Quantum Dynamics, NWI-SM295, exercises week 4

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Question 1: Kinetic energy operator in 3D

In this exercise we derive

$$-\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{l}^2}{2\mu r^2}. \tag{1}$$

The angular momentum operator is defined by

$$\hat{\boldsymbol{l}} = \boldsymbol{r} \times \hat{\boldsymbol{p}}, \tag{2}$$

where the linear momentum operator is

$$\hat{\boldsymbol{p}} = -i\hbar\boldsymbol{\nabla}. \tag{3}$$

The first step is to work out the $\hat{l}^2$ operator and to show that

$$\hat{l}^2 = -\hbar^2(\boldsymbol{r}\times\boldsymbol{\nabla})\cdot(\boldsymbol{r}\times\boldsymbol{\nabla}) = \hbar^2[-r^2\nabla^2 + \boldsymbol{r}\cdot\boldsymbol{\nabla} + (\boldsymbol{r}\cdot\boldsymbol{\nabla})^2]. \tag{4}$$

A convenient way to work with cross products,

$$\boldsymbol{a} = \boldsymbol{b}\times\boldsymbol{c}, \tag{5}$$

is to write the components using the Levi-Civita tensor ϵ_{ijk},

$$a_i = \epsilon_{ijk}b_jc_k \equiv \sum_{j=1}^{3}\sum_{k=1}^{3}\epsilon_{ijk}b_jc_k, \tag{6}$$

where we introduced the Einstein summation convention: whenever an index appears twice one assumes there is a sum over this index.

1a. Write the cross product in components and show that

$$\epsilon_{1,2,3} = \epsilon_{2,3,1} = \epsilon_{3,1,2} = 1, \tag{7}$$

$$\epsilon_{3,2,1} = \epsilon_{2,1,3} = \epsilon_{1,3,2} = -1, \tag{8}$$

and all other component of the tensor are zero. Note: the tensor is $+1$ for $\epsilon_{1,2,3}$, it changes sign whenever two indices are permuted, and as a result it is zero whenever two indices are equal.

Answer: *The cross product in components is:*

$$\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix} = \begin{pmatrix}b_1\\b_2\\b_3\end{pmatrix}\times\begin{pmatrix}c_1\\c_2\\c_3\end{pmatrix} = \begin{pmatrix}b_2c_3-b_3c_2\\b_3c_1-b_1c_3\\b_1c_2-b_2c_3\end{pmatrix}. \tag{9}$$

1b. Check this relation

$$\epsilon_{ijk}\epsilon_{ij'k'} = \delta_{jj'}\delta_{kk'} - \delta_{jk'}\delta_{j'k}. \tag{10}$$

(Remember the implicit summation over index i).

Answer: *First consider $j = j'$, then the equation reads*

$$\epsilon_{ijk}\epsilon_{ijk'} = \delta_{kk'} - \delta_{jk'}\delta_{jk} \tag{11}$$

When $k \neq k'$ we get zero on the left-hand-side (lhs) since i, j, k and at the same time i, j, k' have to be distinct, which is not possible. The right-hand-side (rhs) also gives zero, since $\delta_{jk'}$ and δ_{jk} cannot both be nonzero.

When $k = k'$ we get

$$\sum_i \epsilon_{ijk}^2 = 1 - \delta_{jk}^2 \tag{12}$$

This relation is also correct: if $j = k$ we get zero on both sides, and when $j \neq k$ there is always one i that makes ϵ_{ijk} nonzeros, and we get one on both sides of the equation.

Next, we consider $j \neq j'$, which gives

$$\epsilon_{ijk}\epsilon_{ij'k'} = -\delta_{jk'}\delta_{j'k} \tag{13}$$

When $k = k'$ both sides must be zero.

When $k \neq k'$ we first consider $k = j$, for which both sides are zero (on the lhs ϵ_{ijk} will be zero, and on the rhs $k = j$ means $k \neq j'$, so $\delta_{j'k}$ is zero).

Finally, when $j \neq j'$, $k \neq k'$, and $k \neq j$ we have two cases: $k = j'$ and $k \neq j'$. First, when $k = j'$, we only get nonzero on the lhs when $k' = j$ - and both lhs and rhs will be -1. When $k \neq j'$ (and $k \neq j$), both sides are zero.

1c. Use Eq. (10) to derive Eq. (4).

Answer:

$$
\begin{aligned}
(\boldsymbol{r} \times \boldsymbol{\nabla}) \cdot (\boldsymbol{r} \times \boldsymbol{\nabla}) &= \sum_{i=1}^{3} (\boldsymbol{r} \times \boldsymbol{\nabla})_i \ (\boldsymbol{r} \times \boldsymbol{\nabla})_i && (14)\\
&= \epsilon_{ijk}\, r_j \nabla_k \ \epsilon_{ij'k'}\, r_{j'} \nabla_{k'} && (15)\\
&= [\delta_{jj'}\delta_{kk'} - \delta_{jk'}\delta_{j'k}] r_j \nabla_k r_{j'} \nabla_{k'} && (16)\\
&= \delta_{jj'}\delta_{kk'} r_j \nabla_k r_{j'} \nabla_{k'} - \delta_{jk'}\delta_{j'k} r_j \nabla_k r_{j'} \nabla_{k'} && (17)\\
&= \delta_{jj'}\delta_{kk'} r_j (\delta_{kj'} + r_{j'}\nabla_k) \nabla_{k'} - \delta_{jk'}\delta_{j'k} r_j (\delta_{kj'} + r_{j'}\nabla_k) \nabla_{k'} && (18)\\
&= \delta_{jj'}\delta_{kk'} r_j r_{j'} \nabla_k \nabla_{k'} + (\delta_{jj'}\delta_{kk'} - \delta_{jk'}\delta_{j'k})\delta_{kj'} r_j \nabla_{k'} - \delta_{jk'}\delta_{j'k} r_j r_{j'} \nabla_k \nabla_{k'} && (19)\\
&= r^2\nabla^2 + \underbrace{\delta_{jj'}\delta_{kk'}\delta_{kj'}}_{=\delta_{jk'}} r_j \nabla_{k'} - \delta_{jk'} \underbrace{\delta_{j'k}\delta_{kj'}}_{=3} r_j \nabla_{k'} - \delta_{jk'} r_j (\boldsymbol{r} \cdot \boldsymbol{\nabla}) \nabla_{k'} && (20)\\
&= r^2\nabla^2 - 2\boldsymbol{r} \cdot \boldsymbol{\nabla} - \delta_{jk'} \{ \underbrace{[r_j, \boldsymbol{r} \cdot \boldsymbol{\nabla}]}_{=[r_j, r_j \nabla_j] = -r_j} + (\boldsymbol{r} \cdot \boldsymbol{\nabla}) r_j \} \nabla_{k'} && (21)\\
&= r^2\nabla^2 - 2\boldsymbol{r} \cdot \boldsymbol{\nabla} + \underbrace{\delta_{jk'} r_j \nabla_{k'}}_{=\boldsymbol{r}\cdot\boldsymbol{\nabla}} - (\boldsymbol{r} \cdot \boldsymbol{\nabla}) \underbrace{\delta_{jk'} r_j \nabla_{k'}}_{=\boldsymbol{r}\cdot\boldsymbol{\nabla}} && (22)\\
&= r^2\nabla^2 - \boldsymbol{r} \cdot \boldsymbol{\nabla} - (\boldsymbol{r} \cdot \boldsymbol{\nabla})^2. && (23)
\end{aligned}
$$

1d. Show that

$$r \frac{\partial}{\partial r} = \boldsymbol{r} \cdot \boldsymbol{\nabla} \tag{24}$$

Answer: *The vector $\boldsymbol{r}$ can be written as*

$$\boldsymbol{r} = r \hat{\boldsymbol{r}}, \tag{25}$$

where $r = |\boldsymbol{r}|$ and $\hat{\boldsymbol{r}}$ is the unit vector in the direction $\boldsymbol{r}$. Taking the derivative with respect to r, for a fixed direction $\hat{\boldsymbol{r}}$ gives

$$\frac{\partial}{\partial r} \boldsymbol{r} = \frac{\partial}{\partial r} r \hat{\boldsymbol{r}} = \hat{\boldsymbol{r}}. \tag{26}$$

The may be written in components

$$\frac{\partial}{\partial r} r_i = \frac{r_i}{r}. \tag{27}$$

The chain rule gives

$$\frac{\partial}{\partial r} = \frac{\partial r_i}{\partial r} \frac{\partial}{\partial r_i} = \frac{r_i}{r} \frac{\partial}{\partial r_i} = \frac{1}{r} r_i \nabla_i = \frac{1}{r} \boldsymbol{r} \cdot \boldsymbol{\nabla}. \tag{28}$$

If we multiply this equation with r we get

$$r \frac{\partial}{\partial r} = \boldsymbol{r} \cdot \boldsymbol{\nabla}. \tag{29}$$

1e. Show that

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} r = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \tag{30}$$

Answer:

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}r = \frac{1}{r}\frac{\partial}{\partial r}\left(1 + r\frac{\partial}{\partial r}\right) \tag{31}$$

$$= \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r}\left(\frac{\partial}{\partial r} + r\frac{\partial^2}{\partial r^2}\right) \tag{32}$$

$$= \frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}. \tag{33}$$

1f. Combine the results to derive Eq. (1).

Answer: *From Eq. 4 we get*

$$\hbar^2\nabla^2 = \hbar^2\frac{1}{r^2}[\underbrace{\boldsymbol{r}\cdot\boldsymbol{\nabla}}_{r\frac{\partial}{\partial r}} + \underbrace{(\boldsymbol{r}\cdot\boldsymbol{\nabla})^2}_{(r\frac{\partial}{\partial r})^2}] - \frac{\hat{l}^2}{r^2} \tag{34}$$

$$= \hbar^2[\frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}] - \frac{\hat{l}^2}{r^2} \tag{35}$$

$$= \hbar^2[\frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}] - \frac{\hat{l}^2}{r^2} \tag{36}$$

$$= \hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hat{l}^2}{r^2} \tag{37}$$

so

$$-\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{l}^2}{2\mu r^2}. \tag{38}$$

Question 2: Coupled channels equation for collinear $A + BC$

Three particles move along a line. Their coordinates are x_A, x_B, and x_C, and their masses m_A, m_B, and m_C. The kinetic energy operator is given by

$$\hat{T} = -\frac{\hbar^2}{2m_A}\frac{\partial^2}{\partial x_A^2} - \frac{\hbar^2}{2m_B}\frac{\partial^2}{\partial x_B^2} - \frac{\hbar^2}{2m_C}\frac{\partial^2}{\partial x_C^2}. \tag{39}$$

The center of mass coordinate is

$$X \equiv \frac{m_A x_A + m_B x_B + m_C x_C}{m_A + m_B + m_C} \tag{40}$$

and the Jacobi-coordinates for the $A + BC$ arrangement are

$$r \equiv x_B - x_C. \tag{41}$$

$$R \equiv x_A - \frac{m_B x_B + m_C x_C}{m_B + m_C}. \tag{42}$$

2a. Rewrite the kinetic energy in Jacobi/center-of-mass coordinates (X, R, r).

Answer: *The chain rule gives*

$$\frac{\partial}{\partial x_A} = \frac{\partial X}{\partial x_A}\frac{\partial}{\partial X} + \frac{\partial R}{\partial x_A}\frac{\partial}{\partial R} + \frac{\partial r}{\partial x_A}\frac{\partial}{\partial r} \tag{43}$$

$$\frac{\partial}{\partial x_B} = \frac{\partial X}{\partial x_B}\frac{\partial}{\partial X} + \frac{\partial R}{\partial x_B}\frac{\partial}{\partial R} + \frac{\partial r}{\partial x_B}\frac{\partial}{\partial r} \tag{44}$$

$$\frac{\partial}{\partial x_C} = \frac{\partial X}{\partial x_C}\frac{\partial}{\partial X} + \frac{\partial R}{\partial x_C}\frac{\partial}{\partial R} + \frac{\partial r}{\partial x_C}\frac{\partial}{\partial r} \tag{45}$$

so (with $M = m_A + m_B + m_C$ and $M_{BC} = m_B + m_C$)

$$\frac{\partial}{\partial x_A} = \frac{m_A}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial R} \tag{46}$$
$$\frac{\partial}{\partial x_B} = \frac{m_B}{M}\frac{\partial}{\partial X} - \frac{m_B}{M_{BC}}\frac{\partial}{\partial R} + \frac{\partial}{\partial r} \tag{47}$$
$$\frac{\partial}{\partial x_C} = \frac{m_C}{M}\frac{\partial}{\partial X} - \frac{m_C}{M_{BC}}\frac{\partial}{\partial R} - \frac{\partial}{\partial r} \tag{48}$$

The second derivatives including the mass factors

$$\frac{1}{m_A}\frac{\partial^2}{\partial x_A^2} = \frac{m_A}{M^2}\frac{\partial^2}{\partial X^2} + \frac{1}{m_A}\frac{\partial^2}{\partial R^2} + \frac{2}{M}\frac{\partial^2}{\partial X \partial R} \tag{49}$$
$$\frac{1}{m_B}\frac{\partial^2}{\partial x_B^2} = \frac{m_B}{M^2}\frac{\partial^2}{\partial X^2} + \frac{m_B}{M_{BC}^2}\frac{\partial^2}{\partial R^2} + \frac{1}{m_B}\frac{\partial^2}{\partial r^2} - \frac{2m_B}{MM_{BC}}\frac{\partial^2}{\partial X \partial R} + \frac{2}{M}\frac{\partial^2}{\partial X \partial r} - \frac{2}{M_{BC}}\frac{\partial^2}{\partial R \partial r} \tag{50}$$
$$\frac{1}{m_C}\frac{\partial^2}{\partial x_C^2} = \frac{m_C}{M^2}\frac{\partial^2}{\partial X^2} + \frac{m_C}{M_{BC}^2}\frac{\partial^2}{\partial R^2} + \frac{1}{m_C}\frac{\partial^2}{\partial r^2} - \frac{2m_C}{MM_{BC}}\frac{\partial^2}{\partial X \partial R} - \frac{2}{M}\frac{\partial^2}{\partial X \partial r}. + \frac{2}{M_{BC}}\frac{\partial^2}{\partial R \partial r}. \tag{51}$$

In the sum all the cross terms cancel, and the kinetic energy operator becomes

$$\hat{T} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_{BC}}\frac{\partial^2}{\partial r^2} \tag{52}$$

with the reduced masses

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{M_{BC}} \tag{53}$$
$$\frac{1}{\mu_{BC}} = \frac{1}{m_B} + \frac{1}{m_C}. \tag{54}$$

The potential V is assumed to be independent of X, so the Hamiltonian can be written as

$$\hat{H} = \hat{T} + V(R, r). \tag{55}$$

For large R we find the potential for molecule BC:

$$V_{BC}(r) = \lim_{R\to\infty} V(R, r). \tag{56}$$

2b. Derive the Schrödinger equation for the vibrational wave functions $\phi_v(r)$ of molecule BC.

Answer:

$$\underbrace{\left[-\frac{\hbar^2}{2\mu_{BC}}\frac{\partial^2}{\partial r^2} + V_{BC}(r)\right]}_{\equiv \hat{H}_{BC}} \phi_v(r) = \epsilon_v \phi_v(r). \tag{57}$$

The multichannel expansion is given by

$$\Psi(R, r) = \sum_v \phi_v(r) u_v(R). \tag{58}$$

2c. Derive the coupled channels equation

$$\boldsymbol{u}''(R) = \boldsymbol{W}(R)\boldsymbol{u}(R) \tag{59}$$

and find an expression for the $\boldsymbol{W}$ matrix.

Answer: *In a center-of-mass coordinate system we may drop the C.O.M. kinetic energy term. The* *time-independent Schrödinger equation is*

$$\left[\hat{H} - E\right] \Psi(R, r) = 0 \tag{60}$$

$$\left[\hat{T}_R + \hat{T}_r + V(R, r) - E\right] \Psi(R, r) = 0, \tag{61}$$

where we defined

$$\hat{T}_R = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \tag{62}$$

$$\hat{T}_r = -\frac{\hbar^2}{2\mu_{BC}} \frac{\partial^2}{\partial r^2} \tag{63}$$

We furtermore define the interaction potential

$$\Delta V(R, r) = V(R, r) - V_{BC}(r) \tag{64}$$

so the Schrödinger equation becomes

$$\left[\hat{T}_R + \hat{T}_r + V_{BC}(r) + \Delta V(R, r) - E\right] \Psi(R, r) = 0 \tag{65}$$

$$\left[\hat{T}_R + \hat{H}_{BC} + \Delta V(R, r) - E\right] \sum_v \phi_v(r) u_v(R) = 0. \tag{66}$$

Projecting with $\langle \phi_{v'} |$ *gives*

$$\sum_v \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \delta_{v'v} + \delta_{v'v}(\epsilon_v - E) + \langle \phi_{v'} | \Delta V(R, r) | \phi_v \rangle\right] u_v(R) = 0 \tag{67}$$

or

$$\frac{\partial^2}{\partial R^2} u_{v'}(R) = \frac{2\mu}{\hbar^2} \sum_v \left[\delta_{v'v}(\epsilon_v - E) + \langle \phi_{v'} | \Delta V(R, r) | \phi_v \rangle\right] u_v(R) \tag{68}$$

In matrix notation this becomes Eq. (59) with $\boldsymbol{W}$*-matrix elements*

$$W_{v'v}(R) = \frac{2\mu}{\hbar^2} \left[\delta_{v'v}(\epsilon_v - E) + \langle \phi_{v'} | \Delta V(R, r) | \phi_v \rangle\right]. \tag{69}$$