Quantum Chemistry

Corrections 2C

1. *The Schrödinger equation for a particle of mass m constrained to move on a circle of radius a is*

$$-\frac{\hbar^2}{2I}\frac{d^2\psi(\theta)}{d\theta} = E\psi(\theta) \qquad 0 \le \theta \le 2\pi \qquad \textit{where } I = ma^2$$

This problem is sometimes called the particle-on-a-ring and represents the rotation of a linear molecule in a plane.

Find the solutions to this equation (that is, find the eigenfunctions and eigenvalues), including the normalization constant for the wave function.

Hint: Use the fact that the wave function must be continuous to determine the appropriate boundary conditions needed to solve the problem.

The Schrödinger equation:

$$\hat{H}\psi(\theta) = -\frac{\hbar^2}{2I}\frac{d^2\psi(\theta)}{d\theta^2} = E\psi(\theta) \quad \Rightarrow \quad \frac{d^2\psi(\theta)}{d\theta^2} + \frac{2IE}{\hbar^2}\psi(\theta) = 0$$

The characteristic polynomial of this differential is:

$$r^2 + \frac{2IE}{\hbar^2} = 0 \quad \Rightarrow \quad r = \pm i\frac{\sqrt{2IE}}{\hbar}$$

Therefore, the general solution is:

$$\psi(\theta) = c_1 \cdot e^{i\frac{\sqrt{2IE}}{\hbar}\theta} + c_2 \cdot e^{-i\frac{\sqrt{2IE}}{\hbar}\theta}$$

The condition of the wavefunction being continuous implies that the wavefunction must have the same value in θ and $\theta + 2\pi$:

$$\psi(\theta) = \psi(\theta + 2\pi).$$

We then use the following notation in the general solution,

$$n = \frac{\sqrt{2IE}}{\hbar}$$

And also remembering that $e^{in(\theta+2\pi)} = e^{in\theta}e^{i2\pi n}$:

$$c_1 \cdot e^{in\theta} + c_2 \cdot e^{-in\theta} = c_1 \cdot e^{in\theta}e^{in2\pi} + c_2 \cdot e^{-in\theta}e^{-in2\pi}$$

$$c_1 \cdot e^{in\theta}\left(e^{in2\pi} - 1\right) + c_2 \cdot e^{-in\theta}\left(e^{-in2\pi} - 1\right) = 0$$

This relationship must be true for all values of θ . For example:

$$\begin{cases} \theta = 0 \Rightarrow c_1 \cdot 1 \cdot \left(e^{in2\pi} - 1\right) + c_2 \cdot 1 \cdot \left(e^{-in2\pi} - 1\right) = 0 \\ \theta = \dfrac{\pi}{2n} \Rightarrow c_1 \cdot i \cdot \left(e^{in2\pi} - 1\right) + c_2 \cdot (-i) \cdot \left(e^{-in2\pi} - 1\right) = 0 \end{cases} \quad \Rightarrow \quad \begin{cases} 2c_1 \cdot \left(e^{in2\pi} - 1\right) = 0 \\ 2c_2 \cdot \left(e^{-in2\pi} - 1\right) = 0 \end{cases}$$

$$\theta = 0 \qquad \Rightarrow \quad e^{in\theta} = \cos(n\theta) + i\sin(n\theta) = \cos(0) + i\sin(0) = 1$$

$$\theta = \frac{\pi}{2n} \qquad \Rightarrow \quad e^{in\theta} = \cos(n\theta) + i\sin(n\theta) = \cos(\frac{\pi}{2}) + i\sin(\frac{\pi}{2}) = i$$

There are two possibilities that could arise from the values above:

i) Let $c_1 = c_2 = 0 \quad \Rightarrow \quad \psi(\theta) = 0$, the wavefunction is zero and so, this is not valid.

ii) Let $e^{in2\pi} = e^{-in2\pi} = 1 \quad \Rightarrow \quad \cos(n2\pi) + i\sin(n2\pi) = \cos(n2\pi) - i\sin(n2\pi)$ ssi $\sin(n2\pi) = 0 / \cos(n2\pi) = 1$

n must be an integer (0, ±1, ±2, …) and

$$n = \frac{\sqrt{2IE}}{\hbar},$$

We have $$E_n = \frac{n^2\hbar^2}{2I}$$

which are the eigenvalues of the Hamiltonian.

Again, we see that the quantisation of energy occurs when we apply the boundary conditions.

Now normalise the wavefunctions to find the values of c_1 and c_2 .

$$\int_0^{2\pi} \psi_n^* \psi_n d\theta = 1 \quad \Rightarrow \int_0^{2\pi} \left(c_1^* \cdot e^{-in\theta} + c_2^* \cdot e^{in\theta}\right)\left(c_1 \cdot e^{in\theta} + c_2 \cdot e^{-in\theta}\right) d\theta = 1$$

$$\Rightarrow \int_0^{2\pi} \left(|c_1|^2 + |c_2|^2\right) d\theta + \int_0^{2\pi} \left(c_1^* c_2 \cdot e^{-i2n\theta} + c_2^* c_1 \cdot e^{i2n\theta}\right) d\theta = 1$$

$e^{\pm i2n\theta}$ is a sum of sinusoidal periodic functions $\frac{\pi}{n}$; therefore, its integral from 0 to 2π is zero. :

$$\int_0^{2\pi} e^{\pm i2n\theta} d\theta = \int_0^{2\pi} \cos(2n\theta)d\theta \pm i \int_0^{2\pi} \sin(2n\theta)d\theta = [0-0] \pm [1-1] = 0$$

$$\left(|c_1|^2 + |c_2|^2\right) \int_0^{2\pi} d\theta = \left(|c_1|^2 + |c_2|^2\right) \cdot 2\pi = 1$$

$$|c_1|^2 + |c_2|^2 = \frac{1}{2\pi}$$

Note that both $e^{in\theta}$ and $e^{-in\theta}$ are two eigenfunctions with the same value : they are said to be 'degenerate'.

Any linear combination :

$$\psi_n(\theta) = c_1 \cdot e^{i\frac{\sqrt{2IE_n}}{\hbar}\theta} + c_2 \cdot e^{-i\frac{\sqrt{2IE_n}}{\hbar}\theta},$$

or $|c_1|^2 + |c_2|^2 = \frac{1}{2\pi}$ (normalisation),

is an eigenfunction of the Hamiltonian with an eigenvalue of :

$$E_n = \frac{n^2\hbar^2}{2I} \; .$$

For this reason, any linear combination of wavefunctions can be chosen as the basic solution. For example, if $c_2 = 0$:

$$|c_1|^2 = \frac{1}{2\pi} \quad \Rightarrow \quad c_1 = \frac{1}{\sqrt{2\pi}} \quad \Rightarrow \quad \psi_n(\theta) = \frac{1}{\sqrt{2\pi}} \cdot e^{i\frac{\sqrt{2IE_n}}{\hbar}\theta}$$

2. *Recall the particle on a ring problem from above. The angular momentum operator for a particle on a ring is*

$$\hat{L} = -i\hbar \frac{d}{d\theta}$$

a. *Assume that the system is in an eigenfunction corresponding to* $n = 3$. *What is the angular momentum of the particle with this wave function?*

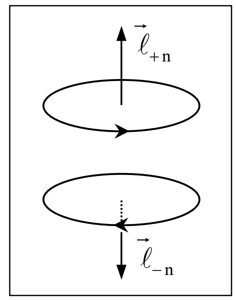
$$\psi_n(\theta) = \frac{1}{\sqrt{2\pi}} e^{in\theta}$$

$$\hat{L}\psi_n(\theta) = -i\hbar \frac{d}{d\theta}\left(\frac{1}{\sqrt{2\pi}} e^{in\theta}\right) = \frac{n\hbar}{\sqrt{2\pi}} e^{in\theta} = n\hbar\psi_n(\theta) = \ell_n\psi_n(\theta)$$

$$\Rightarrow \quad \ell_n = n\hbar \quad \Rightarrow \quad \ell_3 = 3\hbar$$

b. *The problem of the particle-on-a-ring is different from the particle-in-a-box in that the quantum numbers n can take on both positive and negative values. Physically, how would you interpret the difference between a particle on a ring described by wavefunctions with* $n = +3$ *and* $n = -3$ *?*

The positive and negative values of n correspond to the opposite directions of the angular momentum $\vec{\ell}$. From the classical point of view, this represents opposite directions of the particle on the ring.



3. *Consider the situation in which a particle on a ring can be described by the wave function*

$$\Psi(\theta,t) = \frac{\sqrt{3}}{3}\frac{1}{\sqrt{2\pi}} e^{i3\theta} e^{-\frac{iE_3}{\hbar}t} + \frac{\sqrt{3}}{3}\frac{1}{\sqrt{2\pi}} e^{i6\theta} e^{-\frac{iE_6}{\hbar}t} + \frac{\sqrt{3}}{3}\frac{1}{\sqrt{2\pi}} e^{-i6\theta} e^{-\frac{iE_6}{\hbar}t}$$

where the E_n *are the energies of the stationary states for a particle on a ring.*

a. *Is the probability of finding the particle at a particular angle* θ *independent of time if the state is described by the wave function* $\Psi(\theta,t)$ *given above?*

No, the probability of finding the particle at a certain angle is dependent on the time because it is not an eigenfunction of the Hamiltonian, it is a linear combination of the eigenfunctions of Hamiltonian having different eigenvalues (E_3 and E_6). Therefore, the terms depending on time will not end while calculating $\Psi^*(\theta,t)\Psi(\theta,t)$.

b. *If you were to measure the energy of a particle in this state* $\Psi(\theta,t)$*, what value or range of values could you obtain? If your answer includes a range of values, what is the probability for obtaining each value in that range?*

The possible values for the energy measurements are E_3 et E_6 (postulate 3) with a probability of $\left(\frac{\sqrt{3}}{3}\right)^2 = \frac{1}{3}$ for E_3, and with a probability of $2 \cdot \left(\frac{\sqrt{3}}{3}\right)^2 = \frac{2}{3}$ for E_6.

c. *Calculate $\langle E \rangle$, the expectation value of the energy that you would obtain if you were to make repeated measurements on a number of identical systems. (Hint: You can do this without explicitly evaluating any integrals)*

According to the probabilities determined in question b), we can calculate the average value of energy, or we remember that $E_n = \frac{n^2 \hbar^2}{2I}$:

$$\langle E \rangle = \sum_n p(E_n) \cdot E_n = \frac{1}{3} \cdot E_3 + \frac{2}{3} \cdot E_6 = \frac{1}{3} \cdot \frac{9\hbar^2}{2I} + \frac{2}{3} \cdot \frac{36\hbar^2}{2I} = \frac{27\hbar^2}{2I}$$

d. *Let's say you make a measurement of the energy and get $\frac{9\hbar^2}{2I}$ (call this measurement #1). You then make a subsequent measurement (#2) of the energy <u>of the same system you measured the first time</u>. What value or range of values could you obtain in measurement #2?*

We can only obtain the same value $\left(E_3 = \frac{9\hbar^2}{2I}\right)$ in the measurement #2, since the system is in $\Psi_3(\theta,t)$ after measurement #1 (postulate 6).

e. *Would your answer to part c) be any different if <u>in between</u> your two measurements of the energy (#1 and #2) you measured the particle's angular momentum? Why or why not? What possible values could you get for the angular momentum? Recall that the angular momentum operator for the particle on a ring is*

$$\hat{L} = -i\hbar \frac{d}{d\theta}$$

Since $\hat{L}$ and $\hat{H}$ commute, the relative precision that can be obtained in the measurements is not limited. The eigenfunction of $\hat{H}$ and is also an eigenfunction of $\hat{L}$. Therefore, a measurement of the angular momentum between measurements #1 and #2 will give the value $\ell_3 = 3\hbar$. Since the angular momentum measurement will not change the wavefunction, the #2 measurement of the energy will give the same result as in the question (d).

f. *Let's say that after making a measurement of the energy and getting $\frac{9\hbar^2}{2I}$ you measure the angular position and get θ_0 for a result. If your then remeasure the position 10 seconds later, will you get the same result? Why or why not?*

No, because after measuring the angular position the wavefunction becomes an eigenfunction of the angular position operator. This function is a linear combination of the Hamiltonian wavefunctions hence, does not correspond to a stationary state. The probability distribution $\Psi^*(\theta,t)\Psi(\theta,t)$ will evolve with time and a new measurement of the angular position will not necessarily provide the same value..

g. *After making these two measurements of the position (as stated in 3f.), you then measure the energy. What value or range of values could you get?*

We can obtain any value (we cannot predict which) corresponding to the eigenfunctions $\Psi_n(\theta,t)$ contained in the system's function $\Psi(\theta,t)=\sum_n c_n\Psi_n(\theta,t)$. The probability of each of these values will be $|c_n|^2$.

4. *Evaluate the commutator* $\left[\hat{\mathrm{A}},\hat{\mathrm{B}}\right]$ *where* $\hat{\mathrm{A}}$ *and* $\hat{\mathrm{B}}$ *are given below.*

a. $\hat{\mathrm{A}}=\dfrac{d^2}{dx^2}$ $\qquad\hat{\mathrm{B}}=x$

b. $\hat{\mathrm{A}}=\dfrac{d}{dx}-x$ $\qquad\hat{\mathrm{B}}=\dfrac{d}{dx}+x$

a.

$$\left[\hat{A},\hat{B}\right]f(x)=\hat{A}\hat{B}f(x)-\hat{B}\hat{A}f(x)$$

$$\left[\frac{d^2}{dx^2},x\right]f(x)=\left(\frac{d^2}{dx^2}\cdot x\right)f(x)-\left(x\cdot\frac{d^2}{dx^2}\right)f(x)$$

$$=\frac{d}{dx}\cdot\frac{d}{dx}\left(x\cdot f(x)\right)-x\left(\frac{d^2}{dx^2}f(x)\right)$$

$$=\frac{d}{dx}\cdot\left(f(x)+x\cdot\frac{d}{dx}f(x)\right)-x\frac{d^2}{dx^2}f(x)$$

$$=\frac{d}{dx}f(x)+\frac{d}{dx}f(x)+x\cdot\frac{d^2}{dx^2}f(x)-x\cdot\frac{d^2}{dx^2}f(x)=2\frac{d}{dx}f(x)$$

$$\left[\frac{d^2}{dx^2},x\right]=2\frac{d}{dx}$$

b.

$$\left[\frac{d}{dx}-x,\frac{d}{dx}+x\right]f(x)=\left(\frac{d}{dx}-x\right)\cdot\left(\frac{d}{dx}+x\right)f\left(x\right)-\left(\frac{d}{dx}+x\right)\cdot\left(\frac{d}{dx}-x\right)f\left(x\right)$$

$$=\left(\frac{d}{dx}-x\right)\cdot\left(\frac{d}{dx}f\left(x\right)+xf\left(x\right)\right)-\left(\frac{d}{dx}+x\right)\cdot\left(\frac{d}{dx}f\left(x\right)-xf\left(x\right)\right)$$

$$=\left(\frac{d^2}{dx^2}\right)f\left(x\right)+f\left(x\right)+x\frac{d}{dx}f\left(x\right)-x\frac{d}{dx}f\left(x\right)-x^2f\left(x\right)$$

$$-\left(\frac{d^2}{dx^2}\right)f\left(x\right)+f\left(x\right)+x\frac{d}{dx}f\left(x\right)-x\frac{d}{dx}f\left(x\right)+x^2f\left(x\right)=2f(x)$$

$$\left[\frac{d}{dx}-x,\frac{d}{dx}+x\right]=2$$

5. *Answer the following questions TRUE or FALSE and briefly describe the reasoning behind your answer. Be sure to read each question* ***carefully****.*

a. *The wave function for a quantum mechanical system must be an eigenfunction of the Hamiltonian operator.*

FALSE. The wavefunction can be any function provided that it is continuous, finite and normalised, and that its derivation in relation to the position is also continuous. (**postulate 1**)

b. *Every physical observable in classical mechanics can be represented by a Hermitian operator in quantum mechanics.*

TRUE (**postulate 2**).

c. *If the wave function for a system is not an eigenfunction of the operator $\hat{A}$, then a measurement of the observable corresponding to $\hat{A}$ might give a value that is not one of the eigenvalues of $\hat{A}$.*

FALSE. It will definitely give an eigenvalue of the operator $\hat{A}$. We just do not know which one (**postulate 3**). However, if the wavefunction is not an eigenfunction of $\hat{A}$, it will not be known with certainty what the eigenvalue will be measured. For repeated identical measurements, a distribution of values will be obtained.

d. *The wave function for a quantum mechanical system is always equal to a function of time multiplied by a function of the coordinates.*

FALSE. But if this is the case and the Hamiltonian does not depend on time, then the probability distribution does not change over time and the spatial part of the wavefunction satisfies the time-independent Schrödinger equation (**postulate 5**). Such wavefunctions are called the ‘eigenstates’ or ‘stationary states’.

e. *After making a measurement of the observable corresponding to* $\hat{\text{A}}$ *and getting the result* a_n*, the wave function becomes one of the eigenfunctions of* $\hat{\text{A}}$*, but you cannot be certain which one.*

FALSE. We will know exactly which wavefunction it will be : it is the eigenfunction $\Psi_n(\mathbf{r},t)$ corresponding to the eigenvalue a_n measured (**postulate 6**). (We will see later that this is not necessarily the case when the eigenfunctions of $\hat{\text{A}}$ are degenerate).

f. *One can sometimes measure two physical observables with infinite relative precision.*

TRUE. This is the case if the operators can commute (eg. For total energy and angular momentum : $\left[\hat{H},\hat{L}\right]=0$).