F. TRANSLATION VS MOMENTUM AND ROTATION VS ANGULAR MOMENTUM

It was shown in Chapter 2 that the Hamiltonian $\hat{H}$ commutes with any translation (p. 61) or rotation (p. 63) operator, denoted as $\hat{\mathcal{U}}$:

$$[\hat{H}, \hat{\mathcal{U}}] = 0. \tag{F.1}$$

1 THE FORM OF THE $\hat{\mathcal{U}}$ OPERATOR

Below it will be demonstrated for $\boldsymbol{\kappa}$, meaning first a translation vector, and then a rotation angle about an axis in 3D space, that operator $\hat{\mathcal{U}}$ is of the form

$$\hat{\mathcal{U}} = \exp\left(-\frac{i}{\hbar}\boldsymbol{\kappa}\cdot\hat{\boldsymbol{K}}\right), \tag{F.2}$$

where $\hat{\boldsymbol{K}}$ stands for a Hermitian operator (with x, y, z components) acting on functions of points in 3D Cartesian space.

Translation and momentum operators

Translation of a function by a vector $\Delta\boldsymbol{r}$ just represents function f in the coordinate system translated in the opposite direction, i.e. $f(\boldsymbol{r}-\Delta\boldsymbol{r})$, see Fig. 2.3 and p. 62. If vector $\Delta\boldsymbol{r}$ is *infinitesimally small, then, in order to establish the relation between $f(\boldsymbol{r}-\Delta\boldsymbol{r})$ and $f(\boldsymbol{r})$, it is of course sufficient to know the gradient of f* (neglecting, obviously, the quadratic and higher terms in the Taylor expansion):

$$f(\boldsymbol{r}-\Delta\boldsymbol{r}) = f(\boldsymbol{r}) - \Delta\boldsymbol{r}\cdot\nabla f = (1-\Delta\boldsymbol{r}\cdot\nabla)f(\boldsymbol{r}). \tag{F.3}$$

We will compose a large translation of a function (by vector $\boldsymbol{T}$) from a number of small increments $\Delta\boldsymbol{r} = \frac{1}{N}\boldsymbol{T}$, where N is a veeery large natural number. Such a tiny translation will be repeated N times, thus recovering the translation of the function by $\boldsymbol{T}$. In order for the gradient formula to be exact, we have to ensure N tending to infinity. Recalling the definition $\exp(ax) = \lim_{N\to\infty}(1+\frac{a}{x})^N$, we have:

$$\hat{\mathcal{U}}(\boldsymbol{T})f(\boldsymbol{r}) = f(\boldsymbol{r}-\boldsymbol{T}) = \lim_{N\to\infty}\left(1-\frac{\boldsymbol{T}}{N}\nabla\right)^N f(r)$$
$$= \exp(-\boldsymbol{T}\cdot\nabla)f = \exp\left(-\frac{i}{\hbar}\boldsymbol{T}\cdot\hat{\boldsymbol{p}}\right)f(\boldsymbol{r}),$$

where $\hat{\boldsymbol{p}} = -i\hbar\nabla$ is the total momentum operator (see Chapter 1). Thus, for translations we have $\boldsymbol{\kappa} \equiv \boldsymbol{T}$ and $\hat{\boldsymbol{K}} \equiv \hat{\boldsymbol{p}}$.

Rotation and angular momentum operator

Imagine a function $f(\boldsymbol{r})$ of positions in 3D Cartesian space (think, e.g., about a probability density distribution centred somewhere in space). Now suppose the function is to be rotated about the z axis (the unit vector showing its direction is $\boldsymbol{e}$) by an angle α, so we have another function, let us denote it by $\hat{\mathcal{U}}(\alpha; \boldsymbol{e}) f(\boldsymbol{r})$. What is the relation between $f(\boldsymbol{r})$ and $\hat{\mathcal{U}}(\alpha; \boldsymbol{e}) f(\boldsymbol{r})$? This is what we want to establish. This relation corresponds to the opposite rotation (i.e. by the angle $-\alpha$, see Fig. 2.1 and p. 58) of the coordinate system:

$$\hat{\mathcal{U}}(\alpha; \boldsymbol{e}) f(\boldsymbol{r}) = f\big(\boldsymbol{U}^{-1}\boldsymbol{r}\big) = f\big(\boldsymbol{U}(-\alpha; \boldsymbol{e})\boldsymbol{r}\big),$$

where $\boldsymbol{U}$ is a 3×3 orthogonal matrix. The new coordinates $x(\alpha), y(\alpha), z(\alpha)$ are expressed by the old coordinates x, y, z through[1]

$$\boldsymbol{r}' \equiv \begin{pmatrix} x(\alpha) \\ y(\alpha) \\ z(\alpha) \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

Therefore the rotated function $\hat{\mathcal{U}}(\alpha; \boldsymbol{e}) f(\boldsymbol{r}) = f(x(\alpha), y(\alpha), z(\alpha))$. The function can be expanded in the Taylor series about $\alpha = 0$:

$$\begin{aligned}
\hat{\mathcal{U}}(\alpha; \boldsymbol{e}) f(\boldsymbol{r}) &= f\big(x(\alpha), y(\alpha), z(\alpha)\big) = f(x, y, z) + \alpha\left(\frac{\partial f}{\partial \alpha}\right)_{\alpha=0} + \cdots \\
&= f(x, y, z) + \alpha\left(\frac{\partial x(\alpha)}{\partial \alpha}\frac{\partial f}{\partial x} + \frac{\partial y(\alpha)}{\partial \alpha}\frac{\partial f}{\partial y} + \frac{\partial z(\alpha)}{\partial \alpha}\frac{\partial f}{\partial z}\right)_{\alpha=0} + \cdots \\
&= f(x, y, z) + \alpha\left[y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right] f + \cdots
\end{aligned}$$

Now instead of the large rotation angle α, let us consider first an infinitesimally small rotation by angle $\varepsilon = \alpha/N$, where N is a huge natural number. In such a situation we retain only the first two terms in the previous equation:

$$\begin{aligned}
\hat{\mathcal{U}}\left(\frac{\alpha}{N}; \boldsymbol{e}\right) f(\boldsymbol{r}) &= f(x, y, z) + \frac{\alpha}{N}\left[y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right] f(x, y, z) \\
&= \left(1 + \frac{\alpha}{N}\frac{i\hbar}{i\hbar}\left[y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right]\right) f = \left(1 + \frac{\alpha}{N}\frac{1}{i\hbar}\left[x\hat{p}_y - y\hat{p}_x\right]\right) f \\
&= \left(1 - \frac{\alpha}{N}\frac{i}{\hbar}\hat{J}_z\right) f.
\end{aligned}$$

[1] A positive value of the rotation angle means an anticlockwise motion within the xy plane (x axis horizontal, y vertical, z axis pointing to us).

If such a rotation is repeated N times, we recover the rotation of the function by a (possibly large) angle α (the limit assures that ε is infinitesimally small):

$$\hat{\mathcal{U}}(\alpha; \boldsymbol{e}) f(\boldsymbol{r}) = \lim_{N\to\infty} \left[\hat{\mathcal{U}}\left(\frac{\alpha}{N}; \boldsymbol{e}\right)\right]^N f(\boldsymbol{r}) = \lim_{N\to\infty} \left(1 - \frac{\alpha}{N}\frac{i}{\hbar}\hat{J}_z\right)^N f(\boldsymbol{r})$$
$$= \exp\left(-i\frac{\alpha}{\hbar}\hat{J}_z\right) f = \exp\left(-\frac{i}{\hbar}\alpha \boldsymbol{e} \cdot \hat{\boldsymbol{J}}\right) f.$$

Thus for rotations $\hat{\mathcal{U}}(\alpha; \boldsymbol{e}) = \exp(-\frac{i}{\hbar}\alpha \boldsymbol{e} \cdot \hat{\boldsymbol{J}})$, and, therefore, we have $\boldsymbol{\kappa} \equiv \alpha \boldsymbol{e}$ and $\hat{\boldsymbol{K}} \equiv \hat{\boldsymbol{J}}$.

This means that, in particular for rotations about the x, y, z axes (with the corresponding unit vectors $\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{z}$) we have, respectively

$$\left[\hat{\mathcal{U}}(\alpha; \boldsymbol{x}), \hat{J}_x\right] = 0, \tag{F.4}$$

$$\left[\hat{\mathcal{U}}(\alpha; \boldsymbol{y}), \hat{J}_y\right] = 0, \tag{F.5}$$

$$\left[\hat{\mathcal{U}}(\alpha; \boldsymbol{z}), \hat{J}_z\right] = 0. \tag{F.6}$$

Useful relation

The relation (F.1) means that for any translation or rotation

$$\hat{\mathcal{U}}\hat{H}\hat{\mathcal{U}}^{-1} = \hat{H}$$

and taking into account the general form of eq. (F.2) we have for any such transformation a series containing nested commutators (valid for any $\boldsymbol{\kappa}$)

$$\hat{H} = \hat{\mathcal{U}}\hat{H}\hat{\mathcal{U}}^{-1} = \exp\left(-\frac{i}{\hbar}\boldsymbol{\kappa} \cdot \hat{\boldsymbol{K}}\right)\hat{H} \exp\left(\frac{i}{\hbar}\boldsymbol{\kappa} \cdot \hat{\boldsymbol{K}}\right)$$
$$= \left(1 - \frac{i}{\hbar}\boldsymbol{\kappa} \cdot \hat{\boldsymbol{K}} + \cdots\right)\hat{H}\left(1 + \frac{i}{\hbar}\boldsymbol{\kappa} \cdot \hat{\boldsymbol{K}} + \cdots\right)$$
$$= \hat{H} - \frac{i}{\hbar}\boldsymbol{\kappa} \cdot \left[\hat{\boldsymbol{K}}, \hat{H}\right] - \frac{\boldsymbol{\kappa}^2}{2\hbar^2}\left[\left[\hat{\boldsymbol{K}}, \hat{H}\right], \hat{\boldsymbol{K}}\right] + \cdots,$$

where each term in "$+\cdots$" contains $[\hat{\boldsymbol{K}}, \hat{H}]$. This means that to satisfy the equation we necessarily have

$$\left[\hat{\boldsymbol{K}}, \hat{H}\right] = \boldsymbol{0}. \tag{F.7}$$

2 THE HAMILTONIAN COMMUTES WITH THE TOTAL MOMENTUM OPERATOR

In particular this means $[\hat{\boldsymbol{p}}, \hat{H}] = \boldsymbol{0}$, i.e.

$$\left[\hat{p}_\mu, \hat{H}\right] = 0 \tag{F.8}$$

for $\mu = x, y, z$. Of course, we also have $[\hat{p}_\mu, \hat{p}_\nu] = 0$ for $\mu, \nu = x, y, z$.

Since all these four operators mutually commute, the total wave function is simultaneously an eigenfunction of $\hat{H}$ and $\hat{p}_x$, $\hat{p}_y$, $\hat{p}_z$, i.e. the energy and the momentum of the centre of mass can both be measured (without making any error) in a space-fixed coordinate system (see Appendix I). From the definition, the momentum of the centre of mass is identical to the total momentum.[2]

3 THE HAMILTONIAN, $\hat{J}^2$ AND $\hat{J}_z$ DO COMMUTE

Eq. (F.7) for rotations means $[\hat{\boldsymbol{J}}, \hat{H}] = \mathbf{0}$, i.e. in particular

$$\left[\hat{J}_x, \hat{H}\right] = 0, \tag{F.9}$$

$$\left[\hat{J}_y, \hat{H}\right] = 0, \tag{F.10}$$

$$\left[\hat{J}_z, \hat{H}\right] = 0. \tag{F.11}$$

The components of the angular momentum operators satisfy the following commutation rules: [3]

$$\begin{aligned} \left[\hat{J}_x, \hat{J}_y\right] &= i\hbar \hat{J}_z, \\ \left[\hat{J}_y, \hat{J}_z\right] &= i\hbar \hat{J}_x, \\ \left[\hat{J}_z, \hat{J}_x\right] &= i\hbar \hat{J}_y. \end{aligned} \tag{F.12}$$

[2] Indeed the position vector of the centre of mass is defined as $\boldsymbol{R}_{\mathrm{CM}} = \frac{\sum_i m_i \boldsymbol{r}_i}{\sum_i m_i}$, and after differentiation with respect to time $(\sum_i m_i)\dot{\boldsymbol{R}}_{\mathrm{CM}} = \sum_i m_i \dot{\boldsymbol{r}}_i = \sum_i \boldsymbol{p}_i$. The right-hand side represents the momentum of all the particles (i.e. the total momentum), whereas the left is simply the momentum of the centre of mass.

[3] The commutation relations can be obtained by using the definitions of the operators involved directly: $\hat{J}_x = y\hat{p}_z - z\hat{p}_y$, etc. For example,

$$\begin{aligned} [\hat{J}_x, \hat{J}_y] f &= \left[(y\hat{p}_z - z\hat{p}_y)(z\hat{p}_x - x\hat{p}_z) - (z\hat{p}_x - x\hat{p}_z)(y\hat{p}_z - z\hat{p}_y)\right] f \\ &= \left[(y\hat{p}_z z\hat{p}_x - z\hat{p}_x y\hat{p}_z) - (y\hat{p}_z x\hat{p}_z - x\hat{p}_z y\hat{p}_z) \right. \\ &\quad \left. - (z\hat{p}_y z\hat{p}_x - z\hat{p}_x z\hat{p}_y) + (z\hat{p}_y x\hat{p}_z - x\hat{p}_z z\hat{p}_y)\right] f \\ &= (y\hat{p}_z z\hat{p}_x - z\hat{p}_x y\hat{p}_z) f - (yx\hat{p}_z\hat{p}_z - yx\hat{p}_z\hat{p}_z) \\ &\quad - (z^2\hat{p}_y\hat{p}_x - z^2\hat{p}_x\hat{p}_y) + (xz\hat{p}_y\hat{p}_z - x\hat{p}_z z\hat{p}_y) \\ &= (y\hat{p}_z z\hat{p}_x - yz\hat{p}_x\hat{p}_z) f - 0 - 0 + (xz\hat{p}_y\hat{p}_z - x\hat{p}_z z\hat{p}_y) f \\ &= (-i\hbar)^2 \left[y\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial y}\right] = i\hbar \hat{J}_z f. \end{aligned}$$

Eqs. (F.9)–(F.11) are not independent, e.g., eq. (F.11) can be derived from eqs. (F.9) and (F.10). Indeed,

$$\begin{aligned}
\left[\hat{J}_z, \hat{H}\right] &= \hat{J}_z\hat{H} - \hat{H}\hat{J}_z \\
&= \frac{1}{i\hbar}[\hat{J}_x, \hat{J}_y]\hat{H} - \frac{1}{i\hbar}\hat{H}[\hat{J}_x, \hat{J}_y] \\
&= \frac{1}{i\hbar}[\hat{J}_x, \hat{J}_y]\hat{H} - \frac{1}{i\hbar}[\hat{J}_x, \hat{J}_y]\hat{H} \\
&= 0.
\end{aligned}$$

Also, from eqs. (F.9), (F.10) and (F.11) it also follows that

$$\left[\hat{J}^2, \hat{H}\right] = 0, \tag{F.13}$$

because from Pythagoras' theorem $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$.

Do $\hat{J}_x, \hat{J}_y, \hat{J}_z$ commute with $\hat{J}^2$? Let us check the commutator $[\hat{J}_z, \hat{J}^2]$:

$$\begin{aligned}
\left[\hat{J}_z, \hat{J}^2\right] &= \left[\hat{J}_z, \hat{J}_x^2 + \hat{J}_y^2 + \hat{L}_z^2\right] \\
&= \left[\hat{J}_z, \hat{J}_x^2 + \hat{J}_y^2\right] \\
&= \hat{J}_z\hat{J}_x^2 - \hat{J}_x^2\hat{J}_z + \hat{J}_z\hat{J}_y^2 - \hat{J}_y^2\hat{J}_z \\
&= \left(i\hbar\hat{J}_y + \hat{J}_x\hat{J}_z\right)\hat{J}_x - \hat{J}_x\left(-i\hbar\hat{J}_y + \hat{J}_z\hat{J}_x\right) + \left(-i\hbar\hat{J}_x + \hat{J}_y\hat{J}_z\right)\hat{J}_y \\
&\quad - \hat{J}_y\left(i\hbar\hat{J}_x + \hat{J}_z\hat{J}_y\right) \\
&= 0.
\end{aligned}$$

Thus,

$$\left[\hat{J}_z, \hat{J}^2\right] = 0, \tag{F.14}$$

and also by the argument of symmetry (the space is isotropic)

$$\left[\hat{J}_x, \hat{J}^2\right] = 0, \tag{F.15}$$

$$\left[\hat{J}_y, \hat{J}^2\right] = 0. \tag{F.16}$$

Now we need to determine the set of the operators that all mutually commute. Only then can all the physical quantities, to which the operators correspond, have definite values when measured. Also the wave function can be an eigenfunction of all of these operators and it can be labelled by quantum numbers, each corresponding to an eigenvalue of the operators in question. *We cannot choose, for these operators, the whole set of* $\hat{H}, \hat{J}_x, \hat{J}_y, \hat{J}_z, \hat{J}^2$, *because, as was shown above*, $\hat{J}_x, \hat{J}_y, \hat{J}_z$ *do not commute among themselves* (although they do with $\hat{H}$ and $\hat{J}^2$).

The only way is to choose as the set of operators *either* $\hat{H}, \hat{J}_z, \hat{J}^2$ *or* $\hat{H}, \hat{J}_x, \hat{J}^2$ *or* $\hat{H}, \hat{J}_y, \hat{J}^2$. Traditionally, we choose $\hat{H}, \hat{J}_z, \hat{J}^2$ as the set of mutually commuting operators (z is known as the *quantization axis*).

4 ROTATION AND TRANSLATION OPERATORS DO NOT COMMUTE

Now we may think about adding $\hat{p}_x, \hat{p}_y, \hat{p}_z$, to the above set of operators. The operators $\hat{H}$, $\hat{p}_x, \hat{p}_y, \hat{p}_z, \hat{J}^2$ and $\hat{J}_z$ *do not* represent a set of mutually commuting operators. The reason for this is that $[\hat{p}_\mu, \hat{J}_\nu] \neq 0$ for $\mu \neq \nu$, which is a consequence of the fact that, in general, rotation and translation operators do not commute as shown in Fig. F.1.

5 CONCLUSION

It is, therefore, impossible to make all the operators $\hat{H}$, $\hat{p}_x, \hat{p}_y, \hat{p}_z, \hat{J}^2$ and $\hat{J}_z$ commute in a *space fixed coordinate system*. What we are able to do, though, is to write the total wave function Ψ_{pN} in the space fixed coordinate system as a product of the plane wave $\exp(i\boldsymbol{p}_{\mathrm{CM}} \cdot \boldsymbol{R}_{\mathrm{CM}})$ depending on the centre-of-mass variables and on the wave function Ψ_{0N} depending on internal coordinates[4]

$$\Psi_{pN} = \Psi_{0N} \exp(i\boldsymbol{p}_{\mathrm{CM}} \cdot \boldsymbol{R}_{\mathrm{CM}}), \tag{F.17}$$

which is an eigenfunction of the total (i.e. centre-of-mass) momentum operators:

$$\hat{p}_x = \hat{p}_{CM,x}, \quad \hat{p}_y = \hat{p}_{CM,y}, \quad \hat{p}_z = \hat{p}_{CM,z}.$$

The function Ψ_{0N} is the total wave function written in the centre-of-mass coordinate system (a special body-fixed coordinate system, see Appendix I), in which the total angular momentum operators $\hat{J}^2$ and $\hat{J}_z$ are now defined. The three operators $\hat{H}, \hat{J}^2$ and $\hat{J}_z$ commute in any space-fixed or body-fixed coordinate system (including the centre-of-mass coordinate system), and therefore the corresponding physical quantities (energy and angular momentum) have exact values. In this particular coordinate system: $\hat{\boldsymbol{p}} = \hat{\boldsymbol{p}}_{\mathrm{CM}} = \boldsymbol{0}$. We may say, therefore, that

in the centre-of-mass coordinate system $\hat{H}$, $\hat{p}_x, \hat{p}_y, \hat{p}_z, \hat{J}^2$ and $\hat{J}_z$ all do commute.

[4]See Chapter 2 and Appendix I, where the total Hamiltonian is split into the sum of the centre-of-mass and internal coordinate Hamiltonians; N is the quantum number for the spectroscopic states.

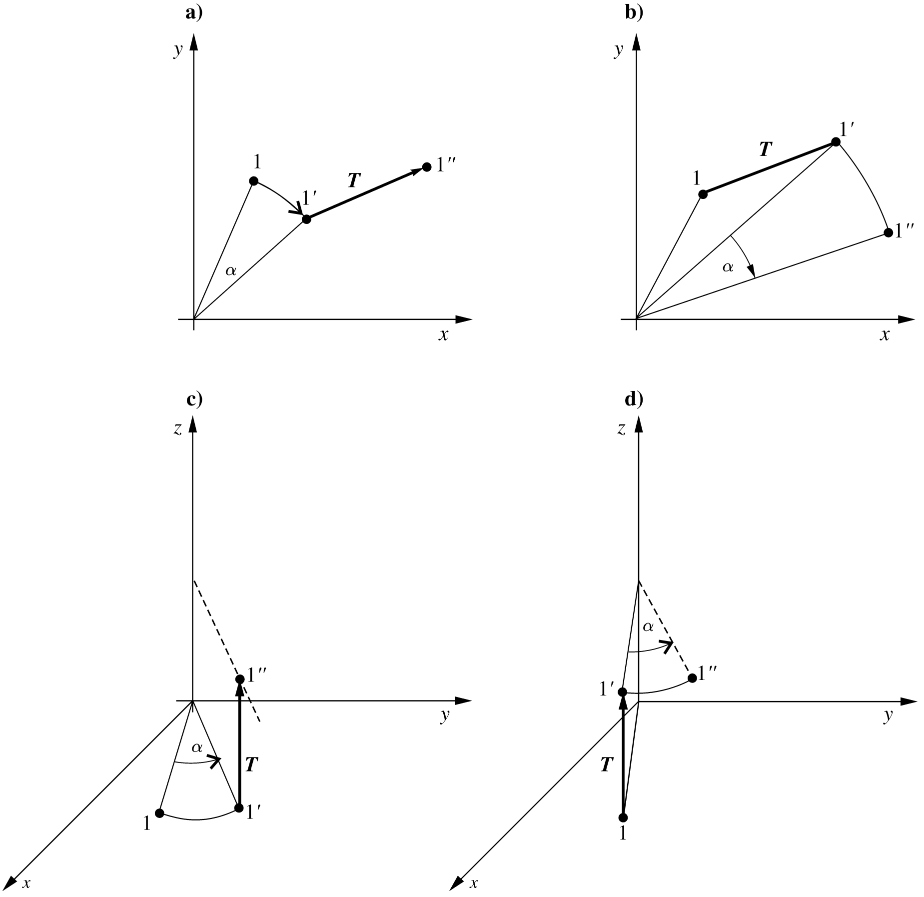

Fig. F.1. In general, translation $\hat{\mathcal{U}}(\boldsymbol{T})$ and rotation $\hat{\mathcal{U}}(\alpha; \boldsymbol{e})$ operators do not commute. The example shows what happens to a point belonging to the xy plane. (a) A rotation $\hat{\mathcal{U}}(\alpha; z)$ by angle α about the z axis takes place first and then a translation $\hat{\mathcal{U}}(\boldsymbol{T})$ by a vector $\boldsymbol{T}$ (restricted to the xy plane) is carried out. (b) The operations are applied in the reverse order. As we can see the results are different (two points $1''$ have different positions in Figs. (a) and (b)), i.e. the two operators do not commute: $\hat{\mathcal{U}}(\boldsymbol{T})\hat{\mathcal{U}}(\alpha; z) \neq \hat{\mathcal{U}}(\alpha; z)\hat{\mathcal{U}}(\boldsymbol{T})$. This after expanding $\hat{\mathcal{U}}(\boldsymbol{T}) = \exp[-\frac{i}{\hbar}(T_x \hat{p}_x + T_y \hat{p}_y)]$ and $\hat{\mathcal{U}}(\alpha; z) = \exp(-\frac{i}{\hbar}\alpha \hat{J}_z)$ in Taylor series, and taking into account that T_x, T_y, α are arbitrary numbers, leads to the conclusion that $[\hat{J}_z, \hat{p}_x] \neq 0$ and $[\hat{J}_z, \hat{p}_y] \neq 0$. Note, that *some* translations and rotations do commute, e.g., $[\hat{J}_z, \hat{p}_z] = [\hat{J}_x, \hat{p}_x] = [\hat{J}_y, \hat{p}_y] = 0$, because we see by inspection (c,d) that any translation by $\boldsymbol{T} = (0, 0, T_z)$ is independent of any rotation about the z axis, etc.