begin{array}{l}(1)\ \text{complex conjugate}:\ \langle f|g\rangle^* = \langle g|f\rangle. \\ (2)\ \text{distributive}:\ \langle f|g\pm h\rangle = \langle f|g\rangle \pm \langle f|h\rangle;\ \langle f\pm g|h\rangle = \langle f|h\rangle \pm \langle g|h\rangle. \\ (3)\ \text{associative}:\ \langle cf|g\rangle = c^*\langle f|g\rangle;\ \langle f|cg\rangle = c\langle f|g\rangle;\ c = \text{any cnst.}\end{array}\right] \tag{7}$$

2. We can define the expectation value of a general operator Q by means of:

$$\underline{\underline{\langle f|Q|g\rangle \equiv \langle f|Qg\rangle \equiv \int_\infty f^*(Qg)\, d^3r}}; \tag{8}$$

So// $\langle Qf|g\rangle = \int_\infty (Qf)^* g\, d^3r = \left[\int_\infty g^*(Qf)\, d^3r\right]^* = \langle g|Qf\rangle^*.$

The condition in Eq.(5) above that the system Hamiltonian $\mathcal{H}$ be Hermitian is:

$$\underline{\mathcal{H}\ \text{Hermitian} \Rightarrow \langle \mathcal{H}\psi|\psi\rangle = \langle \psi|\mathcal{H}\psi\rangle}\ \left(\overset{\text{i.e.}}{=} \int_\infty (\mathcal{H}\psi)^*\psi\, d^3r = \int_\infty \psi^*(\mathcal{H}\psi)\, d^3r\right). \tag{9}$$

3. We shall find use for the "adjoint operator". It is defined by...

→ For any operator Q, the adjoint operator $Q^\dagger$ obeys: $\underline{\langle f|Q^\dagger g\rangle = \langle Qf|g\rangle}$. (10)

This operation resembles complex conjugation, but it is not the same. See this from:

$$\rightarrow \langle g|Qf\rangle^* = \langle Qf|g\rangle = \langle f|Q^\dagger g\rangle. \tag{11}$$

With the Dirac notation in hand, we can now discover some further features of the QM Hamiltonian $\mathcal{H}$ in a succinct fashion.

Connection: Hermitian Operators are Self-Adjoint.

3) We now generalize the notion of Hermitianity in Eq. (4) to the following...

(E) A Hermitian operator $\mathcal{H}$ is "self-adjoint", i.e. $\underline{\mathcal{H}^\dagger = \mathcal{H}}$. For acceptable wavefcns ψ_1 & ψ_2 (generally $\psi_2 \neq \psi_1$): $\underline{\langle\psi_1|\mathcal{H}^\dagger\psi_2\rangle = \langle\mathcal{H}\psi_1|\psi_2\rangle = \langle\psi_1|\mathcal{H}\psi_2\rangle}$.

PROOF: ψ_1 & ψ_2 acceptable wavefcns $\Rightarrow$ so is $\underline{\Psi = c_1\psi_1 + c_2\psi_2}$, w/ c_1 & c_2 arbitrary cnsts. Then $\mathcal{H}$ Hermitian $\Rightarrow \langle\mathcal{H}\Psi|\Psi\rangle = \langle\Psi|\mathcal{H}\Psi\rangle$, by Eq. (9) above. Also, $\mathcal{H}$ Hermitian $\Rightarrow \langle\mathcal{H}\psi_i|\psi_i\rangle = \langle\psi_i|\mathcal{H}\psi_i\rangle$, for $i = 1$ & 2 separately. Now...

$$\langle\mathcal{H}\Psi|\Psi\rangle = \langle\mathcal{H}(c_1\psi_1 + c_2\psi_2)|c_1\psi_1 + c_2\psi_2\rangle \leftarrow \text{use Eq. (7) above}$$

$$= c_1^*\langle\mathcal{H}\psi_1|c_1\psi_1 + c_2\psi_2\rangle + c_2^*\langle\mathcal{H}\psi_2|c_1\psi_1 + c_2\psi_2\rangle$$

i.e.//

$$\rightarrow \langle\mathcal{H}\Psi|\Psi\rangle = |c_1|^2\langle\psi_1|\mathcal{H}\psi_1\rangle + |c_2|^2\langle\psi_2|\mathcal{H}\psi_2\rangle +$$

$$+ c_1^*c_2\langle\mathcal{H}\psi_1|\psi_2\rangle + c_1c_2^*\langle\mathcal{H}\psi_2|\psi_1\rangle. \quad (12A)$$

In a similar fashion, we find...

$$\rightarrow \langle\Psi|\mathcal{H}\Psi\rangle = |c_1|^2\langle\psi_1|\mathcal{H}\psi_1\rangle + |c_2|^2\langle\psi_2|\mathcal{H}\psi_2\rangle +$$

$$+ c_1c_2^*\langle\psi_2|\mathcal{H}\psi_1\rangle + c_1^*c_2\langle\psi_1|\mathcal{H}\psi_2\rangle. \quad (12B)$$

Then $\langle\mathcal{H}\Psi|\Psi\rangle = \langle\Psi|\mathcal{H}\Psi\rangle$ identifies the RHS of (12A) & (12B), with result:

$$\rightarrow c_1^*c_2\langle\mathcal{H}\psi_1|\psi_2\rangle + c_1c_2^*\underbrace{\langle\mathcal{H}\psi_2|\psi_1\rangle}_{=\langle\psi_1|\mathcal{H}\psi_2\rangle^*} = c_1^*c_2\langle\psi_1|\mathcal{H}\psi_2\rangle + c_1c_2^*\underbrace{\langle\psi_2|\mathcal{H}\psi_1\rangle}_{=\langle\mathcal{H}\psi_1|\psi_2\rangle^*}$$

$$\underline{c_1^*c_2\Delta = c_1c_2^*\Delta^*}, \text{ w/ } \underline{\Delta = \langle\mathcal{H}\psi_1|\psi_2\rangle - \langle\psi_1|\mathcal{H}|\psi_2\rangle}. \quad (13)$$

Eq. (13) must hold for *any* choice of the arbitrary cnsts c_1 & c_2. So, we take...

$$\left[\begin{array}{l} c_1 = 1,\ c_2 = 1 \Rightarrow \Delta = (+)\Delta^* \\ c_1 = 1,\ c_2 = i \Rightarrow \Delta = (-)\Delta^* \end{array}\right\| \text{ to avoid contradiction, must have } \Delta \equiv 0. \quad (14)$$

$$\text{BUT, } \Delta \equiv 0 \Longrightarrow \langle\mathcal{H}\psi_1|\psi_2\rangle = \langle\psi_1|\mathcal{H}^\dagger\psi_2\rangle = \langle\psi_1|\mathcal{H}\psi_2\rangle. \text{ so, have } \mathcal{H}^\dagger = \mathcal{H}. \quad \text{QED} \quad (15)$$

General Hermitianity condition. Notion of Eigenfcns & Eigen-energies.

We can now adopt a definition of Hermitianity for a general operator Q...

$$\boxed{\begin{array}{l} Q \text{ is Hermitian iff } Q \text{ is self-adjoint}: Q^\dagger = Q, \\ \text{i.e.}/\!/ \ \langle f|Q^\dagger g\rangle = \langle Qf|g\rangle = \langle f|Qg\rangle,\ f\ \&\ g \text{ "acceptable" fcns.} \end{array}} \tag{16}$$

Note that g can be __different__ from f; we don't need $f = \psi = g$, as in Eq. (9).

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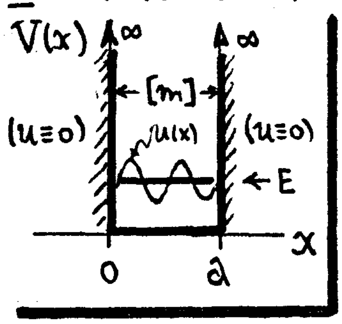
4) Often we are interested in solving the time-independent Schrödinger Eq., i.e.

$$\rightarrow \underline{\mathcal{H}u(\mathbf{r}) = Eu(\mathbf{r})};\ ^{w/\!/}\ \mathcal{H} = -(\hbar^2/2m)\nabla^2 + V(\mathbf{r}),\ ^{\&/\!/}\ E = \langle u|\mathcal{H}u\rangle = \begin{array}{l}\text{time indpt}\\ \text{cnst energy}\end{array} \tag{17}$$

(from Eq. (55) of p. Sch. 21). This PDE for fcns $u(\mathbf{r})$, with particular boundary conditions imposed -- e.g. $u \to 0$ as $r = |\mathbf{r}| \to \infty$, $u \to$ finite as $r \to 0$ -- will generally have a denumerably infinite __set__ of fcns $\{u_n(\mathbf{r})\}$ as solution. The label "n" is __discrete__; conveniently $n = 0, 1, 2, \ldots, \infty$. To each of the discrete "__eigenfunctions__" $u_n(\mathbf{r})$, there will correspond a discrete "__eigen-energy__" E_n.

$\boxed{\text{EXAMPLE}}$ __Particle in a 1D Box.__

__1.__ Box (containment) potential is: $V(x) = \begin{cases} 0, & \text{over } 0 < x < a \ (m \text{ free to move}); \\ \infty, & \text{for } x \leq 0\ \&\ x \geq a \ (m \text{ denied access}). \end{cases}$



$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]u(x) = Eu(x) \Rightarrow \tag{18}$$

$$-(\hbar^2/2m)\frac{d^2u}{dx^2} = Eu,\ ^{n/\!/}\ \underline{\underline{\frac{d^2u}{dx^2} + k^2u = 0}}\ \begin{cases}\text{over } 0 \leq x \leq a, \\ ^{w/\!/}\ u(0) = u(a) = 0; \\ \text{here: } k^2 = \frac{2mE}{\hbar^2}. \end{cases}$$

The boundary conditions are that m's wavefcn $u(x)$ __vanishes__ at all $x \leq 0$ & $x \geq a$... this is the claim that m will never be found outside the box (that __can__ happen when V is finite for $x \leq 0$ & $x \geq a$). So the diff$^{\underline{l}}$ eqtn in (18) need only be solved in $0 \leq x \leq a$; everywhere else, $u \equiv 0$.

__2.__ $u'' + k^2u = 0$ in (18) is a SHO (simple harmonic oscillator) eqtn, [next page]

Example of m-in-a-box. Quantization via boundary conditions.

with solutions: $u(x) \propto \sin kx, \cos kx$. The boundary condition $u(0)=0$ rules out the $\cos kx$ solutions, so: $u(x) = A \sin kx$, w/ A = cnst. Next, the boundary condition $u(a)=0$ generates the eigen-solution...

$$\left.\begin{array}{l} u(a) = A \sin ka = 0 \Rightarrow ka = n\pi, \text{ w/ } n = 1,2,3,\ldots,\infty; \\ \text{i.e.// } k = k_n = n\pi/a, \text{ or// } \underline{E_n = \hbar^2 k_n^2/2m = n^2\left(\frac{\pi^2\hbar^2}{2ma^2}\right)}; \leftarrow \text{eigen-energies} \\ \text{and// } \underline{u_n(x) = A_n \sin k_n x = A_n \sin\left(n\pi \frac{x}{a}\right)}. \leftarrow \text{eigenfunctions.} \end{array}\right\} \quad (19)$$

The above example illustrates the claim that the boundary conditions force the QM system to show its discrete (eigen) solutions. We claim in general:

Solutions to $\mathcal{H}u = Eu$ are generally a set of "eigenfcns" $\{u_n(\mathbf{r})\}$, with corresponding "eigenenergies" $\{E_n\}$, with n = discrete index. The particular form of the set $\{u_n(\mathbf{r}), E_n\}$ is determined by the boundary conditions imposed on the QM system (i.e. on the $\{u_n\}$). One speaks of solving the "eigenvalue equation": $\mathcal{H}u_n(\mathbf{r}) = E_n u_n(\mathbf{r})$.

(20)

We can now prove a ~profound result regarding these eigen-solutions, viz.

(F) Eigenfunctions of $\mathcal{H}$ corresponding to different eigen-energies are "orthogonal": i.e. for $E_m \neq E_n$, we have $\langle u_m | u_n \rangle = 0$.

PROOF This proposition follows from the Hermitianity of $\mathcal{H}$. Start from $\mathcal{H}u_m = E_m u_m$ & $\mathcal{H}u_n = E_n u_n$, $m \neq n$ (distinct eigen-solutions). Form:

$$\underbrace{\langle u_m | \mathcal{H} u_n \rangle} = \langle u_m | E_n u_n \rangle = \underline{E_n \langle u_m | u_n \rangle}, \text{ since } E_n = \text{real cnst};$$

$$= \langle \mathcal{H} u_m | u_n \rangle = \underline{E_m \langle u_m | u_n \rangle}, \text{ by Hermitianity of } \mathcal{H}, \text{ Eq. (16)};$$

∴ Subtract these eqtns $\Rightarrow \underline{(E_m - E_n)\langle u_m | u_n \rangle} = 0$; so// when $E_m \neq E_n$, $\langle u_m | u_n \rangle = 0$. **QED** (21)

Nature of orthogonality. Case of degeneracy.

REMARKS On proposition (E).

1. In detail, the "orthogonality" relation for QM eigenstates $m \neq n$ reads...

$$\rightarrow \langle u_m | u_n \rangle = \int_\infty u_m^*(\mathbf{r})\, u_n(\mathbf{r})\, d^3r = 0, \quad m \neq n. \tag{22}$$

Since the normalization choice is (almost) always $\int_\infty |u|^2 d^3r = 1$, then...

$$\rightarrow \langle u_m | u_n \rangle = \int_\infty u_m^*(\mathbf{r})\, u_n(\mathbf{r})\, d^3r = \delta_{mn}, \text{ Kronecker symbol } \begin{cases} \delta_{mn} = 1, & m = n; \\ \delta_{mn} = 0, & m \neq n. \end{cases} \tag{23}$$

The condition $\langle u_m | u_n \rangle = \delta_{mn}$ is called "orthonormality" for the eigenfcns.

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2. The term "orthogonal" comes from vector analysis...

$\mathbf{A} = (\cdots A_i \cdots)$ & $\mathbf{B} = (\cdots B_i \cdots)$ are orthogonal iff: $\sum_i A_i^* B_i = 0$, i = discrete index.

When $i \rightarrow$ an ∞ (continuous) # of values, the discrete components $A_i \rightarrow A(i)$, a continuous fcn of i, $\sum_i \rightarrow \int di$, and orthogonality $\Rightarrow \int_\infty A^*(i) B(i)\, di = 0$. (24)

So, we can speak of the fcn $A(i)$ being "perpendicular" to the fcn $B(i)$.

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3. The proof of (E) depends on assuming the eigenfcns u_m & u_n, $m \neq n$, correspond to different eigen-energies E_m & $E_n \neq E_m$. However, it can happen that several distinct u's correspond to the same eigen-energy, i.e. u_m & $u_n \neq u_m$ both have energy E_m (i.e. $\mathcal{H} u_m = E_m u_m$ & $\mathcal{H} u_n = E_m u_n$). This situation is called an "energy degeneracy", and the general nomenclature is...

If N independent eigenfcns u_i, $1 \leq i \leq N$, correspond to the same eigenenergy E (i.e. $\mathcal{H} u_i = E u_i$), the state E is called "N-fold degenerate." (25)

The members of the degenerate set $\{u_i\}$ need not be orthogonal [above Eq(21) does not restrict them]. BUT, it is possible to construct linear combinations of the u_i which are orthogonal. This is done by the so-called Schmidt orthogonalization procedure... left as an exercise for the attentive student.