Some observations about MOLPRO

Abstract

In equilibrium, coordinates of atoms in a molecule are expressed with respect to the origin situated at the center–of–mass of the molecule. In the quantum mechanical software MOLPRO, we have found that the center–of–mass of molecule does not coincide with the origin of the coordinate system. Rather it lies in a random manner. The problem becomes more severe when, for example, one wants to know the separation between two interacting particles in the scattering process. There appears need to make amendment in MOLPRO, so that the origin of coordinate system coincides with the center–of–mass of the molecule in equilibrium.

Keywords: ISM: molecules, interaction potential, MOLPRO

Introduction

For quantum mechanical calculations of atomic systems, some software, e.g., Frischet et al.1, Werner et al.2 & Valiey et al.3 etc. are in use in science. For scattering between a molecule of interest and a colliding partner (generally taken as H2 molecule for interstellar medium), a common procedure is to calculate the interaction potential between them. For convenience, the H2 molecule is taken as structure–less particle and is often replaced by He atom, as both of them have 2 electrons and 2 protons.4–15 In the process, the molecule is first optimized and the cartesian coordinates (x_i, y_i, z_i) of the atoms of molecule in equilibrium are obtained. The Cartesian coordinates (x_cm, y_cm, z_cm) of the center–of–mass of the molecule are expressed as

\[ x_{cm} = \frac{\sum m_i x_i}{\sum m_i}, \quad y_{cm} = \frac{\sum m_i y_i}{\sum m_i}, \quad z_{cm} = \frac{\sum m_i z_i}{\sum m_i} \]

where m_i denotes the mass of the i–th atom. The origin of coordinate system is generally taken at the center–of–mass of the molecule, so that x_cm=0, y_cm=0, z_cm=0.

For a clear presentation, in the present discussion, we have taken the case of the interaction between H2CS (thioformaldehyde) and He atom. The H2CS is a planar molecule (say, lying in the yz–plane) as shown in Figure 1 and following the symmetries, the coordinates of its atoms in equilibrium may be expressed as given in Table 1. For coincidence of center–of–mass with the origin of coordinate system, we get the relation

\[ 2m_H x_1 + m_C x_2 = m_S z_3 \]

where m_H, m_C and m_S are atomic masses of hydrogen, carbon and sulphur, respectively. The positions of atoms of H2CS are now kept fix. For calculation of interaction potential between H2CS and He atom, one can put He atom at a point expressed in polar coordinates (r, \theta, \phi) as shown in Figure 2. The Cartesian coordinates (x', y', z') of He atom are

\[ x' = r \sin \theta \cos \phi, \quad y' = r \sin \theta \sin \phi, \quad z' = r \cos \theta \]

Table 1 Atomic coordinates of H2CS in equilibrium.

| Atom | x | y | z |
|------|---|---|---|
| H    | 0 | y | –z |
| H    | 0 | –y | –z |
| C    | 0 | 0 | –z |
| S    | 0 | 0 | z |

Figure 1 Geometry of the H2CS molecule in equilibrium.

Figure 2 Interaction between H2CS and He atom.

For interaction between H2CS and He atom, the coordinates are given in Table 2. Then, the energies are calculated as:

Energy \( E(\mathbf{r}, \theta, \phi) \) of H2CS + He.

Energy \( E(\mathbf{r}, \theta, \phi) \) of H2CS while He atom is present as a ghost atom.
Energy $E(r, \theta, \phi)$ of He atom while all atoms of $H_2CS$ are present as ghost atoms.

### Table 2 Coordinates for interaction between $H_2CS$ and He.

| Atom | x | y | z |
|------|---|---|---|
| H    | 0 | $y_1$ | $-z_1$ |
| H    | 0 | $-y_1$ | $-z_1$ |
| C    | 0 | 0 | $-z_2$ |
| S    | 0 | 0 | $z_1$ |
| He   | $x'$ | $y'$ | $z'$ |

Here, the concept of ghost atom is introduced in order to consider the Basis Set Superposition Error (BSSE). The interaction potential $V(r, \theta, \phi)$ between $H_2CS$ and He atom is

$$V(r, \theta, \phi) = E_1(r, \theta, \phi) + E_2(r, \theta, \phi) - E_3(r, \theta, \phi)$$

The interaction potential $V(r, \theta, \phi)$ is calculated for various positions of He atom and is used as input in the computer code MOLSCAT to calculate the scattering cross sections for collisional transitions between rotational levels, as a function of energy of colliding partner. These cross sections are averaged over the Maxwellian distribution to get the scattering rate coefficients, as a function of kinetic temperature in the medium.

We have found that on optimization of $H_2CS$ with MOLPRO, the center–of–mass does not coincide with the origin of coordinate system. On inclusion of He atom, we do not know if the origin of polar coordinates $(r, \theta, \phi)$ (expressing the position of He atom) is at the center–of–mass of $H_2CS$, or at the origin defined in the MOLPRO, or somewhere else. Under such circumstances, it is difficult to have information about relative separation between the $H_2CS$ molecule and He atom, which is essentially required.

### Optimization of $H_2CS$

On 01 April 2014, we have optimized the $H_2CS$ with MOLPRO (Version 2012.1, Copyright, University College Cardiff Consultants Limited, 2008) by using the method CCSD (T) and basis set cc–pVDZ. The coordinates of atoms obtained are given in Table 3, which provide the center–of–mass at

$$x_{cm} = 0.00, \ y_{cm} = 0.00, \ z_{cm} = 0.4667993088$$  \hspace{1cm} (1)

### Table 3 Atomic coordinates of $H_2CS$ (in Bohr).

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| H    | 0.0 | 1.765973450 | $-3.050725593$ |
| H    | 0.0 | $-1.765973450$ | $-3.050725593$ |
| C    | 0.0 | 0.00 | $-1.940275913$ |
| S    | 0.0 | 0.00 | 1.150376265 |

On 21 September 2017, we have again optimized the $H_2CS$ with MOLPRO (Version 2015.1, Copyright, TTI GmbH Stuttgart, 2015) by using the same method CCSD(T) and the same basis set cc–pVDZ. The coordinates of atoms obtained are given in Table 4, which provide the center–of–mass at

$$x_{cm} = 0.00, \ y_{cm} = 0.00, \ z_{cm} = 0.4667993088$$  \hspace{1cm} (2)

It shows the shifting of the center–of–mass without any reason.

### Table 4 Atomic coordinates of $H_2CS$ (in Bohr).

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| H    | 0.0 | 1.765976499 | $-2.745177869$ |
| H    | 0.0 | $-1.765976499$ | $-2.745177869$ |
| C    | 0.0 | 0.00 | $-1.634732411$ |
| S    | 0.0 | 0.00 | 1.453909829 |

### Discussion

The comparison of $y$–coordinates in Tables 3 & 4 shows that either the values changed or the accuracy of data is up to the 4$^{th}$ or 5$^{th}$ decimal place. The comparison of $z$–coordinates shows a large variation in the values. In equations (1) and (2): (i) The value $x_{cm}=0.00$ is not surprising, as the $H_2CS$ lies in the $yz$–plane. (ii) The two H atoms lie symmetrically opposite on the two sides of $z$–axis and therefore the value $y_{cm}=0.00$, as per expectation. (iii) Non–zero value of $z_{cm}$ is surprising, as the center–of–mass of a molecule (in equilibrium) is generally taken at the origin of coordinate system. Two different values for $z_{cm}$ may be interpreted that the center–of–mass is placed in a random manner in the MOLPRO. There is difference of 0.305536758 Bohr between the positions of center–of–mass when the $H_2CS$ is optimized with the help of MOLPRO on two different dates (01 April 2014 and 21 September 2017). It should not be the case. One may say that the molecule is shifted along the $z$–axis. But, the problem appears to know about the separation between $H_2CS$ and He atom while calculating interaction between them.

This problem was submitted for consideration of the organizers of MOLPRO as well as the MOLPRO users, but no solution emerged out. None of them could tell how to get separation between the $H_2CS$ molecule and He atom.

We have also optimized the Glycolaldehyde ($C_2H_4O_2$) with the help of MOLPRO. The coordinates obtained are given in Table 5. This is case of three–dimensional molecule. These coordinates provide the center–of–mass at

$$x_{cm} = 0.089435584, \ y_{cm} = -0.033493791, \ z_{cm} = 0.000006947$$  \hspace{1cm} (3)

### Table 5 Coordinates of Glycolaldehyde (in Bohr).

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| C    | -0.962276889 | 0.97335635 | 0.00027023 |
| C    | 1.371041657 | $-0.680834308$ | 0.000332592 |
| O    | 3.483477674 | 0.147262577 | 0.000003779 |
| O    | $-3.113843465$ | $-0.620559603$ | $-0.000640617$ |
| H    | 0.978640027 | $-2.736504842$ | 0.000990216 |
| H    | $-0.883628377$ | 2.190534619 | $-1.672012667$ |
| H    | $-0.884340804$ | 2.189412121 | 1.673439411 |
| H    | $-4.620335021$ | 0.387792112 | 0.000922186 |

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It also shows that the center–of–mass of Glycolaldehyde does not coincide with the origin of coordinate system. We have optimized other molecules also with the help of MOLPRO and similar situation of non–coincidence of center–of–mass of molecule and the origin of coordinate system is found.

**Conclusion**

In equilibrium, the center–of–mass of a molecule should coincide with the origin of coordinate system. We have found that for the considered molecules, it is not the case. The problem is found to become more severe, for example, when one wants to know the separation between the two colliding partner for scattering process. There appears need to make amendment in MOLPRO, so that the origin of coordinate system coincides with the center–of–mass of a molecule in equilibrium.

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**Conflict of interest**

Author declares there is no conflict of interest.

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