Chemistry 344

Problem Set 9

A review

Due Oct. 30, 2002

---

1. A hydrogen-like wavefunction is shown below with r in units of a_0.

$$\Psi(r,\theta,\phi) = (1/81)(2/\pi)^{1/2} Z^{3/2} (6\text{-}Zr)\, Zr \exp[-Zr/3] \cos\theta$$

(a) **Determine the values** of the quantum numbers n, ℓ, m for Ψ by inspection. Give the reason for your answers.

n = ℓ = m =

(b) **Determine the most probable value** of r for an electron in the state specified by the $\Psi(r,\theta,\phi)$ given above, when Z = 1.

(c) **Generate** from $\Psi(r,\theta,\phi)$ given above, **another eigenfunction** having the same values of n and ℓ but with the magnetic quantum number equal to m+1.

The Laplacian $\nabla^2 = \{\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2\}$ when transformed to spherical coordinates becomes $\nabla^2 = \{(1/r^2)\{\partial/\partial r\,(r^2\partial/\partial r) - L^2\}$

(d) **Write** down the hamiltonian for a hydrogen-like atom (only the internal motion of the electron relative to the nucleus).

(e) **Determine** whether it is possible to determine simultaneously the energy of a hydrogen atom and its angular momentum.

2. A linear harmonic oscillator is placed in an electric field of strength $\mathcal{E}$. If the oscillating mass has an associated charge -e, the Hamiltonian becomes

$$\mathcal{H} = -(\hbar^2/2\mu)\, d^2/dx^2 + (k/2)x^2 + e\mathcal{E}x.$$

μ is the reduced mass of the oscillator, and k is the Hooke's law force constant. **Solve this problem** by using the coordinate transformation $x = x' - e\mathcal{E}/k$. Of course, $d^2/dx'^2 = d^2/dx^2$ in this case, so the transformation is trivial. Assume that you also know the eigenvalues of

$$\mathcal{H}(x)\Psi(x) = E\Psi(x),$$

that is, $\{-(\hbar^2/2\mu)\, d^2/dx^2 + (k/2)x^2\}\Psi(x) = (n+\frac{1}{2})\hbar\omega\Psi(x)$ where n = 0, 1, 2, 3,...

What then are the eigenvalues of the charged oscillator in an electric field?

3. The general statement of the uncertainty principle is that

$$\sigma_A \cdot \sigma_B \geq (½) \langle [A_{op}, B_{op}]/i \rangle$$

where σ_A is the standard deviation of measurements of values of the observable A and A_{op} is the operator for this observable.

(a) Starting from the above statement, **derive the relationship** between the standard deviations for measurements of position x and linear momentum p_x.

(b) **Derive** the commutator $[L^2, L_z]$. What are the limitations, if any, on the simultaneous measurements of L^2 and L_z?

(c) **Write an explicit equation** stating that the eigenfunctions of L^2 are the spherical harmonics $Y_{\ell m}(\theta,\phi)$.

(d) **Write an explicit equation** stating the result when L_z operates on $Y_{\ell m}(\theta,\phi)$.

(e) A particle of mass m is bouncing elastically on a smooth, flat surface in the earth's gravitational field.
Write down the Schrödinger equation for this system (use z as the vertical distance perpendicular to the flat plane and g is the acceleration of gravity).

What are the boundary conditions on the wavefunction for this particular system?

4. (a)When the hamiltonian is not explicitly dependent on time, **solve the equation**

$$i\hbar(\partial/\partial t)\ \Psi(x, t) = \mathcal{H}(x)\ \Psi(x, t)$$

using the method of **separation of variables**.
Assume that you know the solutions to $\mathcal{H}(x)\psi(x)$.
{Just in case you did not notice, note the difference in the symbols: $\Psi(x, t)$, $\psi(x)$}

The eigenvalues of a linear harmonic oscillator are known.

$$\mathcal{H}(x)\,\psi(x) = E\psi(x)\,,$$

that is, $\{-(\hbar^2/2\mu)\, d^2/dx^2 + (k/2)x^2\}\,\psi(x) = (n+\frac{1}{2})\hbar\omega\,\psi(x)$ where $n = 0, 1, 2, 3,\ldots$

(b) At time zero, a linear harmonic oscillator is in a state that is described by the normalized wavefunction:

$$\Psi(x, 0) = (1/\sqrt{5})\,\psi_0(x) + (1/\sqrt{2})\,\psi_2(x) + c_3\psi_3(x).$$

Determine the numerical value of c_3.

(c) **Write out** the wavefunction at time t.

(d) **What is the expectation value** of the energy of the oscillator <u>at t = 0</u>?

(e) **What is the expectation value** of the energy of the oscillator <u>at t = 1 second</u>?

Possibly useful information:

$(L_x + iL_y)\, Y_{\ell m}(\theta, \phi) = [\ell(\ell+1) - m(m+1)]^{1/2}\, Y_{\ell m+1}(\theta, \phi)$

$(L_x + iL_y) = e^{i\phi}\, \partial/\partial\theta + i\, e^{i\phi} \cdot \cot\theta \cdot \partial/\partial\phi$

$\{-(\hbar^2/2\mu)\, d^2/dx^2 + (k/2)x^2\}\Psi(x) = (n+½)\hbar\omega\Psi(x)$ where $n = 0, 1, 2, 3,...$

$\sigma_A \cdot \sigma_B \geq (½)\, \langle [A_{op}, B_{op}]/i \rangle$

$\nabla^2 = \{\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2\}$

$(2/L)^{1/2} \sin\{(n\pi/L)\, x\}$
$(2\pi)^{-1/2} \exp\{im\phi\}$
$(2\pi)^{-1/2} \exp\{ikx\}$
$(\pi)^{-1/4} \exp\{-x^2/2\}$
$(\pi a_0^3)^{-1/2} \exp\{-r/a_0\}$

$\int_0^\infty x^{2n} \exp(-ax^2)\, dx = \dfrac{1 \cdot 3 \cdot 5 \cdot ... (2n-1)}{2^{n+1} a^n} \left(\dfrac{\pi}{a}\right)^{1/2}$ where n is a positive integer

$\int_0^\infty x^n \exp(-ax)\, dx = n!/a^{n+1}$ for $a > 0$, where n is a positive integer

$\int_0^\infty \exp(-a^2x^2)\, dx = (\pi)^{1/2}/2a$