Hyperspherical coordinates in classical mechanics and applications

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Motivation for Hyperspherical Coordinates (HC) in classical mechanics

Interest in many-body systems justifies the recourse to classical mechanics to simulate, e. g., large atom and molecule clusters, biological molecules ...

Hyperspherical representation of classical dynamics useful:

- to partition kinetic energy into contributions from different kinds of motions (beyond the usual vibration-rotation scheme)

- to understand how energy is shared by different kinds of motions

- to find indicators for critical phenomena (e.g. phase transitions in clusters)

- to study isomerization paths

- to deal simultaneously with different time-scales

This work is inspired by the Smith article* where the *grand angular momentum*, accounting for all kinds of rotations of a many-body system, was first defined

All results are for systems of classical particles in the d-dim Euclidean space R^d, d=1,2,3,4.....

This generalization is suggested by many existing cases or previous works:

- e.g. Wigner Crystals[2] (R^2), planar systems
- continuation of previous works on multidimensional systems in spaces R^d with d > 3, studied for example, in constructions of various hyperspherical coordinate schemes[3,4]
- hyperspherical hydrogen atom as a model of many-particle Coulomb systems[5,6]
- perturbation theory where the dimension d is the perturbation parameter[7]

* F. T. Smith Phys Rev **120**, 1058, 1960

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6 V. Aquilanti et al., Int. Rev. Phys. Chem. 20, 673, 2001

7 *Dimensional Scaling in Chemical Physics*, edited by D. R. Herschbach, J. Avery, and O. Goscinski, Kluwer Academic, Dordrecht, 1993.

Outline

- Coordinates, frames and position matrix
- Basic definitions
- Hyperradius and related quantities
- Invariance properties
- Inequalities and geometry of the space of position matrices
- Energy partitions
- Singular value decomposition (SVD)
- Application

Sevryuk, Lombardi, Aquilanti, *Phys Rev A*, **72**, 033201 (2005)

Coordinates, frames and position matrix

Suppose $N \geqslant 2$ classical particles

Denote by $m_1, \ldots, m_N$ the masses of the particles and by $\mathbf{r}_1, \ldots, \mathbf{r}_N$ their radii-vectors with respect to the center-of-mass.

Define *mass-scaled* radii-vectors

$\mathbf{q}_\alpha = (m_\alpha/M)^{1/2}\mathbf{r}_\alpha$ $(1 \leqslant \alpha \leqslant N)$ where $M = \sum_{\alpha=1}^{N} m_\alpha$
and a *position matrix*:

$$Z = \begin{pmatrix} q_{11} & q_{12} & \cdots & q_{1N} \\ q_{21} & q_{22} & \cdots & q_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ q_{d1} & q_{d2} & \cdots & q_{dN} \end{pmatrix}$$

Coordinates, frames and position matrix

The choice of another Cartesian coordinate frame corresponds to the coordinate change:

- $Z' = R^* Z$ where $R \in \mathrm{O}(d)$
- one can also deal with orthogonal transformations of coordinate frames in the kinematic space by a matrix $Q \in \mathrm{O}(N)$

$$Z' = ZQ$$

Then the position matrices in different allowed frames are connected by coordinate changes of the form $Z' = R^* Z Q$ with $R \in \mathrm{O}(d)$, $Q \in \mathrm{O}(N)$

Coordinates, frames and position matrix

Consider frames from conventional Cartesian ones by transformations Q in the kinematic space of the form

$$Q = \begin{pmatrix} Q_{11} & \cdots & Q_{1,N-1} & (m_1/M)^{1/2} \\ Q_{21} & \cdots & Q_{2,N-1} & (m_2/M)^{1/2} \\ \cdots & \cdots & \cdots & \cdots \\ Q_{N1} & \cdots & Q_{N,N-1} & (m_N/M)^{1/2} \end{pmatrix} \in \mathrm{O}(N).$$

are *privileged coordinate frames*

Coordinates, frames and position matrix

The last column of the matrix Z in a privileged frame is *zero* (center of mass)

- taking only N-1 columns, $d \times (N-1)$ *reduced position matrix*
- In contrast, call the $d \times N$ position matrices in allowed coordinate frames the *full position matrices*

We have two alternative descriptions of a system of N particles in $\mathbb{R}^d$:

- the $d \times N$ full position matrix in an arbitrary allowed coordinate frame
- the $d \times (N-1)$ reduced position matrix in a privileged coordinate frame.

Prototypes of these two descriptions are respectively the collection of N radii-vectors of the particles and the collection of $N-1$ Jacobi vectors

In the following n indicates N or N-1, without distiction

Coordinates, frames and position matrix

The physical space and the kinematic space refer to *dual* ways of treating a system of N particles in $\mathbb{R}^d$:

- by N vectors $\mathbf{q}_\alpha = (q_{1\alpha}, q_{2\alpha}, \ldots, q_{d\alpha})$ belonging to the physical space $\mathbb{R}^d$
- by d vectors $\tilde{\mathbf{q}}_i = (q_{i1}, q_{i2}, \ldots, q_{iN})$ each containing N components (the rows of the position matrix Z) and belonging to the kinematic space $\mathbb{R}^N$

Coordinates, frames and position matrix

Moving systems

If the system rotates around its center-of-mass as a rigid body:

$$Z(t) = R(t)Z(0)$$

where $R(t) \in \mathrm{SO}(d)$ is a special orthogonal matrix for each value of t

Analoguosly, kinematic rotations are motions of the form:

$$Z(t) = Z(0)Q(t)^*$$

Basic definitions

The total *kinetic energy* of a system of $N \geqslant 2$ classical particles in $\mathbb{R}^d$ described by the $d \times n$ position matrix Z is

$$T = \frac{M}{2}\operatorname{Tr}(\dot{Z}\dot{Z}^*) = \frac{M}{2}\sum_{\alpha=1}^{n}|\dot{Z}_\alpha^{\mathrm{c}}|^2 = \frac{M}{2}\sum_{i=1}^{d}|\dot{Z}_i^{\mathrm{r}}|^2 = \frac{M}{2}\sum_{\alpha=1}^{n}\sum_{i=1}^{d}\dot{Z}_{i\alpha}^2,$$

(Tr denotes the trace of a square matrix and the dot above a letter denotes the time derivative)

The classical equations of motion are

$$M\ddot{Z}_{i\alpha} = -\partial U/\partial Z_{i\alpha}, \qquad 1 \leqslant i \leqslant d, \quad 1 \leqslant \alpha \leqslant n,$$

where $U = U(Z)$ is the potential energy of the system

Basic definitions

The total *physical angular momentum* $J \geqslant 0$ of the system in question is given by the formulas

$$J^2 = \sum_{1 \leqslant i < j \leqslant d} J_{ij}^2,$$

$$J_{ij} = M(Z_i^{\mathrm{r}} \cdot \dot{Z}_j^{\mathrm{r}} - Z_j^{\mathrm{r}} \cdot \dot{Z}_i^{\mathrm{r}}) = M \sum_{\alpha=1}^{n} (Z_{i\alpha} \dot{Z}_{j\alpha} - Z_{j\alpha} \dot{Z}_{i\alpha}) = M \sum_{\alpha=1}^{n} \begin{vmatrix} Z_{i\alpha} & \dot{Z}_{i\alpha} \\ Z_{j\alpha} & \dot{Z}_{j\alpha} \end{vmatrix}$$

The dual concept is the total *kinematic angular momentum* $K \geqslant 0$ of the system

$$K^2 = \sum_{1 \leqslant \alpha < \beta \leqslant n} K_{\alpha\beta}^2,$$

$$K_{\alpha\beta} = M(Z_\alpha^{\mathrm{c}} \cdot \dot{Z}_\beta^{\mathrm{c}} - Z_\beta^{\mathrm{c}} \cdot \dot{Z}_\alpha^{\mathrm{c}}) = M \sum_{i=1}^{d} (Z_{i\alpha} \dot{Z}_{i\beta} - Z_{i\beta} \dot{Z}_{i\alpha}) = M \sum_{i=1}^{d} \begin{vmatrix} Z_{i\alpha} & Z_{i\beta} \\ \dot{Z}_{i\alpha} & \dot{Z}_{i\beta} \end{vmatrix}$$

Basic definitions

Finally, the formula for the *grand angular momentum* $\Lambda \geqslant 0$

$$\Lambda^2 = M^2 \sum_{\substack{1\leqslant i,j\leqslant d \\ 1\leqslant \alpha,\beta\leqslant n \\ i<j \text{ or } i=j,\, \alpha<\beta}} (Z_{i\alpha}\dot{Z}_{j\beta} - Z_{j\beta}\dot{Z}_{i\alpha})^2 = M^2 \sum_{\substack{1\leqslant i,j\leqslant d \\ 1\leqslant \alpha,\beta\leqslant n \\ i<j \text{ or } i=j,\, \alpha<\beta}} \begin{vmatrix} Z_{i\alpha} & \dot{Z}_{i\alpha} \\ Z_{j\beta} & \dot{Z}_{j\beta} \end{vmatrix}^2$$

which is equivalent to

$$\Lambda^2 = M^2(\Omega_1\Omega_3 - \Omega_2^2)$$

where

$$\Omega_1 = \mathrm{Tr}(ZZ^*) = \sum_{\alpha=1}^{n}\sum_{i=1}^{d} Z_{i\alpha}^2,$$

$$\Omega_2 = \mathrm{Tr}(Z\dot{Z}^*) = \sum_{\alpha=1}^{n}\sum_{i=1}^{d} Z_{i\alpha}\dot{Z}_{i\alpha},$$

$$\Omega_3 = \mathrm{Tr}(\dot{Z}\dot{Z}^*) = \sum_{\alpha=1}^{n}\sum_{i=1}^{d} \dot{Z}_{i\alpha}^2.$$

Hyperradius and related quantities

The quantity

$$\rho = \left[\mathrm{Tr}(ZZ^*)\right]^{1/2} = \left(\sum_{\alpha=1}^{n}\sum_{i=1}^{d} Z_{i\alpha}^2\right)^{1/2}$$

is called *hyperradius* of the system. The conjugated the linear momentum is

$$P_\rho = M\dot{\rho} = \frac{M}{\rho}\mathrm{Tr}(Z\dot{Z}^*) = \frac{M}{\rho}\sum_{\alpha=1}^{n}\sum_{i=1}^{d} Z_{i\alpha}\dot{Z}_{i\alpha}.$$

In terms of ρ, P_ρ, and T, the variables Ω_1, Ω_2, Ω_3 (previously defined) are

$$\Omega_1 = \rho^2, \qquad \Omega_2 = \rho\dot{\rho} = \rho P_\rho/M, \qquad \Omega_3 = 2T/M.$$

Hyperradius and related quantities

Consequently,

$$\Lambda^2 = 2M\rho^2 T - \rho^2 P_\rho^2.$$

This relation implies immediately the *Smith decomposition* of the total kinetic energy of a system of classical particles:

$$T = T_\Lambda + T_\rho,$$

where

$$T_\Lambda = \frac{\Lambda^2}{2M\rho^2}, \qquad T_\rho = \frac{P_\rho^2}{2M} = \frac{M\dot{\rho}^2}{2}$$

We call T_Λ the *grand angular energy* and T_ρ the *hyperradial energy*

Hyperradius and related quantities

Finally, introduce the quantities

$$T_J = \frac{J^2}{2M\rho^2}, \qquad T_K = \frac{K^2}{2M\rho^2}.$$

- T_J measures the contribution of the external rotations to the total kinetic energy T. We call it the *outer angular energy.*
- T_K is connected with the contribution of the kinematic rotations ("inner motions") to the total kinetic energy T. We call it the *inner angular energy*

Invariance properties

the total kinetic energy T and the grand angular momentum Λ are invariant under orthogonal coordinate transformations in both the physical space and the kinematic space

The physical angular momentum J and each of its $d(d-1)/2$ components J_{12}, J_{13}, ..., $J_{d-1,d}$ are

- invariant under orthogonal coordinate transformations $Q \in \mathrm{O}(n)$ in the kinematic space
- J is also invariant under orthogonal coordinate transformations $R \in \mathrm{O}(d)$ in the physical space

The kinematic angular momentum K and each of its $n(n-1)/2$ components K_{12}, K_{13}, ..., $K_{n-1,n}$ are

- invariant under orthogonal coordinate transformations $R \in \mathrm{O}(d)$ in the physical space
- K is also invariant under orthogonal coordinate transformations $Q \in \mathrm{O}(n)$ in the kinematic space

Invariance properties

Important

Consider a privileged coordinate frame:

- the full position matrix in this frame differs from the reduced position matrix by the presence of an additional zero column
- as a consequence T, J, K, Λ are independent of whether they are determined from the full position matrix or from the reduced position matrix.

In conclusion:

the quantities T, J, K, Λ are instantaneous phase-space invariant of the system of particles

Physical meaning

Some key points

- the physical angular momentum J accounts for *external rotations* of the system (rotations in the physical space $\mathbb{R}^d$)
- the kinematic angular momentum K measures *kinematic rotations* of the system (rotations in the kinematic space $\mathbb{R}^n$ with $n = N$ or $n = N - 1$ (full or reduced Z position matrix)
- the *kinematic rotations* can be understood as a continuous interpolation of the permutations of the particles (connect different Jacobi coupling schemes)
- the *grand angular momentum* $\Lambda^{(**)}$ accounts for all kinds of rotations in the system
- if $\ddot{Z} = 0$, no forces act, $\dot{T} = 0, \dot{\Lambda} = 0$

(**) Λ for the particular case $d = 3$, introduced in F. T. Smith Phys Rev. **120**, 1058 (1960)

Physical meaning

if $\ddot{Z} = 0$, in the case of $T \neq 0$, $\Lambda = 0$ if and only if $Z(t) = 0$ at a certain moment of time. Indeed

$$Z_{i\alpha}(t) = x_{i\alpha} t + y_{i\alpha}$$

where $x_{i\alpha}$ and $y_{i\alpha}$ are constants and

$$\Lambda^2 = M^2 \sum_{\substack{1 \leqslant i,j \leqslant d \\ 1 \leqslant \alpha,\beta \leqslant n \\ i<j \text{ or } i=j,\, \alpha<\beta}} (x_{i\alpha} y_{j\beta} - x_{j\beta} y_{i\alpha})^2$$

if $Z(t) = 0$ for some t, then $\Lambda = 0$
On the other hand suppose $\Lambda = 0$ but $T \neq 0$ then $x_{j\beta} \neq 0$ for some j and β and $y_{i\alpha} = xi\alpha y_{j\beta}/x_{j\beta}$ for any i and α. Consequently $Z(t) = 0$ for $t = -y_{j\beta}/xj\beta$
Then, in the case of free particles, Λ is a measure of how far the trajectory is from the coalescence of all the particles

Inequalities and geometry of the space of position matrices

If a system rotates around its center-of-mass as a rigid body in the space $\mathbb{R}^d$ with $d \geqslant 3$, then

- generically $K > 0$ and $J < \Lambda$ rather than $J = \Lambda$, contrary to what one would probably expect (the opposite inequality $J > \Lambda$ is impossible for any motion of the particles and for any physical

For instance, let $d = 3$, $n = N - 1 = 3$, and

$$Z(t) = \begin{pmatrix} \cos\varphi(t) & \sin\varphi(t) & 0 \\ -\sin\varphi(t) & \cos\varphi(t) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \zeta & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & \theta \end{pmatrix}.$$

Then

$$\begin{aligned} J_{12} &= -\dot\varphi M(\zeta^2 + \eta^2), & J_{13} &= J_{23} = 0, \\ K_{12} &= 2\dot\varphi M\zeta\eta, & K_{13} &= K_{23} = 0, \end{aligned}$$

Inequalities and geometry of the space of position matrices

As a matter of fact

- the outer angular energy T_J underestimates the kinetic energy associated with external rotations of a system of particles for $d \geq 3$. For instance, if the system rotates around its center-of-mass as a rigid body, then $T_\rho = 0$ and $T = T_\Lambda$, but J is generically smaller than Λ (for $d \geq 3$) consequently, T_J is generically smaller than T_Λ
- analogously, the inner angular energy T_K underestimates the kinetic energy associated with kinematic rotations of a system of $N \geq 4$ particles
- we need a more precise account of the energy contributions from different kinds of motion in the system

Inequalities and geometry of the space of position matrices

Introduce the standard *Frobenius inner product* on the space of $d \times n$ position matrices Z

$$(Z^a, Z^b) \mapsto \mathrm{Tr}\big[Z^a (Z^b)^*\big] = \sum_{\alpha=1}^{n} \sum_{i=1}^{d} Z^a_{i\alpha} Z^b_{i\alpha}$$

the corresponding matrix norm is $\|Z\| = \big[\mathrm{Tr}(ZZ^*)\big]^{1/2}$
In this space, there act two orthogonal groups, plus a third one

- the "external rotation group" $\mathrm{SO}(d)$ which acts as $(R,\, Z) \mapsto RZ$ for any $R \in \mathrm{SO}(d)$
- the "kinematic rotation group" $\mathrm{SO}(n)$ which acts as $(Q,\, Z) \mapsto ZQ^*$ for any $Q \in \mathrm{SO}(n)$
- since the "external" and "kinematic" actions thus defined commute: $(RZ)Q^* \equiv R(ZQ^*)$, the direct product $\mathrm{SO}(d) \times \mathrm{SO}(n)$ of these groups also acts in the space of $d \times n$ matrices Z according to the rule $\big((R, Q),\, Z\big) \mapsto RZQ^*$

Inequalities and geometry of the space of position matrices

All the three groups act in the space of $d \times n$ matrices by orthogonal linear transformations in the sense of the Frobenius product, i. e.,

$$\mathrm{Tr}\big[RZ^aQ^*(RZ^bQ^*)^*\big] = \mathrm{Tr}\big[Z^a(Z^b)^*\big]$$

for any $d \times n$ matrices Z^a and Z^b, any $d \times d$ matrix $R \in \mathrm{O}(d)$, and any $n \times n$ matrix $Q \in \mathrm{O}(n)$

Inequalities and geometry of the space of position matrices

Consider

- $\mathfrak{S}_{\mathrm{e}}(Z)$, the orbit of a $d \times n$ matrix Z under the action of the first group, i. e., the manifold of all the matrices of the form RZ, $R \in \mathrm{SO}(d)$
- $\mathfrak{S}_{\mathrm{k}}(Z)$, the orbit of Z under the action of the second group, i. e., the manifold of all the matrices of the form ZQ^*, $Q \in \mathrm{SO}(n)$
- $\mathfrak{S}(Z)$, the orbit of Z under the action of the third group, i. e., the manifold of all the matrices of the form RZQ^* with $R \in \mathrm{SO}(d)$ and $Q \in \mathrm{SO}(n)$

Inequalities and geometry of the space of position matrices

Denote by $\Pi_{\mathrm{e}}(Z)$, $\Pi_{\mathrm{k}}(Z)$, and $\Pi(Z)$ the tangent spaces to $\mathfrak{S}_{\mathrm{e}}(Z)$, $\mathfrak{S}_{\mathrm{k}}(Z)$, and $\mathfrak{S}(Z)$, respectively, at point Z

- the space $\Pi_{\mathrm{e}}(Z)$ is constituted by all the $d \times n$ matrices of the form $Z + \mathcal{R}Z$ with skew-symmetric $\mathcal{R} \in \mathfrak{so}(d)$
- the space $\Pi_{\mathrm{k}}(Z)$ is constituted by all the $d \times n$ matrices of the form $Z + Z\mathcal{Q}$ with skew-symmetric $\mathcal{Q} \in \mathfrak{so}(n)$
- the space $\Pi(Z)$ is constituted by all the $d \times n$ matrices of the form $Z + \mathcal{R}Z + Z\mathcal{Q}$ with $\mathcal{R} \in \mathfrak{so}(d)$ and $\mathcal{Q} \in \mathfrak{so}(n)$

Energy partitions

if $Z = Z(t)$ is the $d \times n$ position matrix of a system of classical particles, we represent the time derivative $\dot{Z}$ of Z in the form

$$\dot{Z} = \dot{Z}^{\mathrm{rot}} + \dot{Z}^{I},$$

where $\dot{Z}^{\mathrm{rot}}$ is the orthogonal projection of $\dot{Z}$ on $\Pi(Z)$ in the sense of the Frobenius product Accordingly, $\dot{Z}^{I}$ is the component of $\dot{Z}$ orthogonal to $\Pi(Z)$
By analogy with the kineti energy formula, we can define the energies

$$T^{\mathrm{rot}} = \frac{M}{2} \operatorname{Tr}\left[\dot{Z}^{\mathrm{rot}} (\dot{Z}^{\mathrm{rot}})^{*}\right] = \frac{M}{2} \sum_{\alpha=1}^{n} \sum_{i=1}^{d} (\dot{Z}^{\mathrm{rot}}_{i\alpha})^2,$$

$$T^{I} = \frac{M}{2} \operatorname{Tr}\left[\dot{Z}^{I} (\dot{Z}^{I})^{*}\right] = \frac{M}{2} \sum_{\alpha=1}^{n} \sum_{i=1}^{d} (\dot{Z}^{I}_{i\alpha})^2.$$

- T^{rot} is the kinetic energy associated with all the kinds of rotation (both external and kinematic). We call it *rotational energy*
- T^{I} will be called the *inertial energy*

Energy partitions

the matrices $\dot{Z}^{\mathrm{rot}}$ and $\dot{Z}^{I}$ are orthogonal in the sense of the Frobenius product:

$$\mathrm{Tr}\big[\dot{Z}^{\mathrm{rot}}(\dot{Z}^{I})^{*}\big] = 0$$

one has an exact decomposition of the total kinetic energy of the system:

$$T = T^{\mathrm{rot}} + T^{I}.$$

We will call this relation the *orthogonal decomposition* of T
Comparing with the terms T_Λ, T_ρ of the Smith decomposition it can be proven that

$$T^{\mathrm{rot}} \leqslant T_\Lambda, \qquad T^{I} \geqslant T_\rho.$$

The corresponding difference

$$T_\xi = T_\Lambda - T^{\mathrm{rot}} = T^{I} - T_\rho$$

is called the *shape energy* On the analogy of the other energy formulas

$$L_\xi = (2M\rho^2 T_\xi)^{1/2},$$

so that

$$T_\xi = \frac{L_\xi^2}{2M\rho^2}.$$

The quantity L_ξ has the dimension of an angular momentum, and we will call it the *singular angular momentum*

Energy partitions

It is now possible to define couplings between internal (kinematic) and external (ordinary) rotations

$$T_{\mathrm{ac}} = T^{\mathrm{rot}} - T_J - T_K.$$

as T_{ac} the *angular coupling energy*
From this one has the *hyperspherical partition* of the kinetic energy T

$$T = T_J + T_K + T_\xi + T_{\mathrm{ac}} + T_\rho$$

intimately connected with the hyperspherical parametrization of the N-body problem

Energy partitions

Consider the orthogonal projections $\dot{Z}^{\mathrm{e}}$ and $\dot{Z}^{\mathrm{k}}$ of $\dot{Z}^{\mathrm{rot}}$ (or of $\dot{Z}$) on the spaces $\Pi_{\mathrm{e}}(Z)$ and $\Pi_{\mathrm{k}}(Z)$, respectively, in the sense of the Frobenius product

$$T^{\mathrm{ext}} = \frac{M}{2}\,\mathrm{Tr}\big[\dot{Z}^{\mathrm{e}}(\dot{Z}^{\mathrm{e}})^{*}\big] = \frac{M}{2}\sum_{\alpha=1}^{n}\sum_{i=1}^{d}(\dot{Z}^{\mathrm{e}}_{i\alpha})^{2}$$

is the energy of the external rotations and is called the *external energy*
Similarly,

$$T^{\mathrm{int}} = \frac{M}{2}\,\mathrm{Tr}\big[\dot{Z}^{\mathrm{k}}(\dot{Z}^{\mathrm{k}})^{*}\big] = \frac{M}{2}\sum_{\alpha=1}^{n}\sum_{i=1}^{d}(\dot{Z}^{\mathrm{k}}_{i\alpha})^{2}$$

is the energy of the kinematic rotations and is called the *internal energy*

It holds $T^{\mathrm{ext}} \geqslant T_J$ and $T^{\mathrm{int}} \geqslant T_K$
The new coupling energy, called the *residual energy*

$$T^{\mathrm{res}} = T^{\mathrm{rot}} - T^{\mathrm{ext}} - T^{\mathrm{int}}$$

The equality

$$T = T^{\mathrm{ext}} + T^{\mathrm{int}} + T^{\mathrm{res}} + T^{I}$$

is named *projective partition* of the kinetic energy T (because of the role played by orthogonal projections in the definition of the terms T^{ext} and T^{int})

Energy partitions

hyperspherical partition

$$T = T_\rho + T_\xi + T_J + T_K + T_{ac}$$

projective partitions

$$T = T_\rho + T_\xi + T^{ext} + T^{int} + T^{res}$$

Singular value decomposition

is the mathematical apparatus the hyperspherical angular momenta an the energy terms of the partitions

The $d \times n$ matrix Z can be decomposed as the product of three matrices (singular value decomposition SVD):

$$Z = D \Upsilon X^*,$$

where $D \in \mathrm{O}(d)$ is a $d \times d$ orthogonal matrix, $X \in \mathrm{O}(n)$ is an $n \times n$ orthogonal matrix, the entries of the $d \times n$ matrix Υ are zeroes, with the possible exception of the diagonal entries

$$\Upsilon_{11} = \xi_1, \ \Upsilon_{22} = \xi_2, \ \ldots, \ \Upsilon_{mm} = \xi_m, \qquad \xi_1 \geqslant \xi_2 \geqslant \ldots \geqslant \xi_m \geqslant 0.$$

The numbers $\xi_1, \xi_2, \ldots, \xi_m$ are called the *singular values* of the matrix Z and are determined uniquely

SVD is closely related to HC, is in fact the way to explicitly obtain HC from Cartesian coordinates

Singular value decomposition

- If $n \geqslant d$ then the d singular values of Z are the square roots of the eigenvalues of the $d \times d$ symmetric matrix ZZ^* (while the eigenvalues of the $n \times n$ symmetric matrix Z^*Z are the squares of the singular values of Z and $n - d$ zeroes)
- If $n \leqslant d$ then the n singular values of Z are the square roots of the eigenvalues of Z^*Z (while the eigenvalues of ZZ^* are the squares of the singular values of Z and $d - n$ zeroes).

Singular value decomposition

(See Kuppermann talk)

For $n > d$, the last $n - d$ columns of the matrix X are irrelevant (Z does not depend on them), we use the so-called thin SVD of Z so the $d \times n$ position matrix Z with $n \geqslant d$ can be decomposed as

$$Z = D \Xi B^*,$$

where $D \in \mathrm{O}(d)$, $\Xi = \mathrm{diag}(\xi_1, \xi_2, \ldots, \xi_d)$ is the $d \times d$ diagonal matrix with and B is an $n \times d$ matrix with orthonormal columns (i.e. $B^* B$ is the $d \times d$ identity matrix)

The matrix B belongs to the quotient spaces $\mathrm{O}(n)/\mathrm{O}(n-d)$

This representation is called the *thin* SVD$^{(**)}$ of Z

(n.b, analogously if $n < d$, the last $d - n$ columns of matrix D are irrelevant)

$^{(**)}$ G.H. Golub and C.F. Van Loan, *Matrix Computations*, 3rd ed. (Johns Hopkins Univ. Press, Baltimore, 1996)

Singular value decomposition

Connection to moments of inertia

In the physically most interesting case $d = 3$, the singular values of the position matrix are connected to the *principal moments of inertia* $I_1 \geqslant I_2 \geqslant I_3$ of the system with respect to its center-of-mass

- If $n \geqslant 3$ then

  $$I_1 = M(\xi_1^2 + \xi_2^2), \qquad I_2 = M(\xi_1^2 + \xi_3^2), \qquad I_3 = M(\xi_2^2 + \xi_3^2),$$

  where $\xi_1 \geqslant \xi_2 \geqslant \xi_3$ are the singular values of the $3 \times n$ position matrix of the system

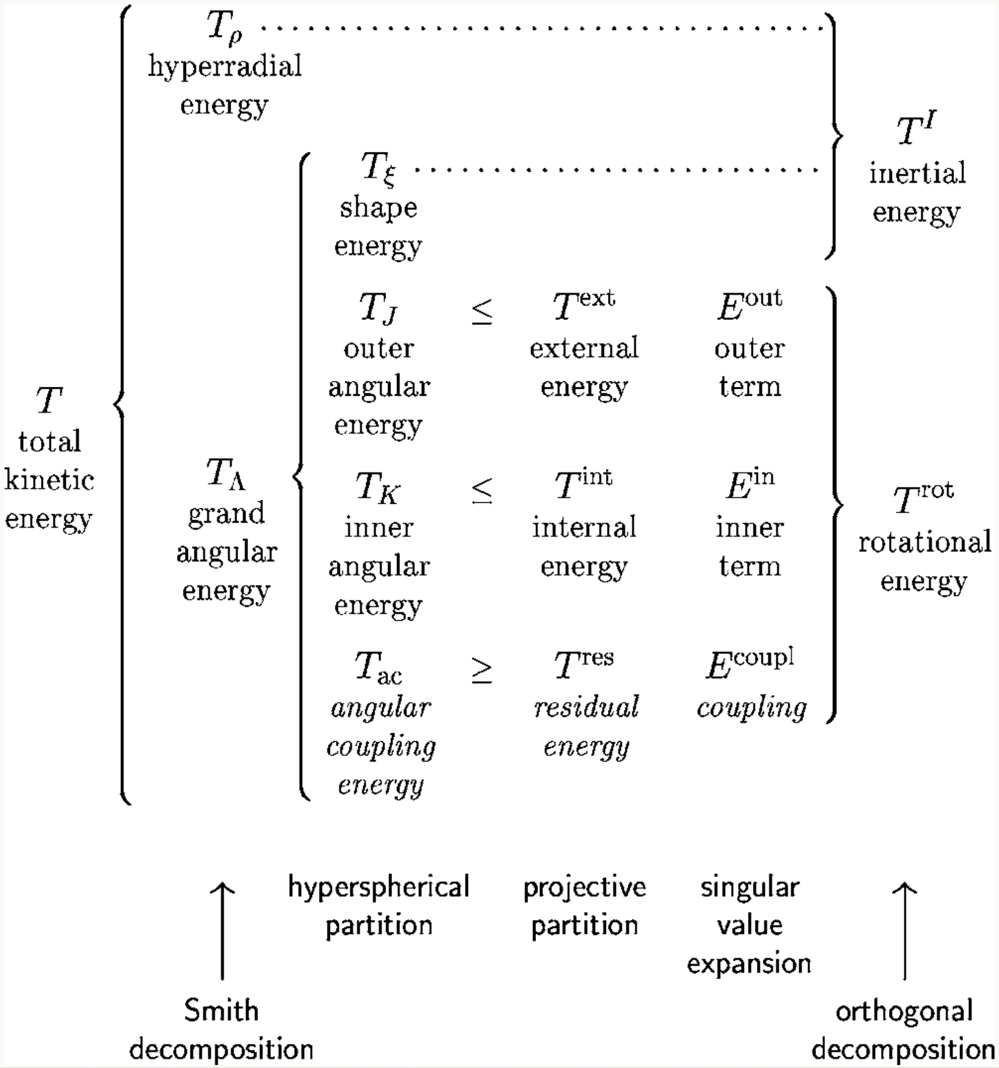
- If $n = 2$ then

  $$I_1 = M(\xi_1^2 + \xi_2^2), \qquad I_2 = M\xi_1^2, \qquad I_3 = M\xi_2^2,$$

- If $n = 1$ then

  $$I_1 = I_2 = M\xi_1^2, \qquad I_3 = 0$$

Schematic representation of partitions



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Physical meaning of the main partition terms

- T_ρ hyperradial energy, overall breathing motion of the system
- T_ξ shape energy, energy spent for the *redistribution* of the inertia among the three principal axis
- T_J, T^{ext} account for the energy of external (ordinary) rotations of the system in the physical space
- T_K, T^{int} account for the energy associated with kinematic (internal) rotations of the system. Physically, kinematic rotations can be understood as a continuous interpolation of the permutations (exchange) of the particles
- T_{ac}, T^{res} cumulatively account for coupling of external, internal rotations and rotations associated to the *singular angular momentum* (shape energy)

Exemplary applications

Rare gas clusters: phase coexistence study[*]

Rare gas clusters can mimic (at nanoscale) rearrangements of solid-like structures and transition to liquid-like behaviour

Ar_n simple model: atoms bound by a pairwise LJ(12,6) potential energy function

$$V = 4\epsilon \sum_{i<j}^{n} \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} + \left(\frac{\sigma}{r} \right)^{6} \right)$$

Caloric curve: temperature as a function of energy, Temp(E)

Temperature is the average kinetic energy <T>, so using partitions we can separate different contribution temperatures

$$T(E) = \sum_i T(E)_i$$

Sampling of phase space by trajectories, microcanonical temperatures

[*] A. Lombardi, V. Aquilanti, E. Yurtsever, M. B. Sevryuk, Chem. Phys. Lett., **430**, 424 (2006)

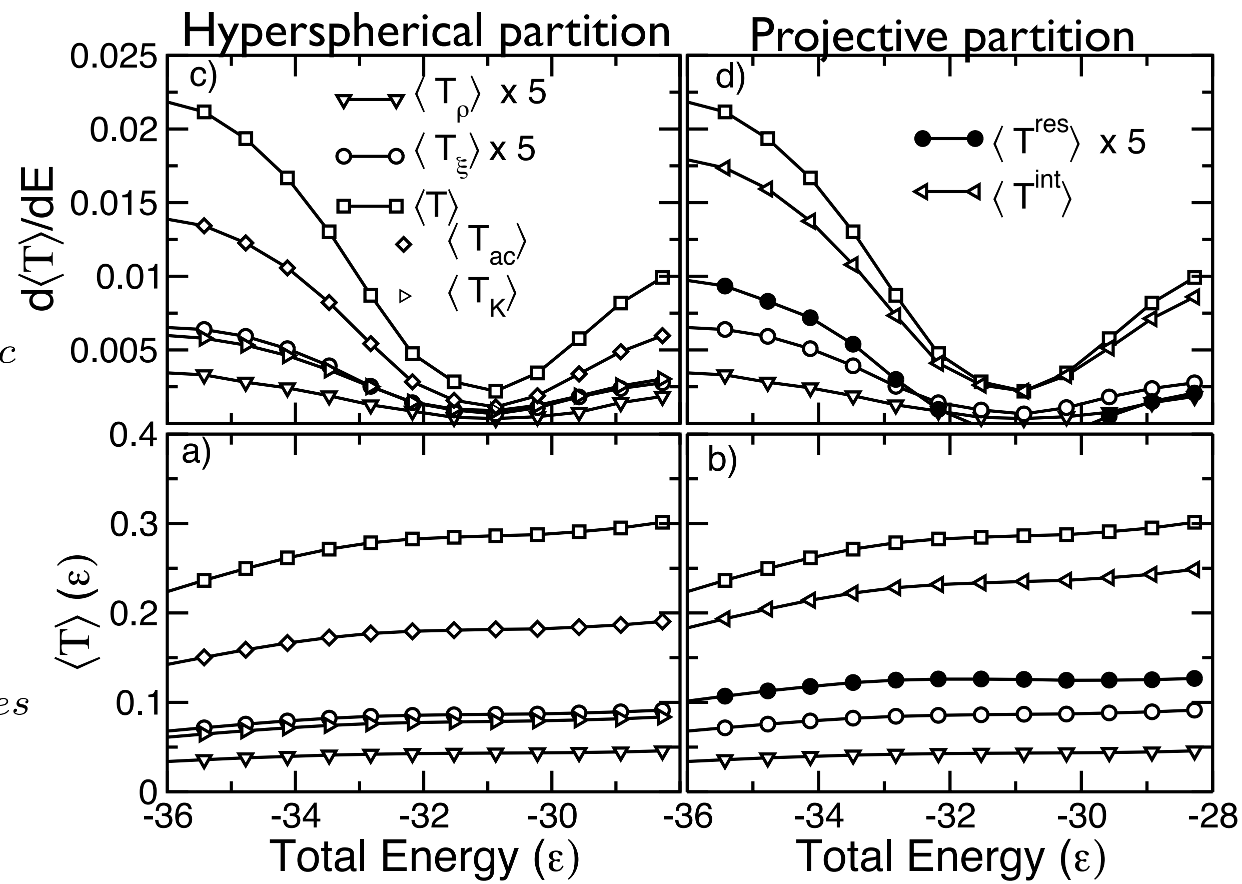
Caloric curves and slopes for Ar_{13}

hyperspherical partition

$$T = T_\rho + T_\xi + T_J + T_K + T_{ac}$$

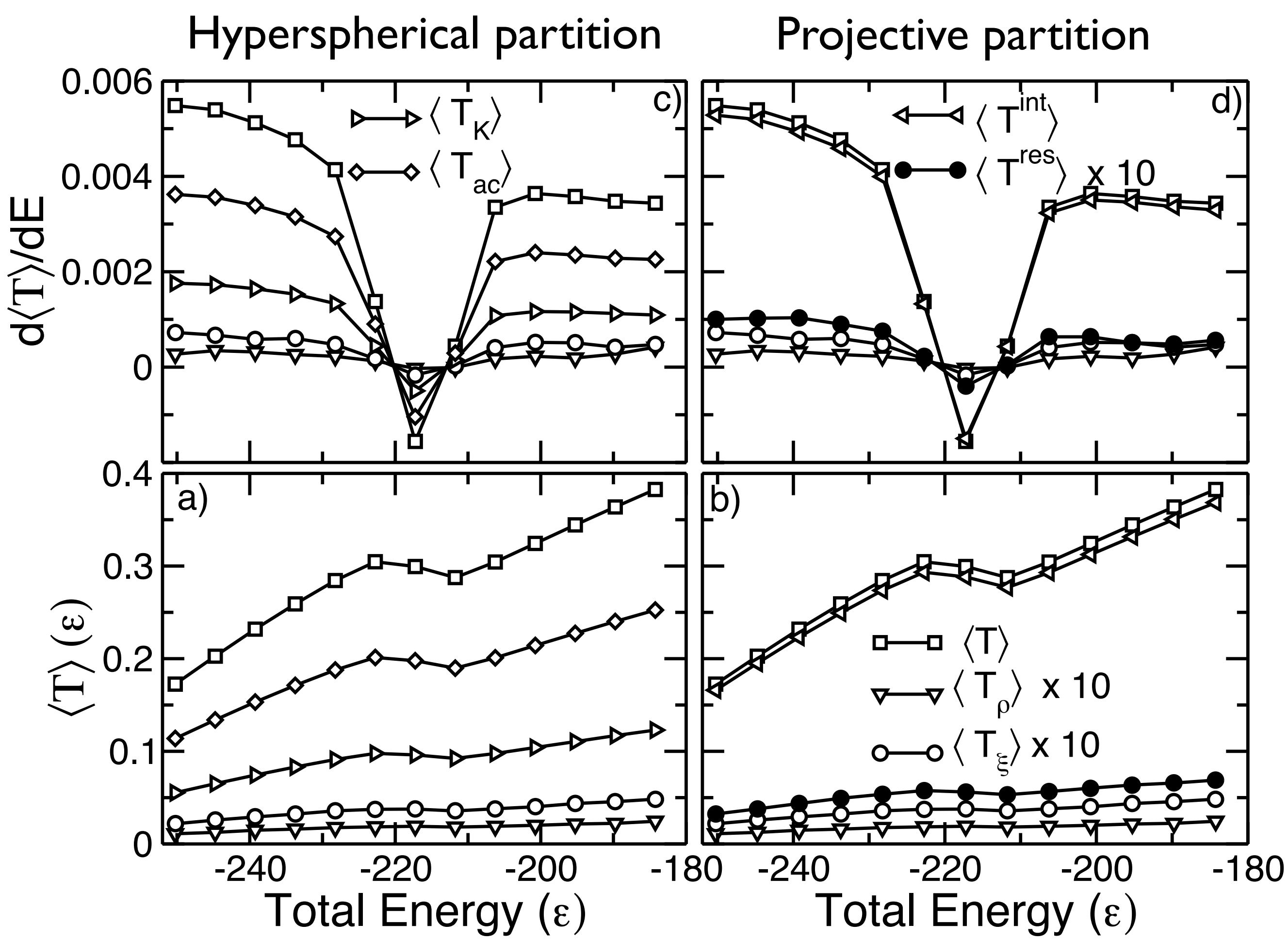
projective partitions

$$T = T_\rho + T_\xi + T^{ext} + T^{int} + T^{res}$$



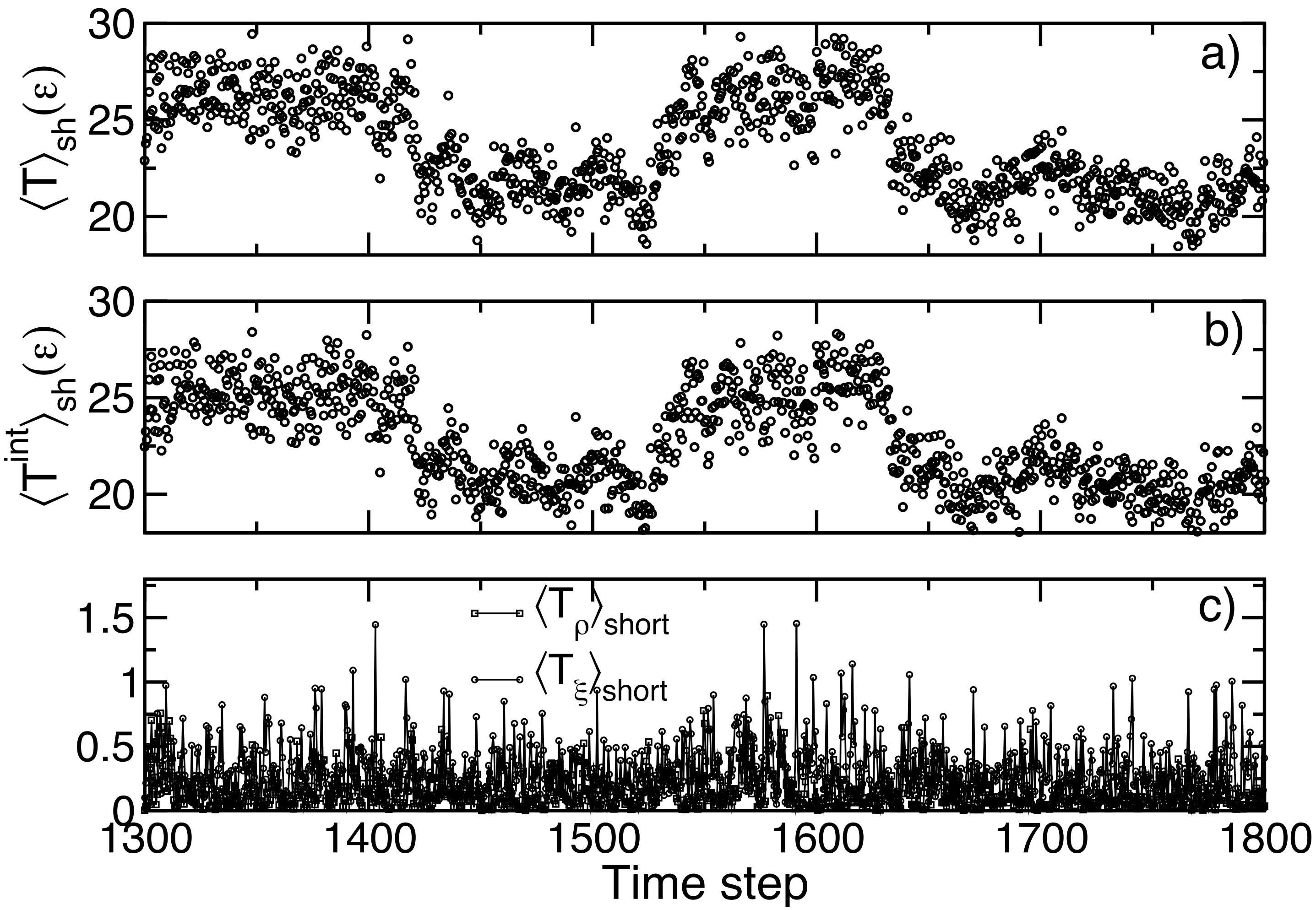
Caloric curves T(E) for Ar_{13} and inverse specific heats dT/dE for various partition terms. The change in the slope is due to a phase-change behavior. Inertial modes contribution terms T_ρ and T_ξ (magnified by a factor of five), common to the two partitions, actually appear to be generally small

Caloric curves and slopes for Ar_{55}



The change in the slope, with backbending (negative heat capacity) is due to a phase-coexistence behavior. Inertial modes contribution terms T_ρ and T_ξ (magnified by a factor of ten), common to the two partitions, actually appear to be generally small. Note that T^{res} is consistently smaller than T_{ac}, this indicate efficient mode-decoupling when phase transition takes place

Short-time averages, from a typical trajectory, for Ar_{55}, for energy terms from the more efficient projective partition



The bimodal behavior in panels a) and b) shows that two temperatures coexist. Coexistence comes from T^{int}, the internal rotation modes (kinematic rotations), while the hyperradial motion (T_ρ, overall breathing mode) and the shape motions (T_ξ) show "chaotic" oscillatory patterns

Conclusions

- The hyperspherical approach introduces a meaningful mode separation scheme, more general than the usual rotation-vibration one
- All the energy terms and hyperangular momenta are rigorously instantaneous phase-space invariants, from where it is easier to look for approximate integrals of the motion
- The introduction of physically meaningful and mathematically well-defined modes of the motion helps the study of the energy sharing and exchange among different degrees of freedom
- Invariant quantities are dynamical quantities that can be useful as indicators in critical phenomena
- All the terms in the various energy partitions can be calculated from the standard output of dynamics simulations, the Cartesian coordinates and momenta, by explicit formulas whose numerical implementation *scales linearly* with the number N of particles (for any fixed dimension d of the physical space) adding only a small computational effort to that involved in current calculation schemes
- Perspective applications include 2D systems (Wigner crystals), biological molecules ..