Hyperspherical methods in reaction dynamics: perspectives of ab-initio quantum reactive scattering calculations

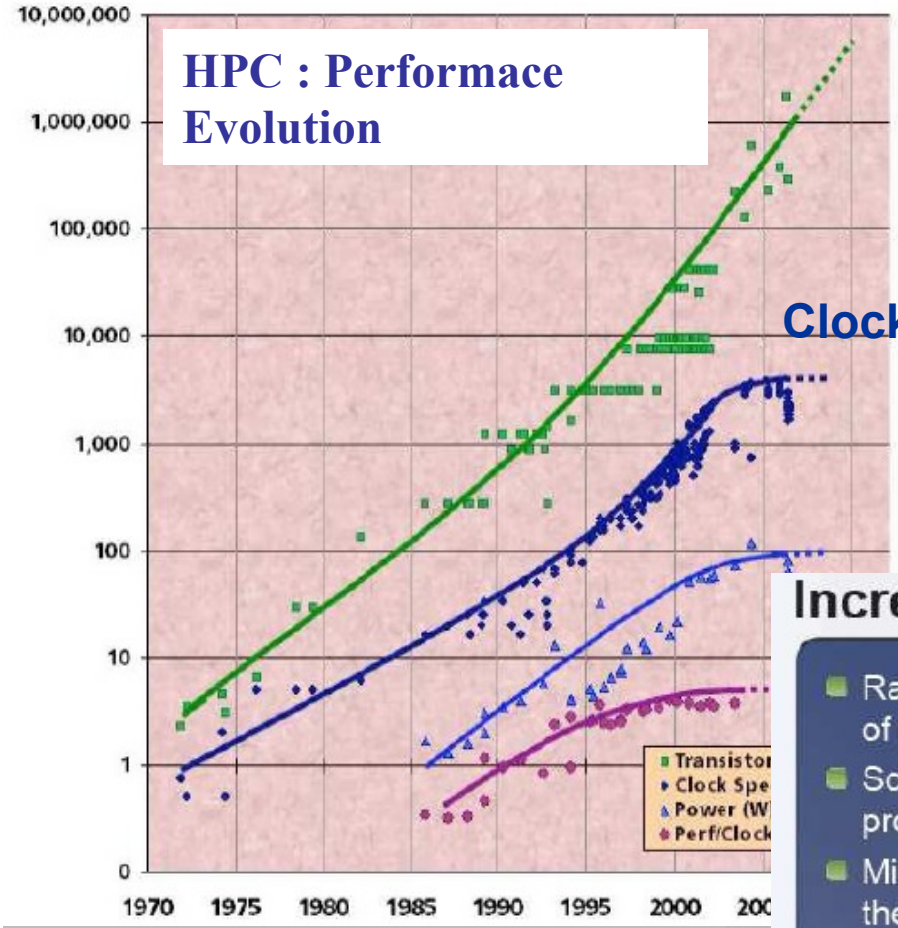
Dario De Fazio

Istituto di Metodologie Inorganiche e dei Plasmi C.N.R., 00016 Roma Italy
Dipartimento di Chimica Università degli Studi,06100 Perugia Italy

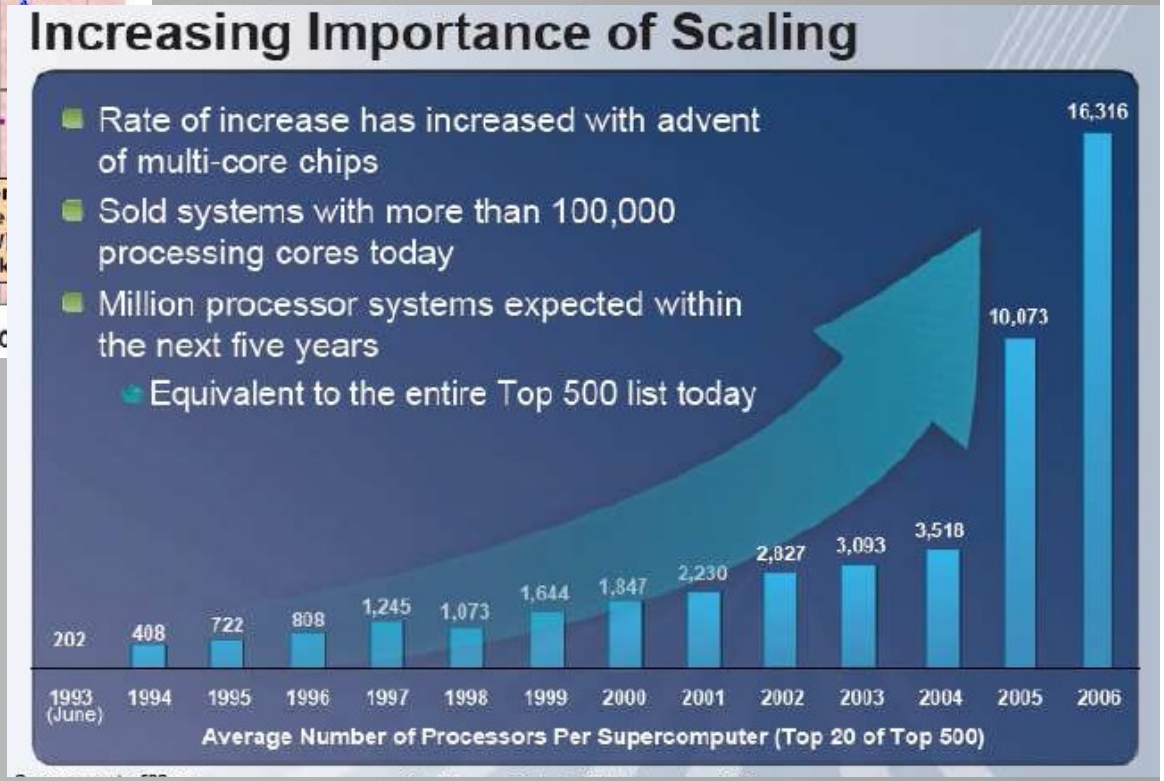
Miguel de Castro Vitores

Universidad Autonoma de Madrid, Madrid Spain

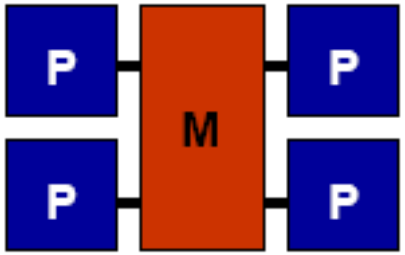
HPC : Performace Evolution



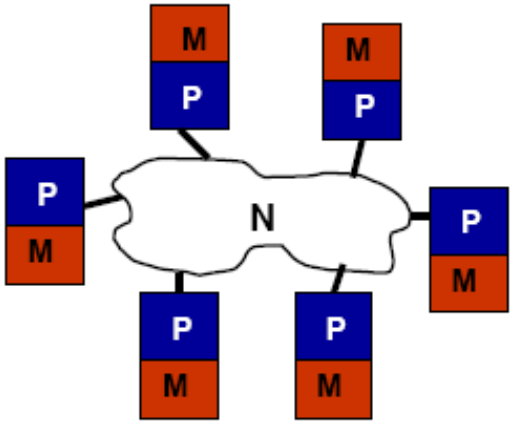
Clock Speed



Shared Memory System

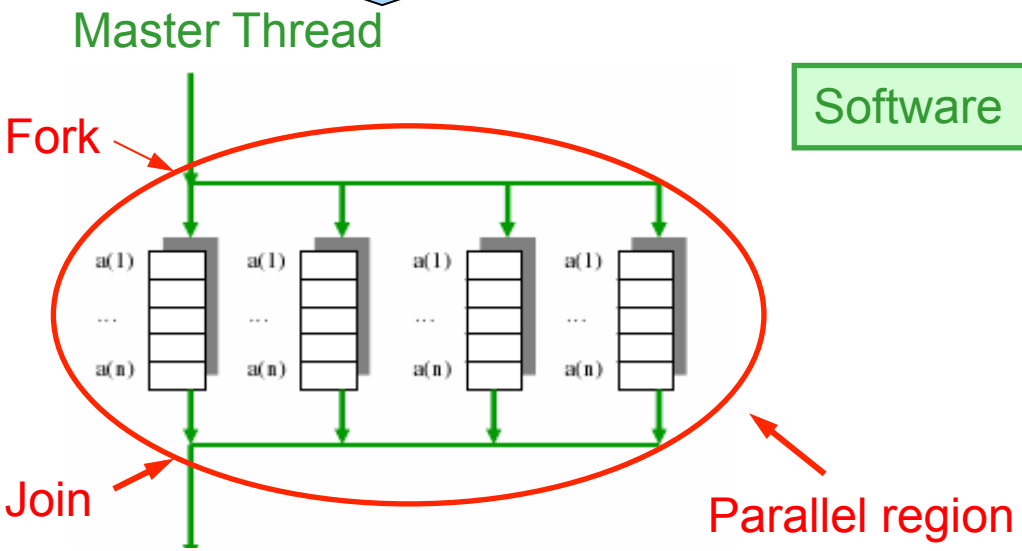


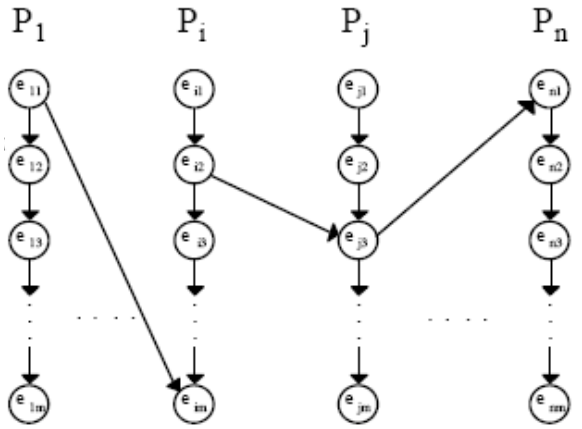
Distributed Memory System



Hardware

Software

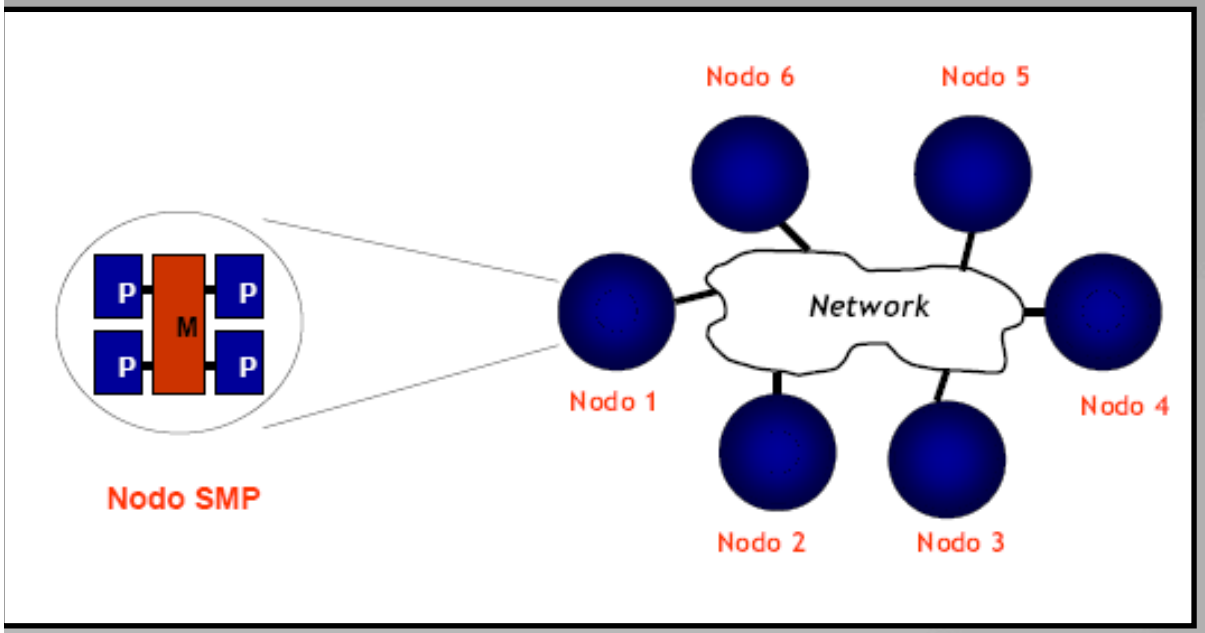




Shared Memory Paradigm (Open-MP)

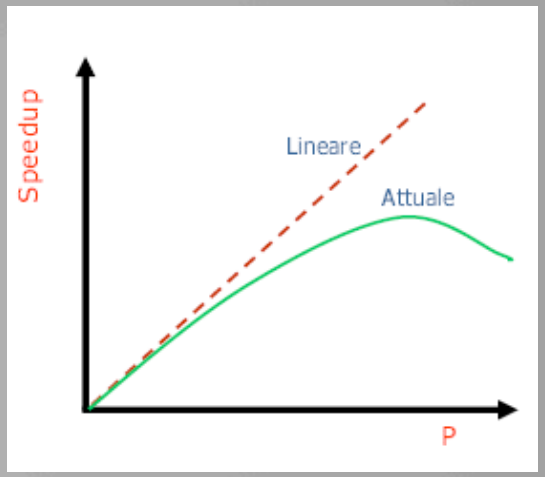
Message-Passing Paradigm (MPI)

Hybrid System

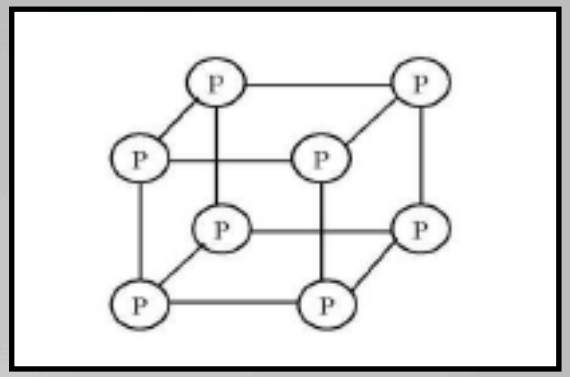


Parallel Performance

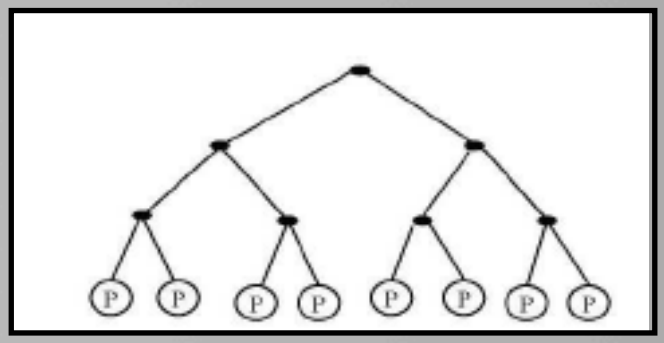
$$S(W,p) = T_s(W) \ / \ T_p(W,p)$$



Hypercube's Topology

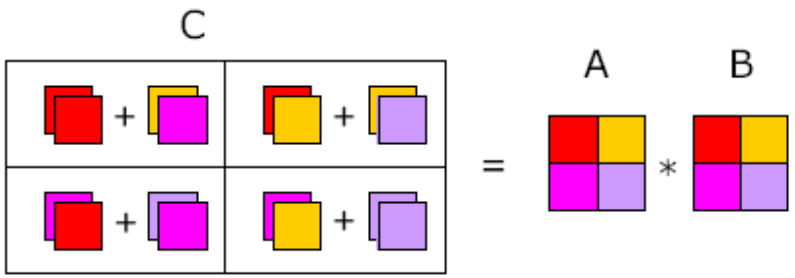


Tree's Topology



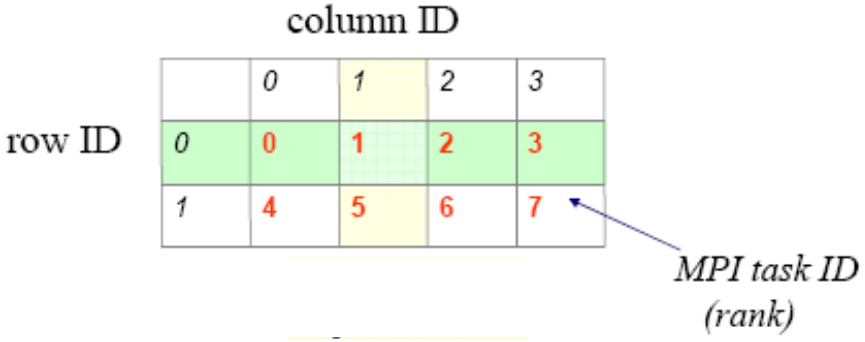
ScaLAPACK

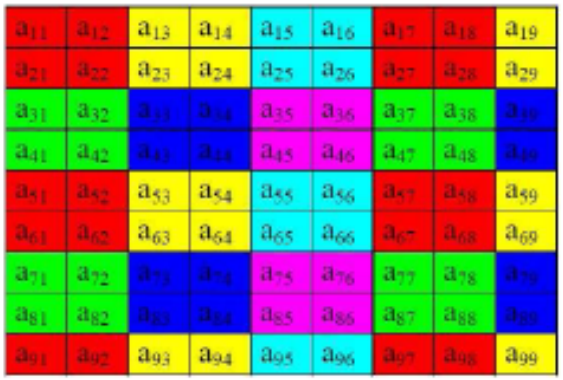
Parallel Linear Algebra



$$c_{ij} = \sum_{k=1}^{N} a_{ik} \cdot b_{kj}$$

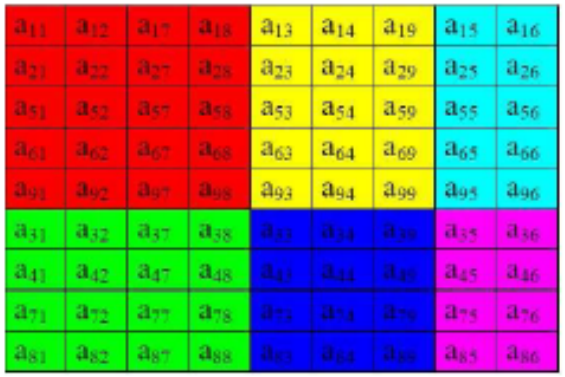
Processor's Grid





Global view

(seen from the matrix)



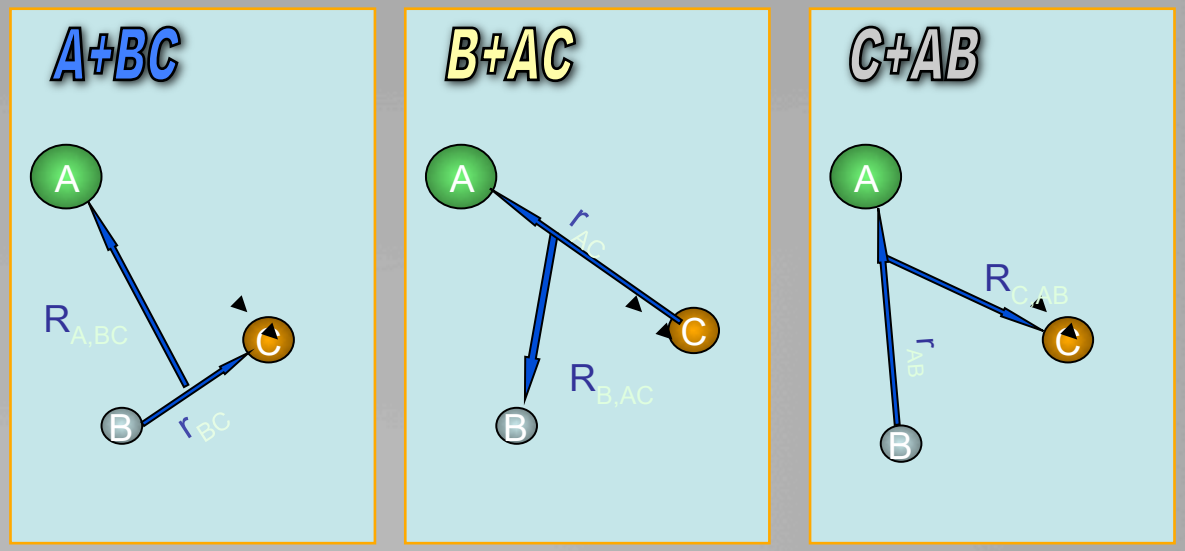
Local view

(seen from the processors)

Block Cyclization of the matrices

The Hyphersperical approach

JACOBI VECTORS



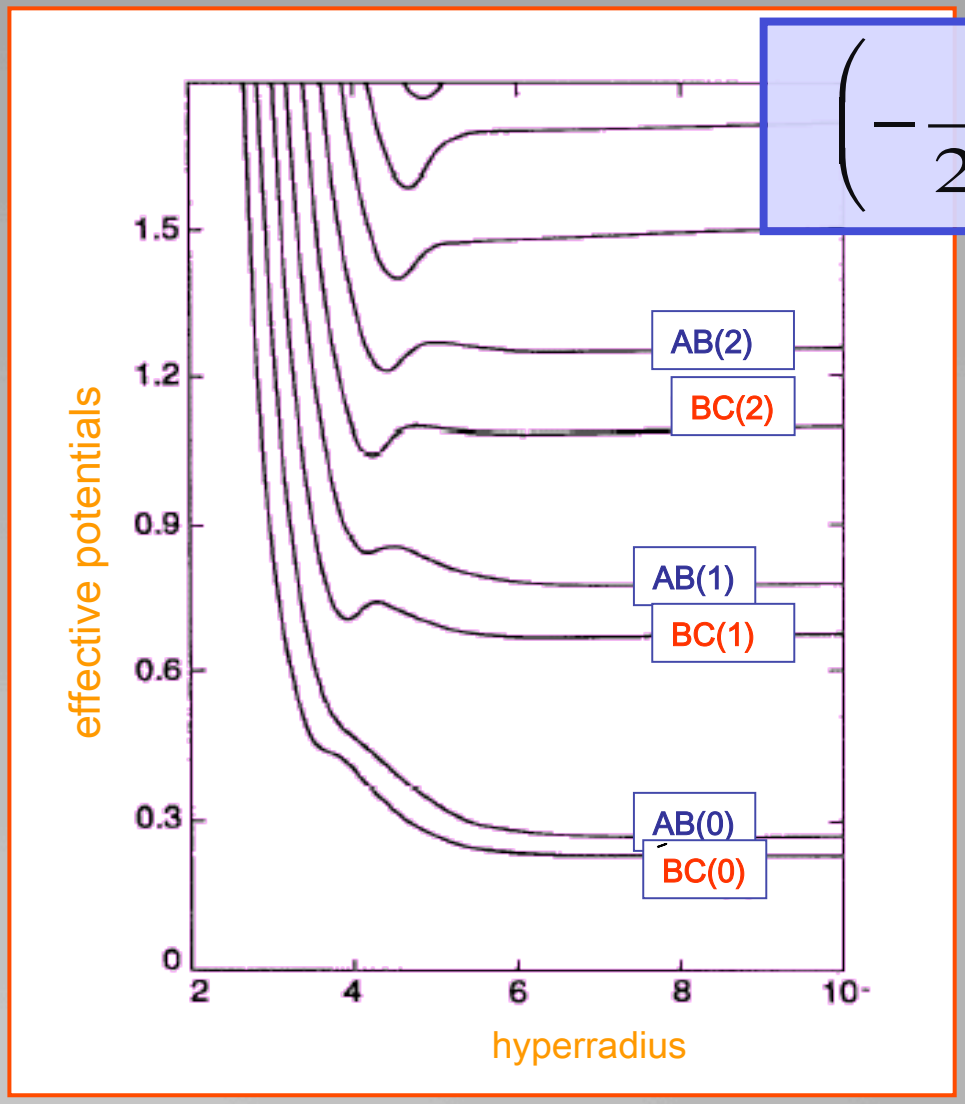
The Jacobi's coordinates are not appropriate in describing the reactive scattering event because a single set of Jacobi's vectors cannot describe well simultaneously reactants and products.

$$\rho = \sqrt{r_{BC}^2 + R_{A,BC}^2} = \sqrt{r_{AC}^2 + R_{B,AC}^2} = \sqrt{r_{AB}^2 + R_{C,AB}^2}$$

European ***ab-initio reactive scattering codes:***

J.M. Launay (Orsay, 1990), Hyperquantization (Perugia, 1998), abc (Oxford, 2000)

The rho-fixed quantization problem



$$\left(-\frac{\hbar^2}{2\mu\rho^2}\Lambda_\Omega^2 + V\right)\phi_n = \varepsilon_n\phi_n$$

Effective potentials employed in the description of the reactive scattering event. When $\rho \to \infty$ they correlate with reactants' and products' ro-vibrational states.

Multichannel scattering as funcion of rho

THE COUPLED CHANNEL EQUATIONS

$$\left[\frac{\partial^2}{\partial\rho^2}+\frac{2\mu}{\hbar^2}\left(E-\varepsilon_n\right)\right]f_{nn'}(\rho)-\sum_{n'=1}^{N}W_{nn'}f_{nn'}(\rho)=0$$

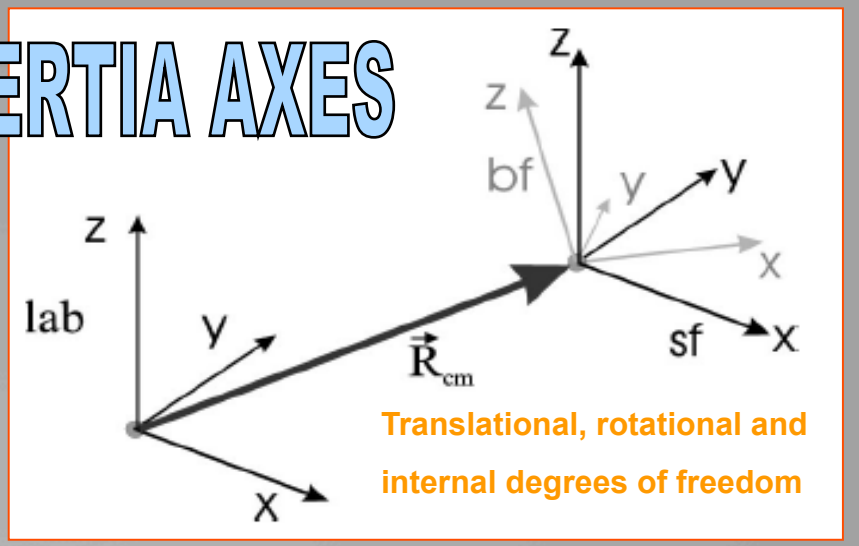
ARE THEN PROPAGATED USING THE LOGARITHMIC DERIVATIVE METHOD AND SOLVED UNDER SCATTERING BOUNDARY CONDITIONS

$$f_{nn'}(\rho)\underset{\rho\to\infty}{\approx}\frac{1}{2ik_n}\left(\delta_{nn'}\exp[-ik_n\rho]-S_{nn'}\exp[ik_n\rho]\right)$$

TO OBTAIN THE SCATTERING MATRIX **S** AT FIXED VALUES OF TOTAL ENERGY E AND TOTAL ANGULAR MOMENTUM J

N_{Max} = 3000-5000 $\quad$ **M_ρ = 10-100 x ρ_{Max}** $\quad$ N = N_{open} + N_{closed}

BODY FRAME: PRINCIPAL INERTIA AXES



PARTITIONING OF THE GRAND-ORBIATAL ANGULAR MOMENTUM

$$\Lambda^2 = \Lambda_\Omega^2 + \mathrm{R}$$

GRAND-ORBITAL ANGULAR MOMENTUM

Ω IS THE PROJECTION OF J ON THE LEAST INERTIA AXIS

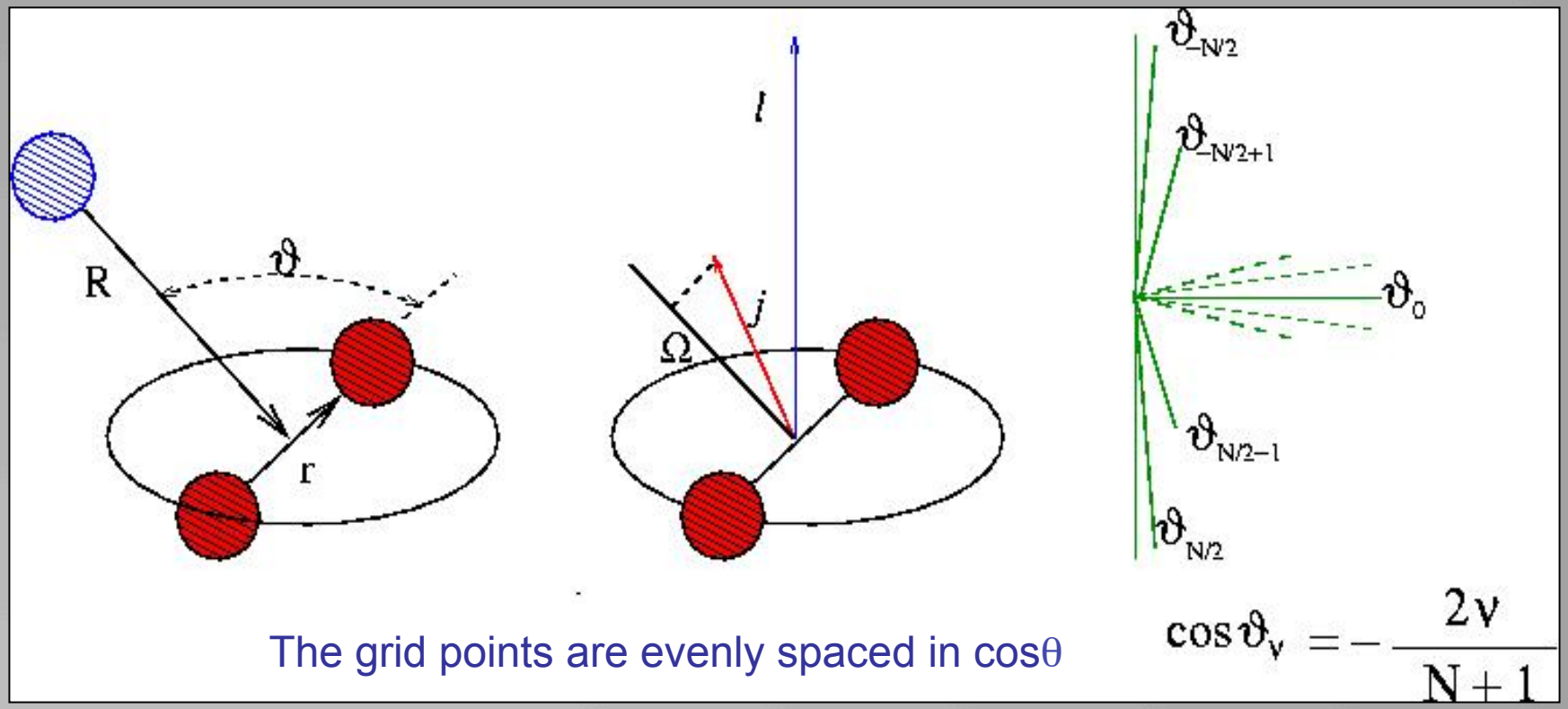
$$\Lambda_\Omega^2 = \frac{1}{\sin 4\Theta}\frac{\partial}{\partial\Theta}\sin 4\Theta\frac{\partial}{\partial\Theta} + \frac{1}{\cos^2 2\Theta}\frac{\partial^2}{\partial\Phi^2} - \frac{4\Omega^2}{\sin^2 2\Theta}$$

ROTATIONAL COUPLING

CORIOLIS COUPLING

$$R = \frac{\hat{J}_y^2}{\cos^2 2\Theta} + \frac{\hat{J}_x^2 + \Omega^2}{\cos^2\Theta} + \frac{2i\sin 2\Theta}{\cos^2 2\Theta}\hat{J}_y\frac{\partial}{\partial\Phi}$$

Discrete analogs of classical orthogonal polynomials

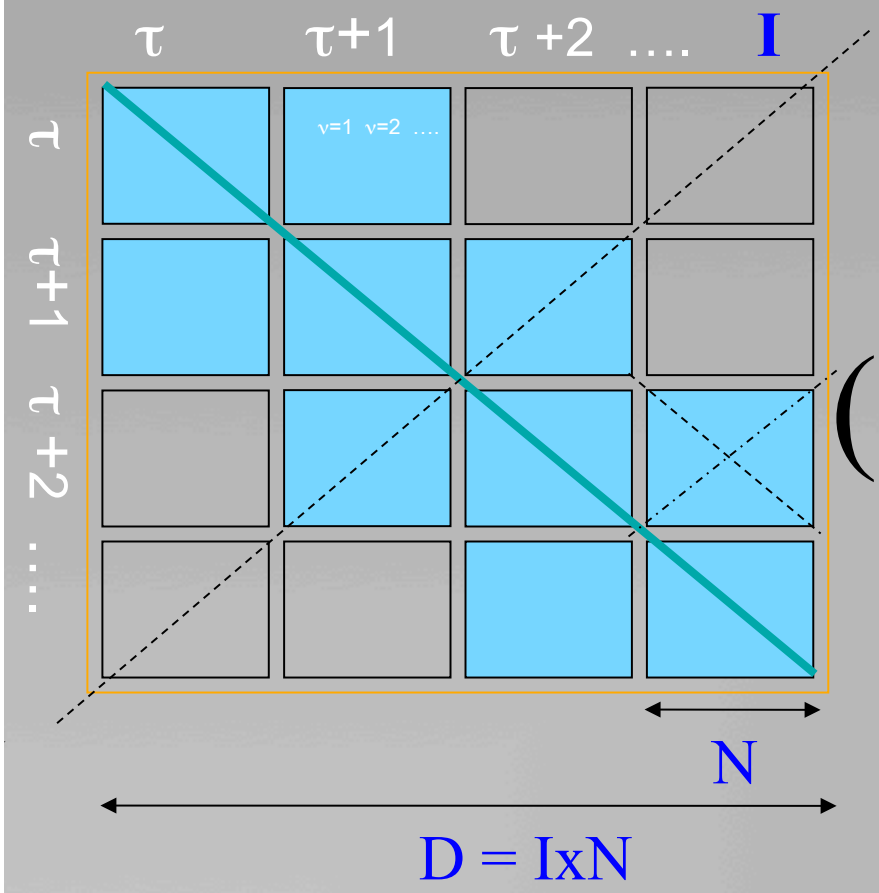


The grid points are evenly spaced in cosθ

$$\cos\vartheta_\nu = -\frac{2\nu}{N+1}$$

$$\left(\frac{N+1}{2}\right)^{-\frac{1}{2}} Y_{j\Omega}(\vartheta_\nu, 0) \sim (-)^{\frac{N}{2}-\nu-j-\Omega}(2j+1)^{\frac{1}{2}} \begin{pmatrix} \frac{N}{2} & \frac{N}{2}+\Omega & j \\ \nu & -\nu & 0 \end{pmatrix}$$

Hamiltonian matrix in the stereo-directed representation



$$(K+V)T = T\varepsilon$$

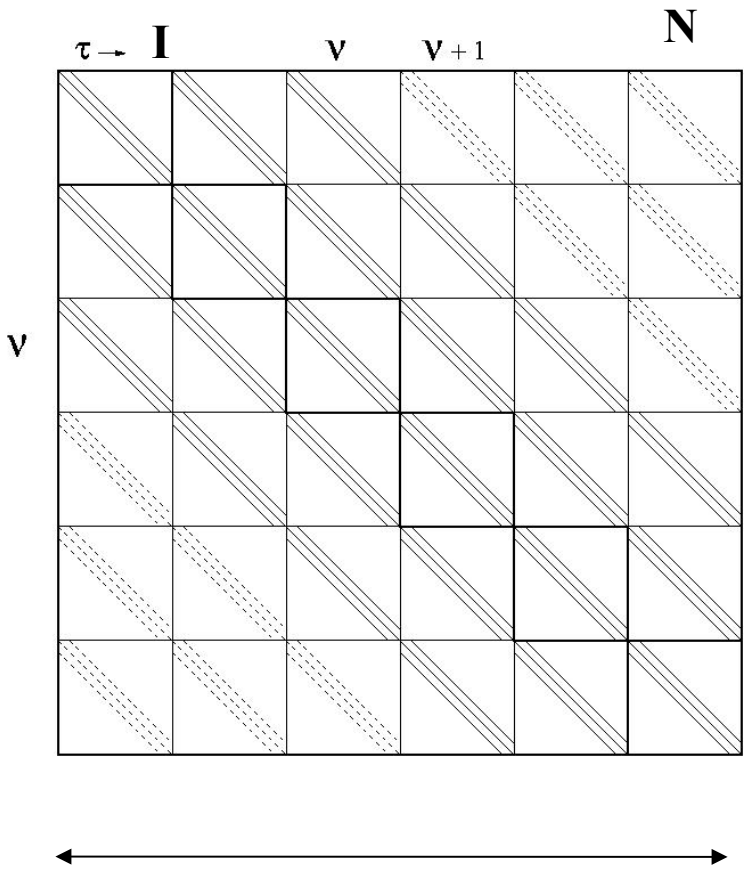
The kinetic energy matrix is block-tridiagonal

The potential matrix is diagonal $V_{\tau\nu,\tau\nu} = V(\rho, \Theta_\tau, \Phi_\nu)$

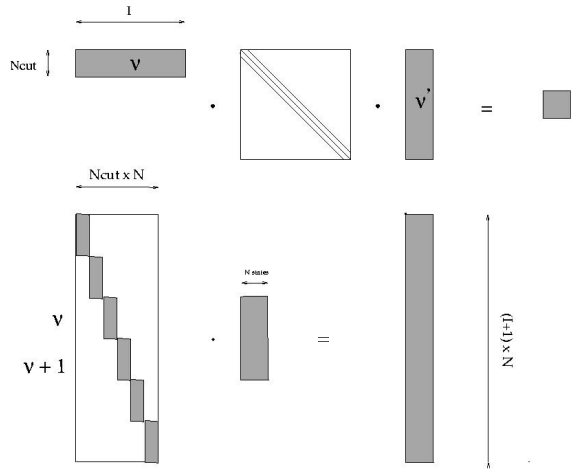
N = 150-500
I = 1500-15000

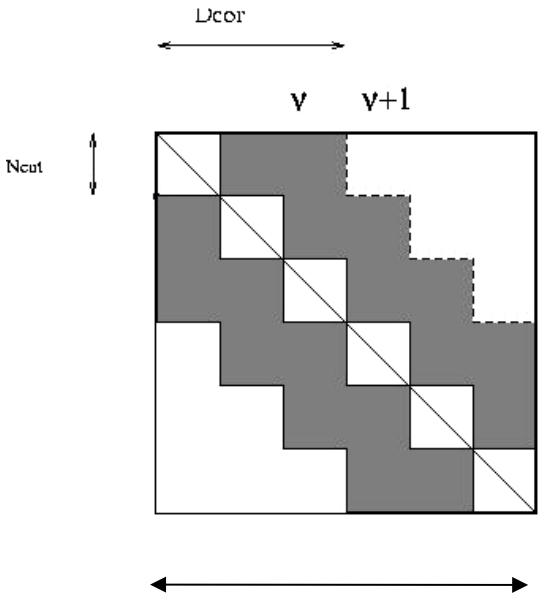
Efficient eigensolver (STLM) based on the Lanczos algorithm

Sequential Diagonalization truncation schemes



D = I x N





I_{vmax} = 200-300

N_{cut} = 40-20

d = I_{vmax} x N_{cut}

Hyperquantization vs abc

Main Benefits

- The body frame used minimize the Ω coupling.
- Avoid to use over-complete basis sets.
- The Hamiltonian matrix is sparse and highly symmetric.
- Calculation of kinetic energy matrix is almost analytical.
- No integrals have to be calculated.
- Two alternative schemes to reduce the dimension of the Hamiltonian matrix.

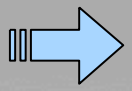
Costs

- large number of grid points, matrices of large dimension.
- lattice angular points evenly spaced in the cosine .
- The convergence of the Hyperquantization parameters change with ρ.

Parallelization Strategy

Conservation of the Total Angula momentum

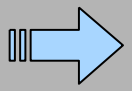
$$\sigma_{vj}(E) = \frac{\pi}{k_{vj}^2} \sum_{J\Omega\Omega' v' j'} (2J+1) \left| S^J_{vj\Omega, v' j' \Omega'} \right|^2$$



MPI no communication

Principal Axis Body-frame Projections

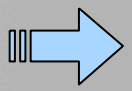
$$R = \frac{\hat{J}_y^2}{\cos^2 2\Theta} + \frac{\hat{J}_x^2 + \Omega^2}{\cos^2 \Theta} + \frac{2i \sin 2\Theta}{\cos^2 2\Theta} \hat{J}_y \frac{\partial}{\partial \Phi}$$



MPI near neighboor communication

Propagation of closed couled equations

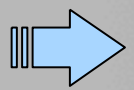
$$\left[\frac{\partial^2}{\partial \rho^2} + \frac{2\mu}{\hbar^2} (E - \varepsilon_n) \right] f_{nn'}(\rho) - \sum_{n'} W_{nn'} f_{nn'}(\rho) = 0$$



OpenMP linear algebra libraries

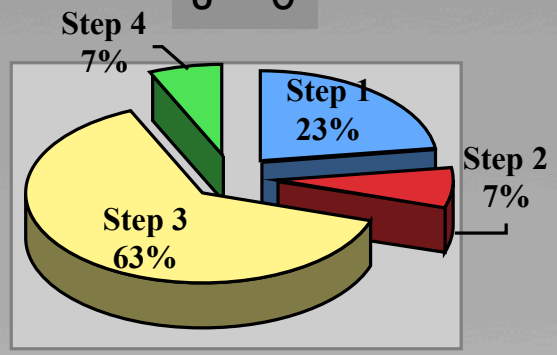
The rho-fixed problem

$$\left(-\frac{\hbar^2}{2\mu\rho^2} \Lambda_\Omega^2 + V \right) \varphi_n = \varepsilon_n \varphi_n$$

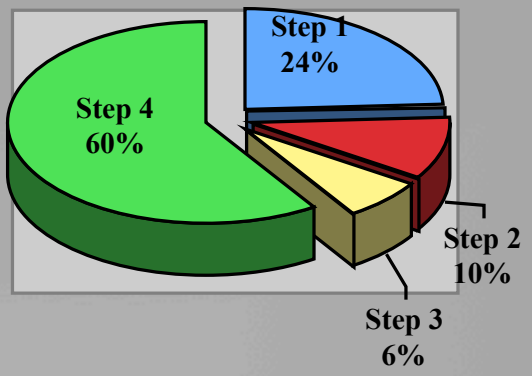


MPI-based linear algebra libraries
(Scalapack, PETSc, SLEPc) +
OpenMP loop calling sequential libraries

J = 0



J = 8



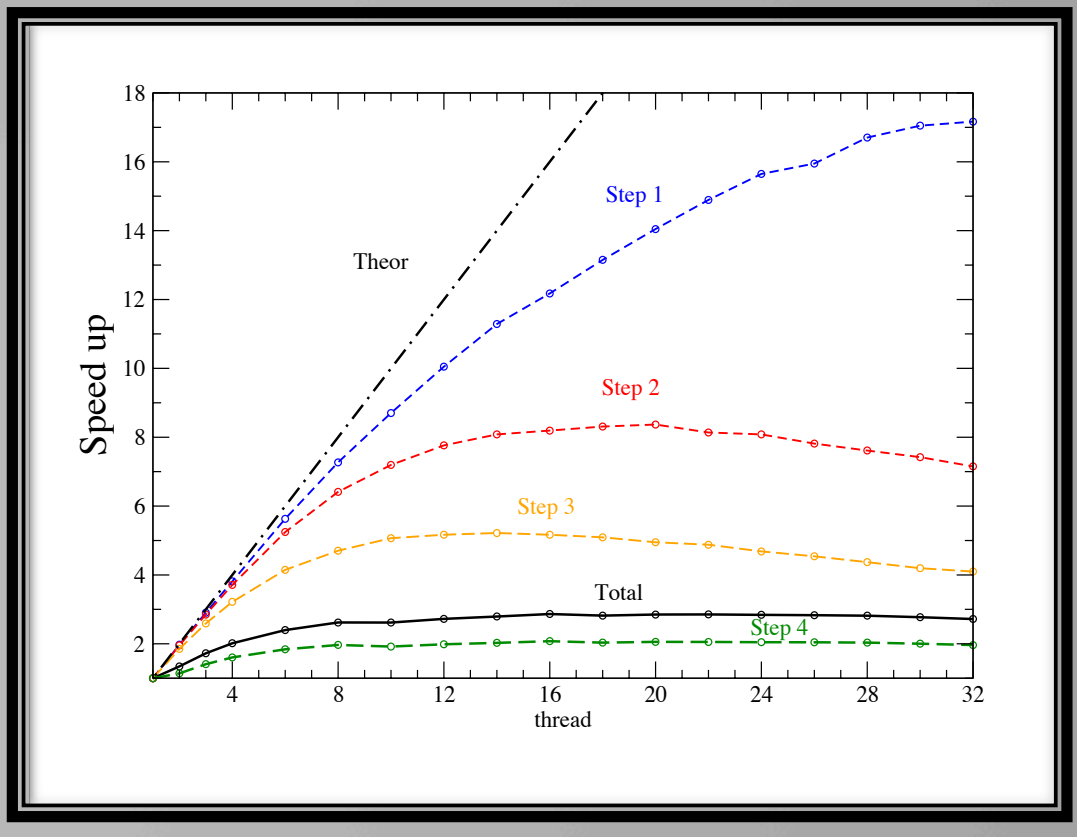
abc code

System Clock-Time (sec)

Step 1 = Propag.
Step 2 = Overlap
Step 3 = H Build-up
Step 4 = H diagonalization

Parallel Performance

$S(W,p) = T_s(W) \;/\; T_p(W,p)$



Computational Performances

Hyperquantization Algorithm

$$Li^+ + HD \longrightarrow LiH(D)^+ + D(H)$$

Sequential Code

Step	1	2	3	4	Total
ρ = 30	527	5	417	1	950
ρ = 9	62	47	1387	51	1537

Pure Open-MP (64 Threads)

Step	1	2	3	4	Total
ρ = 30	10	0	10	1	22
ρ = 9	1	1	33	15	50

Scalapack Code (16 MPI tasks + 4 Threads)

Step	1	2	3	4	Total
ρ = 9	18	17	9	4	48

System Clock-Time (sec)

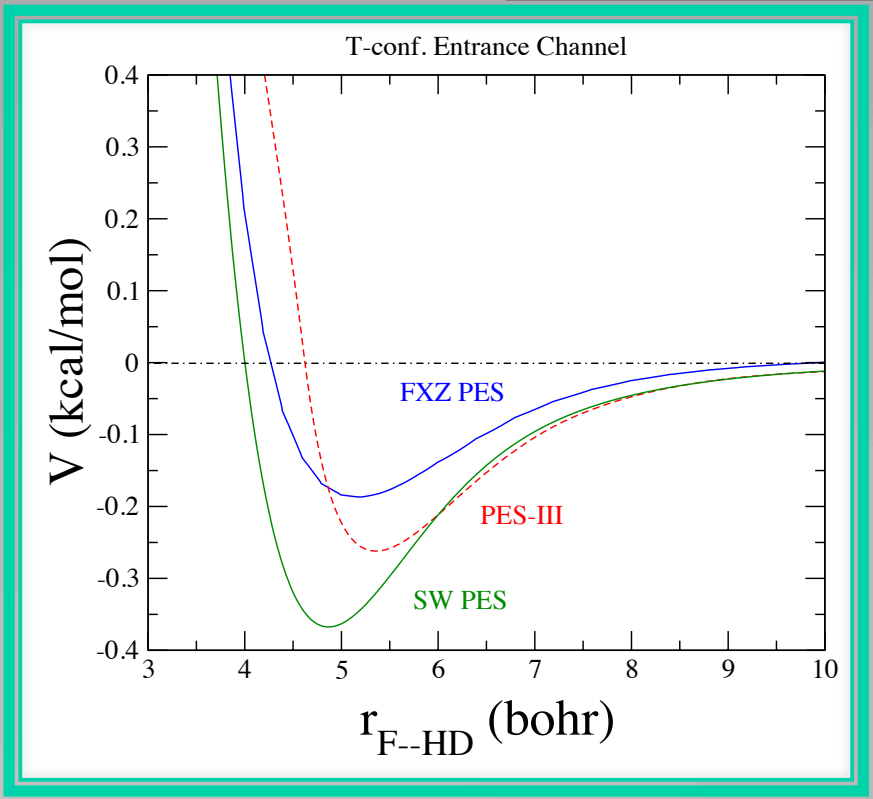
Step 1 = V
Step 2 = Pre-diagonalization
Step 3 = H Build-up
Step 4 = H diagonalization

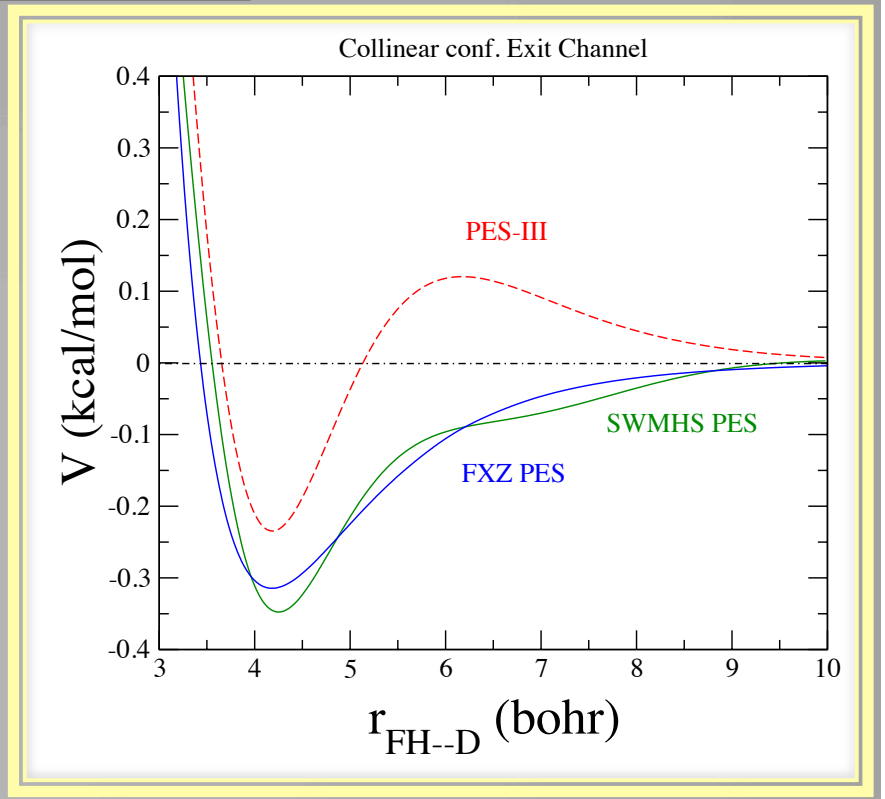
Matrix Dimension

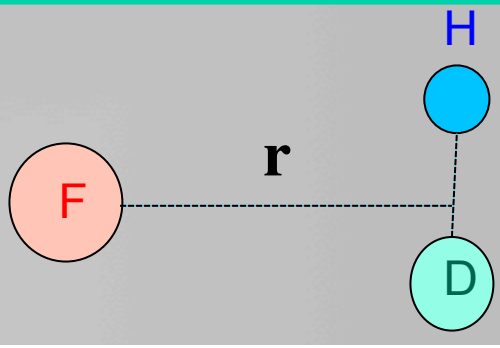
ρ	H	Hrid
30	393037	1574
9	1495023	5039

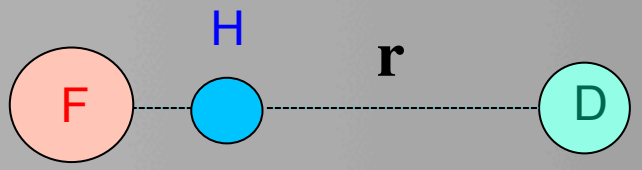
F + HD → HF + D

The Long-range Interaction

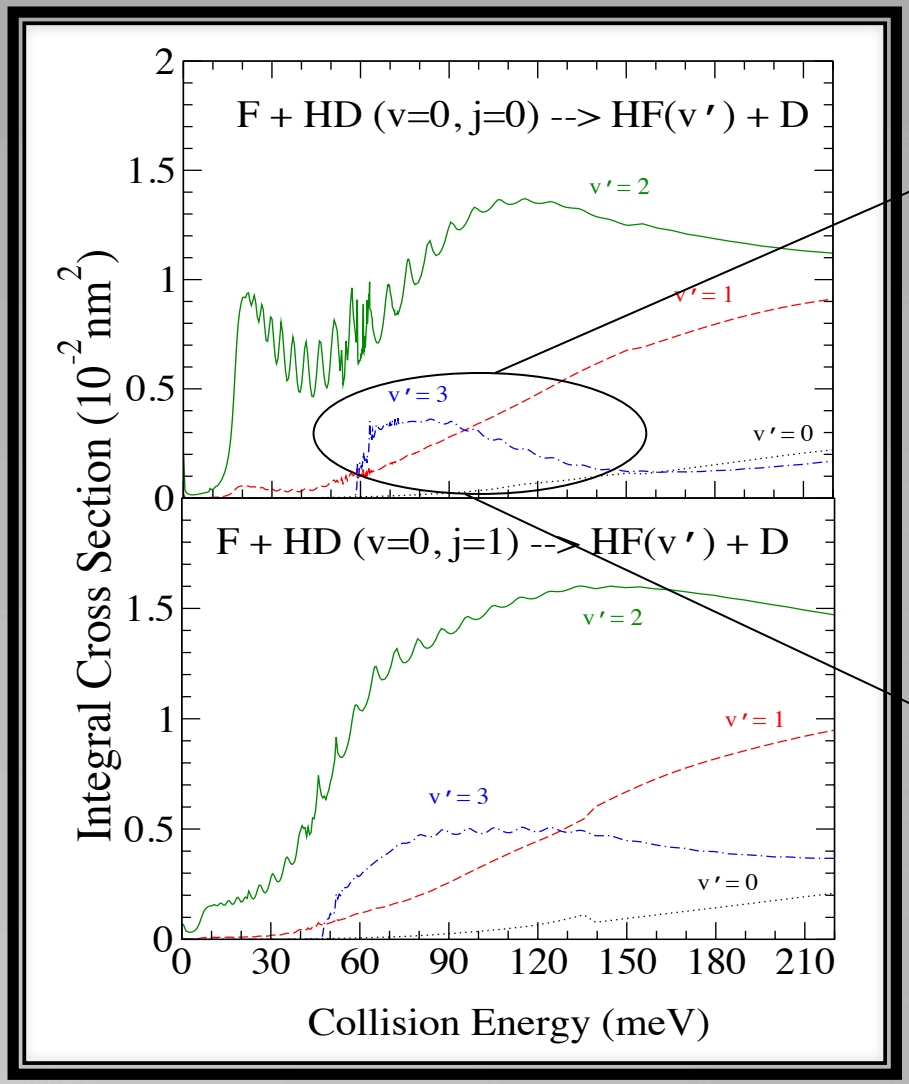




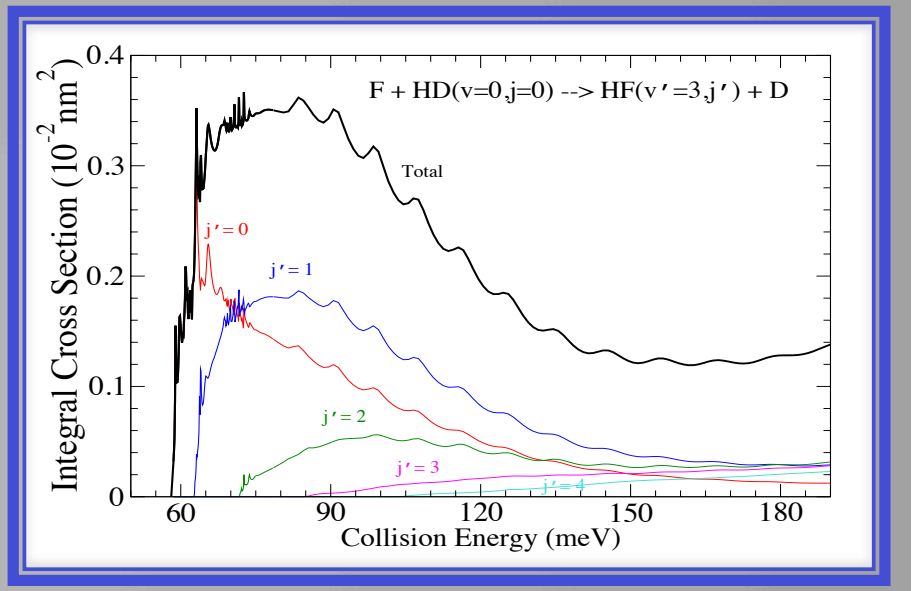




FXZ PES

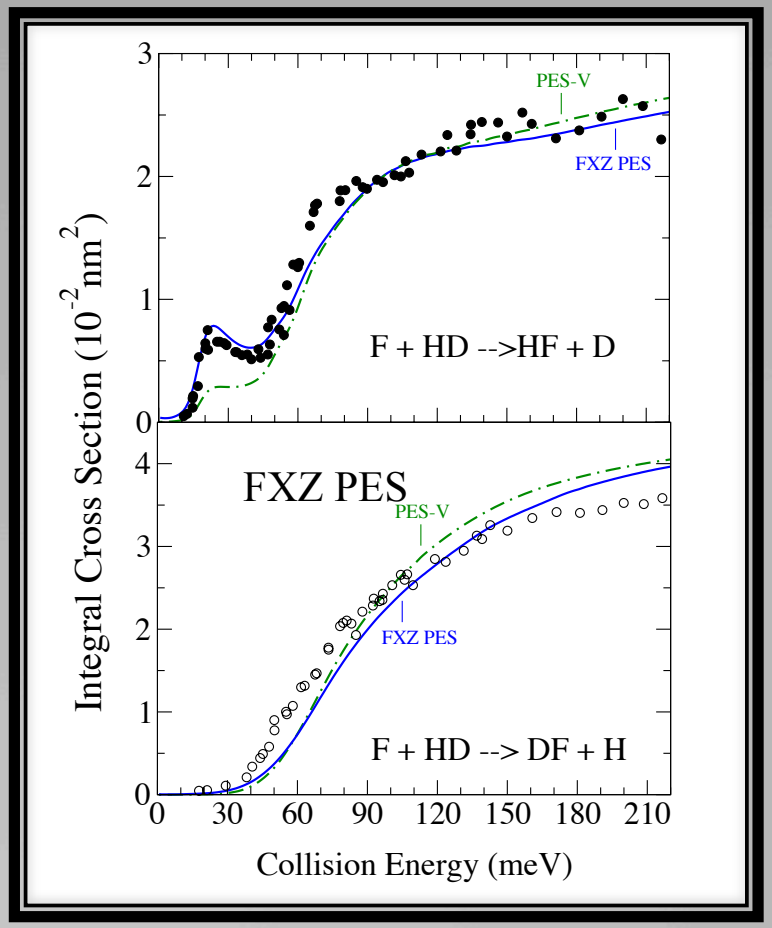


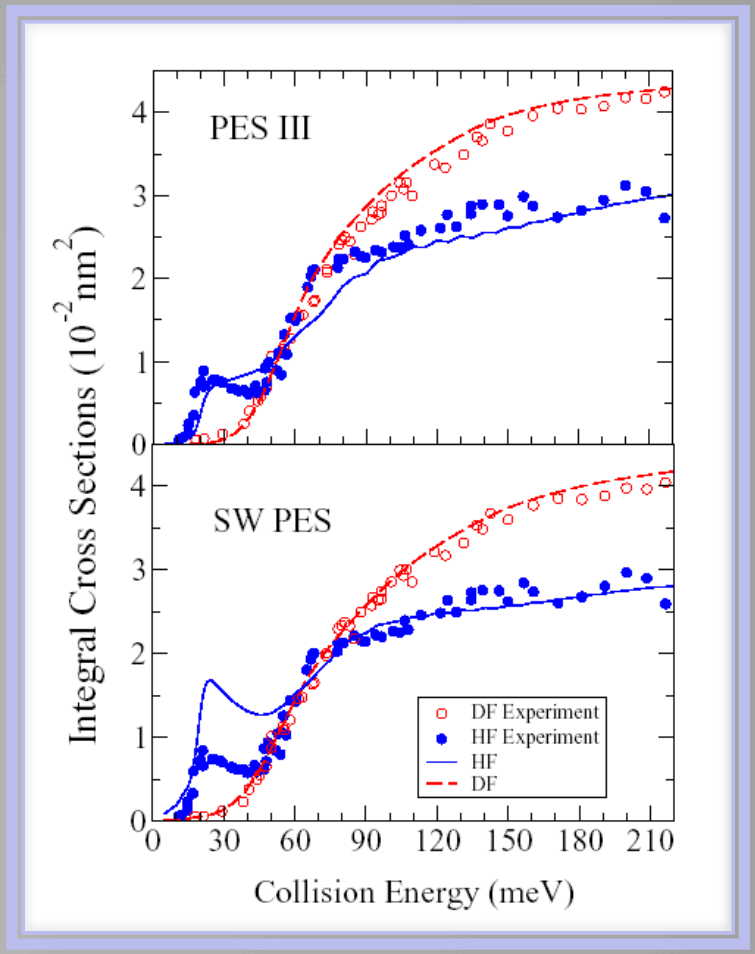
State-to-state ics



F + HD(J=0,1) ⟶ HF + D

K. Liu et al (2000)

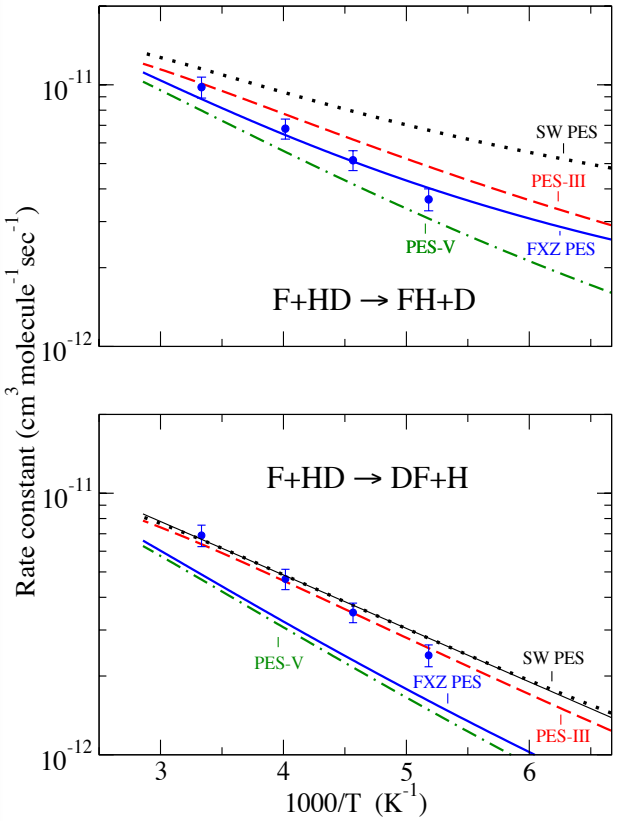




$\sigma = 4$ meV

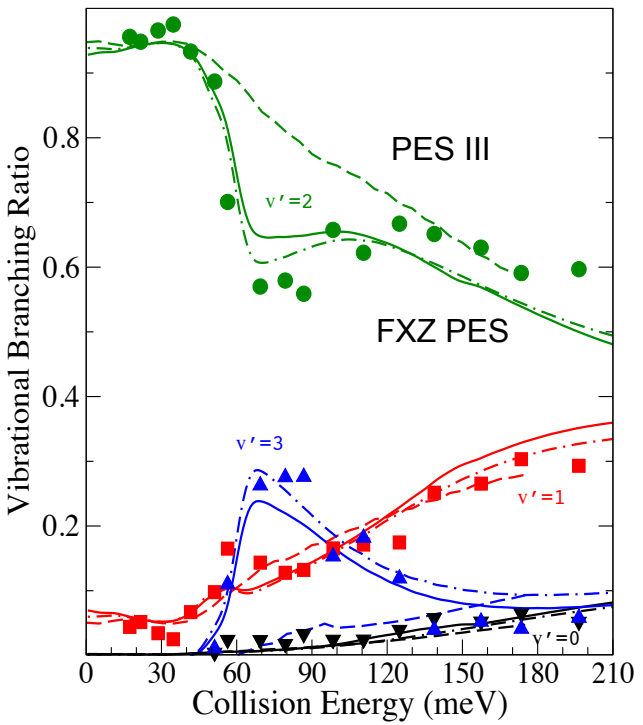
Rate constants

Persky (2005)



Vibrational Branching Ratios

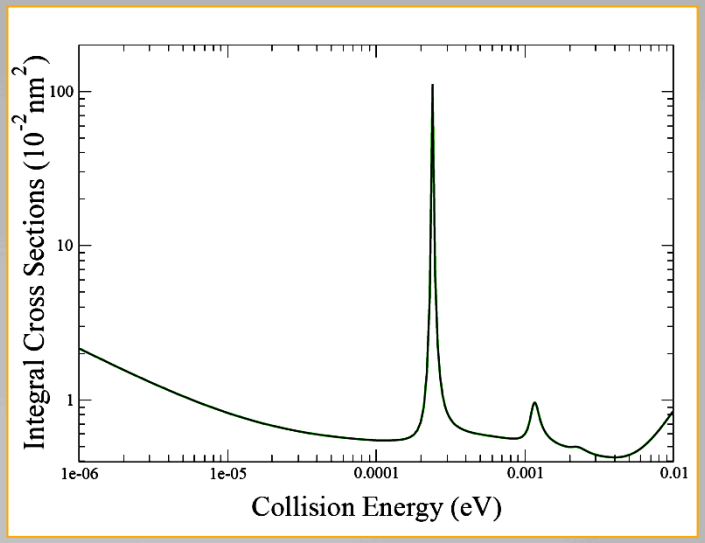
K. Liu et al (2002)



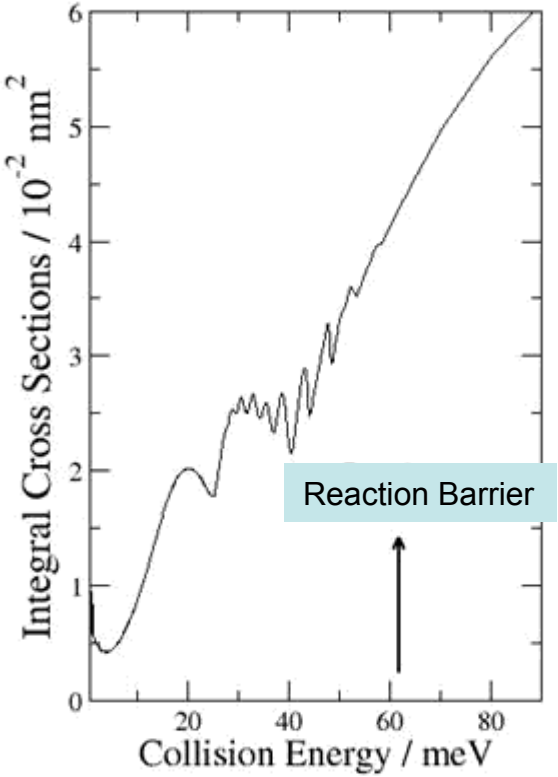
J_{max} = 20-30 Ω_{max} = 3-5

INTEGRAL CROSS SECTION

$$\sigma_{vj}(E) = \frac{\pi}{k_{vj}^2} \sum_{J\Omega\Omega' v' j'} (2J+1) \left| S^J_{vj\Omega, v' j' \Omega'} \right|^2$$



$F + H_2(v=0,j=0) \rightarrow HF(all) + H$



Conclusions and Perspectives

- The Hyperquantization Algorithm is particularly suitable to fully exploit the new hardware and software available in the H.P.C. facilities.
- In the next future all 3-atoms reactions can be computed including ion-molecule systems and chemistry in cold and ultra-cold conditions.
- The Hyperquantization can be formally extended to solve higher dimensional problems so that the good performances reached in the treatment of the three bodies dynamics, encourage the development of hyperspherical computer codes for reactions involving 4 or 5 atoms.
- To obtain a close agreement with the molecular beam and kinetic experimental data high accuracy description (of the order of few meV) of the interaction , in the long range as well as in the transition state regions of the rection, is required.
- The large improvement of the computational performances will permit to use hyperspherical techniques to solve 3-centers reactions including perturbatively additional degrees of freedom.

Acknowledgments:

- HPC-Europa2 program
- *Thanks to the organizer*