Quantum Mechanics: Problems 2

1. The Hamiltonian for a harmonic oscillator is

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

where μ is the reduced mass and k is the force constant.

(a) By defining $\omega = (k/\mu)^{1/2}$ and $s = (\hbar^2/k\mu)^{1/4}$ show that

$$\frac{H}{\hbar\omega} = -\frac{1}{2}\frac{d^2}{dq^2} + \frac{1}{2}q^2$$

where $q = x/s$. (The unit s of length and the unit $\hbar\omega$ of energy are the natural units for the harmonic oscillator.)

(b) Show that $\psi_0(q) = N_0 \exp(-q^2/2)$ is an eigenfunction of H. Calculate the corresponding energy eigenvalue and the normalization constant N_0.

$$\textit{Note:} \quad \int_{-\infty}^{\infty} e^{-\alpha q^2}\, dq = \sqrt{\frac{\pi}{\alpha}}.$$

(c) Show that a classical oscillator with the same total energy as $\psi_0(q)$ oscillates in the range $-1 \le q \le 1$. Determine $d^2\psi_0/dq^2$ at $q = \pm 1$ and comment on your result.

(d) Sketch $|\psi_0|^2$ as a function of q, and estimate (e.g. by counting squares) the probability that the quantum oscillator will be found in a classically forbidden region.

2. The Hamiltonian for a particle of mass m moving freely in two dimensions is

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right).$$

(a) Use the chain rule

$$\left(\frac{\partial}{\partial x}\right)_y = \left(\frac{\partial r}{\partial x}\right)_y \left(\frac{\partial}{\partial r}\right)_\phi + \left(\frac{\partial \phi}{\partial x}\right)_y \left(\frac{\partial}{\partial \phi}\right)_r,$$

$$\left(\frac{\partial}{\partial y}\right)_x = \left(\frac{\partial r}{\partial y}\right)_x \left(\frac{\partial}{\partial r}\right)_\phi + \left(\frac{\partial \phi}{\partial y}\right)_x \left(\frac{\partial}{\partial \phi}\right)_r,$$

to transform this Hamiltonian into polar coordinates $r = (x^2 + y^2)^{1/2}$ and $\phi = \arctan(y/x)$, and hence show that the Hamiltonian for a particle of mass m confined to a ring of radius r can be written as

$$H = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2},$$

where $I = mr^2$ is the moment of inertia of the particle about the origin.

(b) Evaluate the commutator $[H, L_z]$, where

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

is the operator for the z component of the angular momentum, and comment on the physical significance of your result.

(c) Verify that the functions

$$\psi_m(\phi) = (2\pi)^{-1/2}\, e^{+im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots$$

are simultaneous eigenfunctions of H and L_z subject to the periodic boundary condition $\psi(\phi + 2\pi) = \psi(\phi)$, and determine the corresponding energy and angular momentum eigenvalues. Is $\sin(m\phi)$ also a simultaneous eigenfunction of H and L_z?

3. The angular momentum $\mathbf{L}$ of a particle about the origin is given classically by the vector product

$$\mathbf{L} = \mathbf{r} \wedge \mathbf{p},$$

where $\mathbf{r}$ is the position of the particle and $\mathbf{p}$ is its linear momentum. The quantum mechanical operators for the components L_x, L_y and L_z of the angular momentum are therefore given in terms of the position operators x, y and z and the linear momentum operators p_x, p_y and p_z of the particle as

$$L_x = yp_z - zp_y,$$
$$L_y = zp_x - xp_z,$$
$$L_z = xp_y - yp_x.$$

Note the cyclic symmetry, which you should exploit as much as possible in the following:

(a) Use the chain rule to show that this expression for L_z is equivalent to the simpler expression $L_z = -i\hbar\partial/\partial\phi$ when p_x and p_y are written out explicitly as $p_x = -i\hbar\partial/\partial x$ and $p_y = -i\hbar\partial/\partial y$.

(b) Use these definitions of p_x and p_y to show that $[x, p_x] = i\hbar$, $[x, p_y] = 0$ and $[p_x, p_y] = 0$, and hence go on to show that

$$[L_x, L_y] = i\hbar\, L_z$$
$$[L_y, L_z] = i\hbar\, L_x$$
$$[L_z, L_x] = i\hbar\, L_y.$$

(c) Verify the commutator identity $[A, B^2] = [A, B]B + B[A, B]$ for two operators A and B, and use this identity to show that

$$[L_z, L_x^2] = +i\hbar\,(L_x L_y + L_y L_x)\,,$$
$$[L_z, L_y^2] = -i\hbar\,(L_x L_y + L_y L_x)\,.$$

(d) Hence show that the squared angular momentum operator

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

commutes with each component L_x, L_y and L_z of the angular momentum. What is the significance of this result in light of your answer to part (b)?

(e) In spherical polar coordinates,

$$L^2 = -\hbar^2 \left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right)$$

and

$$L_z = -i\hbar\frac{\partial}{\partial\phi}.$$

Show that the function $Y_{?,?}(\theta, \phi) = \sin\theta\, e^{+i\phi}$ is a simultaneous eigenfunction of both of these operators and identify the appropriate values of the quantum numbers ℓ and m by comparing with the eigenvalue equations

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

and

$$L_z\, Y_{\ell,m} = \hbar\, m\, Y_{\ell,m}.$$

$Y_{?,?}(\theta, \phi)$ is the angular part of what kind of hydrogenic orbital?

4. Treating the nucleus as infinitely heavy, the Hamiltonian for the hydrogen atom is

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ and $r^2 = x^2 + y^2 + z^2$.

(a) Defining

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \quad \text{and} \quad E_h = \frac{e^2}{4\pi\epsilon_0 a_0},$$

show that

$$\frac{H}{E_h} = -\frac{1}{2}\nabla'^2 - \frac{1}{r'},$$

where $\nabla'^2 = \partial^2/\partial x'^2 + \partial^2/\partial y'^2 + \partial^2/\partial z'^2$ and $r'^2 = x'^2 + y'^2 + z'^2$ with $x' = x/a_0$, $y' = y/a_0$, $z' = z/a_0$. (The system of *atomic units* in which the unit of length is a_0 (the bohr) and the unit of energy is E_h (the hartree) is the natural system to use in electronic structure calculations.)

(b) Show that the wavefunction

$$\psi_{1s} = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} e^{-Zr}$$

(with r in bohr) is a normalized eigenfunction of the Schrödinger equation for a one-electron atom having a nuclear charge of Z atomic units. What is the corresponding energy in hartrees?

(c) Find the probability that an electron described by this wavefunction lies in a thin spherical shell of radius r and thickness dr and hence show that the most probable distance of the electron from the nucleus is $1/Z$ bohr.

(d) Calculate the expectation values of the potential energy $\langle V\rangle = \langle -Z/r\rangle$ and the kinetic energy $\langle T\rangle = \langle H\rangle - \langle V\rangle$ of a 1s electron and confirm that they satisfy the virial theorem $\langle T\rangle = -(1/2)\langle V\rangle$.

Note: Remember that in spherical polar coordinates

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2},$$

and the volume element for integrations is $r^2\sin\theta\, dr d\theta d\phi$. Also

$$\int_0^\infty r^n e^{-\alpha r}\, dr = \frac{n!}{a^{n+1}}.$$