PROBLEMS

CHEMISTRY 163A

18. If ψ_1 and ψ_2 are eigenfunctions of $\hat{H}$ with different eigenvalues $E_1 \neq E_2$, prove that ψ_1 and ψ_2 are orthogonal.

19. McQ 5-18.

20. (a) If x_{tp} is the classical turning point for a harmonic oscillator, set up the integral which represents the probability that an oscillator with ψ_v will be found at classically forbidden values of x.

*(b) Calculate the probability that a harmonic oscillator in the first excited vibrational state (v = 1) is found outside of the classical turning points.

For this state:

$$\psi_1 = \left(\frac{\alpha}{4\pi}\right)^{1/4} 2\alpha^{1/2} x \exp\left(-\frac{\alpha x^2}{2}\right) \text{ and } E = \frac{3}{2} h\nu_0$$

use $\int_u^\infty z^2 \exp(-z^2)dz = \frac{\pi^{1/2}}{4}\operatorname{erfc}(u) + \frac{u}{2}\exp(-u^2)$

where $\frac{2}{\pi^{1/2}}\int_u^\infty \exp(-z^2)dz = \operatorname{erfc}(u)$

is the complementary error function

and $\operatorname{erfc}(3^{1/2}) = 0.0142$.

21. For the second eigenfunction of the harmonic oscillator:

$$\psi_2 = B\exp(-\xi^2/2)(4\xi^2 - 2) \qquad \xi = \alpha^{1/2} x$$

(a) Evaluate the normalization constant *B*.

(b) Show that ψ_2 satisfies the Schrödinger equation for a harmonic oscillator. What is the energy eigenvalue?

*(c) Using the energy eigenvalue (and thus λ in eq 5-68) from part b, show that if $a_0 = -2$, a_2 follows from the recursion relationship (5-80).

22. (a) Evaluate $\langle$K.E.$\rangle$ for the harmonic oscillator with v = 2. (NOTE: You may use results for $\frac{d^2\psi_2}{dx^2}$ correctly obtained in prob. 21(b).)

$$\psi_2 = \left(\frac{\alpha}{64\pi}\right)^{1/4} \exp(-\xi^2/2)(4\xi^2 - 2)$$

*(b) Evaluate $\langle$P.E.$\rangle$ for this state of the harmonic oscillator.

*(c) Are your (correct) results surprising?