APPENDIX I

Space- and Body-Fixed Coordinate Systems

Space-Fixed Coordinate System (SFCS)

A planetoid (or molecule) moves through empty space, and we are observing it from our (inertial[1]) spaceship. In order to carry out observations of the planetoid (molecule), we have to install some gear on our spaceship and install a Cartesian coordinate system that will enable us to describe the planetoid whatever happens to it. This is the space-fixed coordinate system (SFCS), whose orientation with respect to distant stars does not change with time.

If the molecule does not interact with anything, then with respect to the SFCS (see Chapter 2), note the following:

- Its *total energy* remains invariant (because of the homogeneity of time).
- Its *total momentum* remains invariant (because of the homogeneity of space).
- Its *total angular momentum vector* remains invariant (because of the isotropy of space).

An observer on another spaceship (inertial as well) will see the same phenomena in exactly the same way[2]: the energy, momentum, and angular momentum also will be invariant, but in general, it will be different from what was measured in the first spaceship.

Let us introduce in the SFCS the vectors $\boldsymbol{r}_i = (x_i, y_i, z_i)$ showing from the origin the particles from which our molecule is composed (i.e., the electrons and the nuclei), $i = 1, 2, \ldots N$. Then, using the SFCS, we write down the Hamiltonian of the system and the operators of the mechanical quantities we are interested in, we calculate all the wave functions we need, we compare them with spectra measured in the SFCS, etc.

---

1 That is, it is not rotating. We will convince ourselves that our SFCS is inertial by measuring how a pointlike mass (assumed to not be interacting with the rest of the spaceship) moves. If it moves along a straight line with a constant velocity, then the SFCS is inertial. In a *non-inertial* coordinate system, the description of the physical phenomena in the molecule will be different.

2 That is, in the non-relativistic approximation. The Doppler effect, with the change of the electromagnetic wave frequency due to the motion (even uniform) of the emitting object, *is seen* in the experiment. The effect is of the relativistic character; i.e., it vanishes if we assume the infinite velocity of light.

Ideas of Quantum Chemistry, Second Edition. http://dx.doi.org/10.1016/B978-0-444-59436-5.00029-5

Body-Fixed Coordinate System (BFCS)

One day, however, we may feel that we do not like the SFCS because it has too many variables. Of course, this is not a sin, but it does waste our forces. Indeed, since in all inertial systems we have the same physics, we can separate the motion of the center of mass[3] (the total mass $M = \sum_i m_i$). The center of mass with position

$$\boldsymbol{R}_{CM} = \frac{\sum_i m_i \boldsymbol{r}_i}{M}$$

moves in the SFCS with a constant velocity along a straight line, which can be easily taken into account after the solution is obtained, and which in most cases is irrelevant. This is why we decide to introduce the Cartesian coordinates $\left(X_{CM}, Y_{CM}, Z_{CM}\right) = \boldsymbol{R}_{CM}$ in the hope that in the future, we will be able to get rid of them. Now, we need to introduce a coordinate system (of the lacking $3N - 3$ variables) located in the molecule, the so-called *body-fixed coordinate system* (BFCS). How should this be defined? Well, it should be a coordinate system that will define unambiguously any configuration of the particles in the molecule. There are many such coordinate systems. Here, you have some of the possibilities for the BFCS (*in all of them, their axes are parallel to the corresponding axes of the SFCS*[4]). We may choose one of the following sets[5] of position vectors:

- With $\boldsymbol{R}_{CM}$, we locate the BFCS *on any of the particles* (this is indicated by vector $\boldsymbol{r}_1$), and the BFCS positions of the other particles are shown by $\boldsymbol{r}'_i = \boldsymbol{r}_i - \boldsymbol{r}_1$ for $i = 2, 3, \ldots N$.
- With $\boldsymbol{R}_{CM}$, the vector $\boldsymbol{R} = \boldsymbol{r}_2 - \boldsymbol{r}_1$ *indicates particle* 2 from *particle* 1, and the remaining particles are shown by the vectors that begin in the center of the section linking particles 1 and 2: $\boldsymbol{r}'_i = \boldsymbol{r}_i - \frac{(\boldsymbol{r}_1 + \boldsymbol{r}_2)}{2}$ for $i = 3, 4, \ldots N$.
- With $\boldsymbol{R}_{CM}$, all the vectors show the particles from the center of mass (except particle 1): $\boldsymbol{r}'_i = \boldsymbol{r}_i - \boldsymbol{R}_{CM}$ for $i = 2, 3, \ldots N$. The position vector of the particle 1 can be calculated from the coordinates already given.

Center-of-Mass Separation

After writing the Hamiltonian $\hat{\mathcal{H}}$ in the SFCS, and then introducing *any of the above choices* of the coordinate system, we obtain $\hat{\mathcal{H}} = \hat{H}_{CM} + \hat{H}$,
where

[3] The exact separation of the center of mass motion in SFCS, as well as the exact separation of rotation of the molecule (which is not shown in this appendix) have been shown for the first time in R.T. Pack and J.O. Hirschfelder, *J.Chem.Phys.*, *49*, 4009 (1968).

[4] Only after introducing the axes of the coordinate system associated to the particles, and not with the SFCS, is separation of rotation possible.

[5] Other are other choices are possible.

with any of the choices, the operator $\hat{H}$ is identical but the mathematical formula for $\hat{H}$ will be different because different coordinates are used.

Thus, the total Hamiltonian in the SFCS is

$$\hat{\mathcal{H}} = \hat{H}_{CM}(X_{CM}, Y_{CM}, Z_{CM}) + \hat{H}(\boldsymbol{r}),$$

where $\boldsymbol{r}$ *symbolizes*[6] all the other variables. The key result is that the two operators on the right side *depend on different variables*.

The goal of the above changes of the coordinate system was to show that the Schrödinger equation written in the SFCS; i.e., $\hat{\mathcal{H}}\Psi = \mathcal{E}\Psi$ splits into *two* Schrödinger equations ("*separation of variables*") as follows:

- $\hat{H}_{CM}\psi_{CM} = E_{CM}\psi_{CM}$ describes the motion of a free "*particle*" of mass M and the coordinates X_{CM}, Y_{CM}, Z_{CM} (the "*center-of-mass motion*"), with $\psi_{CM} = \exp(i\boldsymbol{p}_{CM} \cdot \boldsymbol{R}_{CM})$, where $\boldsymbol{p}_{CM}$ stands for the total momentum of the system.
- $\hat{H}\psi = E\psi$,

where

$$\mathcal{E} = E + E_{CM}$$
$$\Psi(\boldsymbol{R}_{CM}, \boldsymbol{r}) = \psi_{CM}(\boldsymbol{R}_{CM}) \cdot \psi(\boldsymbol{r}).$$

The proof is simple. Let us check that the product wave function satisfies the Schrödinger equation. The left side is

$$\begin{aligned}
&\hat{\mathcal{H}}[\psi_{CM}(\boldsymbol{R}_{CM}) \cdot \psi(\boldsymbol{r})] \\
&\quad = \hat{H}_{CM}[\psi_{CM}(\boldsymbol{R}_{CM}) \cdot \psi(\boldsymbol{r})] + \hat{H}[\psi_{CM}(\boldsymbol{R}_{CM}) \cdot \psi(\boldsymbol{r})] \\
&\quad = \psi(\boldsymbol{r}) \cdot \hat{H}_{CM}\psi_{CM}(\boldsymbol{R}_{CM}) + \psi_{CM}(\boldsymbol{R}_{CM}) \cdot \hat{H}\psi(\boldsymbol{r}) \\
&\quad = \psi(\boldsymbol{r}) \cdot E_{CM}\psi_{CM}(\boldsymbol{R}_{CM}) + \psi_{CM}(\boldsymbol{R}_{CM}) \cdot E\psi(\boldsymbol{r}) \\
&\quad = \left(E + E_{CM}\right)[\psi_{CM}(\boldsymbol{R}_{CM}) \cdot \psi(\boldsymbol{r})]
\end{aligned}$$

and this equals the right side $\mathcal{E}\Psi$.

Example 1. ***Center-of-Mass Separation for the First Choice of the Coordinates***

We use the first choice of the coordinates for the system of *two* particles. In the SFCS, $\hat{\mathcal{H}} = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 + V$. The new coordinates are

$$X_{CM} = \frac{\sum_i m_i x_i}{M}, Y_{CM} = \frac{\sum_i m_i y_i}{M}, Z_{CM} = \frac{\sum_i m_i z_i}{M},$$

$$x = x_2 - x_1,$$
$$y = y_2 - y_1,$$
$$z = z_2 - z_1.$$

[6] For the sake of brevity.

Then[7]

$$\frac{\partial}{\partial x_1} = \frac{\partial X_{CM}}{\partial x_1}\frac{\partial}{\partial X_{CM}} + \frac{\partial Y_{CM}}{\partial x_1}\frac{\partial}{\partial Y_{CM}} + \frac{\partial Z_{CM}}{\partial x_1}\frac{\partial}{\partial Z_{CM}} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial y}{\partial x_1}\frac{\partial}{\partial y} + \frac{\partial z}{\partial x_1}\frac{\partial}{\partial z}$$
$$= \frac{m_1}{M}\frac{\partial}{\partial X_{CM}} + 0 + 0 - \frac{\partial}{\partial x} + 0 + 0 = \frac{m_1}{M}\frac{\partial}{\partial X_{CM}} - \frac{\partial}{\partial x},$$

and similarly for y_1 and z_1. Further,

$$\frac{\partial}{\partial x_2} = \frac{\partial X_{CM}}{\partial x_2}\frac{\partial}{\partial X_{CM}} + \frac{\partial Y_{CM}}{\partial x_2}\frac{\partial}{\partial Y_{CM}} + \frac{\partial Z_{CM}}{\partial x_2}\frac{\partial}{\partial Z_{CM}} + \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} + \frac{\partial y}{\partial x_2}\frac{\partial}{\partial y} + \frac{\partial z}{\partial x_2}\frac{\partial}{\partial z}$$
$$= \frac{m_2}{M}\frac{\partial}{\partial X_{CM}} + 0 + 0 + \frac{\partial}{\partial x} + 0 + 0 = \frac{m_2}{M}\frac{\partial}{\partial X_{CM}} + \frac{\partial}{\partial x},$$

and similarly for y_2 and z_2.

Hence, the kinetic energy operator (after constructing the proper Laplacians from the above operators) is

$$\hat{T} = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 = -\frac{\hbar^2}{2m_1}\left[\left(\frac{m_1}{M}\right)^2\frac{\partial^2}{\partial X_{CM}^2} + \frac{\partial^2}{\partial x^2} - 2\frac{m_1}{M}\frac{\partial^2}{\partial X_{CM}\partial x}\right]$$
$$+ (\text{similarly for } y \text{ and } z) +$$
$$-\frac{\hbar^2}{2m_2}\left[\left(\frac{m_2}{M}\right)^2\frac{\partial^2}{\partial X_{CM}^2} + \frac{\partial^2}{\partial x^2} + 2\frac{m_2}{M}\frac{\partial^2}{\partial X_{CM}\partial x}\right]$$
$$+ (\text{similarly for } y \text{ and } z) \; = -\frac{\hbar^2}{2M}\Delta_{CM} - \frac{\hbar^2}{2\mu}\Delta,$$

where the reduced mass μ of the two particles: $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$, and $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

[7] According to the mathematical analysis, we have to write down the contributions of all the differential operators $\frac{\partial}{\partial u}$ of the new coordinates u multiplied by their "*coupling constants*" $\frac{\partial u}{\partial x_1}$ with the coordinate x_1.

Our derivation is now over. The operator $\hat{H}$ has been found. It turned out to take the following form[8] (note, that the new coordinates have to be introduced also in the potential energy V) of the form:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\Delta + V.$$

Example 2. ***Center-of-Mass Separation for the Third Choice of the Coordinates***

Let us take again the same two particles, but this time use the third choice of the coordinate system:

$$X_{CM} = \frac{\sum_i m_i x_i}{M}, Y_{CM} = \frac{\sum_i m_i y_i}{M}, Z_{CM} = \frac{\sum_i m_i z_i}{M},$$

$$x = x_2 - X_{CM},$$
$$y = y_2 - Y_{CM},$$
$$z = z_2 - Y_{CM}.$$

Then,

$$\frac{\partial}{\partial x_1} = \frac{\partial X_{CM}}{\partial x_1}\frac{\partial}{\partial X_{CM}} + \frac{\partial Y_{CM}}{\partial x_1}\frac{\partial}{\partial Y_{CM}} + \frac{\partial Z_{CM}}{\partial x_1}\frac{\partial}{\partial Z_{CM}} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial y}{\partial x_1}\frac{\partial}{\partial y} + \frac{\partial z}{\partial x_1}\frac{\partial}{\partial z}$$
$$= \frac{m_1}{M}\frac{\partial}{\partial X_{CM}} + 0 + 0 - \frac{m_1}{M}\frac{\partial}{\partial x} + 0 + 0 = \frac{m_1}{M}\left(\frac{\partial}{\partial X_{CM}} - \frac{\partial}{\partial x}\right),$$

and similarly for y_1 and z_1. Further,

$$\frac{\partial}{\partial x_2} = \frac{\partial X_{CM}}{\partial x_2}\frac{\partial}{\partial X_{CM}} + \frac{\partial Y_{CM}}{\partial x_2}\frac{\partial}{\partial Y_{CM}} + \frac{\partial Z_{CM}}{\partial x_2}\frac{\partial}{\partial Z_{CM}} + \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} + \frac{\partial y}{\partial x_2}\frac{\partial}{\partial y} + \frac{\partial z}{\partial x_2}\frac{\partial}{\partial z}$$

[8] The kinetic energy operator has a very interesting form. Particle 1 *rests* right in the origin of the BFCS ($x = 0$, $y = 0$, $z = 0$), and therefore its kinetic energy operator is absent in $\hat{H}$. There is the kinetic energy of particle 2, *but its mass is equal to* μ, not to m_2. The coordinates x, y, and z (measured from the origin of the BFCS) correspond to particle 2. For example, for the hydrogen-like atom, if someone takes the nucleus as particle 1, and the electron as particle 2, then x, y, and z show the *electron* from the Cartesian coordinate system BFCS located on the nucleus. The potential energy operator $V = -\frac{Ze^2}{\sqrt{(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2}} = -\frac{Ze^2}{\sqrt{x^2+y^2+z^2}}$ corresponds to the Coulombic interaction of the electron of charge $-e$ and the nucleus of the charge Ze. After separation of the center of mass, we are left with equation $\hat{H}\psi = E\psi$. The electron of mass μ is described by the wave function ψ. In the ground state, $\psi = \frac{1}{\sqrt{\pi}}e^{-\sqrt{x^2+y^2+z^2}}$. This is the description of the hydrogen-like atom *according to an observer sitting at the nucleus*.

If another observer puts his armchair (with the axes of the BFCS carved on it) at the *electron*, then he would see the hydrogen-like atom "*according to the electron*." Since in V there are squares of x, y, and z, and in the kinetic energy operator, there are the *second* derivatives with respect to x, y, and z, then we would obtain the same wave function as before: $\psi = \frac{1}{\sqrt{\pi}}e^{-\sqrt{x^2+y^2+z^2}}$, where the particle moving with respect to the electron is the *nucleus*, but with the mass equal to μ (i.e., the same as before). By the way, this μ is almost equal to the mass of the *electron*.

Thus, the two descriptions mean the same thing.

$$= \frac{m_2}{M}\frac{\partial}{\partial X_{CM}} + 0 + 0 + \left(1 - \frac{m_2}{M}\right)\frac{\partial}{\partial x} + 0 + 0$$
$$= \frac{m_2}{M}\frac{\partial}{\partial X_{CM}} + \left(1 - \frac{m_2}{M}\right)\frac{\partial}{\partial x} = \frac{m_2}{M}\frac{\partial}{\partial X_{CM}} + \frac{m_1}{M}\frac{\partial}{\partial x},$$

and similarly for y_2 and z_2.

Thus, the kinetic energy operator takes the following form (after inserting the squares of the corresponding operators):

$$\hat{T} = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 = -\frac{\hbar^2}{2m_1}\left[\left(\frac{m_1}{M}\right)^2\left(\frac{\partial^2}{\partial X_{CM}^2} + \frac{\partial^2}{\partial x^2} - 2\frac{\partial^2}{\partial X_{CM}\partial x}\right)\right]$$
$$+ (\text{similarly for } y \text{ and } z)$$
$$+ -\frac{\hbar^2}{2m_2}\left[\left(\frac{m_2}{M}\right)^2\frac{\partial^2}{\partial X_{CM}^2} + \left(\frac{m_1}{M}\right)^2\frac{\partial^2}{\partial x^2} + 2\frac{m_1 m_2}{M^2}\frac{\partial^2}{\partial X_{CM}\partial x}\right] + (\text{similarly for } y \text{ and } z)$$
$$= -\frac{\hbar^2}{2M}\Delta_{CM} - \frac{\hbar^2}{2m_1}\left(\frac{m_1}{M}\right)^2\Delta_{xyz} - \frac{\hbar^2}{2m_2}\left(\frac{m_1}{M}\right)^2\Delta_{xyz} - \frac{\hbar^2}{2m_1}\left(\frac{m_1}{M}\right)^2\left(-2\frac{\partial^2}{\partial X_{CM}\partial x}\right)$$
$$+ \cdots - \frac{\hbar^2}{2m_2}2\frac{m_1 m_2}{M^2}\frac{\partial^2}{\partial X_{CM}\partial x} + \ldots = -\frac{\hbar^2}{2M}\Delta_{CM} - \frac{\hbar^2}{2m_1}\left(\frac{m_1}{M}\right)^2\Delta_{xyz}$$
$$- \frac{\hbar^2}{2m_2}\left(\frac{m_1}{M}\right)^2\Delta_{xyz} = -\frac{\hbar^2}{2M}\Delta_{CM} - \frac{\hbar^2}{2}\left(\frac{m_1}{m_2 M}\right)\Delta_{xyz}.$$

It is seen that once again, we have reached the situation that allows us to separate the motion of the center of mass in the Schrödinger equation. This time, however, the *form* of the operator $\hat{H}$ is different (e.g., Δ_{xyz} formally takes the same form as Δ), only because the variables are different (the operator remains *the same*). Once again, this is the kinetic energy of a pointlike particle[9] with the coordinates x, y, and z (defined in *this* example) and the mass is equal to $\frac{m_2 M}{m_1}$.

[9] Let us first denote the nucleus as particle 1 and the electron as particle 2. Then $\boldsymbol{R}_{CM}$ shows almost the position of the nucleus, and x, y, and z are nearly the coordinates of the electron measured from the nucleus, while $\frac{m_2 M}{m_1}$ is almost equal to the mass of the electron. Thus, we have a situation that resembles Example 1.

If the particles are chosen in the other way (the electron is particle 1 and the nucleus is particle 2), then the same physical situation looks completely different. The values of x, y, and z are very close to 0, while the mass of the effective pointlike particle becomes very large.

Note that the new coordinates describe the potential energy in a more complex way. We need the differences of the kind $x_2 - x_1$, in order to insert them into the Pythagorean formula for the distance. We have $x_1 = X_{CM}\frac{m_1+m_2}{m_1} - \frac{m_2}{m_1}x_2 = X_{CM}\frac{m_1+m_2}{m_1} - \frac{m_2}{m_1}\left(x + X_{CM}\right) = X_{CM} - \frac{m_2}{m_1}x$,

$x_1 - x_2 = X_{CM} - \frac{m_2}{m_1}x - x - X_{CM} = -x\left(1 + \frac{m_2}{m_1}\right)$.

This gives immediately (r stands for the electron-center of mass distance): $V\left(\text{new}\right) = -\frac{Ze^2}{\left(1+\frac{m_2}{m_1}\right)r}$.