I. SPACE- AND BODY-FIXED COORDINATE SYSTEMS

Space-fixed coordinate system (SFCS)

A planetoid (or molecule) moves through empty space, we observe it from our (inertial[1]) space ship. To carry out observations of the planetoid (molecule), we have to install some equipment in our space ship and to fix a Cartesian coordinate system on it. This will enable us to describe the planetoid whatever happens to it. This is the Space-Fixed Coordinate System (SFCS), its orientation with respect to distant stars does not change in time.

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

- 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 space ship (also inertial) will see the same phenomena in exactly the same way,[2] the energy, momentum and angular momentum will also be invariant, but in general they will be different from what was measured in the first space ship.

Let us introduce the vectors $\boldsymbol{r}_i = (x_i, y_i, z_i)$ into the SFCS showing (from the origin of the coordinate system) 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 the Hamiltonian of the system, the operators of the mechanical quantities we are interested in, we calculate all the wave functions we need, compare with spectra measured in the SFCS, etc.

Body-fixed coordinate system (BFCS)

One day, however, we may feel that we do not like the SFCS, because to describe the molecule we use too many variables. Of course, this is not a sin, but only a

[1] No rotation. We will convince ourselves that our SFCS is inertial by measuring how a point-like mass moves (assumed to be non-interacting with the rest of the space ship). If it moves along a straight line with a constant velocity, the SFCS is inertial. In a *non-inertial* coordinate system the description of the physical phenomena in the molecule will look different.

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

waste of our time. Indeed, since in all inertial systems we have the same physics, we can separate the motion of the centre of mass[3] (the total mass $M = \sum_i m_i$). The centre of mass with position

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

moves with a constant velocity along a straight line in the SFCS, which can easily be taken into account after the solution is obtained, and in most cases it is irrelevant. This is why we decide to introduce the Cartesian coordinates $(X_{\mathrm{CM}}, Y_{\mathrm{CM}}, Z_{\mathrm{CM}}) = \boldsymbol{R}_{\mathrm{CM}}$ in the hope that in future we will be able to get rid of them. Now we need to introduce a coordinate system (of the missing $3N-3$ variables) located on the molecule, called the *body-fixed coordinate system* (BFCS). How to define this? Well, it should be a coordinate system that will define any configuration of the particles in the molecule unambiguously. There are a lot of 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:

- $\boldsymbol{R}_{\mathrm{CM}}$, then, we locate in the BFCS *on any of the particles* (say, the one 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 $i = 2, 3, \ldots, N$.
- $\boldsymbol{R}_{\mathrm{CM}}$, the vector $\boldsymbol{R} = \boldsymbol{r}_2 - \boldsymbol{r}_1$ *indicating particle* 2 *from particle* 1, and the remaining particles are shown by the vectors which begin in the centre of the section linking particles 1 and 2: $\boldsymbol{r}'_i = \boldsymbol{r}_i - \frac{(\boldsymbol{r}_1+\boldsymbol{r}_2)}{2}$ for $i = 3, 4, \ldots, N$.
- $\boldsymbol{R}_{\mathrm{CM}}$, and all the vectors showing the particles (except particle 1): $\boldsymbol{r}'_i = \boldsymbol{r}_i - \boldsymbol{R}_{\mathrm{CM}}$ for $i = 2, 3, \ldots, N$. the position vector of the particle 1 can be calculated from the coordinates already given.

Centre-of-mass separation

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

$$\hat{H}_{\mathrm{CM}} = -\frac{\hbar^2}{2M}\Delta_{\mathrm{CM}}$$

with $\Delta_{\mathrm{CM}} = \frac{\partial^2}{\partial X_{\mathrm{CM}}^2} + \frac{\partial^2}{\partial Y_{\mathrm{CM}}^2} + \frac{\partial^2}{\partial Z_{\mathrm{CM}}^2}$, and $\hat{H}$ that does not contain X_{CM}, Y_{CM}, Z_{CM}.

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

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

[5]There are other possible choices.

At 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

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

where ***r*** *symbolizes*[6] all the other variables. The key result is that the two operators on the right *do depend on different variables*.

The goal of the above changes to 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"):

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

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

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

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

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

Example 1. ***Centre-of-mass separation for the first choice of the coordinates.*** We use the first choice of 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:

$$X_{\mathrm{CM}} = \frac{\sum_i m_i x_i}{M}, \qquad Y_{\mathrm{CM}} = \frac{\sum_i m_i y_i}{M}, \qquad Z_{\mathrm{CM}} = \frac{\sum_i m_i z_i}{M},$$
$$x = x_2 - x_1, \quad y = y_2 - y_1, \quad z = z_2 - z_1.$$

[6] For the sake of brevity.

Then,[7]

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

and similarly for y_1 and z_1. Further,

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

and similarly for y_2 and z_2.

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

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

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

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

[7] According to the mathematical analysis we have to write 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.

[8] The kinetic energy operator has a quite interesting form. Particle 1 *rests* right at 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, 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, z show the *electron*

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

Example 2. ***Centre-of-mass separation for the third choice of coordinates.*** Let us take the same two particles again, but this time use the third choice of coordinate system.

$$X_{\mathrm{CM}} = \frac{\sum_i m_i x_i}{M}, \qquad Y_{\mathrm{CM}} = \frac{\sum_i m_i y_i}{M}, \qquad Z_{\mathrm{CM}} = \frac{\sum_i m_i z_i}{M},$$
$$x = x_2 - X_{\mathrm{CM}}, \quad y = y_2 - Y_{\mathrm{CM}}, \quad z = z_2 - Y_{\mathrm{CM}}.$$

Then,

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

and similarly for y_1 and z_1. Further,

$$\frac{\partial}{\partial x_2} = \frac{\partial X_{\mathrm{CM}}}{\partial x_2}\frac{\partial}{\partial X_{\mathrm{CM}}} + \frac{\partial Y_{\mathrm{CM}}}{\partial x_2}\frac{\partial}{\partial Y_{\mathrm{CM}}} + \frac{\partial Z_{\mathrm{CM}}}{\partial x_2}\frac{\partial}{\partial Z_{\mathrm{CM}}} + \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} + \frac{\partial y}{\partial x_2}\frac{\partial}{\partial y} + \frac{\partial z}{\partial x_2}\frac{\partial}{\partial z}$$
$$= \frac{m_2}{M}\frac{\partial}{\partial X_{\mathrm{CM}}} + 0 + 0 + \left(1 - \frac{m_2}{M}\right)\frac{\partial}{\partial x} + 0 + 0 = \frac{m_2}{M}\frac{\partial}{\partial X_{\mathrm{CM}}} + \left(1 - \frac{m_2}{M}\right)\frac{\partial}{\partial x}$$
$$= \frac{m_2}{M}\frac{\partial}{\partial X_{\mathrm{CM}}} + \frac{m_1}{M}\frac{\partial}{\partial x}$$

and similarly for y_2 and z_2.

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

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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 charge Ze. After the separation of the centre 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 a 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, z, and in the kinetic energy operator there are the *second* derivatives with respect to x, y, z, 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 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.

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

It is seen that once again we have reached a situation allowing us to separate the motion of the centre of mass in the Schrödinger equation. This time, however, the *form* of the operator $\hat{H}$ is different (e.g., Δ_{xyz} has only formally 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 point-like particle[9] with coordinates x, y, z (defined in *this* example) and mass 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, $\boldsymbol{R}_{\mathrm{CM}}$ almost shows the position of the nucleus, and x, y, z are almost 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 which resembles Example 1.

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

Note, that the new coordinates describe the potential energy in a more complex way. We need differences of the kind $x_2 - x_1$, to insert them into Pythagoras' formula for the distance. We have

$$
x_1 = X_{\mathrm{CM}}\frac{m_1 + m_2}{m_1} - \frac{m_2}{m_1}x_2 = X_{\mathrm{CM}}\frac{m_1 + m_2}{m_1} - \frac{m_2}{m_1}(x + X_{\mathrm{CM}}) = X_{\mathrm{CM}} - \frac{m_2}{m_1}x,
$$

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

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