Quantum Chemistry by Levine

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1 Chapter 7 Theorems of Quantum Mechanics

7.1
(a) True
(b) True
(c) False

7.2
c is real number

7.3
(a) $< m|n >= \int f_m^* f_n d\tau$
$< n|m > * = (\int f_n^* f_m d\tau)^* = \int f_m^* f_n d\tau$
(b) $< f|B|g >= \int f^* B g d\tau$
$< cf|B|g >= \int c^* f^* B g d\tau = c^* \int f^* B g d\tau = c^* < f|B|g >$

7.4
unity operator

7.5
if B is Hermitian
$< f|B|g >= \int f^* Bg =< g|B|f >^* = (\int g^* Bf) * = \int (Bf)^* g =< Bf|g >$

7.6
Given $\hat{A}$ is Hermitian:
(a) $< f|A|g >=< g|A|f >^*$
$< f|cA|g >= c < f|A|g >$
$< g|cA|f >^* = (\int g * cAf)^* = c^* \int (Af)^* g = c^* < g|A|f >$
so the equation only holds when c is real number

(b) given $< f|A|g >$ and $< f|B|g >$
$< f|A+B|g >= \int f^*(A+B)g = \int f^*Ag + \int f^*Bg$

7.7
(a)verify that $\frac{d^2}{dx^2}$ is Hermitian
$\int f * \frac{d^2}{dx^2} g = f^* \frac{dg}{dx}|_{-\inf}^{\inf} - \int \frac{df^*}{dx} \frac{dg}{dx}$
$= - \int \frac{df^*}{dx} \frac{dg}{dx} = \int \frac{d^2 f}{dx^2} g$
from **7.6**
$-\frac{\hbar^2}{2m}$ is real number
(b)$< T_x >= \int \Psi^*(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2})\Psi$
$= -\frac{\hbar^2}{2m}(\Psi \frac{d\Psi}{dx}|_{-\inf}^{\inf} - \int \frac{d\Psi^*}{dx} \frac{d\Psi}{dx})$
$= \frac{\hbar^2}{2m} \int \frac{d\Psi^*}{dx} \frac{d\Psi}{dx}$
(c)$< T >=< T_x > + < T_y > + < T_z >$
(d)Given each component nonnegative, $< T >>= 0$

7.8
(a) $\int f^* \frac{dg}{dx} = f^* g|_{-\inf}^{\inf} - \int \frac{df^*}{dx} g$
there is an extra negative sign
not Hermitian
(b) $\int f^* \frac{idg}{dx} = \int \frac{df^*}{dx} g$
so $i\frac{d}{dx}$ is Hermitian
(c) $\frac{d^2}{dx^2}$ is Hermitian
(d) $i\frac{d^2}{dx^2}$ is not Hermitian

7.9
representing a physical quantity means is Hermitian operator
(a) false
(b) false
(c) true
(d) true

7.11
Given $< A^2 >= \int \Psi^* A^2 \Psi = \int \Psi^* A(A\Psi)$
then $f = \Psi, g = A\Psi$ for $< f|A|g >$
for Hermitian A:
$= \int (A\Psi) * (A\Psi) = \int |A\Psi|^2$

7.12
(a) given A and B are Hermitian

$\int f^*ABg = \int(Af) * Bg = \int(BAf) * g$
if AB is also Hermitian:
$\int f^*ABg = \int(ABf) * g$
So we need $AB = BA$, which means A, B commute
(b)$\int f^*(AB + BA)g = \int f^*ABg + \int f^*BAg$
(c) both x and p_x are Hermitian
but they do not commute due to uncertainty
So xp_x not Hermitian
(d) $\frac{1}{2}(xp_x + p_x x)$ is Hermitian

7.13
(a)$\int f^* \frac{dg}{dx} = f^*g|_{-\inf}^{\inf} - \int \frac{df^*}{dx}g = -< g|\frac{d}{dx}|f >$
(b)$\int f^*(AB - BA)g = \int f^*ABg - \int f^*BAg = \int(Af)^*Bg - \int(Bf)^*Ag = \int(BAf)^*g - \int(ABf)^*g =< g|BA|f >^* - < g|AB|f >^* = - < g|(AB - BA)|f >^*$
So $AB - BA$ is anti-Hermitian

7.15
(a) the eigenfunctions are orthogonal
given $\hat{H}\Psi = E\Psi$ at stationary wave state:
$\hat{H}\Psi = (n + \frac{1}{2})hv\Psi$
$< \Psi|\hat{H}|\Psi >= (n + \frac{1}{2})hv\delta_{mn}$
(b) the eigenfunctions are orthogonal
given $\hat{H}\Psi = E\Psi$ at stationary wave state:
$\hat{H}\Psi = \frac{n^2h^2}{8ml^2}\Psi$
$< \Psi|\hat{H}|\Psi >= \frac{n^2h^2}{8ml^2}\delta_{mn}$

7.16
$< \Psi_2|H|f(x) >=< f(x)|H|\Psi_2 >^*$
where $H\Psi_2 = (2 + \frac{1}{2})hv\Psi$
the above equation becomes:
$= \frac{5}{2}hv < f(x)|\Psi_2 >^*$

7.19
given the simulation equation:
$f = \Sigma < g_i|f > g_i$
given $g_i = \sqrt{\frac{2}{l}}sin(\frac{n\pi x}{l})$
so $< g_i|f >= \int_0^{l/2} g_i(-1)dx + \int_{l/2}^{l} g_i dx$

7.20

(a) F.
like Y_0^0
(b) F.
only a complete set of eigenfunctions.
(c) T.
L_z and H commute.

7.21

if m is odd, $\prod^m = \prod$
if m is even, $\prod^m = \hat{1}$

7.22

(a) s has the wave function like a sphere as even function
(b) $2p_x$ is odd function.
(c) $2s + 2p_x$ are linear combination of $\hat{H}$ under the same energy level
but $2s$ is even parity and $2p_x$ is odd parity, so they are not under the same eigenvalue of $\prod$

7.23

if $m! = n$ ψ_m and ψ_n are orthogonal
$\int \psi_m^* \prod \psi_n = 0$
if $m = n$
since vibration wave function is either an odd or even function
$\prod$ has eigenvalue as $+1 or - 1$

7.24

(a) $< 2s|x|2p_x >$ since $\hat{x}2p_x$ is even, so when it integrate with 2s, the result is an even function
integral not zero
(b) $< 2s|x^2|2p_x >$ since both are odd function, integral is zero
(c) $< 2p_y|x|2p_x >$ is an odd function, integral is zero

7.25

same as calculation of $\prod$
given $\hat{R}f = rf$
$\hat{R}^n f = r^n f = f$
then $r^n = 1$

7.26

prove that $\prod$ is both linear and Hermitian
(a)$\prod(f(x)+g(x)) = f(-x)+g(-x) = \prod f(x) + \prod g(x)$
(b)$< f(x)|\prod|g(x) >= \int f(x)^* \prod g(x) = \int f(-x)^* \prod g(-x) d(-x) = \int f(-x)^* g(x) d(-x) = \int (\prod f(x))^* g(x) dx$

7.27
intuitively, $\prod f = +1f$ so f is even function
$\prod g = -1g$ so g is odd function
then $\int f * g = 0$ is an odd function

7.28
$< v_1|x|v_2 >$ where v_1 and v_2 are either odd or even according to quantum number
so if v_1 and v_2 both odd, or both even, integral is zero
otherwise, not zero

7.29
(a) do not need to calculate, can just imagine in 3-d cartisan coordinate.
$r = \sqrt{x^2+y^2+z^2}$ does not change
$\theta = \pi - \theta$
$\phi = \phi + \pi$
(b)$\prod e^{im\phi} = e^{im\phi+\pi} = e^{im\phi}e^{im\pi} = (-1)^m e^{im\phi}$

7.30
$\int\int \dots (\int f(q_1, q_2, \dots, q_m) dq_1 dq_2 \dots dq_k) \dots dq_m = 0$

7.32
the prob of getting $L_z = \hbar$ is $|\frac{1}{\sqrt{6}}|^2 + |\frac{1}{\sqrt{3}}|^2 = \frac{1}{2}$
the prob of getting $L_z = 0$ is $|\frac{1}{\sqrt{3}}|^2 = \frac{1}{3}$
so the average $< L_z >= \frac{1}{2}\hbar$

7.33
The p_0 and p_1 state has $L^2 = 2\hbar^2$
The d_0 has $L^2 = 2 * 3\hbar^2$
$< L^2 >= (\frac{1}{6} + \frac{1}{2}) * 2\hbar + \frac{1}{3} * 6\hbar = \frac{10}{3}\hbar$

7.34
for both p state:

$E_1 = -\frac{e^2}{4\pi\epsilon_0 8a}$
for d state:
$E_2 = -\frac{e^2}{4\pi\epsilon_0 18a}$
So $< E >= (\frac{1}{6} + \frac{1}{2})E_1 + \frac{1}{3}E_2$

7.35
Given $L^2 = 2\hbar$
So $l = 1$
then $m = -1, 0, 1$
So the measurement of L_x is $-\hbar, 0, \hbar$

7.36
the first term is $n = 1$ stationary state
the second term is $n = 2$ stationary state
So $\frac{1}{4}E_{n=1} + \frac{3}{4}E_{n=2} = \frac{13h^2}{32ml^2}$

7.37
Given the wave function $g_i = \sqrt{\frac{2}{l}} sin(\frac{n\pi x}{l})$
any non-stationary can be written as its combination
So each index, i.e. possibility is:
$|c_i^2| = \int g_i^* \Psi$

7.38
Shown as above:
$|c_i^2| = \int g_i^* \Psi$

7.42
(a)1
(b)0
(c)1
(d)0

7.43
$\int_{-\infty}^{\infty} \delta(x-a)dx = \int_{-\infty}^{\infty} \delta(x)^2 dx$
$= \delta(0) \int_{-\infty}^{\infty} \delta(x)dx = \inf$

7.44
$\int_0^{\infty} f(x)\delta(x)$ is not the same as $\int_{-\infty}^{\infty} f(x)\delta(x)$

$\int_0^\infty f(x)\delta(x) = f(x)H(x)|_0^\infty - \int_0^\infty f'(x)H(x)dx$
$= f(\infty) - \frac{1}{2}f(0) - f(x)|_0^\infty = \frac{1}{2}f(0)$

7.49

(a) $\begin{pmatrix} 6 & 2 \\ -12 & -12 \end{pmatrix}$

(b) $\begin{pmatrix} 2 & 4 \\ 8 & -8 \end{pmatrix}$

(c) $\begin{pmatrix} 3 & 0 \\ 4 & 1 \end{pmatrix}$

(d) $\begin{pmatrix} 6 & 3 \\ 0 & -9 \end{pmatrix}$

(e) $\begin{pmatrix} -2 & 5 \\ -16 & -19 \end{pmatrix}$

7.50

$CD =$
$\begin{pmatrix} 5i & 10 & 5 \\ 0 & 0 & 0 \\ -i & -2 & -1 \end{pmatrix}$
$DC =$
$\begin{pmatrix} 5i - 1 \end{pmatrix}$

7.51

all the unity orthogonal vector

7.52

$< f_i|P|f_j >=< f_i|sC|f_j >= c < f_i|C|f_j >$
i.e. $P_{ij} = sC_{ij}$

7.53

Given $< f_i|A|f_j >= a_i\delta_{ij}$
Given f_i is a complete orthogonal set
Let $Af_j = \Sigma_k c_k f_k$
$< f_i|A|f_j >= \Sigma_k c_k < f_i|f_k >= \Sigma_k c_k \delta_{ik} = c_i$
So:
$Af_j = \Sigma_k < f_k|A|f_j > f_k = \Sigma_k a_i \delta_{ij} f_k = a_i f_j$
So a_i is the eigenvalue.

7.63

Given Hermitian:
$< f_i|A|f_j >=< Af_i|f_j >$
$\int f_i^* Af_j = \int(Af_i) * f_j$
So A has eigenvalue a has to be real

7.64

(a)F.
It can be a linear combination of time term prod stationary wave function
(b) T.
(c) F.
needs to be a stationary function
(d) F.
These eigenfunctions need to have the same eigenvalue
(e) F.
The measurement has to be a eigenvalue.
(f) T.
$|\Psi|^2$ is independent of time, which is what stationary means
(g) F.
They can have one common eigenfunction, but not a common complete set of eigenfunction.
(h) F.
They can have the same eigenfunction under different eigenvalue
(i) F.
It does not ensure they are non-degenerate
(j) F.
(k) T.
(l) F.
It does not have a fixed unit.
(m) F.
$< \Psi|A|\Psi >$ is real does not ensure Ψ is real
(n) T.
(o) T
(p) F.
It holds for all well-behaved functions as long as B is Hermitian
(q) T.
(r) F.
only for stationary states