

MOLECULAR DYNAMICS IN HYPERSPHERICAL COORDINATES

DINÁMICA MOLECULAR EN COORDENADAS HIPERESFÉRICAS

V. M. FREIXAS LEMUS, A. MARTÍNEZ MESA AND L. URANGA PIÑA[†]

Facultad de Física, Universidad de La Habana, Cuba. llinersy@fisica.uh.cu[†]

[†] corresponding author

(Recibido 25/3/2014 ; Aceptado 22/7/2014)

PACS: Hyperspherical methods (atomic physics), 31.15.xj; Scattering in atomic and molecular collisions, 34.80.-i; Molecular dynamics calculations in atomic and molecular physics, 31.15.xv

The remarkable progress experienced during the last decade by the set of experimental techniques known as femtosecond spectroscopy, has significantly stimulated the investigation of dynamical processes at the molecular scale, especially via computer simulations. Ultrafast spectroscopy experiments provide direct information on the evolution of molecular phenomena in the femtosecond time-scale. On the other hand, theoretical studies allow to translate the experimental information into an explicit representation of atomic motion. These data may be used to design control strategies to manipulate the dynamics of the molecular systems in order to optimize, for instance, the formation of a target molecule. Computer simulations exhibit some additional advantages, such as the possibility to address the calculation of observables that can not be accessed empirically. It is also useful to carry out an artificial separation of the different components of the intermolecular interactions (e.g., the isotropically averaged potential, anisotropic contributions, local minima, etc.), and to evaluate the influence of each one of these contributions on the calculated observables.

Reactive collisions, i.e., those where bond breaking and formation occur, constitute examples of dynamical processes that can not be treated properly within the standard scattering theory. For example, for triatomic systems, the change in the bonding character enforces it to be treated explicitly as a three-body problem. Because of the rapid increase of the computational resources necessary to undertake the simulations of a molecular system as its size becomes larger, it is very important to find a representation of the molecular motion that enables the solution of the resulting equations of motion to be handled efficiently.

The purpose of this paper is to discuss the advantages of hyperspherical coordinates for the study of molecular dynamics, with emphasis on the case of triatomic systems. Hyperspherical coordinates constitute alternative representations of the molecular motion [1-6]. These

generalized coordinates transform the problem of n particles moving in a D -dimensional space, after the elimination of the motion of the centre of mass, into that of a single particle of mass $\mu = \sqrt{m_a m_b m_c / (m_a + m_b + m_c)}$ that moves in a d -dimensional hypersphere ($d=(n-1)D$) whose variable (hyper)radius is ρ . The position on the hypersurface is specified by $d-1$ hyperangles.

There are many different angular parametrizations, such as the asymmetric (or Fock), symmetric (or Smith) and Johnson coordinates [3]. The freedom to choose the parametrization which is better suited for every possible application is one of the more appealing features the method. The majority of the investigations carried out so far in the hyperspherical framework are based on the time-independent scattering theory. Therefore, the unique perspective emerging from the time-dependent approach to quantum dynamics has remained practically unexplored. The study of the time evolution of reactive collisions in the hyperspherical formalism to be addressed here, is performed by means of the Classical Molecular Dynamics method. As it will be explained below, the deviations arising from neglecting quantum effects are alleviated by the particular choice of the potential energy surface.

As a numerical example, we will focus our attention in the $F + HCl \rightarrow FH + Cl$ exchange reaction. Owing to the availability of experimental and theoretical results, this kind of reactive collisions constitute an ideal benchmark to test novel algorithms, for which an application to the numerical simulation of dynamical processes of molecular systems in the gas phase is envisaged. From the practical point of view, this reaction also has potential applications in the design and fabrication of chemical lasers [8,9].

Jacobi vectors are the most widely used set of dynamical variables to specify the configuration of polyatomic systems. This preference is due to the simplicity of the classical and the

quantum equations of motion in this configuration space, since the kinetic energy is a homogeneous quadratic form of the conjugate momenta. The Jacobi coordinates for a triatomic system are defined as follows:

$$\vec{X} = \vec{r}_c - \frac{m_a \vec{r}_a + m_b \vec{r}_b}{m_a + m_b} \quad (1)$$

$$\vec{x} = \vec{r}_b - \vec{r}_a \quad (2)$$

$$\varphi = \arccos \left(\frac{\vec{X} \cdot \vec{x}}{|\vec{X}| |\vec{x}|} \right). \quad (3)$$

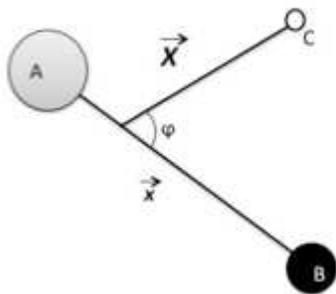


Figure 1. Definition of Jacobi coordinates.

One of the key ingredients for the solution of any dynamical problem is the evaluation of the interaction potential, which demands to express the interparticle distances as a function of the generalized coordinates. For Jacobi coordinates, this can be achieved without too much effort by using the cosine law. However, one of the main difficulties associated to the use of Jacobi's vectors is that they depend on the preselected order of the particles, i.e., they depend on how do we chose A, B and C. Albeit some strategies have being devised to overcome this problem [11], such asymmetry often affects the numerical convergence of quantum mechanical calculations on exchange processes. This situation can be avoided by introducing the hyperspherical coordinates, which are defined in terms of the rescaled Jacobi's vectors \vec{r} and \vec{R} [10, 11].

In the following, we will make use of the so called Smith hyperspherical coordinates ρ , Θ , Φ , defined as:

$$\rho = \sqrt{|\vec{R}|^2 + |\vec{r}|^2} \quad (4)$$

$$\sin(2\Theta) = 2 \frac{|\vec{R} \times \vec{r}|}{\rho^2} \quad (5)$$

$$\tan(2\Phi) = 2 \frac{\vec{R} \cdot \vec{r}}{|\vec{R}|^2 - |\vec{r}|^2}. \quad (6)$$

These coordinates can describe the time evolution of the internal degrees of freedom, after decoupling them from the motion of the centre of mass and from the rotations of the whole system. The hyperspherical coordinates present some properties that make these generalized coordinates very attractive for the description of reactive collisions. For example, the hyperradius ρ is independent of the way of choosing the Jacobi vectors. It also provides an intuitive time-evolving description of the process, that is, this quantity takes

large values for the asymptotic rearrangement regions of the reactants and the products, whereas the small values of the hyperradius correspond to the three atoms located within the strong interaction region. Moreover, the two hyperangles Θ and Φ are related to the area of the triangle formed by the three particles and the geometric shape of this triangle, respectively. In this work, the equations of motion are solved in an effective Cartesian configuration space, defined through the transformation:

$$\xi = \rho \cos(2\Theta) \sin(2\Phi) \quad (7)$$

$$\eta = \rho \sin(2\Theta) \quad (8)$$

$$\zeta = \rho \cos(2\Theta) \cos(2\Phi). \quad (9)$$

In this configuration space, the equations of motion for the variables $s = \xi, \eta, \zeta$ take the form:

$$\dot{s} = \frac{1}{\mu} [4P_s - 3Ws] \quad (10)$$

$$\dot{P}_s = \frac{3W}{\mu} [P_s - Ws] - \frac{\partial V}{\partial s} \quad (11)$$

$$W = \frac{xP_x + yP_y + zP_z}{x^2 + y^2 + z^2}. \quad (12)$$

The analysis of the structure of the system of equations (10) makes the pragmatic advantage of introducing this new configuration space to become striking: the numerical solution of these differential equations is only slightly more difficult than integrating the equations of motion of a single particle in the ordinary three-dimensional space. Nevertheless, because of the abstract nature of the generalized Cartesian coordinates (7), it is simpler to generate the initial conditions in the phase space associated to the Jacobi coordinates. The initial values of the intramolecular distance $|\vec{r}|$ and its conjugate momentum $|\vec{P}_r|$ are generated by sampling the ground state initial wave function and its Fourier transform, respectively. A similar procedure was used to generate the coordinates $|\vec{R}|$ (distributed following a Gaussian centred at a sufficiently large separation, 15\AA , with a standard deviation of 0.5\AA), while the momenta $|\vec{P}_R|$ were selected according to a Boltzmann velocity distribution corresponding to the temperature of 300K . The initial angular momentum quantum number was also chosen according to a Boltzmann distribution. The rotational eigenstate corresponding to this quantum number was used to generate the initial value of the Jacobi angle φ .

Finally, the potential energy surface of the triatomic system was modelled using a London-Eyring-Polanyo-Sato (LEPS) function:

$$V(r_1, r_2, r_3) = Q_1 + Q_2 + Q_3 - \sqrt{J_1^2 + J_2^2 + J_3^2 - J_1 J_2 - J_2 J_3 - J_3 J_1}. \quad (13)$$

This functional expression consist in a superposition of both coulombic (Q_i) and electron exchange (J_i) terms. Explicit equations specifying the dependence of each of these terms on the interatomic distances have been given elsewhere [10].

The parameter values, which determine the shape of the LEPS potential energy surface, were taken from the literature [4]. This particular potential energy surface was designed to optimize the correspondence between the results of Quasi-Classical Trajectory (QCT) calculations and the experimental data available for the F+HCl reaction. The resulting potential landscape does not show any significant barrier, thus the possible role played by tunnelling at low collision energies can be disregarded. Because of the fitting of the experimental results, any other quantum effects are masked in the interaction potential. This feature guarantees the validity of the results presented below, which were computed using the QCT method.

In Figures 2 and 3, the time evolution of the Smith hyperspherical coordinates is illustrated by three representative trajectories, corresponding to different collision energies. From top to bottom, they are shown the cases of collisions taking place at small, intermediate and large incident energies. In Figure 2, the differences in the initial energy of the F atom impinging on the HCl molecule become striking from the shortening of the elapsed time before the collision takes place. The collision times corresponds to the point in time when the hyperradius attains its minimal value.

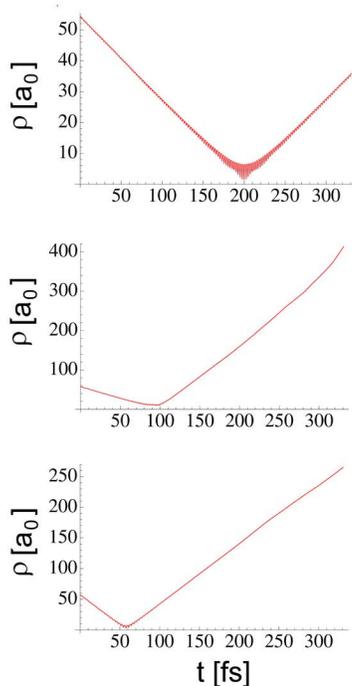


Figure 2. Time evolution of the hyperradius for representative trajectories in the hyperspherical configuration space corresponding to low ($E_{col} = 0.4 \text{ kcal}\cdot\text{mol}^{-1}$, top panel), intermediate ($E_{col} = 1.5 \text{ kcal}\cdot\text{mol}^{-1}$, middle panel) and high ($E_{col} = 5.0 \text{ kcal}\cdot\text{mol}^{-1}$, bottom panel) collision energies.

On the other hand, the time evolution of the coordinates Θ and Φ , plotted in Figure 3, reveal the connection between the shape of trajectories in the hyperspherical configuration space and the physical characteristics of the scattering process. For example, the oscillations in the hyperangular coordinates are a fingerprint of molecular vibrations. The hyperangle Θ is

related to the area of the triangle formed by the three particles (Eqn. (5)), so the amplitude of Θ oscillations enlarges when the atoms are closer (for such configurations, the distortions of the shape of the triangle are more pronounced), as it can be seen in Figure 3.

Moreover, the relationship between the hyperangle Φ and the particles ordering can be exploited to describe the process of HCl bond breaking and the formation of the HF molecule in terms of the time evolution of Φ . Discontinuities in $\Phi(t)$ happens whenever the F atom crosses the plane perpendicular to the HCl molecular axis. Likewise, the comparison between the initial and final values of this coordinate allows to identify the reactive and the non-reactive trajectories. It can be seen, that the three trajectories represented in Figure 3 correspond to scattering events without exchange.

Finally, at high and intermediate collision energies, the variations of the hyperangles Θ and Φ are noticeable during a narrow time interval of about 100 fs centred at the point in time when collision occurs. At small incident energies, however, the oscillations of the hyperangles take place during a larger interval of around 300 fs. Hence, the trajectory in the hyperspherical space provides a way to differentiate quantitatively between direct reactions from those proceeding through an insertion mechanism, i.e., with the formation of an intermediate triatomic complex.

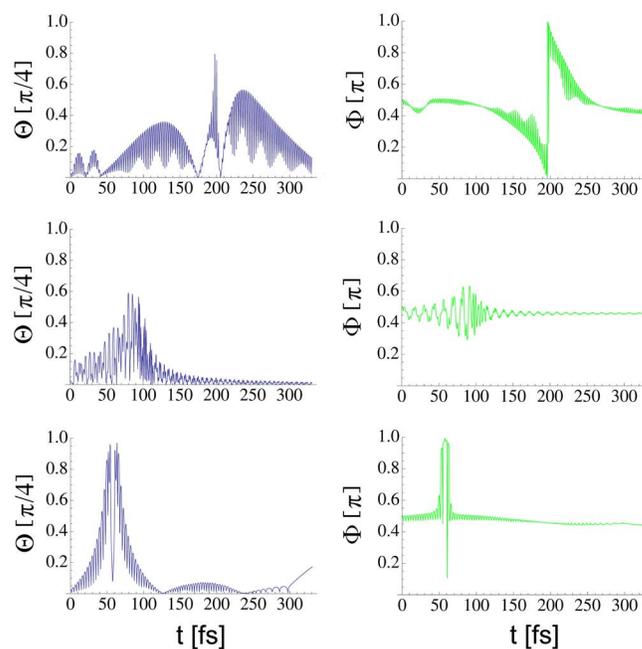


Figure 3. Time evolution of the hyperangles and Φ , for representative trajectories corresponding to low ($E_{col} = 0.4 \text{ kcal}\cdot\text{mol}^{-1}$, top panel), intermediate ($E_{col} = 1.5 \text{ kcal}\cdot\text{mol}^{-1}$, middle panel) and high ($E_{col} = 5.0 \text{ kcal}\cdot\text{mol}^{-1}$, bottom panel) collision energies.

The overall behaviour of the triatomic system can be described by the average trajectory $\langle \rho \rangle(t)$, $\langle \Phi \rangle(t)$, represented in Figure 4. It can be noticed, that there is only a slight variation of the average hyperangle $\Delta\Phi \sim \pi/50$. This small shift indicates that the exchange reaction is unlikely to occur at $T = 300\text{K}$. It is

also apparent that the change of $\langle\Phi\rangle$ does not take place in a single step, but the system visit configurations with smaller hyperangles instead, as it is shown in Figure 4 (inset).

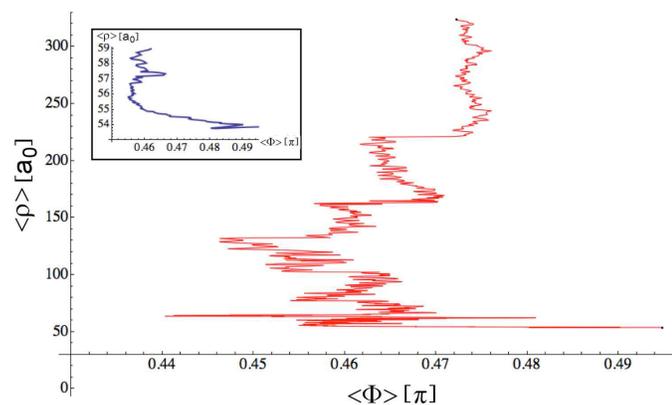


Figure 4. Average trajectory $\langle\rho\rangle(t)$, $\langle\Phi\rangle(t)$ of the triatomic system.

Summing up, we have developed an algorithm for the application of the Classical Molecular Dynamics method to the study of the time evolution of reactive collisions in triatomic systems. The methodology was applied to the particular case of the $F + HCl \rightarrow HF + Cl$ exchange reaction. We have shown that this formalism provides a geometrical representation of the molecular motion in the hyperspherical configuration space, that can be interpreted to retrieve information on the dynamical properties of the system. The probability of occurrence of the exchange reaction is found to be negligible at room temperature. As an outlook, we plan to carry out the study of the state-to-state reaction probabilities for different

initial vibrational and rotational quantum numbers for low collision energies, for which the particle exchange is more likely to occur. In addition, the symmetric hyperspherical coordinates allow to establish quantitative criteria in order to distinguish between different types of reactions (e.g., reactive and non-reactive scattering, direct or insertion reactions, etc).

[1] V. Aquilanti, S. Cavalli, J. Chem. Soc., Faraday Trans. **93**, 801 (1997)

[2] S. K. Gray, G. G. Balint-Kurti, J. Chem. Phys. **108**, 950 (1998)

[3] V. Aquilanti, S. Cavalli, D. De Fazio, J. Chem. Phys. **109**, 3792 (1998)

[4] P. Palmieri et al., Mol Phys. **98**, 1835 (2000)

[5] D. De Fazio, V. Aquilanti, S. Cavalli, J. Chem. Phys. **125**, 133109 (2006)

[6] D. De Fazio et al., J. Chem. Phys. **129**, 064303 (2008)

[7] B. R. Johnson, J. Chem. Phys. **79**, 1906 (1983)

[8] H. Kornweitz, A. Persky, J. Phys. Chem. A **108**, 140 (2004)

[9] H. Kornweitz, A. Persky, J. Phys. Chem. A **108**, 8599 (2004)

[10] L. Alfonso Hernández, Diploma thesis, Universidad de la Habana (2010)

[11] D. De Fazio, Ph.D. thesis, University of Perugia (1996)

[12] S. Lahmar et al. (eds.), *Topics in the Theory of Chemical and Physical Systems*, (123D146. Springer, 2007)