Commutator theorem (W1L2)

If $[\hat{A}, \hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ have a set of nontrivial common eigenstates. ($\exists$ a set of common eigenstates)

there exists

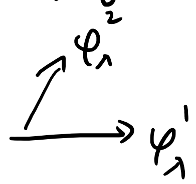
- Complete set of commuting observables (C.S.C.O.) – Liboff
- Hamiltonian — a very important operator
- Hydrogen atom as an example — Ch 4 Griffiths (excluding spin)

Complete set of commuting observables (C.S.C.O.)

Definition An exhaustive set of commuting operators whose common eigenstates are uniquely determined by the eigenvalues of these operators

Earlier, we learnt that some operators have degenerate eigenvalues λ.
Then, given λ, we cannot completely determine the eigenstate ψ.

Eg.



Any $\psi = \alpha_1 \varphi_\lambda^1 + \alpha_2 \varphi_\lambda^2$ is an eigenstate with eigenvalue λ. $(\alpha_1, \alpha_2 \in \mathbb{C})$

Let $\hat{A}$ be an operator with degenerate eigenvalue a.
Let $\hat{B}$ be another operator that commutes with $\hat{A}$.
Then $\exists$ eigenstates $\{\varphi_{a,b}\}$ that are common to $\hat{A}$ and $\hat{B}$.

$\{\varphi_{a,b}\}$ is a subset (v= to) OR of the set of degenerate eigenstates of $\hat{A}$ with eigenvalue a.

Eg $\hat{H} = \hat{P}^2$. $\hat{P}$ $a = E = \frac{\hbar^2 k^2}{2m}$

Eg. $\hat{H} = \frac{\hat{p}^2}{2m}$, $\hat{p}$

$a = E = \frac{\hbar^2 k^2}{2m}$

$b = \hbar k$

$\{\varphi_{a,b}\}$ is a subset of $\{\varphi_a\}$.

$\hookrightarrow \varphi_{\frac{\hbar^2k^2}{2m}, \hbar k}$ or $\varphi_{\frac{\hbar^2k^2}{2m}, -\hbar k}$

$\uparrow$ e^{ikx} $\qquad$ $\uparrow$ e^{-ikx}

Q) Does $a = \frac{\hbar^2 k^2}{2m}$ and $b = \hbar k$ uniquely determine the common eigenstates of $\hat{H} = \frac{\hat{p}^2}{2m}$ and $\hat{p}$?

("uniquely determined" means there is only one linearly independent eigenstate; dimension of the space of $\{\varphi_{a,b}\}$ = 1)

A) Yes $\{\varphi_{a,b}\} = \mu e^{ikx}$

Likewise, $a = \frac{\hbar^2 k^2}{2m}$ and $b = -\hbar k$ uniquely determines

$$\{\varphi_{a,b}\} = \mu e^{-ikx}$$

Therefore $\hat{H} = \frac{\hat{p}^2}{2m}$ and $\hat{p}$ are a C.S.C.O.

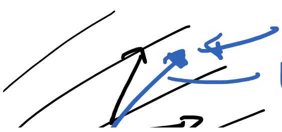
If $\{\varphi_{a,b}\}$ still has dimension >1,

and if $\hat{C}$ commutes with both $\hat{A}$ and $\hat{B}$,

Then we can find eigenstates $\{\varphi_{a,b,c}\} \in \{\varphi_{a,b}\}$ that is common to $\hat{A}$, $\hat{B}$ and $\hat{C}$.

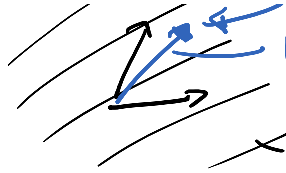
If this $\{\varphi_{a,b,c}\}$ has dimension 1, ie. the state is uniquely determined by a, b, c, $\{\hat{A}, \hat{B}, \hat{C}\}$ is a C.S.C.O.

Eg



labelled by a, b

If $[\hat{A}, \hat{B}] = 0$, $\hat{B}$ can "pick up" a subset for its eigen space. $\hat{B}\psi = b\psi$



labelled by a, b

for its eigenspace. $\hat{B}\psi = b\psi$

all vectors in this plane are eigenstates of $\hat{A}$ with eigenvalue a.

Good quantum numbers

Definition: An independent set of parameters that can be simultaneously specified (and which are maximally informative)

Eg. Above $\{a, b, c\}$ are good quantum numbers.

Hamiltonian

Why is the Hamiltonian so important?

1) The eigenstates $|\psi\rangle$ of the time-independent Hamiltonian are the stationary states; every expectation value associated with $|\psi\rangle$ is independent of time.

2) The Hamiltonian governs the dynamics of the system.

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

Eigenstates:

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi.$$

$$|\psi(t)\rangle = e^{-iEt/\hbar} |\psi(0)\rangle \quad \text{(stationary states)}$$

Expectation value

c.c.

$$\langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle e^{-iEt/\hbar} \psi(0) | \hat{A} | e^{-iEt/\hbar} \psi(0) \rangle$$

$$= \langle \psi(0) | \underbrace{e^{iEt/\hbar}}_{\text{scalar}} \hat{A} \underbrace{e^{-iEt/\hbar}}_{\text{scalar}} | \psi(0) \rangle$$

$$= \langle \psi(0) | \hat{A} | \psi(0) \rangle.$$

Hydrogen atom - 1 proton, 1 electron.

$\oplus$ e

To find the stationary states, we need the Hamiltonian

$$\hat{H} = \frac{\hat{p}_1^2}{2m_p} + \frac{\hat{p}_2^2}{2m_e} + V(|\vec{r}_1 - \vec{r}_2|),$$

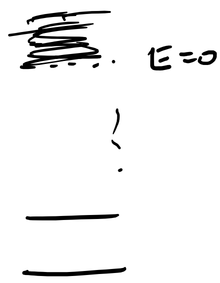
$\uparrow$ KE proton $\quad$ $\uparrow$ KE e^-

$$V(|\vec{r}_1 - \vec{r}_2|) \equiv V(r) = -\frac{e^2}{r} \quad \text{(CGS units)}$$

Coulomb

(later: more terms, but small changes)

<u>Only</u> Hamiltonian of an atom, a molecule or a solid that can be solved exactly.



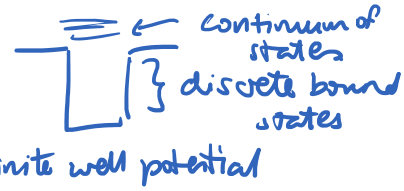
Eigenenergies of bound states (E<0)

are $E_n = -\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2}$, $n = 1, 2, 3, \ldots$

$\uparrow$ 13.593 eV

(E_n is quantized)

c.f.



$$\mu = \frac{m_e m_p}{m_e + m_p} \quad \text{reduced mass}$$

Note: $\frac{m_e}{m_p} \sim \frac{1}{1800}$

$$\mu = \frac{m_e m_p}{m_e + m_p} = \frac{m_e}{\frac{m_e}{m_p} + 1} \simeq m_e\left(1 - \underbrace{\frac{m_e}{m_p}}_{\sim \frac{1}{1800}}\right) \simeq m_e$$

$$E_n \approx -\frac{m_e e^4}{2\hbar^2}\frac{1}{n^2}, \quad n = 1, 2, 3, \ldots$$

$\leftarrow$ 13.6 eV (1 Rydberg)

$\approx$ ~0.05% error in $E_{n=1}$ if we take $\mu \approx m_e$.

i.e. treating the centre of mass of the system as the proton.

$\Rightarrow$ This approximation is known as the <u>Born-Oppenheimer approximation</u>

<u>Definition</u> The approximation that the electron motion and the nuclear motion can be separated.

Eg. where this fails — proton tunneling in enzymes.

See slides.

States of the hydrogen atom (ignoring spin) can be labelled as $\psi_{n\ell m}$ or $|n\ell m\rangle$

$n = 1, 2, 3, \ldots$
$\ell = 0, 1, \ldots, (n-1)$
$m = -\ell, -\ell+1, \ldots, \ell$.

For the hydrogen atom, ignoring spin,

$\{H, \hat{L}^2, L_z\}$ form a C.S.C.O.

$$H|n\ell m\rangle = \frac{1}{2m_e}\left(-\hbar^2 \frac{1}{r}\frac{d^2}{dr^2} r + V(r)\right)|n\ell m\rangle + \underbrace{\frac{\hbar^2 \ell(\ell+1)}{2m_e r^2}}|n\ell m\rangle$$

(Born-Oppenheimer approx)

for $\ell > 0$, repulsive term.

Q) Do stationary states depend on time?

A) Yes $|\psi(t)\rangle = e^{-iEt/\hbar}|\psi(0)\rangle$.

Consider $|\phi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$

stationary states

E_1 $E_2 \neq E_1$

$$|\phi(t)\rangle = c_1 e^{-iE_1t/\hbar}|\psi_1(0)\rangle + c_2 e^{-iE_2t/\hbar}|\psi_2(0)\rangle$$

Q) Can we find an eigenstate of $\hat{H}$ that is not an eigenstate of $\hat{L}^2$? Hydrogen atom: $[\hat{H}, \hat{L}^2] = 0$

A) Yes, eg. $|\psi\rangle = c_1|\overset{n}{3}\,\overset{\ell}{1}\,\overset{m}{0}\rangle + c_2|\overset{n}{3}\,\overset{\ell}{2}\,\overset{m}{0}\rangle$

where $|c_1|^2 + |c_2|^2 = 1$ and c_1 and c_2 are non-zero.

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and c_1 and c_2 are non-zero.

$$H|\psi\rangle = E_n|\psi\rangle, \quad n = 3$$

$$\hat{L}^2|\psi\rangle = c_1 \hbar^2 \underset{l_1=1}{l_1}(l_1+1)|3\ 1\ 0\rangle + c_2 \hbar^2 \underset{l_2=2}{l_2}(l_2+1)|3\ 2\ 0\rangle$$

$$\neq \lambda|\psi\rangle.$$