PROBLEM SET SOLUTIONS

Chapter 7, *Quantum Chemistry*, 5th Ed., Levine

7.6 Which of the following operators are Hermitian?

For a Hermitian operator, $<A> = <A>^*$, or

$<f|A|g> = <g|A|f>^*$. Assume f & g are well-behaved at limits of integration.

Integration by parts: $\int u\, v' = uv - \int v\, u'$

(a) $<f|d/dx|g> = \int f^* (dg/dx)\, d\tau = f^*g\, | - \int g\, (df/dx)^*\, d\tau$

$= - <g|d/dx|f>^*$ NO

(b) $<f|i\, d/dx|g> = \int f^* (i\, dg/dx)\, d\tau = i\, f^*g\, | + \int g\, (i\, df/dx)^* d\tau$

$= <g|i\, d/dx|f>^*$ YES

(c) $<f|4\, d^2/dx^2|g> = \int f^* (4\, d^2g/dx^2)\, d\tau$; $[u = f,\ v' = d^2g/dx^2,$

$v = dg/dx,\ u' = df/dx]$

$= 4\, f^*dg/dx\, | - 4 \int (dg/dx)\, (df/dx)^* d\tau$; $[u = df^*/dx,\ v' = dg/dx,$

$v = g,\ u' = d^2f^*/dx^2]$

$= -4\, (df^*/dx)g\, | + 4 \int g\, d^2f^*/dx^2\, d\tau$

$= <g|4\, d^2/dx^2|f>$ YES

(d) $<f|i\, d^2/dx^2|g> = \int f^* (i\, d^2g/dx^2)\, d\tau$; $[u = f,\ v' = d^2g/dx^2,$

$v = dg/dx,\ u' = df/dx]$

$= i\, f^*dg/dx\, | - i \int (dg/dx)\, (df/dx)^* d\tau$; $[u = df^*/dx,\ v' = dg/dx,$

$v = g,\ u' = d^2f^*/dx^2]$

$= -i\, (df^*/dx)g\, | + i \int g\, d^2f^*/dx^2\, d\tau = -\int g\, (i\, d^2f/dx^2)^*\, d\tau$

$= - \langle g \mid i\, d^2/dx^2 \mid f \rangle^*$ NO

7.9 Which of the following operators meet all the requirements for a quantum mechancal operator that is to represent a physical quantity?

Operator must be linear & Hermitian

(a) SQRT = $(\quad)^{1/2}$ NOT LINEAR

(b) d/dx LINEAR, NOT HERMITIAN

(c) d^2/dx^2 LINEAR & HERMITIAN

(d) i d/dx LINEAR & HERMITIAN

7.17 For the hydrogenlike atom,

$$V = -Z (e')^2 (x^2 + y^2 + z^2)^{-1/2}$$

And the potential energy is an even function of the coordinates.

(a) What is the parity of ψ_{2s}?

$\psi_{2s} = 1/[4(2\pi)^{1/2}] (Z/a)^{3/2} (2 - Zr/a) e^{-Zr/(2a)}$

$\Pi (x) = -x, \Pi (y) = -y, \Pi (z) = -z,$

$\Pi (r) = r, \Pi (\theta) = \pi - \theta, \Pi (\phi) = \pi + \phi$

$\Pi \psi_{2s} = 1/[4(2\pi)^{1/2}] (Z/a)^{3/2} \Pi \{(2 - Zr/a) e^{-Zr/(2a)}\}$

$= 1/[4(2\pi)^{1/2}] (Z/a)^{3/2}(2 - Zr/a) e^{-Zr/(2a)}$

$= \psi_{2s}$ EVEN

(b) What is the parity of ψ_{2px}?

$\psi_{2px} = 1/[4(2\pi)^{1/2}] (Z/a)^{5/2} r e^{-Zr/(2a)} \sin \theta \cos \phi$

$\Pi \psi_{2px} = 1/[4(2\pi)^{1/2}] (Z/a)^{5/2} \Pi \{ r e^{-Zr/(2a)} \sin \theta \cos \phi\}$

$= 1/[4(2\pi)^{1/2}] (Z/a)^{5/2} r e^{-Zr/(2a)} \sin (\pi - \theta) \cos (\pi + \phi)$

$\sin (\pi - \theta) = \sin \pi \cos \theta - \cos \pi \sin \theta = 0 - (-1) \sin \theta = \sin \theta$

$\cos (\pi + \phi) = \cos \pi \cos \phi - \sin \pi \sin \phi = - \cos \phi - 0 = - \cos \phi$

$\Pi \psi_{2px} = 1/[4(2\pi)^{1/2}] (Z/a)^{5/2} r e^{-Zr/(2a)} \sin \theta (- \cos \phi)$

$= - \psi_{2px}$ ODD

(c) $\psi_{2s} + \psi_{2px} = 1/[4(2\pi)^{1/2}] (Z/a)^{3/2} e^{-Zr/(2a)}$

$x\{2 - Zr/a + rZ/a \sin \theta \cos \phi\}$

$H (\psi_{2s} + \psi_{2px}) = H \psi_{2s} + H \psi_{2px} = E_2\psi_{2s} + E_2\psi_{2px}$

$= E_2 (\psi_{2s} + \psi_{2px})$ Yes, eigenfunction

$\Pi (\psi_{2s} + \psi_{2px}) = \Pi \psi_{2s} + \Pi \psi_{2px} = \psi_{2s} - \psi_{2px}$

neither even nor odd, no parity

We showed previously that when V is even, the wavefunctions of a system with non-degenergate energy levels must be of definite parity. Here, the n=2 level is degenerate, hence no definite parity.

7.26 For a hydrogen atom in a p state, the possible outcomes of a measurement of L_z are $-\underline{h}$, 0, and $\underline{h}$. For each of the following wavefunctions give the probabilities of each of these three results.

$L_z\ \psi_{2pm} = m\ \underline{h}\ \psi_{2pm}$; for a p state, m = -1, 0, 1

Write ψ as a linear combination of eigenfunctions of L_z. The probability of getting a particular value when the property is measured is the square of the corresponding coefficient.

Probability of measuring property i = $|c_i|^2$

$1 = \Sigma\ |c_i|^2$

(a) $\psi_{2pz} = \psi_{2p0} = c_1\ \psi_{2p-1} + c_2\ \psi_{2p0} + c_3\ \psi_{2p1}$

$c_1 = c_3 = 0.\ c_2 = 1$

Probability of measuring $\underline{h}$ is square of coefficient of ψ_{2p1} : 0

Probability of measuring $-\underline{h}$ is square of coefficient of ψ_{2p-1} : 0

Probability of measuring 0 is square of coefficient of ψ_{2p0} : 1.

Note: $c_1^2 = c_2^2 + c_3^2 = 1 = 0 + 1 + 0$

(b) $\psi_{2py} = -i/\surd 2\ \psi_{2p1} + i/\surd 2\ \psi_{2p-1}$

Probability of measuring $\underline{h}$ is square of coefficient of ψ_{2p1} :

$|-i/\surd 2|^2 = (-i/\surd 2)\ (-i/\surd 2)^* = 1/2$

Probability of measuring $-\underline{h}$ is square of coefficient of ψ_{2p-1} :

$|i/\surd 2|^2 = (i/\surd 2)\ (i/\surd 2)^* = 1/2$

Probability of measuring 0 is square of coefficient of ψ_{2p0} : 0

Note: $c_1^2 = c_2^2 + c_3^2 = 1 = 1/2 + 1/2 + 0$

(c) $\psi_{2p1} = c_1\ \psi_{2p-1} + c_2\ \psi_{2p0} + c_3\ \psi_{2p1}$

$c_1 = 0 = c_2,\ c_3 = 1\ \&\ c_1^2 = c_2^2 + c_3^2 = 1$

Probability of measuring $\underline{h}$ is square of coefficient of ψ_{2p1} : 1

Probability of measuring $-\underline{h}$ is square of coefficient of ψ_{2p-1} : 0

Probability of measuring 0 is square of coefficient of ψ_{2p0} : 0.

7.27 (3rd Ed.; like example, p. 185, 5th Ed.) Consider a particle in a nonstationary state in a one-dimensional box of length L with infinite walls. Suppose at time t_0 its state function is the parabolic function

$$\psi(t_0) = N\,x\,(L - x) \qquad 0 \leq x \leq L$$

where N is the normalization constant. If at time t_0 we were to make a measurement of the particle's energy, what would be the possible outcomes of the measurement & what would be the probability for each such outcome?

For a 1D particle in a box, $H = -\underline{h}^2/(2m)\, d^2/dx^2$;

$V = 0\ (0 \leq x \leq L)$, $V = \infty\ (x < 0, x > L)$

The complete set of eigenfunctions of the H operator for a 1D particle in a box are the ψ_n

$\psi_n = (2/L)^{1/2} \sin(n\pi x/L) \qquad 0 \leq x \leq L$

$\psi_n = 0 \qquad x < 0, x > L$

Since $\psi(t_0)$ is an arbitrary function, we can expand it in terms of the eigenfunctions of H:

$\psi(t_0) = \Sigma\, c_n\, \psi_n$, where $c_n = \langle\psi(t_0)\,|\psi_n\rangle$.

The probability of obtaining the eigenfunction E_n when making a measurement is $|c_n|^2$. Find c_n:

$c_n = \langle\psi(t_0)\,|\psi_n\rangle$

$= \int_0^L \psi(t_0)\, \psi_n\, dx = \int_0^L N\, x\, (L - x)\, (2/L)^{1/2} \sin(n\pi x/L)\, dx$

$= N\, (2/L)^{1/2}\, \{L \int_0^L x \sin(n\pi x/L)\, dx - \int_0^L x^2 \sin(n\pi x/L)\, dx\}$

$= N\, (2/L)^{1/2}\, [L/(n\pi)]^3\, \{-(n\pi)^2 \cos(n\pi)$

$\qquad + [(n\pi)^2 - 2] \cos(n\pi) + 2\}$

$= N\, (2/L)^{1/2}\, [L/(n\pi)]^3\, 2\, (1 - \cos(n\pi))$

If n = 1, 3, 5…, cos (nπ) = -1. If n = 2, 4, 6…, cos (nπ) = 1.

$c_n = N\, 2^{3/2}\, L^{5/2}/\, (n\pi)^3\, (1 - (-1)) = N\, 2^{5/2}\, L^{5/2}/\, (n\pi)^3$,

n = 1, 3, 5…,

$c_n = N\, 2^{3/2}\, L^{5/2}/\, (n\pi)^3\, (1 - 1) = 0$, n = 2, 4, 6…,

Probability of measuring E_n is $|c_n|^2$.

$|c_n|^2 = 0$, n = 2, 4, 6…,

$\psi(t_0) = N\, x\, (L - x)$, $0 \le x \le L$, is odd function

$\psi_n = (2/L)^{1/2} \sin (n\pi x/L)$, $0 \le x \le L$, is even & so doesn't contribute to $\psi(t_0)$

$|c_n|^2 = N^2\, 2^5\, L^5/\, (n\pi)^6$, n = 1, 3, 5…,

To evaluate c_n need normalization constant N:

$<\psi(t_0)\, |\, \psi(t_0)> = \int_0^L N^2\, x^2\, (L - x)^2\, dx$

$= \int_0^L N^2\, x^2\, (L^2 - L\, x + x^2)\, dx$

$= N^2\, (L^2 \int_0^L x^2\, dx - 2L \int_0^L x^3\, dx + \int_0^L x^4\, dx)$

$= N^2\, \{L^2\, (x^3/3)\, |_0^L - 2L\, (x^4/4)\, |_0^L + (x^5/5)\, |_0^L\}$

$= N^2\, \{L^5/3 - 2\, L^5/4 + L^5/5\}$

$= N^2\, L^5\{1/3 - 2/4 + 1/5\} = N^2\, L^5/30 = 1$, if N = SQRT $(30/\, L^5)$

$|c_n|^2 = (30/\, L^5)\, 2^5\, L^5/\, (n\pi)^6$, n = 1, 3, 5…,

$= (30)\, (32)/(n\pi)^6$

$|c_1|^2 = (30)\, (32)/(\pi)^6 = 0.99855$

$|c_3|^2 = (30)\, (32)/(2\pi)^6 = 0.001370$

$|c_5|^2 = (30)\, (32)/(4\pi)^6 = 0.000064$

Most of the contribution comes from ψ_1 because it losely resembles $\psi(t_0)$--See Fig. 7.3, p. 186, 5th Ed.