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.

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

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

n = 3 $\quad$ ℓ = 1 $\quad$ m = 0 because ϕ does not appear.

The exponential in the radial function is $-Zr/na_0$

also see polynomial in r is power $n-\ell=2$

(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.

Probability density $\Psi^*\Psi$. Regardless of θ and ϕ radial probability density $4\pi r^2 \Psi^*\Psi$

Most probable r occurs when probability is maximum

$\frac{\partial}{\partial r}(\text{Probability}) = 0 \qquad \frac{\partial}{\partial r}\left[(6-r)r^2 e^{-r/3}\right] = e^{-r/3}\left(\frac{r^3}{3} - 5r^2 + 12r\right)$

{Since $r^2\psi^2$ is max. when $r\psi$ is max., $\therefore$ need only $\frac{\partial}{\partial r}(r\psi) = 0$}

$r^2 - 15r + 36 = 0$

$(r-12)(r-3) = 0 \quad \therefore r = 12$ or 3 in units of a_0. Look at function, see maximum at $12a_0$

(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.

$L_+ \Psi_{lm} = \underbrace{[l(l+1) - m(m+1)]^{1/2}}_{\text{here } \sqrt{1(1+1)-0} = \sqrt{2}} \Psi_{l\,m+1}$

Given $L_+ = e^{i\phi}\frac{\partial}{\partial\theta} + i e^{i\phi}\cot\theta\frac{\partial}{\partial\phi}$

gives zero derivative when ϕ is not showing in the function

$L_+\Psi = L_+ F(r)\cos\theta$

$= e^{i\phi} F(r)(-\sin\theta) = \sqrt{2}\,\Psi_{l\,m+1}$

$\therefore \Psi_{l,m+1} = \frac{-e^{i\phi}}{\sqrt{2}} F(r) \sin\theta$

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).

$$\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{r}\right)\Psi = E\Psi$$

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

Uncertainty principle: need to know if $[H, L^2] = 0$?
Here with transformed coords we see that
$[H, L^2] = 0$ because $\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Ze^2}{r}$ commutes with L^2 and L^2 commutes with itself.
YES $\sigma_E \cdot \sigma_{L^2} = 0$

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?

Transform Coords:

$$\left\{-\frac{\hbar^2}{2\mu}\frac{d^2}{dx'^2} + \underbrace{\frac{k}{2}\left(x'-\frac{e\mathcal{E}}{k}\right)^2}_{\frac{k}{2}x'^2 - e\mathcal{E}x' + \frac{e^2\mathcal{E}^2}{2k}} + \underbrace{e\mathcal{E}\left(x'-\frac{e\mathcal{E}}{k}\right)}_{e\mathcal{E}x' - \frac{e^2\mathcal{E}^2}{k}}\right\}\Psi(x') = E\Psi(x')$$

$$\left\{-\frac{\hbar^2}{2\mu}\frac{d^2}{dx'^2} + \frac{k}{2}x'^2 - \frac{e^2\mathcal{E}^2}{2k}\right\}\Psi(x') = E\Psi(x')$$

a constant

$$\left\{-\frac{\hbar^2}{2\mu}\frac{d^2}{dx'^2} + \frac{k}{2}x'^2\right\}\Psi(x') = \left(E + \frac{e^2\mathcal{E}^2}{2k}\right)\Psi(x')$$

Solutions given $\rightarrow$ $(n+\frac{1}{2})\hbar\omega\Psi(x')$

$$\therefore\ E + \frac{e^2\mathcal{E}^2}{2k} = (n+\tfrac{1}{2})\hbar\omega$$

eigenvalues $E = (n+\frac{1}{2})\hbar\omega - e^2\mathcal{E}^2/2k$

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.

Need $[x, p_x]\psi = x\frac{\hbar}{i}\frac{\partial \psi}{\partial x} - \frac{\hbar}{i}\frac{\partial (x\psi)}{\partial x} = x\frac{\hbar}{i}\frac{\partial \psi}{\partial x} - \frac{\hbar}{i}x\frac{\partial \psi}{\partial x} - \frac{\hbar}{i}\psi$

$= -\frac{\hbar}{i}\psi$

$[x, p_x] = -\frac{\hbar}{i} = i\hbar$

$\sigma_x \cdot \sigma_{p_x} \geq \frac{1}{2}\left\langle \frac{[x, p_x]}{i} \right\rangle$

$\sigma_x \cdot \sigma_{p_x} \geq \frac{1}{2}\hbar$

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

$[L^2, L_z] = (L_x^2 + L_y^2 + L_z^2)L_z - L_z(L_x^2 + L_y^2 + L_z^2)$

$= L_x(L_xL_z) + L_y(L_yL_z) + L_z^3 - (L_zL_x)L_x - (L_zL_y)L_y - L_z^3$

But $L_zL_x - L_xL_z = i\hbar L_y$ or $L_zL_x = L_xL_z + i\hbar L_y$ or $L_xL_z = L_zL_x - i\hbar L_y$

and $L_yL_z - L_zL_y = i\hbar L_x$ or $L_zL_y = L_yL_z - i\hbar L_x$ or $L_yL_z = L_zL_y + i\hbar L_x$

$[L^2, L_z] = L_x(L_zL_x - i\hbar L_y) + L_y(L_zL_y + i\hbar L_x) - (L_xL_z + i\hbar L_y)L_x$
$- (L_yL_z - i\hbar L_x)L_y$

$= -i\hbar L_xL_y + i\hbar L_yL_x - i\hbar L_yL_x + i\hbar L_xL_y$

$= 0$

Therefore there are no limitations on the simultaneous measurements of L^2 and L_z, i.e.

$\sigma_{L^2} \cdot \sigma_{L_z} \geq 0$

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

$$L^2 Y_{\ell m}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\phi)$$

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

$$L_z Y_{\ell m}(\theta,\phi) = m\hbar\, Y_{\ell m}(\theta,\phi)$$

(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).

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + mgz\right]\cdot\psi(z) = E\psi(z)$$

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

$V(z) = \infty$ for $z \leq 0$ $\quad \psi(z<0) = 0$ single-valued and continuous

$\psi(z)$ must go to zero as $z \to \infty$, $\psi(z) = 0$ at $z=0$.

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: $\Psi(x,t)$, $\psi(x)$}

Let $\Psi(x,t) = F(t)\cdot\psi(x)$ since $H(x)$ has no t in it.

$$i\hbar\frac{\partial}{\partial t}F(t)\cdot\psi(x) = H(x)\,F(t)\cdot\psi(x)$$

$$\frac{\psi(x)\, i\hbar\,\partial F(t)/\partial t}{F(t)\cdot\psi(x)} = \frac{F(t)\,H(x)\cdot\psi(x)}{F(t)\cdot\psi(x)}$$

Divide both sides by function $F(t)\cdot\psi(x)$

$$\frac{i\hbar\,\frac{\partial F(t)}{\partial t}}{F(t)} = \frac{H(x)\,\psi(x)}{\psi(x)} = E \quad \text{since } H(x)\psi(x) = E\psi(x)$$

$$\therefore \frac{\partial F(t)}{\partial t} = \frac{E}{i\hbar}F(t) \qquad \therefore F(t) = \exp^{-iEt/\hbar}$$

$$\therefore \Psi(x,t) = \exp^{-iEt/\hbar}\,\psi(x)$$

The eigenvalues of a linear harmonic oscillator are known.

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

that is, $\{-(\hbar^2/2\mu)\, d^2/dx^2 + (k/2)x^2\}\, \psi(x) = (n+½)\hbar\omega\, \psi(x)$ 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.

Normalization: $\int_{-\infty}^{+\infty} \Psi^*(x,0)\,\Psi(x,0)\,dx = 1$

terms like this all zero! ORTHOGONAL

$$1 = \frac{1}{5}\underbrace{\int_{-\infty}^{+\infty} \psi_0^*(x)\,\psi_0(x)\,dx}_{1} + \frac{1}{2}\underbrace{\int \psi_2^*(x)\,\psi_2(x)\,dx}_{1} + c_3^2\underbrace{\int \psi_3^*(x)\,\psi_3(x)\,dx}_{\text{NORMALIZED } 1} + \frac{1}{\sqrt{10}}\int \psi_0^*(x)\,\psi_2(x)\,dx + \ldots$$

$$1 = \frac{1}{5} + \frac{1}{2} + c_3^2 \qquad c_3 = \sqrt{\frac{3}{10}}$$

(c) **Write out** the wavefunction at time t. (need $-iE_nt/\hbar$ in exponent of time part)

$$\Psi(x,t) = \sqrt{\frac{1}{5}}\,\psi_0(x)\,e^{-i\frac{1}{2}\hbar\omega t} + \frac{1}{\sqrt{2}}\,\psi_2(x)\,e^{-i\frac{5}{2}\omega t} + \sqrt{\frac{3}{10}}\,\psi_3(x)\,e^{-i\frac{7}{2}\omega t}$$

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

$$\langle E\rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t)\,\mathcal{H}\,\Psi(x,t)\,dx = \frac{1}{5}\int_{-\infty}^{+\infty} \psi_0(x)\,\overbrace{\mathcal{H}\psi_0(x)}^{E_0\psi_0}\,dx + \frac{1}{2}\int_{-\infty}^{+\infty} \psi_2(x)\,\mathcal{H}\psi_2(x)\,dx$$

$$+ \frac{3}{10}\int_{-\infty}^{+\infty} \psi_3(x)\,\underbrace{\mathcal{H}\psi_3(x)}_{E_3\psi_3}\,dx + \frac{1}{\sqrt{10}}\int \psi_0(x)\,\underbrace{\mathcal{H}\psi_2(x)}_{E_2\psi_2(x)}\,dx + \ldots$$

ORTHOGONAL ZERO!

$$\langle E\rangle = \frac{1}{5}\left(\frac{1}{2}\hbar\omega\right) + \frac{1}{2}\left(\frac{5}{2}\hbar\omega\right) + \frac{3}{10}\left(\frac{7}{2}\hbar\omega\right) = \frac{12}{5}\hbar\omega$$

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

The same, $\frac{12}{5}\hbar\omega$

$\langle E\rangle$ is independent of time since energy is conserved (a constant of the motion).