

Molecular Dynamics of Chiral Molecules in Hyperspherical Coordinates

Andrea Lombardi[1,2(✉)], Federico Palazzetti[1], and Vincenzo Aquilanti[1]

[1] Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Perugia, Italy
ebiu2005@gmail.com, {federico.palazzetti,vincenzo.aquilanti}@unipg.it
[2] Consortium for Computational Molecular and Materials Sciences (CMS)[2], Via Elce di Sotto, 8, 06123 Perugia, Italy
http://www.chm.unipg.it/gruppi?q=node/48

Abstract. The role of chirality in molecular collisions, in connection to chiral discrimination, lacks a striking experimental demonstration. This is due to difficulties in setting up apparatuses allowing for a strict control of the spatial distribution and alignment of the molecules and to lack of adequate theoretical and computational approaches to design experiments, anticipate results and interpret data. Here we illustrate a theoretical approach to the description of chiral effects in collisions to search for a stereo-directional origin of chiral discrimination.

Keywords: Molecular chirality · Chiral discrimination · Chiral recognition · Hyperspherical coordinates · Intermolecular interactions · Molecular collisions

1 Introduction

The quantum mechanical treatment of N-body problems is the theoretical background of quantum reactive scattering calculations. It can be formulated in terms of hyperspherical functions, an optimal choice for the expansion basis sets [1–4], and for the representation of intermolecular and intramolecular interactions. Hyperspherical and related techniques refer to a wide class of curvilinear coordinates for which the construction of relevant operators and functionals of interest in quantum and classical mechanics is relatively straightforward. Although the practical feasibility of full quantum treatments limits the use to three- or four-atom systems, one might go beyond this restriction by extending the hyperspherical approach to classical mechanics, so that applications to dynamics simulations of clusters and large molecules would become feasible, benefiting of the computational ease of classical trajectories. In the case of classical mechanics, the added value of the hyperspherical method is the separation of the degrees of freedom into homogeneous sets of variables corresponding to well defined kinetic energy terms, representing deformations, ordinary rotations and kinematic rotations [3,4].

© Springer Nature Switzerland AG 2019
S. Misra et al. (Eds.): ICCSA 2019, LNCS 11624, pp. 413–427, 2019.
https://doi.org/10.1007/978-3-030-24311-1_30

The hyperspherical formulation grounds on "classical" definitions of the hyperangular momenta and other dynamic quantities. The classical hyperspherical equation of motion can be consequently written, although terms dependent upon angular variables and singularities in the corresponding Hamilton function make it convenient integration in Cartesian coordinates. A proper matrix transformation permits the evaluation, as a function of time, of the terms appearing in the hyperspherical Hamilton function.

The peculiar feature of hyperspherical coordinates to be considered in this work is the definition of a chiral degree of freedom corresponding to the chiral sign of a given molecular system [5–7]. Such coordinates make the hyperspherical representation suited for studying chiral effects in collisions. To identify the microscopic mechanisms inducing chiral selection it is necessary to investigate how chiral molecules collide with atomic or molecular targets and their behaviour in gaseous environments. The transition to gas phase is crucial in order to single out the fundamental elementary molecular processes. Intriguing is the idea that the effects associated to the true chiral influence of roto-translational motions [8–10], proved for liquids phase, might occur also in gas phase. The sense of rotation of a vortex in gas phase could act selectively on the direction of a chiral molecule rotation. This affirmation is strengthened by the experimental observation that in supersonic beams of gaseous mixtures the component in excess induces directionality and orientation in dragging molecules [11], as amply discussed, for example in Ref. [12] and elsewhere. Molecular alignment is actually a powerful allied in the search for an experimental proof of chiral selection in collisions, being molecular rotations a source of averaging of orientation and stereodynamics effects, since in case of fast rotations the vector correlation of the specific polarization directions to the physically significant vector quantities in the body frame gets lost in the laboratory reference frame.

The aspects of collisions of molecules to put into relation to chirality are the intermolecular interactions driving molecular encounters and the stereodynamics of collisions involving different enantiomers. Although chiral effects are well known in the interaction of molecules with light (e.g. natural optical activity, dichroism), they are still nearly disregarded in the context of molecular collisions, since the molecular scattering theory has not been provided with an explicit description of chirality, for which the introduction of new parameters and methodologies is still required. In fact, the only efforts to set up reliable full quantum mechanical scattering calculations in the previous decades have been dedicated to the study of three-atom reactions, where chirality is not present (three atoms always lie on a plane), leaving aside more complex systems –mostly due to the exceedingly high computational costs– involving more than three atoms (or centers) for which chiral configurations exist [13–15].

In the following Sections, it will be given a description of the hyperspherical coordinates applied to chiral systems and of the related approach to the modeling of the interactions. Finally, a model system, prototype of chiral collisions, will be examined.

2 Theoretical Background

The tetrahedron is the simplest chiral polyhedron in the three-dimensional space, considering as distinguishable its four vertexes. Accordingly, tetratomic molecules are the simplest chiral systems. As a general consequence, chiral manifestations in elementary processes and interactions can in principle be reduced to four-center problems.

Quantum mechanical theory of molecular scattering, applied to four-atom systems, does not contain an explicit description of the effects of the chirality in collisions and it still requires the introduction of new parameters and methodologies. Indeed, when collision processes involve more than three atoms, simulations and related systematic computations cannot be efficiently grounded on quantum mechanics, since the feasibility of full quantum treatments is limited by the number of degrees of freedom. Because of this, related computations are usually carried out resorting to the so called quasi-classical trajectory calculations (QCT) (see e.g. [16] for a QCT program) or sometimes by combining quantum mechanics treatments (for selected bound degrees of freedom) with classical mechanics ones (for the remainder), the so-called quantum-classical methods (see e.g. [17]). A variety of semiclassical methods are also available [18–24]. Rarely, and almost exclusively for three atom systems, the calculation is performed using exact quantum full-dimensional treatments [25] and this excludes chirality.

To provide a theoretical background, we show how to identify a single chiral degree of freedom in four-center problems, within the hyperspherical coordinate framework, as a tool for molecular dynamics studies and structural recognition of chiral properties in dimers and clusters.

2.1 Coordinates for Chiral Molecules

Different enantiomers are commonly distinguished attributing them a sign, + or −, accounting for the sense of rotation of the plane of polarization of light, in their optical activity. A chiral coordinate must be a variable that changes its sign according to the chiral sign of the enantiomer. An appropriate mathematical tool for the representation of four-center chiral systems is the *singular value decomposition* [26], a matrix decomposition theorem that can be applied to any given set of N atoms, after assigning to them a properly defined position matrix.

Given a system of $N \geq 2$ particles, let us denote by $m_1, \cdots, m_N$ the particle masses and by $\mathbf{r_1}, \cdots, \mathbf{r_N}$ the corresponding radii vectors in the center of mass reference system. A set of *mass scaled* radii vectors $\mathbf{q}_\alpha = (m_\alpha/M)^{1/2}\mathbf{r}_\alpha$ ($1 \leq \alpha \leq N$), can be constructed, where $M = \sum_\alpha^N m_\alpha$ is the total mass of the system.

The $3N$ components of the mass-scaled vectors are then arranged columnwise to form a $3 \times N$ position matrix as follows:

$$Z = \begin{pmatrix} q_{1,1} & q_{1,2} & \cdots & q_{1,N} \\ q_{2,1} & q_{2,2} & \cdots & q_{2,N} \\ q_{3,1} & q_{3,2} & \cdots & q_{3,N} \end{pmatrix}. \tag{1}$$

A matrix $Z' = R^t Z$ corresponds to the coordinate change occurring in passing to a rotated coordinate frame placed at the center of mass of the system, by the action of a rotation matrix R^t, transpose of a matrix $R \in O(3)$. A rotation of the coordinate frame can also be performed in the so called *kinematic space* [14,15,27], by action of an orthogonal matrix (right-multiplication) $K \in O(N)$ on the position matrix Z, $Z' = ZK$.

A reduced set of K matrices having the following form (see last column):

$$K = \begin{pmatrix} k_{1,1} & k_{1,2} & \cdots & (m_1/M)^{1/2} \\ k_{2,1} & k_{2,2} & \cdots & (m_2/M)^{1/2} \\ \cdots & \cdots & \cdots & \cdots \\ k_{N,1} & k_{N,2} & \cdots & (m_N/M)^{1/2} \end{pmatrix} \tag{2}$$

generates a special subset of the possible Cartesian frames. Since the mass-scaled vectors sum to zero [27], $\sum_\alpha^N m_\alpha^{1/2} \mathbf{q}_\alpha = 0$, as a consequence of the rotation through K as in Eq. 2, the last column of Z' is invariably the zero-vector. In this special case, one only has to deal with a $3 \times (N-1)$ reduced Z matrix, meaning that the variables representing the motion of the center of mass have been separated. This smaller matrix Z is called *reduced position matrix*.

The set of (N-1) Jacobi vectors, adopted in the representation of molecular collision dynamics, forms a reduced matrix. The Jacobi vectors are obtained as a linear combinations of the N Cartesian particle position vectors, in which the coefficients are defined in terms of the particle masses [28,29]. There is no unique set of such vectors, each of them corresponds to a different coupling scheme of the particles. The different sets are connected by kinematic rotations.

The *singular value decomposition* applied to the $3 \times n$ position matrix Z (where $n = N$ or $n = N-1$) leads to the following product of three matrices:

$$Z = R\Lambda K^t \tag{3}$$

where $R \in O(3)$ and $K \in O(n)$ are 3×3 and $3 \times n$ orthogonal matrices, respectively. The $3 \times n$ matrix Λ is such that its entries are zeroes, with the possible exception of the diagonal ones, $\Lambda_{11} = \lambda_1, \Lambda_{22} = \lambda_2, \Lambda_{33} = \lambda_3$, which are subjected to the inequality $\lambda_1 \geq \lambda_2 \geq \lambda_3 \geq 0$.

The values λ_i, $(i = 1, 2, 3)$ are called the *singular values* of the matrix Z and are uniquely determined, although the factors R and K in Eq. 3 are not. If $N \leq 3$ and Z is the full $3 \times N$ position matrix, then the smallest singular value λ_3 is necessarily zero. The λ's are invariant under both physical space and kinematic rotations [14,27,30,31], a remarkable property, with possible applications to molecular collision dynamics [29,32–35].

The case $n = 3$, corresponding to four particles or four centers, is peculiar, since R and K cannot be chosen to be *special orthogonal* matrices, $R \in SO(3)$ and $K \in SO(n)$, but must be orthogonal matrices. In this case, when the determinant of Z, denoted by $\det(Z)$ is lower than zero, its sign depends on the sign

of $\det(\Lambda)$, see Eq. 3, meaning that one of the singular values must be negative: $\lambda_3 \leq 0$. This fact is directly connected to the mirror image of the system and relevant for chiral molecules.

Indeed, in a generic trajectory of a 4-atom system, the behaviour of the singular values is such that at a given time the λ_3 can approach the zero value and become negative (or positive), meaning the system has changed its chirality sign.

An alternative valid interpretation of the sign of λ_3 (namely the sign of $\det(Z)$) resorts to the volume in the physical space of the tetrahedron identified by the four centers. Considering the matrix Z^t, its determinant is equivalent to the scalar "triple" product of the three Jacobi vectors, say $\mathbf{Q}_1, \mathbf{Q}_2, \mathbf{Q}_3$, describing the system. Such a product, $\mathbf{Q} \cdot (\mathbf{Q}_2 \times \mathbf{Q}_3)$, is actually equivalent to the volume delimited by the tetrahedron defined by the same three vectors. By the way, the two "chiral" triple products are interconverted by space inversion (parity), but not by time reversal combined with any proper spatial rotation, so satisfying the Barron definition of true chirality, mentioned in Sect. 1, see Refs. [8–10].

2.2 The Characterization of the Interactions

Collision dynamics calculations require an accurate characterization of the intermolecular interactions. In order to build up reliable Potential Energy Surfaces (PESs) it is necessary to match experimental information to calibrate *ab initio* techniques. To meet this target, one relies on a representation of the potentials in appropriate analytic forms, in which interaction parameters connected to collision observables can be directly incorporated [5].

The interaction occurring between a rare-gas atom and hydrogen peroxide and persulfide molecules, has been considered in previous works [36–38], motivated by the interesting problem of large amplitude motions–torsion motion around the O-O and S-S bonds–as a chirality inversion mechanism (note that these two molecules are chiral). In Fig. 2 a sketch of the coordinate system used to represent the corresponding intermolecular potential energy surface is shown. The distance r and the two polar angles α ($0 \leq \alpha \leq 2\pi$) and β ($0 \leq \beta \leq \pi$) are the variables which are used in the analytic representation of the potential energy surface and to which a further angle γ is to be added to describe low-frequency mode corresponding to the torsion around the middle O-O or S-S bond. A complete torsion connects the two chiral forms. In Fig. 3 the corresponding calculated potential energy profiles connecting the two enantiomeric forms are represented, as obtained by using different basis sets.

The expression of the potential energy of the H_2S_2 (or H_2O_2) is as follows:

$$V = V_{ext}(r; \alpha, \beta) + V_{int}(r; \gamma) \tag{4}$$

where the intermolecular potential V_{ext} is a function of the atom distance r and its position with respect to the molecule and the intramolecular energy V_{int} depends on the dihedral angle γ and has an expected mild dependence on the atomic distance r. It can be shown that the potential energy, so formulated, can

be expressed in terms of combinations of real-valued hyperspherical harmonics [39–43], denoted by $R^{\mu}_{MM'}$, obtained by combination of complex-valued Wigner D-functions [44,45], as follows:

$$V(r;\alpha,\beta,\gamma) = \sum_{\mu,M,M'} v^{\mu}_{M,M'}(r) R^{\mu}_{MM'}(\alpha,\beta,\gamma) \tag{5}$$

where $\mu = 0, 1, 2, \cdots$, $M(M') = -\mu, -\mu+1, \cdots, 0, 1, \cdots, \mu$ and the radial coefficients $v^{\mu}_{MM'}(r)$ are the expansion moments. For additional details about hyperspherical harmonics see Refs. [14,27,30,31,46,47] and references therein. For a given geometry of the atom-molecule system and a given value of the torsion dihedral angle γ, the harmonic functions take a defined value, then, if the corresponding value of the $V(r;\alpha,\beta,\gamma)$ function is known over a range of the distance r, the only remaining unknown quantities are the radial coefficients. In practice, for any given atom-molecule mutual orientation, a system of linear equations can be set up and solved for the coefficients $v^{\mu}_{M,M'}$ as a function of r. This procedure allows to build up an analytic potential energy surface.

The number of harmonic functions in the above expansion is finite and limited by the number of the specific configurations. These are selected based on physical meaning to capture the essential of the problem to be studied. We remark that the torsion angle γ appearing in the analytic expression of the potential energy function is the chiral coordinate of the system.

The radial coefficients of the hyperspherical expansion in Eq. 5, describe the radial dependence of the different components of the intermolecular interaction, for example dispersion and induction forces, repulsion due to the overlap of the electron clouds, electrostatic contributions. The spherical average of the function in Eq. 5 defines the radial coefficient $v^{0}_{00}(r)$, which represent the isotropic contribution to the interaction (well representative of the van der Waals forces), directly connected to measurable features of the cross sections which are observed in the molecular beam collision experiments (see Ref. [5] and reference therein).

In general, a tentative set of energy profiles, needed to set up the system of linear equations from which a PES can be obtained, is provided by ab initio methods and further refined by comparison of the available experimental data with the corresponding quantities obtained by theoretical methods, using the PES. For example, the accuracy of the $v^{0}_{00}(r)$ coefficient, can be checked directly by comparison with molecular beam experiments.

The method described here for the modelling of the intermolecular interaction, can be extended to a variety of different cases involving more complex molecules [48–52], including interactions with ions and surfaces and in liquid phase [53–58]. For a representative set of the applications to practical cases of collision studies, see Refs. [48,49,58–70].

3 Dynamics Simulations of Collisions of Chiral Molecules

The hypothesis that alignment and orientation in gaseous streams could not only minimize averaging effects due to molecular rotations but crucially propitiate chiral effects in the differential scattering by oriented molecules (see Refs. [71,72] and references therein) has been assessed in previous work [5,73].

The simplest model of a chiral collision is given by a target chiral molecule well oriented or aligned with respect to an incoming stream of atoms. Accordingly, we make the hypothesis that a sample of chiral molecules in a collision chamber is under a controlled orientation distribution, achieved by one of the spatial control techniques illustrated in Ref. [5], and is the target of a beam of velocity selected atoms, coming along a specific direction.

The appropriate set of coordinates describing the orientation of the molecules with respect to the incoming atom directions is made up by a set of Euler angles, i.e. three angular variables denoted here by α, β, and Φ, ranging from 0 to 2π, π and 2π respectively. These angles actually set the orientation of the molecular frame with respect to a space fixed frame, whose z-axis coincides with the incoming molecule or atom propagation direction.

Euler angles varying within a narrow interval around some specific values describe a sharp molecular orientation distribution, so that the simulated processes can be thought of as "oriented collisions".

As a target chiral molecule, we choose the hydrogen persulfide, H_2S_2, for which the potential energy surface, describing the interaction with Rare-gas atoms, has been described in Sect. 2.2, and is available at Ref. [37].

The hydrogen peroxide, H_2O_2, also might have been chosen, at the price of a more complicated interpretation of the collision simulations, being fast interconversion expected as a consequence of a low torsion energy barrier (see Ref. [36]).

The coordinate system for the chiral collisions is shown in Fig. 4, where the molecular reference frame, the Euler orientation coordinates and the parameters of the collision are pictured. The orientation of the velocity vector of the Rg atom with respect to the molecule is given by a polar and an azimuthal angle, coinciding with the α and β angles previously mentioned. A further coordinate is represented by the azimuthal angle Φ (see the figure), accounting for rotations around the y-axis, determining the intersection point of the atom velocity direction line with a circle, of radius the impact parameter b, lying on the xz plane (see Fig. 1). Actually, the three angles, (α, β, Φ) parametrize the rotation needed to bring into coincidence the body frame of the molecule with the arrangement of Fig. 4, where the y-axis corresponds to the incoming atom direction in the laboratory frame.

The cross section of the collision depends on the collision energy E, the total angular momentum denoted by J, and the actual configuration of the molecule (dihedral angle between the two SH bonds and the central S–S bond, that we denoted as γ, see Sect. 2.2). The total angular momentum J can be expressed as

the sum of the molecular angular momentum, here denoted by j, and the orbital angular momentum, associated to the rotation of the vector joining the centers of mass of the colliding bodies, during the collision. In classical mechanics the orbital angular momentum is given by the product $\mu v b$ of the reduced mass of the colliding particles μ, the collision velocity v and the impact parameter b (see Fig. 1). Except for the torsion around the central bond, the molecule is frozen (see Sect. 2.2), so that a quantum number formally associated to the torsion vibration mode, denoted as n, is sufficient to identify the quantum state of the molecule.

The scattering probability at an angle Θ can be defined as the fraction of collisions with impact parameter b that are deflected at Θ (see Fig. 1). Accordingly, we denote as $P^{E,J,n}_{\alpha,\beta}(\Phi, b, \Theta)$ the probability function. Note that all the relevant quantities illustrated above are contained in this expression, as variables or labels. Collisions correspond to a specific axial distribution of the molecules and therefore the collision observables are labelled by the orientation angles. So for example is the differential cross sections, which, as a function of the scattering angle Θ, is written as follows:

$$\sigma^{E,J,n}_{\alpha,\beta}(\Theta) = 2\pi \int_{b=0}^{b=b_{max}} \int_{0}^{2\pi} \int_{\gamma+}^{\gamma-} P^{E,J,n}_{\alpha,\beta}(\Phi, b, \Theta) b db d\gamma d\phi \tag{6}$$

The values $\gamma+$ and $\gamma-$ are the classical turning points of the torsion coordinate γ.

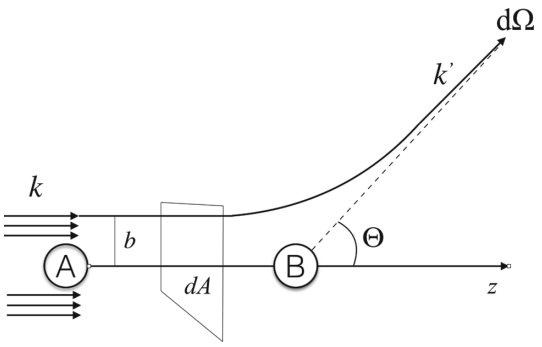

Fig. 1. Scheme of collision of structureless particles. k and k' are wavevectors before and after collision, b is the impact parameter, and $d\Omega$ is the differential solid angle receiving the scattered particles. dA is an area.

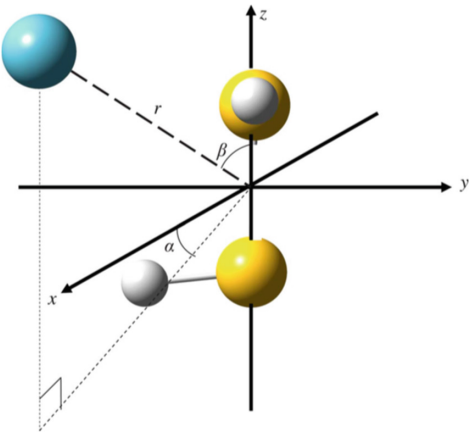

Fig. 2. Sketch of the coordinates parametrizing the interaction between a Rare-gas atom (pale blue particle) and the H_2S_2 (or H_2O_2) molecule. A vector **r** specifying the position of the atom with respect to the center of mass of the molecule (in its equilibrium geometry) is expressed in terms of its modulus r and polar angles α and β, with the axis z lying on the molecular axis. Reproduced with permission from Ref. [37]

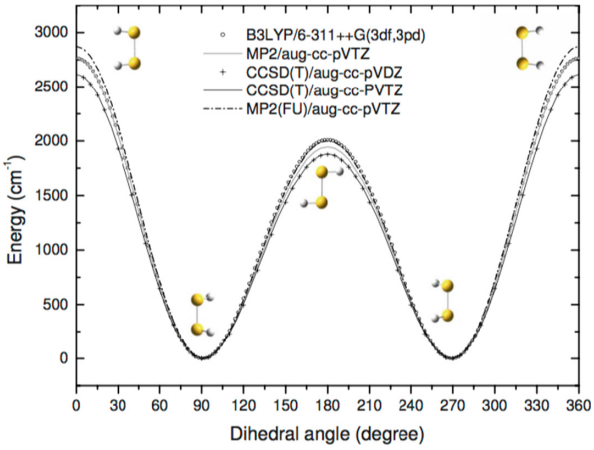

Fig. 3. Variation of the energy profile of the H_2S_2 molecule as a function of the dihedral angle γ for different theory levels and basis sets. The two different chiral forms are indicated corresponding to the two symmetric potential wells. The experimental barriers are of 2800(90) and 1990(15) cm^{-1} for cis and trans configurations, respectively [74]. Reproduced with permission from Ref. [37]

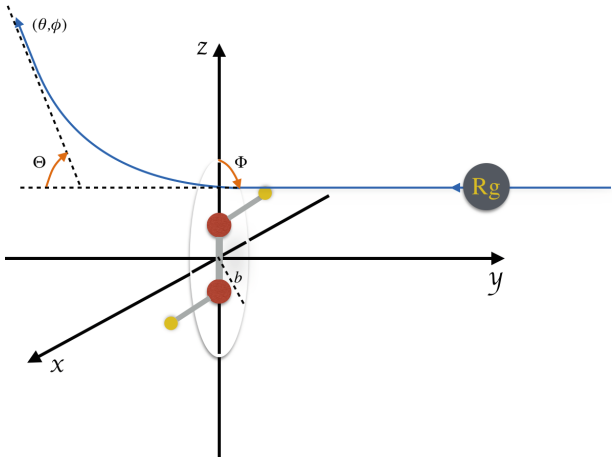

Fig. 4. Sketch of the geometry of an oriented collision involving a chiral molecule of type ABBA (e.g. H_2O_2 or H_2S_2) and a Rare-gas atom (Rg). The atom comes from the y direction, perpendicular to the xz plane. The orientation of the molecular O-O (or S-S) bond defines the z-axis. A circle in the xz plane of radius equal to the impact parameter b is shown along with a perpendicular line corresponding to the direction of motion of the incoming atom, intersecting the circle in a point defined by the azimuthal angle Φ. The scattering angle Θ between the initial and final velocities, and the recoil direction defined by the polar angles θ and ϕ, are indicated.

4 Conclusions

This account was dedicated to the theoretical study of the manifestations of chirality in molecular collisions, following the idea that chiral effects must occur in gaseous flows and streams. Systematic theoretical simulations are intended to inspire and address possible experimental efforts to reveal mechanisms of chiral generation and recognition, still a challenge in the field of molecular collision dynamics.

Acknowledgments. The authors acknowledge financial support from MIUR PRIN 2010-2011 (contract 2010ERFKXL_002) and from "Fondazione Cassa di Risparmio di Perugia (Codice Progetto: 2015.0331.021 Ricerca Scientifica e Tecnologica)". They also acknowledge the Italian Ministry for Education, University and Research, MIUR, for financial supporting through SIR 2014 "Scientific Independence for young Researchers" (RBSI14U3VF). Thanks are due to the Dipartimento di Chimica, Biologia e Biotecnologie dell'Università di Perugia (FRB, Fondo per la Ricerca di Base 2017) and to the MIUR and the University of Perugia for the financial support of the AMIS project through the program "Dipartimenti di Eccellenza". A. L. acknowledges financial support from MIUR PRIN 2015 (contract 2015F59J3R_002). A.L. thanks the OU Supercomputing Center for Education & Research (OSCER) at the University of Oklahoma, for allocated computing time.

References

1. Aquilanti, V., Beddoni, A., Cavalli, S., Lombardi, A., Littlejohn, R.: Collective hyperspherical coordinates for polyatomic molecules and clusters. Mol. Phys. **98**(21), 1763–1770 (2000)
2. Aquilanti, V., Beddoni, A., Lombardi, A., Littlejohn, R.: Hyperspherical harmonics for polyatomic systems: basis set for kinematic rotations. Int. J. Quantum Chem. **89**(4), 277–291 (2002)
3. Aquilanti, V., Lombardi, A., Littlejohn, R.: Hyperspherical harmonics for polyatomic systems: basis set for collective motions. Theoret. Chem. Acc. **111**(2–6), 400–406 (2004)
4. Sevryuk, M.B., Lombardi, A., Aquilanti, V.: Hyperangular momenta and energy partitions in multidimensional many-particle classical mechanics: the invariance approach to cluster dynamics. Phys. Rev. A **72**(3), 033201 (2005)
5. Lombardi, A., Palazzetti, F.: Chirality in molecular collision dynamics. J. Phys.: Condens. Matter **30**(6), 063003 (2018)
6. Lombardi, A., Palazzetti, F., Peroncelli, L., Grossi, G., Aquilanti, V., Sevryuk, M.: Few-body quantum and many-body classical hyperspherical approaches to reactions and to cluster dynamics. Theoret. Chem. Acc. **117**(5–6), 709–721 (2007)
7. Aquilanti, V., Lombardi, A., Yurtsever, E.: Global view of classical clusters: the hyperspherical approach to structure and dynamics. Phys. Chem. Chem. Phys. **4**(20), 5040–5051 (2002)
8. Barron, L.D.: True and false chirality and absolute asymmetric synthesis. J. Am. Chem. Soc. **108**, 5539–5542 (1986)
9. Barron, L.D.: True and false chirality and absolute enantioselection. Rend. Fis. Acc. Lincei **24**, 179–189 (2013)
10. Ribó, J.M., Crusatz, J., Sagués, F., Claret, J., Rubires, R.: Chiral sign induction by vortices during the formation of mesophases in stirred solutions. Science **292**, 2063–2066 (2001)
11. Aquilanti, V., Ascenzi, D., Cappelletti, D., Pirani, F.: Velocity dependence of collisional alignment of oxygen molecules in gaseous expansions. Nature **371**, 399–402 (1994)
12. Aquilanti, V., Grossi, G., Lombardi, A., Maciel, G.S., Palazzetti, F.: Aligned molecular collisions and a stereodynamical mechanism for selective chirality. Rend. Fis. Acc. Lincei **22**, 125–135 (2011)
13. Zhao, B., Guo, H.: State-to-state quantum reactive scattering in four-atom systems. WIREs Comput. Mol. Sci. **7**, e1301 (2017)
14. Aquilanti, V., Beddoni, A., Lombardi, A., Littlejohn, R.: Hyperspherical harmonics for polyatomic systems: basis set for kinematic rotations. Int. J. Quantum Chem. **89**, 277–291 (2002)
15. Aquilanti, V., Beddoni, A., Cavalli, S., Lombardi, A., Littlejohn, R.: Collective hyperspherical coordinates for polyatomic molecules and clusters. Mol. Phys. **98**, 1763–1770 (2000)
16. Hase, W., et al.: J. Quantum. Chem. Program Exch. Bull. **16**, 671 (1996)
17. Billing, G.: Comput. Phys. Rep. **1**, 239–296 (1984)
18. Laganà, A., Crocchianti, S., Faginas Lago, N., Pacifici, L., Ferraro, G.: A nonorthogonal coordinate approach to atom-diatom parallel reactive scattering calculations. Collect. Czech. Chem. Commun. **68**, 307–330 (2003)
19. Lago, N.F., Laganà, A., Garcia, E., Gimenez, X.: Thermal rate coefficients for the $N + N$¡Subscript¿2¡/Subscript¿ reaction: quasiclassical, semiclassical and quantum calculations. In: Gervasi, O., et al. (eds.) ICCSA 2005. LNCS, vol. 3480, pp. 1083–1092. Springer, Heidelberg (2005). https://doi.org/10.1007/11424758_113

20. Faginas-Lago, N., Laganá, A.: A comparison of semiclassical IVR and exact quantum collinear atom diatom transition probabilities for mixed reactive and non reactive regimes. In: AIP Conference Proceedings, vol. 762, p. 920 (2005)
21. Faginas-Lago, N., Laganà, A.: On the semiclassical initial value calculation of thermal rate coefficients for the N + N_2 reaction. J. Chem. Phys. **125**, 114311 (2006)
22. Faginas-Lago, N., Costantini, A., Huarte-Larrañaga, F.: Direct calculation of the rate coefficients on the grid: exact quantum versus semiclassical results for N+ N2. Int. J. Quantum Chem. **110**(2), 422–431 (2010)
23. Faginas, N., Huarte-Larranaga, F., Laganà, A.: Full dimensional quantum versus semiclassical reactivity for the bent transition state reaction N + N_2. Chem. Phys. Lett. **464**, 249–255 (2008)
24. Rampino, S., Faginas-Lago, N., Laganà, A., Huarte-Larrañaga, F.: An extension of the grid empowered molecular simulator to quantum reactive scattering. J. Comput. Chem. **33**, 708–714 (2012)
25. De Fazio, D.: The H + HeH^+ → He + H_2^+ + reaction from the ultra-cold regime to the three-body breakup: exact quantum mechanical integral cross sections and rate constants. Phys. Chem. Chem. Phys. **16**, 11662–11672 (2014)
26. Horn, R.A., Johnson, C.R.: Matrix Analysis, 2nd edn. University Press, Cambridge (1990)
27. Sevryuk, M.B., Lombardi, A., Aquilanti, V.: Hyperangular momenta and energy partitions in multidimensional many-particle classical mechanics: the invariance approach to cluster dynamics. Phys. Rev. A **72**, 033201 (2005)
28. Gatti, F., Lung, C.: Vector parametrization of the *n*-atom problem in quantum mechanics. I. Jacobi vectors. J. Chem. Phys. **108**, 8804–8820 (1998)
29. Aquilanti, V., Lombardi, A., Yurtsever, E.: Global view of classical clusters: the hyperspherical approach to structure and dynamics. Phys. Chem. Chem. Phys. **4**, 5040–5051 (2002)
30. Aquilanti, V., Lombardi, A., Sevryuk, M.B.: Phase-space invariants for aggregates of particles: hyperangular momenta and partitions of the classical kinetic energy. J. Chem. Phys. **121**, 5579 (2004)
31. Aquilanti, V., Lombardi, A., Littlejohn, R.G.: Hyperspherical harmonics for polyatomic systems: basis set for collective motions. Theoret. Chem. Acc. **111**, 400–406 (2004)
32. Aquilanti, V., Carmona Novillo, E., Garcia, E., Lombardi, A., Sevryuk, M.B., Yurtsever, E.: Invariant energy partitions in chemical reactions and cluster dynamics simulations. Comput. Mater. Sci. **35**, 187–191 (2006)
33. Aquilanti, V., Lombardi, A., Sevryuk, M.B., Yurtsever, E.: Phase-space invariants as indicators of the critical behavior of nanoaggregates. Phys. Rev. Lett. **93**, 113402 (2004)
34. Calvo, F., Gadea, X., Lombardi, A., Aquilanti, V.: Isomerization dynamics and thermodynamics of ionic argon clusters. J. Chem. Phys. **125**, 114307 (2006)
35. Lombardi, A., Aquilanti, V., Yurtsever, E., Sevryuk, M.B.: Specific heats of clusters near a phase transition: energy partitions among internal modes. Chem. Phys. Lett. **30**, 424–428 (2006)
36. Barreto, P.R.P., Vilela, A.F.A., Lombardi, A., Maciel, G.S., Palazzetti, F., Aquilanti, V.: The hydrogen peroxide-rare gas systems: quantum chemical calculations and hyperspherical harmonic representation of the potential energy surface for atom-floppy molecule interactions. J. Phys. Chem. A **111**, 12754–12762 (2007)
37. Maciel, G.S., Barreto, P.R.P., Palazzetti, F., Lombardi, A., Aquilanti, V.: A quantum chemical study of h_2s_2: intramolecular torsional mode and intermolecular interactions with rare gases. J. Phys. Chem. A **129**, 164302 (2008)

38. Barreto, P.R.P., Palazzetti, F., Grossi, G., Lombardi, A., Maciel, G., Vilela, A.F.A.: Range and strength of intermolecular forces for van der Waals complexes of the type H_2X_n-Rg, with x = o, s and n = 1, 2. Int. J. Quantum Chem. **110**, 777–786 (2010)
39. Palazzetti, F., Munusamy, E., Lombardi, A., Grossi, G., Aquilanti, V.: Spherical and hyperspherical representation of potential energy surfaces for intermolecular interactions. Int. J. Quantum Chem. **111**, 318–332 (2011)
40. Aquilanti, V., Cavalli, S.: The quantum-mechanical Hamiltonian for tetraatomic systems in symmetric hyperspherical coordinates. J. Chem. Soc. Faraday Trans. **93**, 801–809 (1997)
41. Barreto, P.R.P., Albernaz, A.F., Palazzetti, F.: Potential energy surfaces for van der Waals complexes of rare gases with H_2S and H_2S_2: extension to xenon interactions and hyperspherical harmonics representation. Int. J. Quantum Chem. **112**, 834–847 (2012)
42. Lombardi, A., et al.: Spherical and hyperspherical harmonics representation of van der Waals aggregates. In: AIP Conference Proceedings, vol. 1790, p. 020005 (2016)
43. Aquilanti, V., Caglioti, C., Lombardi, A., Maciel, G.S., Palazzetti, F.: Screens for displaying chirality changing mechanisms of a series of peroxides and persulfides from conformational structures computed by quantum chemistry. In: Gervasi, O., et al. (eds.) ICCSA 2017. LNCS, vol. 10408, pp. 354–368. Springer, Cham (2017). https://doi.org/10.1007/978-3-319-62404-4_26
44. Aquilanti, V., Cavalli, S., Coletti, C., di Domenico, D., Grossi, G.: Int. Rev. Phys. Chem. **20**, 673 (2001)
45. Varshalovich, D.A.: Quantum Theory of Angular Momentum. World Scientific, Singapore (1958)
46. Castro-Palacio, J.C., Velasquez Abad, L., Lombardi, A., Aquilanti, V.: Normal and hyperspherical mode analysis of NO-doped Kr crystals upon Rydberg excitation of the impurity. J. Chem. Phys. **126**, 174701 (2007)
47. Castro Palacio, J.C., Rubayo-Soneira, J., Lombardi, A., Aquilanti, V.: Molecular dynamics simulations and hyperspherical mode analysis of NO in Kr crystals with the use of ab initio potential energy surfaces for the Kr-NO complex. Int. J. Quantum Chem. **108**, 1821–1830 (2008)
48. Lombardi, A., Lago, N.F., Laganà, A., Pirani, F., Falcinelli, S.: A bond-bond portable approach to intermolecular interactions: simulations for N-methylacetamide and carbon dioxide dimers. In: Murgante, B., et al. (eds.) ICCSA 2012. LNCS, vol. 7333, pp. 387–400. Springer, Heidelberg (2012). https://doi.org/10.1007/978-3-642-31125-3_30
49. Lombardi, A., Laganà, A., Pirani, F., Palazzetti, F., Lago, N.F.: Carbon oxides in gas flows and earth and planetary atmospheres: state-to-state simulations of energy transfer and dissociation reactions. In: Murgante, B., et al. (eds.) ICCSA 2013. LNCS, vol. 7972, pp. 17–31. Springer, Heidelberg (2013). https://doi.org/10.1007/978-3-642-39643-4_2
50. Lago, N.F., Albertí, M., Laganà, A., Lombardi, A.: Water $(H_2O)m$ or Benzene $(C_6H_6)n$ aggregates to solvate the K^+? In: Murgante, B., et al. (eds.) ICCSA 2013. LNCS, vol. 7971, pp. 1–15. Springer, Heidelberg (2013). https://doi.org/10.1007/978-3-642-39637-3_1
51. Faginas-Lago, N., Albertí, M., Costantini, A., Laganá, A., Lombardi, A., Pacifici, L.: An innovative synergistic grid approach to the computational study of protein aggregation mechanisms. J. Mol. Model. **20**(7), 2226 (2014)

52. Faginas-Lago, N., Yeni, D., Huarte, F., Alcamì, M., Martin, F.: Adsorption of hydrogen molecules on carbon nanotubes using quantum chemistry and molecular dynamics. J. Phys. Chem. A **120**, 6451–6458 (2016)
53. Faginas-Lago, N., Lombardi, A., Albertí, M., Grossi, G.: Accurate analytic intermolecular potential for the simulation of Na+ and K^+ ion hydration in liquid water. J. Mol. Liq. **204**, 192–197 (2015)
54. Albertí, M., Faginas Lago, N.: Competitive solvation of k^+ by C_6H_6 and H_2O in the $k^+-(C_6h_6)_n-(H_2O)_m$ $(n = 1-4; m = 1-6)$ aggregates. Eur. Phys. J. D **67**, 73 (2013)
55. Albertí, M., Faginas Lago, N.: Ion size influence on the ar solvation shells of M^+-C_6F_6 clusters (m = na, k, rb, cs). J. Phys. Chem. A **116**, 3094–3102 (2012)
56. Albertí, M., Faginas Lago, N., Pirani, F.: Ar solvation shells in K^+-HFBz: from cluster rearrangement to solvation dynamics. J. Phys. Chem. A **115**, 10871–10879 (2011)
57. Lago, N.F., Albertí, M., Laganà, A., Lombardi, A., Pacifici, L., Costantini, A.: The molecular stirrer catalytic effect in methane ice formation. In: Murgante, B., et al. (eds.) ICCSA 2014. LNCS, vol. 8579, pp. 585–600. Springer, Cham (2014). https://doi.org/10.1007/978-3-319-09144-0_40
58. Faginas-Lago, N., Huarte Larrañaga, F., Albertí, M.: On the suitability of the ILJ function to match different formulations of the electrostatic potential for water-water interactions. Eur. Phys. J. D **55**(1), 75 (2009)
59. Bartolomei, M., Pirani, F., Laganà, A., Lombardi, A.: J. Comput. Chem. **33**, 1806 (2012)
60. Albertí, M., Faginas-Lago, N., Laganà, A., Pirani, F.: A portable intermolecular potential for molecular dynamics studies of NMA-NMA and NMA-H_2O aggregates. Phys. Chem. Chem. Phys. **13**(18), 8422–8432 (2011)
61. Albertí, M., Faginas-Lago, N., Pirani, F.: J. Phys. Chem. A **115**(40), 10871–10879 (2011)
62. Albertí, M., Faginas-Lago, N.: Eur. Phys. J. D **67**, 73 (2013)
63. Albertí, M., Faginas-Lago, N., Pirani, F.: Chem. Phys. **399**, 232 (2012)
64. Falcinelli, S., et al.: Modeling the intermolecular interactions and characterization of the dynamics of collisional autoionization processes. In: Murgante, B., et al. (eds.) ICCSA 2013. LNCS, vol. 7971, pp. 69–83. Springer, Heidelberg (2013). https://doi.org/10.1007/978-3-642-39637-3_6
65. Lombardi, A., Faginas-Lago, N., Pacifici, L., Costantini, A.: Modeling of energy transfer from vibrationally excited CO_2 molecules: cross sections and probabilities for kinetic modeling of atmospheres, flows, and plasmas. J. Phys. Chem. A **117**(45), 11430–11440 (2013)
66. Lombardi, A., Pirani, F., Laganà, A., Bartolomei, M.: Energy transfer dynamics and kinetics of elementary processes (promoted) by gas-phase CO_2-N_2 collisions: selectivity control by the anisotropy of the interaction. J. Comput. Chem. **37**, 1463–1475 (2016)
67. Pacifici, L., Verdicchio, M., Faginas-Lago, N., Lombardi, A., Costantini, A.: A high-level ab initio study of the N_2 + N_2 reaction channel. J. Comput. Chem. **34**(31), 2668–2676 (2013)
68. Lombardi, A., Faginas-Lago, N., Pacifici, L., Grossi, G.: Energy transfer upon collision of selectively excited CO_2 molecules: state-to-state cross sections and probabilities for modeling of atmospheres and gaseous flows. J. Chem. Phys. **143**, 034307 (2015)

69. Lombardi, A., Faginas-Lago, N., Pacifici, L., Costantini, A.: Modeling of energy transfer from vibrationally excited CO_2 molecules: cross sections and probabilities for kinetic modeling of atmospheres, flows, and plasmas. J. Phys. Chem. A **117**, 11430–11440 (2013)
70. Celiberto, R., et al.: Atomic and molecular data for spacecraft re-entry plasmas. Plasma Sources Sci. Technol. **25**, 033004 (2016)
71. Musigmann, M., Busalla, A., Blum, K., Thompson, D.G.: Enantio-selective collisions between unpolarized electrons and chiral molecules. J. Phys. Chem. B **34**, L79–L85 (2001)
72. Aquilanti, V., Grossi, G., Lombardi, A., Maciel, G.S., Palazzetti, F.: The origin of chiral discrimination: supersonic molecular beam experiments and molecular dynamics simulations of collisional mechanisms. Phys. Scr. **78**, 058119 (2008)
73. Lombardi, A., Palazzetti, F., Maciel, G.S., Aquilanti, V., Sevryuk, M.B.: Simulation of oriented collision dynamics of simple chiral molecules. Int. J. Quantum Chem. **111**, 1651–1658 (2011)
74. Herbst, E., DeFrees, D.J., McLean, A.D.: Ab initio determination of mode coupling in HSSH: the torsional splitting in the first excited S-S stretching state. J. Chem. Phys. **91**, 5905 (1989)