APPENDIX F

Translation versus Momentum and Rotation versus Angular Momentum

In Chapter 2, it was shown that the Hamiltonian $\hat{H}$ commutes with any translation (p. 68) or rotation (p. 69) operator, denoted as $\hat{\mathcal{U}}$:

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

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 the 3-D space,) that operator $\hat{\mathcal{U}}$ takes 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 (having the x-, y-, and z- components) acting on functions of points in the 3-D Cartesian space.

Translation and Momentum Operators

Translation of a function by a vector $\Delta\boldsymbol{r}$ is equivalent to the function f in the coordinate system translated in the opposite direction; i.e., $f(\boldsymbol{r} - \Delta\boldsymbol{r})$–see Fig. 1.3 and p. 68. If the 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 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, one has to ensure that N tends to infinity. Recalling the definition

Ideas of Quantum Chemistry, Second Edition. http://dx.doi.org/10.1016/B978-0-444-59436-5.00026-X

$\exp(ax) = \lim_{N\to\infty}\left(1+\frac{a}{x}\right)^N$, 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 the 3-D Cartesian space (think, for example, about a probability density distribution centered somewhere in the space). Now, suppose that 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, which we will denote 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. 1.1 and p. 89) of the coordinate system:

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

where $\boldsymbol{U}$ is a 3×3 orthogonal matrix. The new coordinates $x(\alpha)$, $y(\alpha)$, and $z(\alpha)$ are expressed by the old coordinates x, y, and 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 $\alpha = 0$:

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

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

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:

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

If such a rotation is repeated N times, then we recover the rotation of the function by a (possibly large) angle α (the symbol of limit ensures 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 $\hat{\mathcal{U}}(\alpha;\boldsymbol{e}) = \exp\left(-\frac{i}{\hbar}\alpha\boldsymbol{e}\cdot\hat{\boldsymbol{J}}\right)$, 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-, and z-axes (with the corresponding unit vectors $\boldsymbol{x}$, $\boldsymbol{y}$, and $\boldsymbol{z}$) we have, respectively,

$$[\hat{\mathcal{U}}(\alpha;\boldsymbol{x}),\,\hat{J}_x] = 0, \tag{F.4}$$
$$[\hat{\mathcal{U}}(\alpha;\boldsymbol{y}),\,\hat{J}_y] = 0, \tag{F.5}$$
$$[\hat{\mathcal{U}}(\alpha;\boldsymbol{z}),\,\hat{J}_z] = 0. \tag{F.6}$$

Useful Relation

Eq. (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 $\boldsymbol{\kappa}$):

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

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

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

Hamiltonian Commutes with the Total Momentum Operator

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

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

for $\mu = x, y, z$. Of course, we have also $[\hat{p}_\mu, \hat{p}_\nu] = 0$ 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 center of mass can both be measured (without making any error) in a space-fixed coordinate system (see Appendix I available at booksite.elsevier.com/978-0-444-59436-5). From its definition, the momentum of the center of mass is identical with the total momentum.[2]

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,

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

$$[\hat{J}_y, \hat{H}] = 0, \quad \text{and} \tag{F.10}$$

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

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

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

---

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

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

For instance, $[\hat{J}_x, \hat{J}_y]f$

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

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

$$[\hat{J}_z, \hat{H}] = \hat{J}_z\hat{H} - \hat{H}\hat{J}_z = \frac{1}{i\hbar}[\hat{J}_x, \hat{J}_y]\hat{H} - \frac{1}{i\hbar}\hat{H}[\hat{J}_x, \hat{J}_y] = \frac{1}{i\hbar}[\hat{J}_x, \hat{J}_y]\hat{H} - \frac{1}{i\hbar}[\hat{J}_x, \hat{J}_y]\hat{H} = 0.$$

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

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

because from the Pythagorean 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 $[\hat{J}_z, \hat{J}^2]$:

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

Thus,

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

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

$$[\hat{J}_x, \hat{J}^2] = 0, \quad \text{and} \tag{F.15}$$

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

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 labeled by the quantum numbers, each corresponding to an eigenvalue of the operators in question. *We cannot choose as these operators the whole set of* $\hat{H}, \hat{J}_x, \hat{J}_y, \hat{J}_z, \hat{J}^2$, *because as it was shown earlier,* $\hat{J}_x, \hat{J}_y, \hat{J}_z$ *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 the 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, one chooses as the set of the mutually commuting operators $\hat{H}, \hat{J}_z, \hat{J}^2$ (z is known as the *quantization axis*).

Rotation and Translation Operators Do Not Commute

Now, we may think to add $\hat{p}_x, \hat{p}_y, \hat{p}_z$ to the above set of the 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 result of the fact that in general, rotation and translation operators do not commute, as shown in Fig. F.1.

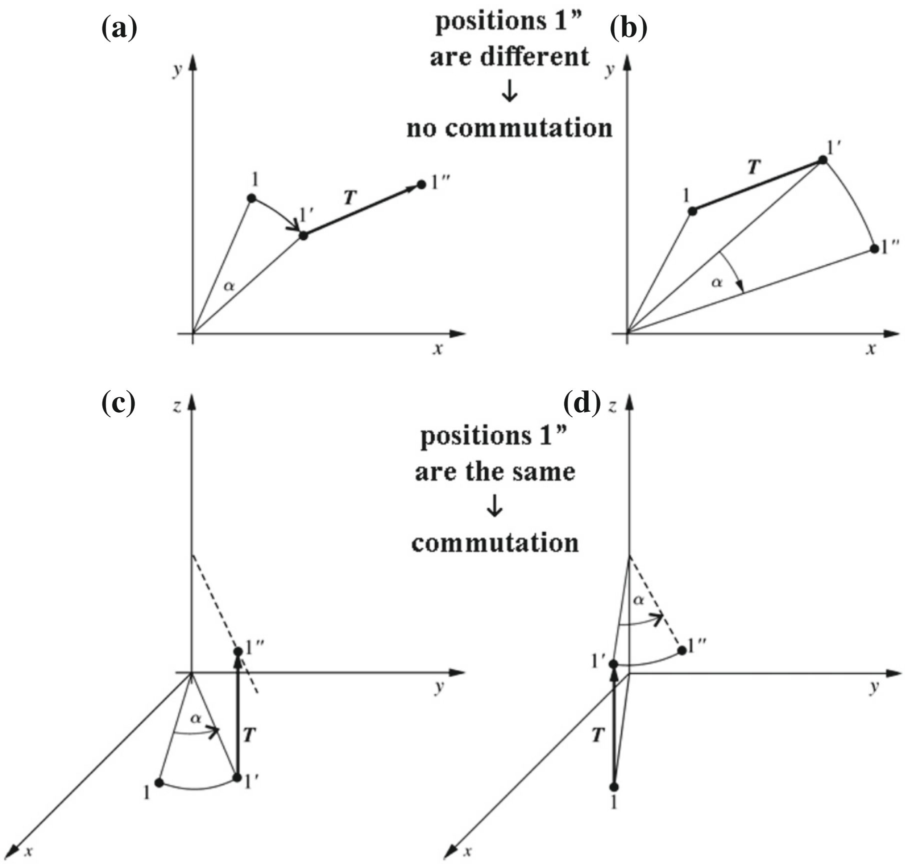

Fig. F.1. In general, translation $\hat{\mathcal{U}}(\boldsymbol{T})$ and rotation $\hat{\mathcal{U}}(\alpha; \boldsymbol{e})$ operators do not commute. The example shows what happens to a point belonging to the xy plane. (a) If a rotation $\hat{\mathcal{U}}(\alpha; \boldsymbol{z})$ by angle α about 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, and (b) shows what happens if the operations are applied in the reverse order. As we can see, the results are different (two points $1''$ have different positions in panels a and b); i.e., the two operators do not commute: $\hat{\mathcal{U}}(\boldsymbol{T})\hat{\mathcal{U}}(\alpha; \boldsymbol{z}) \neq \hat{\mathcal{U}}(\alpha; \boldsymbol{z})\hat{\mathcal{U}}(\boldsymbol{T})$. Expanding $\hat{\mathcal{U}}(\boldsymbol{T}) = \exp[-\frac{i}{\hbar}(T_x \hat{p}_x + T_y \hat{p}_y)]$ and $\hat{\mathcal{U}}(\alpha; \boldsymbol{z}) = \exp(-\frac{i}{\hbar}\alpha \hat{J}_z)$ in a 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 [as shown in panels (c) and (d)] that any translation by $\boldsymbol{T} = (0, 0, T_z)$ is independent of any rotation about the z-axis, etc.

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 down the total wave function Ψ_{pN} in the space-fixed coordinate system as a product of the plane wave $\exp(i\boldsymbol{p}_{CM} \cdot \boldsymbol{R}_{CM})$, which depends on the center-of-mass variables, and the wave function Ψ_{0N}, which depends on internal coordinates[4] as follows:

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

which is an eigenfunction of the total (i.e., center-of-mass) momentum operators: $\hat{p}_x = \hat{p}_{CM,x}$, $\hat{p}_y = \hat{p}_{CM,y}$, $\hat{p}_z = \hat{p}_{CM,z}$. The function Ψ_{0N} is the total wave function written in the center-of-mass coordinate system (a special body-fixed coordinate system; see Appendix I available at booksite.elsevier.com/978-0-444-59436-5), 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 center-of-mass coordinate system), and therefore, the corresponding physical quantities (energy and angular momentum) have exact values. In this particular coordinate system, $\hat{\boldsymbol{p}} = \hat{\boldsymbol{p}}_{CM} = \boldsymbol{0}$. We may say, therefore, that

> *in the center-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 see Appendix I available at booksite.elsevier.com/978-0-444-59436-5, where the total Hamiltonian is split into a sum of the center-of-mass and internal coordinate Hamiltonians; N is the quantum number for the spectroscopic states.