Exam 1 and Answers

1. Evaluate the commutator between the z-components of linear momentum and angular momentum. Comment on whether it should be possible to simultaneously measure these two variables for a particle.

The operators are

$$\hat{p}_z = -i\hbar\frac{\partial}{\partial z} \qquad \text{and} \qquad \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

No derivative operator encounters any function of its own variable, thus

$$\left[\hat{p}_z, \hat{L}_z\right] = 0$$

and both variables can be specified simultaneously.

2. In a certain Compton-scattering event, an x-ray photon of wavelength 1 nm knocks an electron out of the atom. The scattered x-ray photon has a wavelength of 2 nm. Calculate the kinetic energy of the ejected electron in electron volts. You may assume that the initial KE of the electron is negligible.

By conservation of energy

$$E(\text{xray}_{\text{in}}) = E(\text{xray}_{\text{out}}) + E(\text{electron})$$

$$\frac{hc}{\lambda_{\text{in}}} = \frac{hc}{\lambda_{\text{out}}} + \frac{1}{2}mv^2$$

$$\frac{1}{2}mv^2 = (6.626 \times 10^{-27})(2.998 \times 10^{8})\left(\frac{1}{1 \times 10^{-9}} - \frac{1}{2 \times 10^{-9}}\right)$$

$$= 9.932 \times 10^{-17}\,\text{J}/1.602 \times 10^{-19}\,\text{J}\,\text{eV}^{-1} = 620\,\text{eV}$$

3. For the operator

$$\frac{1}{2}\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r}$$

$\psi(r) = e^{-r}$ is known to be an eigenfunction. Find the corresponding eigenvalue. Normalize $\psi(r)$ in spherical polar coordinates, so that

$$\int_0^\infty |\psi(r)|^2 \, 4\pi r^2 \, dr = 1$$

You might need the definite integral

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

Evaluate the deriviatives

$$\frac{d}{dr}e^{-r} = -e^{-r} \qquad \text{and} \qquad \frac{d^2}{dr^2}e^{-r} = +e^{-r}$$

Therefore

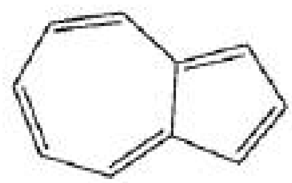
$$\{\text{operator}\}e^{-r} = \frac{1}{2}e^{-r}$$

and the eigenvalue equals $\frac{1}{2}$. To normalize, write $\psi(r) = A\, e^{-r}$ so

$$\int_0^\infty |\psi(r)|^2 \, 4\pi r^2 \, dr = 4\pi A^2 \int_0^\infty r^2 \, e^{-2r} \, dr = 4\pi A^2 \times \frac{2!}{2^3} = 1$$

giving $A = 1/\sqrt{\pi}$.

4. Azulene $C_{10}H_8$, shown below, is an aromatic hydrocarbon containing delocalized π-electrons.



(i) How many π-electrons does azulene have? 5 double bonds, thus 10 π-electrons.

As a model for this π-electron system, consider the mobile electrons in a rectangular two-dimensional box of dimensions 5.00 Å by 4.65 Å.

For the two-dimensional particle-in-a-box,

$$E_{n_1,n_2} = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2}\right)$$

(ii) Identify the quantum numbers of the HOMO and LUMO of the π-electron system.

The levels E_{11}, E_{12}, E_{21} and E_{22} are all doubly filled, accounting for 8 electrons. The HOMO and LUMO are E_{13} and E_{31}—which is which depends on your numbering.

(iii) Calculate the wavelength (in nm) of the lowest-energy π-electron transition.

For *one* electron jumping from HOMO to LUNO

$$\frac{hc}{\lambda} = |E_{13} - E_{31}| = \frac{h^2}{8m}\left|\frac{3^2}{a^2} + \frac{1^2}{b^2} - \frac{1^2}{a^2} - \frac{3^2}{b^2}\right|$$

where a, $b = 5.00 \times 10^{-10}$, 4.65×10^{-10}. The absolute value bracket works out to 0.0499×10^{20}. Using the constant $h/mc = 2.426 \times 10^{-12}$

$$\lambda = \frac{8}{(2.426 \times 10^{-12})(0.0499 \times 10^{20})} \times 10^9 \approx 660\,\text{nm}$$

(iv) Should azulene be a colored compound? If so, what color?

Yes, since it absorbs in the visible region 400–700 nm. Since it takes out light near the red end of the spectrum, the compound should be blue. Actually "azulene" is named for its blue color! (y'know "azure").

5. After separation of variables in the Schrödinger equation for the hydrogen molecule-ion H_2^+ (which we will study in a couple of weeks), the equation for the variable denoted by λ is given by:

$$\frac{d}{d\lambda}\left[(\lambda^2-1)\frac{d\Lambda}{d\lambda}\right]+\left[A+2R\lambda-\frac{R^2|E|\lambda^2}{4}-\frac{m^2}{\lambda^2-1}\right]\Lambda(\lambda)=0$$

where R, A, E and m are all constants. Deduce the $\lambda\to\infty$ asymptotic form for $\Lambda(\lambda)$.

As $\lambda\to\infty$, the equation reduces approximately to

$$\lambda^2\frac{d^2\Lambda}{d\lambda^2}-\frac{R^2|E|\lambda^2}{4}\Lambda\approx 0$$

Cancelling the λ^2 and noting that E is negative for bound states,

$$\Lambda(\lambda)\approx\exp\left(-\frac{R}{2}\sqrt{|E|}\,\lambda\right)$$

6. Before quantum mechanics, many of the properties of matter could be accounted for by a model in which the electrons in an atom were treated as harmonic oscillators. Suppose the electron in hydrogen atom were bound with a force constant

$$k=\frac{9e^2}{64(4\pi\epsilon_0)a_0^3}$$

where e is the electron charge 1.602×10^{-19} C, a_0 is the Bohr radius 0.529×10^{-10} m and $1/4\pi\epsilon_0=8.99\times10^9$ in compatible units, such that k comes out in N m^{-1}.

(i) Assuming that the electron behaves as a quantum-mechanical harmonic oscillator, derive a formula for the wavelength of the radiation which can be emitted or absorbed by a hydrogen atom.

The natural frequency of the oscillator is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

The energy-level separation equals $h\nu = hc/\lambda$. Thus

$$\lambda = 2\pi c\sqrt{\frac{m}{k}}$$

(ii) Calculate this wavelength in nm.

Putting in the numbers, we find $\lambda = 121.6$ nm. This is the actual value for the Lyman alpha transition in hydrogen. (OK, so we fudged a little on the constants!)