PROBLEM SET SOLUTIONS

Chapter 3, *Quantum Chemistry*, 5th Ed., Levine

3.23Which of the following functions are eigenfunctions of d^2/dx^2?

To be an eigenfunction of d^2/dx^2, the function must satisfy the following relationship, where k is a constant:

$$d^2/dx^2 \ \psi = k\ \psi.$$

(A) $d^2/dx^2\ (e^x) = d/dx\,(e^x) = e^x$. Yes it is an eigenfunction with eigenvalue = 1.

(B) $d^2/dx^2\ (x^2) = d/dx\ (2x) = 2$. No

3.27 Evaluate the commutators:

(A) $[x, p_x]\ \psi = x\ p_x\ \psi - p_x\ (x\ \psi) = x\ (-i\underline{h}\ d/dx)\ \psi - (-i\underline{h}\ d/dx)\ (x\ \psi)$

$$= (-i\underline{h})\ (x\ d\psi/dx - (1 \cdot \psi + x\ d\psi/dx)) = (i\underline{h})\ \psi$$

$$[x, p_x] = i\underline{h}$$

(B) $[x, p_x^2]\ \psi = x\ p_x^2\ \psi - p_x^2\ (x\ \psi) = x\ (-\underline{h}^2\ d^2/dx^2)\ \psi - (-\underline{h}^2\ d^2/dx^2)\ (x\ \psi)$

$$= (-\underline{h}^2)\ (x\ d^2\psi/dx^2 - d/dx\ (x\ d\psi/dx + \psi \cdot 1)$$

$$= (-\underline{h})^2\ (x\ d^2\psi/dx^2 - (d\psi/dx + x\ d^2\psi/dx^2 + d\psi/dx))$$

$$= (-\underline{h}^2)\ (-2\ d\psi/dx) = 2\ \underline{h}^2\ d\psi/dx$$

$$[x, p_x^2] = 2\ \underline{h}^2\ d/dx$$

3.36 The terms *state* and *energy* level are not synonymous in quantum mechanics. For the particle in a cubic box, consider the energy range $E < 15\ h^2/(8ma^2)$.

(A) How many states lie in this range?
(B) How many energy levels lie in this range?

For a particle in a cubic box of length a on a side,

$$E = (n_x^2 + n_y^2 + n_z^2)\ h^2/(8ma^2).$$

Rearranging gives

$$E\ (8ma^2)/\ h^2 = (n_x^2 + n_y^2 + n_z^2)$$

Rephrase the question: How many states lie in the range $(n_x^2 + n_y^2 + n_z^2) < 15$?

n_x, n_y, n_z,	1,1,1	2,1,1	1,2,1	1,1,2	1,2,2	2,1,2	2,2,1	1,1,3	1,3,1	3,1,1
$E(8ma^2)/\ h^2$	3	6	6	6	9	9	9	11	11	11

n_x, n_y, n_z,	2,2,2	2,1,3	1,2,3	3,2,1	2,3,1	1,3,2	3,1,2	2,2,3	2,3,2	3,2,2
$E(8ma^2)/\ h^2$	12	14	14	14	14	14	14	17	17	17

n_x, n_y, n_z,	1,1,4	4,1,1	1,4,1	1,3,3	3,1,3	3,3,1
$E(8ma^2)/\ h^2$	18	18	18	19	19	19

TOTAL: 17 states and 6 energy levels lie within this range.

For example, one level has 6 states with $E\ (8ma^2)/\ h^2 = 14$

3.39 For the particle confined to a box with dimensions a, b, and c, find the following values for the state with quantum numbers n_x, n_y, n_z. (NOTE: $\langle x \rangle$ & $\langle p_x \rangle$ are done in Example, p. 56)

For the particle in a 3D box,

$E = (n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2)\ (h/8m)$;

$\psi\ (x,y,z) = \sqrt{(8/(abc))}\ \sin (n_x\pi x/a)\ \sin (n_y\pi y/b)\ \sin (n_z\pi z/c) = f(x)\ g(y)\ h(z);\ d\tau = dx\ dy\ dz$

$\int_0^a f^*(x)\ f(x)\ dx = 1 = \int_0^b g^*(y)\ g(y)\ dy = \int_0^c h^*(z)\ h(z)\ dz$

(A) $\langle x \rangle = \int \psi^* x \psi\ d\tau = \int_0^a f^*(x)\ x\ f(x)\ dx\ \int_0^b g^*(y)\ g(y)\ dy\ \int_0^c h^*(z)\ h(z)\ dz$

$= \int_0^a x\ (2/a)\ \sin^2 (n_x\pi x/a)\ dx = a/2$ (For ground state, $n_x = 1$)

(B) $\langle y \rangle$ & $\langle z \rangle$ have exactly the same mathematical form as $\langle x \rangle$ so $\langle y \rangle = b/2$ & $z = c/2$.

(C) $\langle p_x \rangle = = \int \psi^*\ p_x\ \psi\ d\tau = \int_0^a f^*(x)\ p_x\ f(x)\ dx\ \int_0^b g^*(y)\ g(y)\ dy\ \int_0^c h^*(z)\ h(z)\ dz$

$= \int_0^a f^*(x)\ p_x\ f(x)\ dx = -i\underline{h} \int_0^a f^*(x)\ df(x)/dx\ dx = -i\underline{h} \int_0^a f^*(x)\ df(x) = -i\underline{h}\ f^2\ (x)/2\ \Big|_0^a$

$= -(i\underline{h}/2)\ (\sin n_x\pi - \sin 0) = 0$

(D) $\langle x^2 \rangle = \int \psi^* x^2 \psi\ d\tau = \int_0^a f^*(x)\ x^2\ f(x)\ dx\ \int_0^b g^*(y)\ g(y)\ dy\ \int_0^c h^*(z)\ h(z)\ dz$

$= (2/a) \int_0^a x^2\ \sin^2 (n_x\pi x/a)\ dx$

$= (2/a)\ (x^3/6 - (x^2a/(4n_x\pi) - a^3/(8n_x^2\pi^2))\ \sin (2n_x\pi x/a) - xa^2/(4n_x^2\pi^2)\ \cos (2n_x\pi x/a)\ \Big|_0^a)$ (A4)

$= (2/a)\ (a^3/6 - (a^3/(4n_x\pi) - a^3/(8n_x^2\pi^2))\ \sin (2n_x\pi) - a^3/(4n_x^2\pi^2)\ \cos (2n_x\pi)) - 0 - 0)$

$= (2/a)\ (a^3/6 - (a^3/(4n_x\pi) - a^3/(8n_x^2\pi^2)) \cdot 0 - a^3/(4n_x^2\pi^2) \cdot 1)$

$= (2/a)\ (a^3/6 - a^3/(4n_x^2\pi^2))$

$= a^2/3 - a^2/(2n_x^2\pi^2) = (1 - 3/(2n_x^2\pi^2))\ a^2/3$

Does $\langle x^2 \rangle = \langle x \rangle^2$? No because $\langle x \rangle = a/2$ & $\langle x \rangle^2 = a^2/4$.

Does $\langle xy \rangle = \langle x \rangle \langle y \rangle$?

Yes, because $\langle xy \rangle = (8/(abc))\ (a^2/4)\ (b^2/4)\ (c^2/4) = ab/4 = (a/2)\ (b/2) = \langle x \rangle \langle y \rangle$.