CTC2, exercises week 1, NWI-MOL176

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Question 1: Chapter 1

The harmonic oscillator Hamiltonian for a particle with mass m and a harmonic potential with force constant k is

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2.$$
(1)

1a. Find a coordinate transformation, $x = \alpha y$, to rewrite the Hamiltonian as

$$\hat{H}_0 = A\left(-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2\right) \tag{2}$$

and determine A as a function of m and k. Note that y must be dimensionless (why?).

Answer: With $x = \alpha y$ we have

$$\frac{\partial}{\partial x} = \frac{\partial y}{\partial x}\frac{\partial}{\partial y} = \frac{1}{\alpha}\frac{\partial}{\partial y}$$
(3)

 $and \ for \ the \ second \ derivative$

$$\frac{\partial^2}{\partial x^2} = \frac{1}{\alpha^2} \frac{\partial^2}{\partial y^2} \tag{4}$$

so the Hamiltonian becomes

$$\hat{H}_0 = -\frac{\hbar^2}{2m\alpha^2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}k\alpha^2 y^2 \tag{5}$$

To write this Hamiltonian in the form Eq. (2) we need to have

$$A = \frac{\hbar^2}{m\alpha^2} = k\alpha^2. \tag{6}$$

We can solve this for α

$$\alpha^4 = \frac{\hbar^2}{mk} \tag{7}$$

$$\alpha^2 = \frac{\hbar}{\sqrt{mk}} \tag{8}$$

(9)

so

$$A = k\alpha^2 = \hbar \sqrt{\frac{k}{m}}.$$
(10)

For convenience, we define

$$\omega \equiv \sqrt{\frac{k}{m}} \tag{11}$$

so the Hamiltonian can be written as

$$\hat{H}_0 = \hbar\omega \left(-\frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 \right).$$
(12)

1b. Show that Hamilton's classical equations of motion for one particle in one dimension is equivalent to Newton's equation.

Answer: The classical Hamiltonian is

$$H = \frac{p^2}{2m} + V(x).$$
 (13)

Hamilton's equations of motion are

$$\frac{\partial x}{\partial t} = \frac{\partial H(x,p)}{\partial p} = \frac{p}{m} \tag{14}$$

$$\frac{\partial p}{\partial t} = -\frac{\partial H(x,p)}{\partial x} = -\frac{\partial V(x)}{\partial x}.$$
(15)

From the first equation we have

$$p = m \frac{\partial x}{\partial t} \tag{16}$$

and from the second we find the force

$$F = -\frac{\partial V(x)}{\partial x} = \frac{\partial}{\partial t}p = m\frac{\partial^2 x}{\partial t^2}.$$
(17)

With acceleration defined as $a = \frac{\partial^2 x}{\partial t^2}$, we get Newton's equation of motion

$$F = ma. \tag{18}$$

Question 2: Chapter 4

2a. Use first order perturbation theory to show that the energy levels of a diatomic molecule can be written as

$$E_{vl} = \epsilon_v + B_v l(l+1), \tag{19}$$

where v = 0, 1, 2, ... is the vibrational quantum number and l = 0, 1, 2, ... is the rotational quantum number. Take the vibrational Schrödinger equation with l = 0 as the zeroth order problem, and treat the centrifugal term as a perturbation. Assume that the solutions $\chi_v(r)/r$ of the zeroth-order problem are known and give the expression for B_v .

Reminder first order perturbation theory: Assume the Hamiltonian can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$
 (20)

and we want to find approximate solutions of

$$\hat{H}\Psi_n = E_n\Psi_n. \tag{21}$$

We assume that the zeroth-order problem has been solved

$$H_0\phi_n = \epsilon_n\phi_n \tag{22}$$

In first order perturbation theory, the energies E_n are given by

$$E_n = \epsilon_n + \frac{\langle \phi_n | \hat{H}_1 | \phi_n \rangle}{\langle \phi_n | \phi_n \rangle}.$$
(23)

A Morse potential has the functional form

$$V(r) = D_e [1 - e^{-\alpha(r - r_e)}]^2.$$
(24)

Answer: The Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hat{l}^2}{2\mu r^2} + V(r)$$
(25)

We take as zeroth order Hamiltonian

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + V(r)$$
(26)

and we take the centrifugal term as perturbation

$$\hat{H}_1 = \frac{\hat{l}^2}{2\mu r^2}.$$
(27)

The l = 0 zeroth order vibrational wave function $\chi_v(r)/r$ is an eigenfunction of \hat{H}_0 with energy ϵ_v . We assume this wave function to be normalized. As zeroth order wave function for rotational level l we take

$$\chi_{v,l}^{(0)}(r) = \frac{\chi_v(r)}{r} Y_{l,m}(\theta,\phi).$$
(28)

Note that the rotational part is exact, and the vibrational part is an approximation when l > 0. The first order energy perturbation is

$$\epsilon_v^{(1)} = \langle vlm | \hat{H}_1 | vlm \rangle \tag{29}$$

$$= \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} \frac{\chi_{v}(r)}{r} Y_{l,m}^{*}(\theta,\phi) \frac{\dot{l}^{2}}{2\mu r^{2}} \frac{\chi_{v}(r)}{r} Y_{lm}(\theta,\phi) \sin\theta \, d\theta \, d\phi \, r^{2} \, dr$$
(30)

$$= l(l+1) \int_0^\infty \frac{\hbar^2}{2\mu r^2} |\chi_v(r)|^2 dr$$
(31)

so

$$B_v \approx \frac{\hbar^2}{2\mu} \int_0^\infty \frac{|\chi_v(r)|^2}{r^2} dr.$$
 (32)

2b. Derive an expression for the vibrational energies ϵ_v , for given parameters D_e , r_e , and α , and assuming the reduced mass of the diatom is μ . To simplify the problem, make an harmonic approximation of the Morse potential, i.e., make a Taylor expansion up to second order around the minimum, and use that as the potential.

Answer: For $r = r_e$ the Morse potential is zero. Since the potential is non-negative, the minimum must be at $r = r_e$. The second derivative of the potential in the minimum is

$$\frac{\partial^2}{\partial r^2} V(r) = \frac{\partial^2}{\partial r^2} D_e [1 - e^{-\alpha(r - r_e)}]^2$$
(33)

$$= 2\alpha D_e \frac{\partial}{\partial r} [1 - e^{-\alpha(r - r_e)}]$$
(34)

$$=2\alpha^2 D_e \tag{35}$$

so the Taylor expansion of the potential to second order is

$$V(r) \approx \frac{1}{2}k(r - r_e)^2, \quad with \ k = 2\alpha^2 D_e.$$
(36)

In this approximation the vibrational energies are

$$\epsilon_v = (v + \frac{1}{2})\hbar\omega \tag{37}$$

with

$$\omega = \sqrt{\frac{k}{\mu}} = \alpha \sqrt{\frac{2D_e}{\mu}}.$$
(38)

so

$$\epsilon_v = (v + \frac{1}{2})\hbar\alpha \sqrt{\frac{2D_e}{\mu}}.$$
(39)

2c. Give the expression for B_v in terms of the Morse parameters and the reduced mass using the harmonic approximation.

Answer:

$$B = \frac{\hbar^2}{2\mu r_e^2} \tag{40}$$

2d. Show that the wave functions in Eq. (4.66) of the lecture notes are solutions to the Schrödinger equation (4.54).

Answer:

$$\hat{H}\Psi_{vlm} = \left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{l}^2}{2\mu r^2} + V(r)\right]\frac{\chi_{vl}(r)}{r}Y_{lm}(\theta,\phi)$$
(41)

First, we note that the spherical harmonic Y_{lm} is an eigenfunction of the \hat{l}^2 with eigenvalue $\hbar^2 l(l+1)$, so

$$\hat{H}\Psi_{vlm}(r,\theta,\phi) = \left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)\right]\frac{\chi_{vl}(r)}{r}Y_{lm}(\theta,\phi)$$
(42)

$$=\frac{1}{r}Y_{lm}(\theta,\phi)\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}+\frac{\hbar^2 l(l+1)}{2\mu r^2}+V(r)\right]\chi_{vl}(r)$$
(43)

$$=\frac{1}{r}Y_{lm}(\theta,\phi)\epsilon_{vl}\chi_{vl}(r) \tag{44}$$

$$=\epsilon_{vl}\Psi_{vlm}(r,\theta,\phi).$$
(45)

Question 3: Chapter 4: "left as an exercise" in lecture notes

When studying chapter 4 you will find some of the math "left as an exercise". These exercises are collected here. The answers will be put online, use this question if you want to give it a try yourself.

3a. Show that

$$\epsilon_{ijk}\epsilon_{ij'k'} = \delta_{jj'}\delta_{kk'} - \delta_{jk'}\delta_{kj'}.$$
(46)

Answer: On the left-hand-side (lhs) there is a summation over *i*, so the quation has to be checked for all possible values of *j*, *j'*, *k*, and *k'*. One way is to tabulate the lhs and rhs for all 3^4 possible sets of *j*, *j''*, *k*, and *k'*. The alternative is a bit of reasoning:

(i) First, consider all cases with j = k. The lhs will be zero. The rhs will also be zero:

$$\delta_{jj'}\delta_{jk'} - \delta_{jk'}\delta_{jj'} = 0, \tag{47}$$

(ii)Next, consider $j \neq k$. On the lhs if $j' \neq j$ and $j' \neq k$, the result will be zero, since j' must have the only value of i for which $\epsilon_{ijk} \neq 0$. On the rhs, if $j' \neq j$ and $j' \neq k$, then both terms on are zero. Thus, we need to check the equation for either j' = j or j' = k (and $j \neq k$):

(iiia)Consider j' = j. The lhs will only be nonzero if k' = k. On the rhs, if j' = j

$$\delta_{jj}\delta_{kk'} - \delta_{jk'}\delta_{jk} = \delta_{kk'} - \delta_{jk'}\delta_{jk}.$$
(48)

The second term is zero since we are considering $j \neq k$, so the result is $\delta_{kk'}$, just as on the lhs. (*iiib*)Consider j' = k. The lhs will only be nonzero if k' = j, in which case the result is $\epsilon_{ijk}\epsilon_{ikj} = -1$. On the rhs, if j' = k we get (remember $j \neq k$)

$$\delta_{jk}\delta_{kk'} - \delta_{jk'}\delta_{kk} = -\delta_{jk'},\tag{49}$$

which is also -1 when k' = j.

3b. Show that

$$p_r \equiv \hat{\boldsymbol{r}} \cdot \boldsymbol{p} \tag{50}$$

is the moment conjugate to the coordinate $r = |\mathbf{r}|$.

Answer: The conjugate momentum is defined as

$$p_r = \frac{\partial T}{\partial \dot{r}},\tag{51}$$

where

$$T = \frac{1}{2}\mu |\dot{\boldsymbol{r}}|^2. \tag{52}$$

The vector \mathbf{r} in spherical polar coordinates is

$$\boldsymbol{r} = r \begin{pmatrix} \cos \phi \sin \theta \\ \sin \phi \sin \theta \\ \cos \theta \end{pmatrix} = r \hat{\boldsymbol{r}}, \tag{53}$$

so

$$\dot{\boldsymbol{r}} = \dot{r}\hat{\boldsymbol{r}} + r\phi\boldsymbol{r}_{\phi} + r\theta\boldsymbol{r}_{\theta} \tag{54}$$

where

$$\boldsymbol{r}_{\phi} = \frac{\partial \hat{\boldsymbol{r}}}{\partial \phi} = \begin{pmatrix} -\sin\phi\sin\theta\\\cos\phi\sin\theta\\0 \end{pmatrix}$$
(55)

and

$$\boldsymbol{r}_{\theta} = \frac{\partial \hat{\boldsymbol{r}}}{\partial \theta} = \begin{pmatrix} \cos \phi \cos \theta \\ \sin \phi \cos \theta \\ -\sin \theta \end{pmatrix}.$$
 (56)

Note that $\hat{\mathbf{r}}$, \mathbf{r}_{ϕ} , and \mathbf{r}_{θ} are an orthogonal set of vectors, with

$$|\hat{\boldsymbol{r}}| = 1 \tag{57}$$

$$|\boldsymbol{r}_{\phi}| = \sin\theta \tag{58}$$

$$|\boldsymbol{r}_{\theta}| = 1 \tag{59}$$

so

$$T = \frac{1}{2}\mu \dot{\boldsymbol{r}} \cdot \dot{\boldsymbol{r}} \tag{60}$$

$$= \frac{1}{2}\mu(\dot{r}\hat{r} + r\dot{\phi}r_{\phi} + r\dot{\theta}r_{\theta}) \cdot (\dot{r}\hat{r} + r\dot{\phi}r_{\phi} + r\dot{\theta}r_{\theta})$$
(61)

$$= \frac{1}{2}\mu\dot{r}^2 + r^2\dot{\phi}^2\sin^2\theta + r^2\dot{\theta}^2.$$
 (62)

So the momentum p_r is

$$p_r = \frac{\partial T}{\partial \dot{r}} = \mu \dot{r} \tag{63}$$

This is equal to Eq. (50), since

$$\hat{\boldsymbol{r}} \cdot \boldsymbol{p} = \mu \hat{\boldsymbol{r}} \cdot \dot{\boldsymbol{r}} = \mu \dot{\boldsymbol{r}},\tag{64}$$

where we used Eq. (54) in the last step.

This derivation can be simplified by noting that since the length of the vector $|\hat{\mathbf{r}}| = 1$, its timederivative must be perpendicular to it. So, we do not have to introduce the angles, but instead start from

$$\dot{\boldsymbol{r}} = \frac{\partial}{\partial t} r \hat{\boldsymbol{r}} = \dot{r} \hat{\boldsymbol{r}} + r \dot{\hat{\boldsymbol{r}}}$$
(65)

 $and \ use$

$$\dot{\boldsymbol{r}}\dot{\boldsymbol{r}} = \dot{r}^2 + r^2 |\dot{\hat{\boldsymbol{r}}}|^2, \tag{66}$$

where the second term does not depend on \dot{r} .

3c. Derive this commutation relation

$$[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}.$$
(67)

Answer: On the lhs we have

$$[\hat{A}, \hat{B}\hat{C}] = \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A}.$$
(68)

On the rhs of Eq. (67) we have

$$\hat{B}[\hat{A},\hat{C}] + [\hat{A},\hat{B}]\hat{C} = \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A} + \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C}$$
(69)

$$=\hat{A}\hat{B}\hat{C}-\hat{B}\hat{C}\hat{A},\tag{70}$$

q.e.d.

3d. Using Levi-Civita tensors, show that

$$[\hat{l}_i, \hat{l}_{i'}] = i\hbar\epsilon_{ii'j}\hat{l}_j. \tag{71}$$

Answer:		
	$[\hat{l}_i,\hat{l}_{i'}]=\epsilon_{ijk}\epsilon_{i'j'k'}[r_j\hat{p}_k,r_{j'}\hat{p}_{k'}]$	(72)
	$=\epsilon_{ijk}\epsilon_{i'j'k'}(r_j[\hat{p}_k,r_{j'}]\hat{p}_{k'}+r_{j'}[r_j,\hat{p}_{k'}]\hat{p}_k)$	(73)
	$=i\hbar\epsilon_{ijk}\epsilon_{i'j'k'}(-\delta_{kj'}r_j\hat{p}_{k'}+\delta_{jk'}r_{j'}\hat{p}_k)$	(74)
	$=i\hbar(-\epsilon_{ijk}\epsilon_{i'kk'}r_j\hat{p}_{k'}+\epsilon_{ijk}\epsilon_{i'j'j}r_{j'}\hat{p}_k)$	(75)
	$=i\hbar(-\epsilon_{ijk}\epsilon_{k'i'k}r_j\hat{p}_{k'}+\epsilon_{ijk}\epsilon_{j'ji'}r_{j'}\hat{p}_k)$	(76)
	$=i\hbar(-[\delta_{ik'}\delta_{ji'}-\delta_{ii'}\delta_{jk'}]r_j\hat{p}_{k'}+[\delta_{ij'}\delta_{ki'}-\delta_{ii'}\delta_{j'k}]r_{j'}\hat{p}_k)$	(77)
	$=i\hbar(-\delta_{ik'}\delta_{ji'}r_j\hat{p}_{k'}+\delta_{ij'}\delta_{ki'}r_{j'}\hat{p}_k)$	(78)
	$=i\hbar(-\delta_{ik}\delta_{ji'}r_j\hat{p}_k+\delta_{ij}\delta_{ki'}r_j\hat{p}_k)$	(79)
	$= i\hbar (\delta_{ij}\delta_{i'k} - \delta_{ik}\delta_{i'j})r_j\hat{p}_k$	(80)
	$=i\hbar\epsilon_{mii'}\epsilon_{mjk}r_j\hat{p}_k$	(81)
	$= i\hbar\epsilon_{ii'm}\hat{l}_m.$	(82)

In step Eq. (75-76) and in the last step we used that the Levi-Civita tensor is invariant under cyclic permutations of the indices.

3e. Show that

$$\hat{t}^2 = r^2 \hat{p}^2 + \hbar^2 (\boldsymbol{r} \cdot \boldsymbol{\nabla})^2 + \hbar^2 \boldsymbol{r} \cdot \boldsymbol{\nabla}.$$
(83)

Use the Levi-Civita tensor relation

$$\epsilon_{ijk}\epsilon_{ij'k'} = \delta_{jj}\delta_{kk} - \delta_{jk'}\delta_{j'k}.$$
(84)

Answer:

$$\hat{l}^2 = l \cdot l \tag{85}$$

$$=\epsilon_{ijk}\epsilon_{ij'k'}r_j\hat{p}_kr_{j'}\hat{p}_{k'} \tag{86}$$

$$= (\delta_{jj'}\delta_{kk'} - \delta_{jk'}\delta_{j'k})r_j\hat{p}_k r_{j'}\hat{p}_{k'}$$
(87)

$$=\underbrace{\delta_{jj'}\delta_{kk'}r_jp_kr_{j'}p_{k'}}_{A} - \underbrace{\delta_{jk'}\delta_{j'k}r_jp_kr_{j'}p_{k'}}_{B}.$$
(88)

The first term (A) gave r^2p^2 in the classical expression, but here we must change the order of \hat{p}_k and $r_{j'}$ to get this, so we use

$$\hat{p}_k r_{j'} = r_{j'} \hat{p}_k + [\hat{p}_k, r_{j'}]. \tag{89}$$

The first term on the rhs will lead to the r^2p^2 classical contribution and we get a new contribution from the commutator:

$$[\hat{p}_k, r_{j'}] = -i\hbar\delta_{kj'}.\tag{90}$$

If we use this in A we get

$$-i\hbar\delta_{jj'}\delta_{kk'}\delta_{kj'}r_j\hat{p}_{k'} = -i\hbar r_j\hat{p}_j = -i\hbar \boldsymbol{r}\cdot\hat{\boldsymbol{p}}.$$
(91)

Taken together we get for A,

$$A = r^2 \hat{p}^2 - i\hbar \boldsymbol{r} \cdot \hat{\boldsymbol{p}},\tag{92}$$

where $\hat{p}^2 = \hat{p} \cdot \hat{p}$. The second term in Eq. (88), B, gave $r^2(\hat{r} \cdot p)^2 = (\mathbf{r} \cdot p)^2$ in the classical derivation, but again, we have to change the order, and we will get extra terms from the commutators needed to do that. Since momentum operators commute with eachother, we only have to commute $r_{j'}$ and $\hat{p}_{k'}$, and also the order of \hat{p}_k and $r_{j'}$ must be changed. Thus,

$$B = \delta_{jk'} \delta_{j'k} r_j \hat{p}_k (\hat{p}_{k'} r_{j'} + [r_{j'}, \hat{p}_{k'}])$$
(93)

$$=\delta_{jk'}r_j\hat{p}_{k'}\delta_{j'k}\hat{p}_kr_{j'} + i\hbar\delta_{jk'}\delta_{j'k}\delta_{j'k'}r_j\hat{p}_k \tag{94}$$

$$= (\boldsymbol{r} \cdot \boldsymbol{p})\delta_{j'k}(r_{j'}\dot{p}_k + [\dot{p}_k, r_{j'}]) + i\hbar\boldsymbol{r} \cdot \boldsymbol{p}$$
(95)

$$= (\boldsymbol{r} \cdot \boldsymbol{p})^2 - i\hbar (\boldsymbol{r} \cdot \hat{\boldsymbol{p}})\delta_{j'k}\delta_{kj'} + i\hbar \boldsymbol{r} \cdot \hat{\boldsymbol{p}}$$
(96)

In the second term we have

$$\delta_{j'k}\delta_{kj'} = \delta_{j'k}^2 = \sum_{j'=1}^3 \sum_{k'=1}^3 \delta_{j'k} = \sum_{j'=1}^3 1 = 3,$$
(97)

so

$$B = (\boldsymbol{r} \cdot \hat{\boldsymbol{p}})^2 - 2i\hbar \boldsymbol{r} \cdot \hat{\boldsymbol{p}}$$
(98)

and together with A,

$$\hat{l}^2 = A - B = r^2 \hat{p}^2 - (\boldsymbol{r} \cdot \hat{\boldsymbol{p}})^2 + i\hbar \boldsymbol{r} \cdot \hat{\boldsymbol{p}}.$$
(99)

With $\hat{p} = -i\hbar \nabla$ we get the final result

$$\hat{l}^2 = r^2 \hat{p}^2 + \hbar^2 (\boldsymbol{r} \cdot \boldsymbol{\nabla})^2 + \hbar^2 \boldsymbol{r} \cdot \boldsymbol{\nabla}.$$
(100)

3f. For the vector \boldsymbol{r} , defined by spherical polar angles θ , ϕ , and length r, calculate the Jacobian,

$$\boldsymbol{J} = \begin{bmatrix} \frac{\partial \boldsymbol{r}}{\partial r} \frac{\partial \boldsymbol{r}}{\partial \theta} \frac{\partial \boldsymbol{r}}{\partial \phi} \end{bmatrix},\tag{101}$$

show that the columns of \boldsymbol{J} are orthogonal, and calculate their lengths.

Answer:

$$\frac{\partial \boldsymbol{r}}{\partial r} = \begin{pmatrix} \cos\phi\sin\theta\\\sin\phi\sin\theta\\\cos\theta \end{pmatrix}$$
(102)

$$\frac{\partial \boldsymbol{r}}{\partial \theta} = r \begin{pmatrix} \cos \phi \cos \theta \\ \sin \phi \cos \theta \\ -\sin \theta \end{pmatrix}$$
(103)

$$\frac{\partial \boldsymbol{r}}{\partial \phi} = r \begin{pmatrix} -\sin\phi\sin\theta\\\cos\phi\sin\theta\\0 \end{pmatrix}. \tag{104}$$

 $The \ scalar \ products:$

$$\frac{\partial \boldsymbol{r}}{\partial r} \cdot \frac{\partial \boldsymbol{r}}{\partial r} = \cos^2 \phi \sin^2 \theta + \sin^2 \phi \sin^2 \theta + \cos^2 \theta$$

$$= (\cos^2 \phi + \sin^2 \phi) \sin^2 \theta + \cos^2 \theta = \sin^2 \theta + \cos^2 \theta = 1$$
(105)
(106)

$$\frac{\partial \boldsymbol{r}}{\partial \theta} \cdot \frac{\partial \boldsymbol{r}}{\partial \theta} = r^2 (\cos^2 \phi \cos^2 \theta + \sin^2 \phi \cos^2 \theta + \sin^2 \phi \cos^2 \theta + \sin^2 \phi) = r^2 (\cos^2 \theta + \sin^2 \theta) = r^2 \quad (107)$$

$$\frac{\partial \boldsymbol{r}}{\partial \phi} \cdot \frac{\partial \boldsymbol{r}}{\partial \phi} = r^2 (\sin^2 \phi \sin^2 \theta + \cos^2 \phi \sin^2 \theta) = r^2 \sin^2 \theta \tag{108}$$

$$\frac{\partial \boldsymbol{r}}{\partial r} \cdot \frac{\partial \boldsymbol{r}}{\partial \theta} = r(\cos^2 \sin \theta \cos \theta + \sin^2 \phi \sin \theta \cos \theta - \cos \theta \sin \theta) = 0$$
(109)

$$\frac{\partial \boldsymbol{r}}{\partial r} \cdot \frac{\partial \boldsymbol{r}}{\partial \phi} = r(-\cos\phi\sin\phi\sin^2\theta + \sin\phi\cos\phi\sin^2\theta) = 0$$
(110)

$$\frac{\partial \boldsymbol{r}}{\partial \theta} \cdot \frac{\partial \boldsymbol{r}}{\partial \phi} = r^2 (-\cos\phi\sin\phi\cos\theta\sin\theta + \sin\phi\cos\phi\cos\theta\sin\theta) = 0.$$
(111)

So, the columns are orthogonal, and their lengths are 1, r, and $r\sin\theta$.