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GRID-TECHNOLOGY FOR NUMERICAL SIMULATION OF CHEMICAL REACTIONS

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Abstract

We discuss a possible strategy for implementing a grid-based approach to realizing the immense computational resources required to compute reactive molecular scattering cross sections and rate constants .

Description of reactive scattering problem

$$A+(BC)_m \rightarrow \begin{cases} A+(BC)_n \\ (AB)_n + C \\ (AC)_p + B \\ A+B+C \\ (ABC)^* \rightarrow \begin{cases} A+(BC)_n \\ (AB)_n + C \\ (AC)_p + B \\ A+B+C \end{cases} \end{cases}$$

Formulation of the problem and calculation formulas

The quantum mechanical Hamiltonian in the curvilinear coordinate system may be written in the form

$$\hat{H}_s = -\frac{\hbar^2}{2m}\sum_{i,j}^{5}\frac{1}{\sqrt{g}}\frac{\partial}{\partial x_s^i}g^{ij}\sqrt{g}\,\frac{\partial}{\partial x_s^j} + U\left(x^0(s), x^1, x^2\right),$$

$$\vec{x}_s = \left\{x_s^i\right\} = (x^0(s), x^1, \ldots, x^5),$$

with the metric tensor defined by

$$g_{ij}\left(x^0(s), x^1, x^2\right) = \sum_k \frac{\partial x_s^i}{\partial q_k}\frac{\partial x_s^j}{\partial q_k} \qquad g = Det\left(g_{i,j}\right)$$

Formulation of the problem and calculation formulas

The multi-channel scattering problem in the three-body system is described by the Schredinger equation

$$\left(\hat{H}_s - E \right) \Psi = 0$$

The full wave function should obey boundary conditions

$$\lim_{x^0 \to -\infty} \Psi^{(+)}(m, x_s) = \Psi_{in}(m, x_s) + \sum_{n \neq m} R_{nm} \Psi_{in}(n, x_s)$$

$$\lim_{x^0 \to +\infty} \Psi^{(+)}(m, x_s) = \sum_{n} S_{nm} \Psi_{out}(n, x_s)$$

$$G(X,X') = \int dX \exp\left\{ i/\hbar S_d(X,X') \right\}$$

Problem with $t \to \pm\infty$ remains:

at $t \to \pm\infty$ P,P' - fixed

but $E=E'$, so path undetermined

Solution: $S \to T$, extracting δ-functions

$$A = \int dX\, G^{+}(P',X) G(X,P)$$

$$G(X,P) = \int DPDX/(2\pi\hbar)^{s} \exp\left\{ i/\hbar \int X\,dP - i/\hbar \int H\,dt + i\phi \right\}$$

$$(P,X) \rightarrow (QY)$$

$$H(P,X) \rightarrow \tilde{H}(Q,Y)=H(X, \partial F_1/\partial t) + \partial F_1/\partial t|_{Q,Y}$$

$$\tilde{S} = -P_* X_* + \int dF_1 + \int Q dY$$

$$G(P_* X) = \exp\left\{ -i/h\, P_* X_* + i/h F_1 \Big|_*^0 + i/h Q_* (Y_0 - Y_*) \right\}$$

$$A(P_i \rightarrow P_f) = \int dX_0 C\, d(X_0 P_0) \exp\left\{ i/h (P_f X_f - P_i X_i) \right.$$

$$\left. + i/h F_1 \Big|_*^0 + i/h F_1 \Big|_*^f + i/h Q_i (Y_0 - Y_i) + i/h Q_f (Y_f - Y_0) \right\}$$

$$F_1: \quad H(X, \partial F_1/\partial x) = E$$

The sequential computational scheme

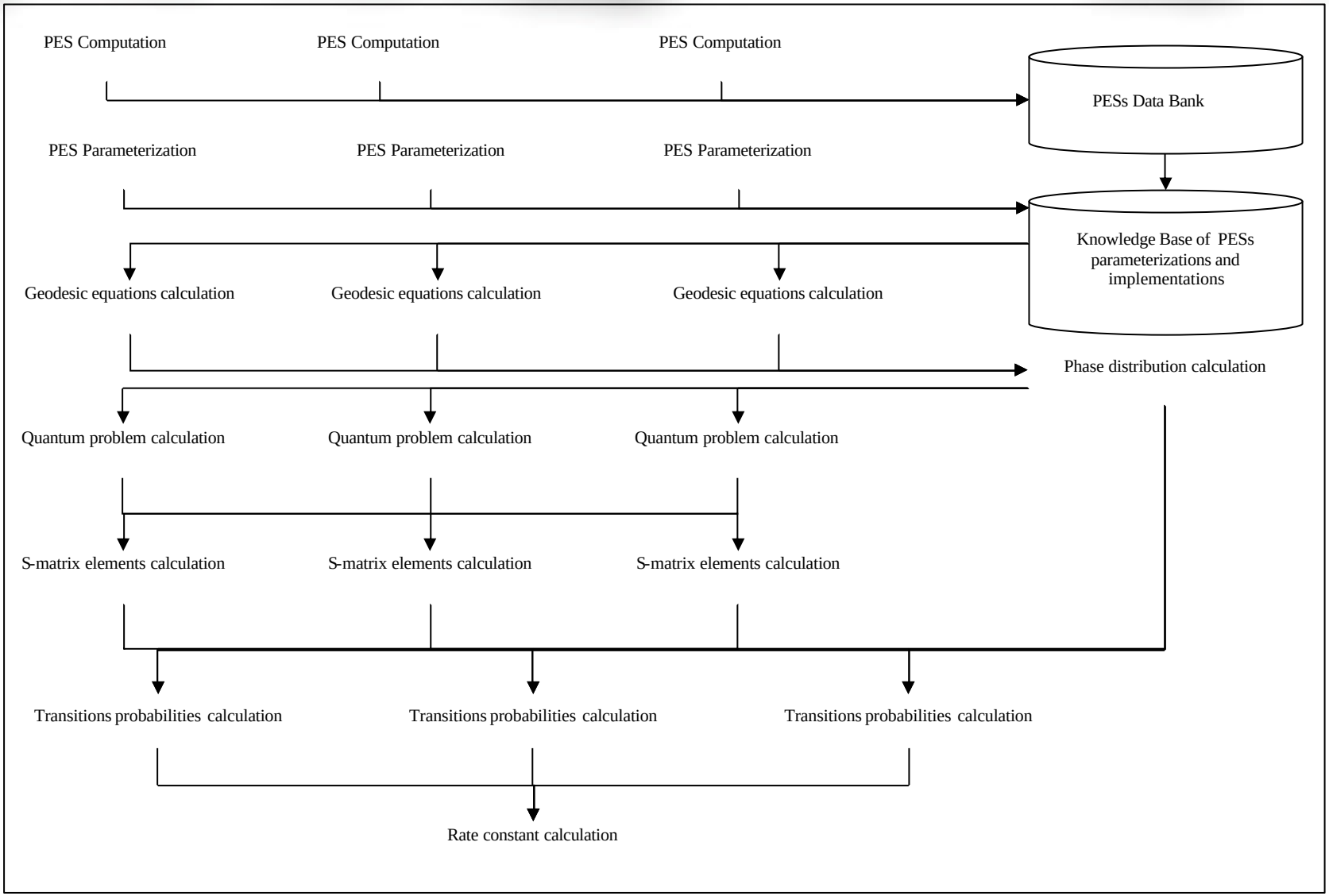
- PES computation,
- PES parametrization,
- Lagrangian surface computation,
- Action increment computation,
- Integral representation for S-matrix and probabilities computation

Grid for chemical reactions calculation

Steps for the solution of the reactive scattering problem

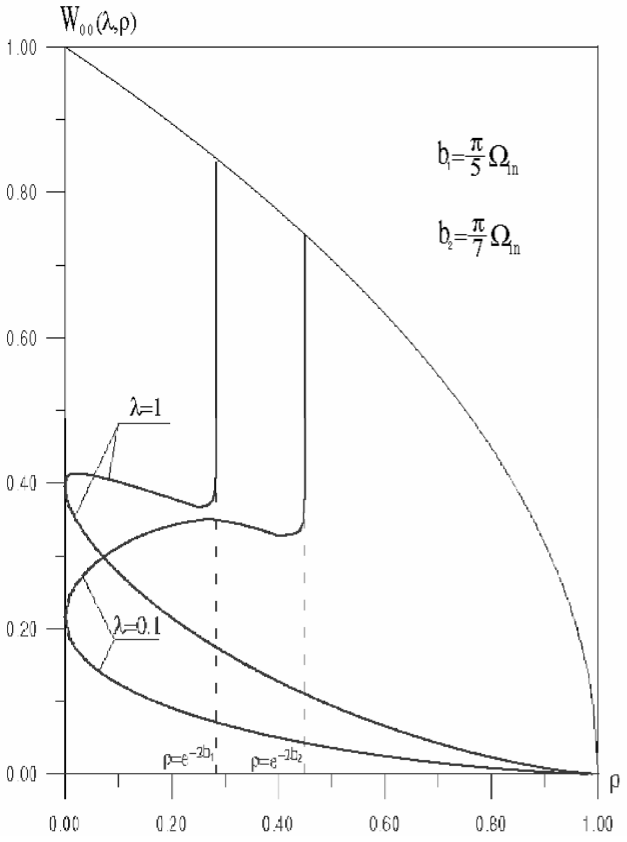
- *Computation of PES.*
- *Parameterization of PES.*
- *Solution of geodesic trajectory problems on Lagrange surfaces of the three-body system and the construction of the trajectory tubes distribution.*
- *Calculation of the quantum system evolution on the trajectory tubes.*
- *Computation of -matrix elements and reaction probabilities for a set of initial phases and collision energies .*
- *Averaging of -matrix element amplitudes over distribution of trajectory tubes, i.e. calculation of probabilities of elementary reactive quantum transitions.*
- *Visualization of the results.*

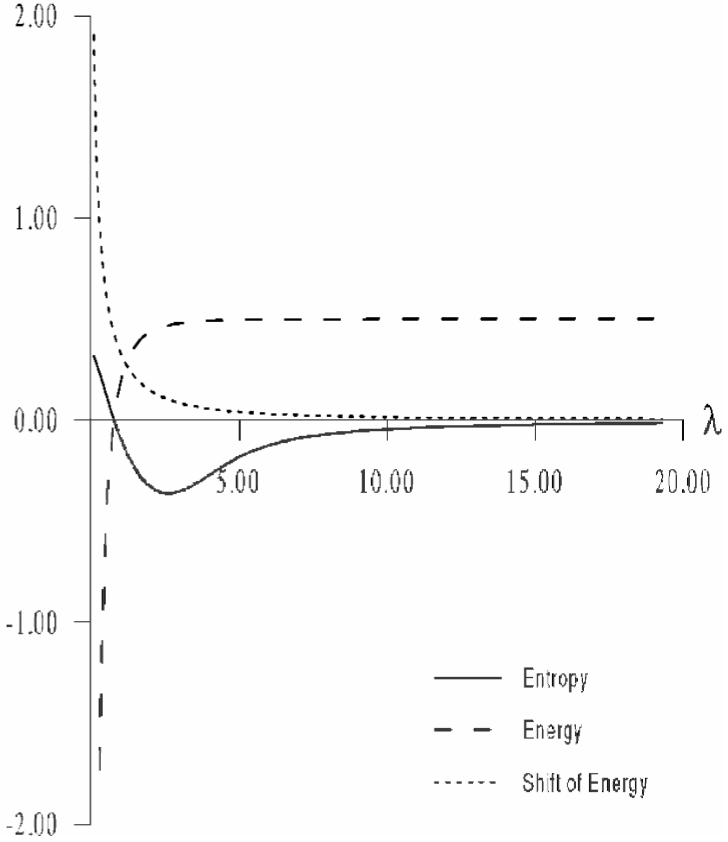
The computational scheme for the problem solution on the grid

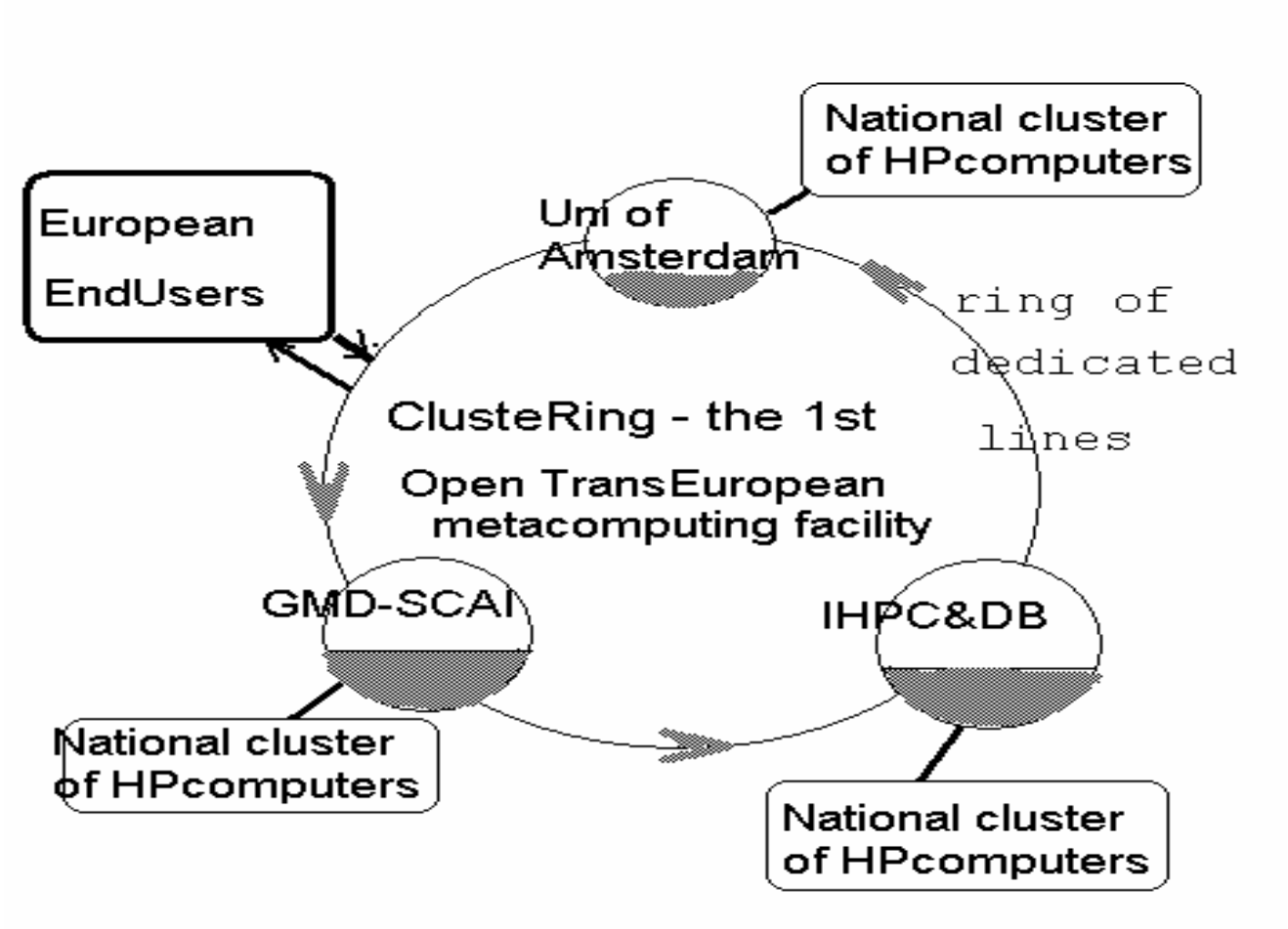


Numerical Example:

Li + (FH) → (LiFH)* → (LiF) + H.






National cluster
of HPcomputers
European
EndUsers
Uni of
Amsterdam
ring of
dedicated
lines
ClusteRing - the 1st
Open TransEuropean
metacomputing facility
GMD-SCAI
IHPC&DB
National cluster
of HPcomputers
National cluster
of HPcomputers

Conclusion

In this paper we have discussed a possible strategy for solving the reactive scattering problem using Grid technology. We believe that this approach offers the best possibility for the practical realization of the immense computational requirements needed for the solution of this problem. Unfortunately, as in many other cases the effective use of grid possibilities makes it necessary to build new problem solving environment for each particular class of problems and substantially change applied codes and sometimes even pertinent algorithms