

# Chimie quantique ab-initio: code DIRCCR12-OS explicitement corrélé

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- Une collaboration européenne
  - J. Noga, Bratislava, Pr invité 2/3 mois par an depuis 4 ans sur contingent UFR de Physique
  - COST chemistry action D26/012/02
    - Wim Klopper, U. Karlsruhe...
  - Ouverture du PAI Stefanik avec la Slovaquie en 2004
- Manuel et source sur le web depuis fin novembre 2003:  
<http://www-laog.obs.ujf-grenoble.fr/~valiron/ccr12>

# Approximation de Born-Oppenheimer (BO)

- Les noyaux étant beaucoup plus lourds que les électrons,

$$\frac{m_p}{m_e} \approx 1830$$

– *en première approximation* – la distribution des électrons s'adapte adiabatiquement au mouvement des noyaux

→ une surface de potentiel qui dépend uniquement de la position instantanée des noyaux

→ une dynamique collisionnelle sur cette surface

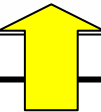
# L'équation de Schrödinger *électronique*

Soit  $\Psi(\mathbf{r}, \mathbf{R}) = \Psi_e(\mathbf{r}, \mathbf{R})\Psi_N(\mathbf{R})$

alors dans l'approximation BO :

$$\hat{H}_e \Psi_e(\mathbf{r}, \mathbf{R}) = E^{\text{eff}}(\mathbf{R}) \Psi_e(\mathbf{r}, \mathbf{R})$$

$$\hat{T}_e = - \left( \frac{\hbar^2}{2m_e} \right) \sum_i^{\text{electrons}} \Delta_i$$

$$\hat{V} = - \sum_i^{\text{electrons}} \sum_k^{\text{noyaux}} \frac{Z_k e^2}{r_{ik}} + \sum_{i < j}^{\text{electrons}} \frac{e^2}{r_{ij}} + \sum_{k < l}^{\text{noyaux}} \frac{Z_k Z_l e^2}{R_{kl}}$$


# Synoptique des approximations en ab-initio non relativiste

	Hartree-Fock	<i>Amélioration du traitement de la corrélation électronique</i> →	Full CI
<i>Amélioration de la base</i> ↓		<i>Plus une 3e dimension du tableau pour la prise en compte des effets relativistes, etc.</i>	
Base infinie	Limite Hartree-Fock	<b>DIRCCR12-OS</b>	Solution « exacte »

# R12 theory in a nutshell !

Electron-electron cusp condition (T. Kato, 1957)

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \left(1 + \frac{1}{2}r_{12}\right)\Psi(\vec{r}_1, \vec{r}_1, \dots, \vec{r}_n) + \mathcal{O}(r_{12}^2)$$

which implies

*See a nice proof in I. Mayer's book*

$$\lim_{r_{12} \rightarrow 0} \left( \frac{\partial \Psi}{\partial r_{12}} \right)_{av} = \frac{1}{2} \Psi(r_{12} = 0).$$

is not fulfilled by any conventional CI-like approach

*R12 methods avoid explicitly correlated geminals and corresponding many-electron integrals by introducing an approximate one-electron ansatz (W. Kutzelnigg, 1985).*

Max angular momentum **L** on atoms → truncation error

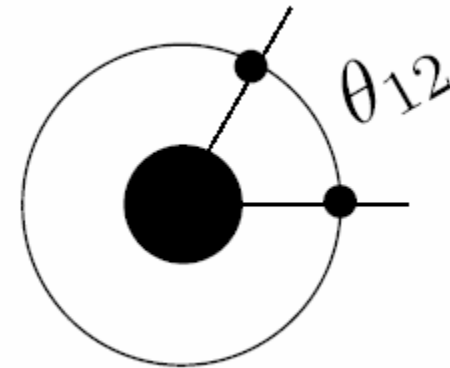
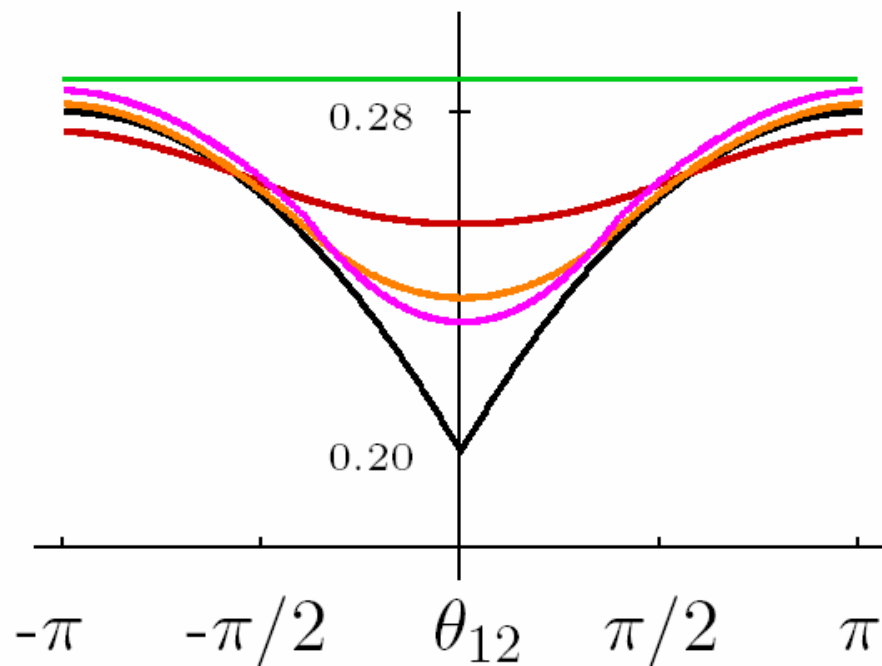
**(L+1)<sup>-3</sup>** for any conventional CI-type expansions

**(L+1)<sup>-7</sup>** for R12-type methods

*Same behaviour for intra- and inter-molecular properties...*

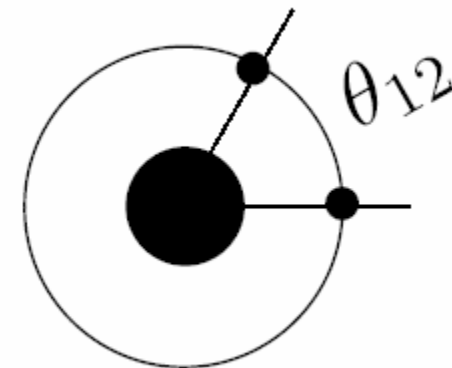
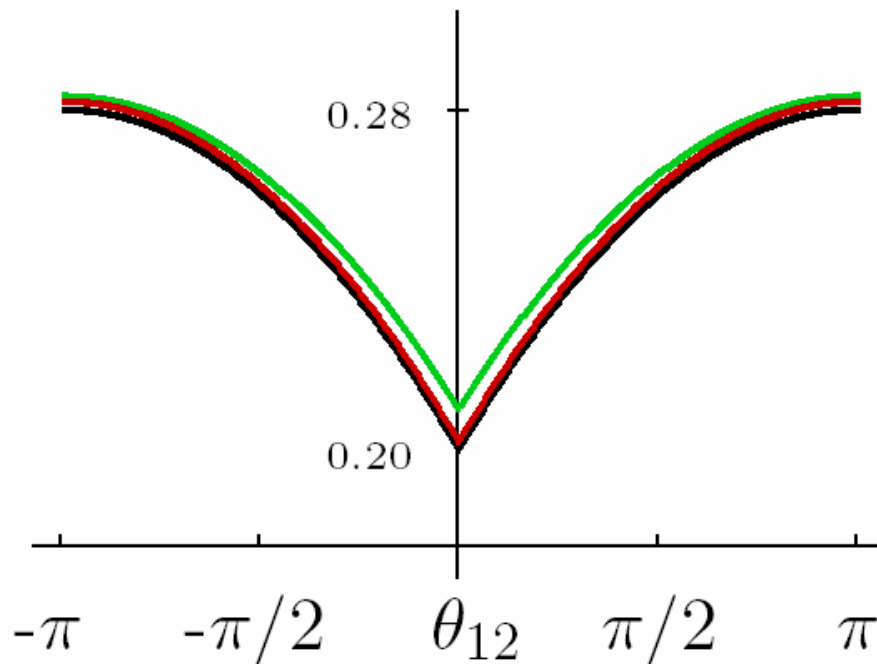
*R12 corrects for basis set angular incompleteness and (mostly) for BSSE*

# He angular cusp with saturated **s**, **sp**, **spd**, **spdf**



*Picture borrowed from S. Kedzuch's diploma.*

# He angular cusp with R12-saturated **s**, **sp**, **spd**, **spdf**



*Picture borrowed from S. Kedzuch's diploma.*

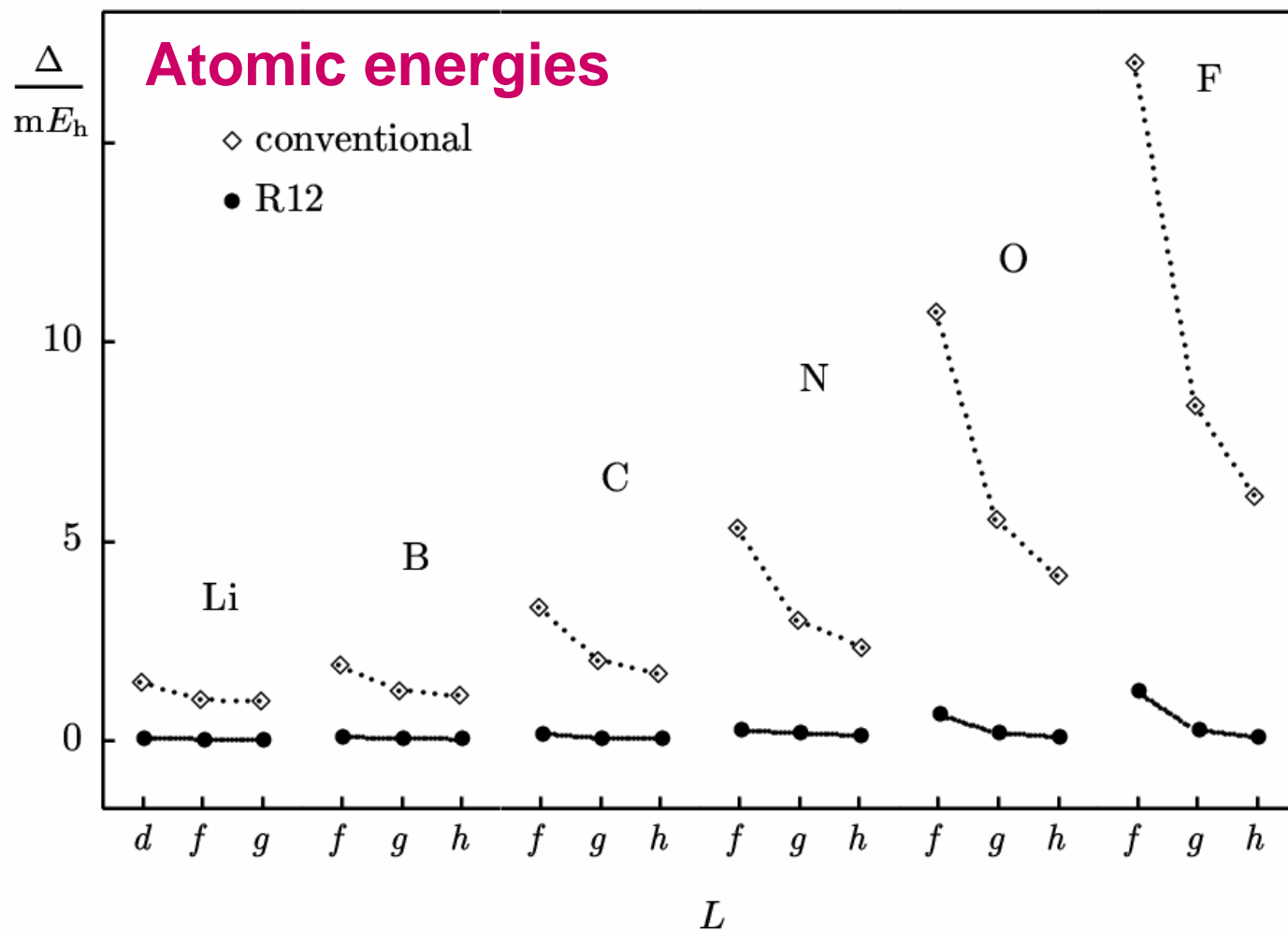


Fig. 1 Errors ( $\Delta$ ) of the CCSD and CCSD-R12 atomic energies with increasing maximum angular momentum functions included in the basis. Subsets of the  $19s11p6d5f4g$  parent basis set for Li and  $19s13p8d6f4g2h$  bases for other atoms were used.  $\Delta$ s are with respect to the estimated basis set limit CCSD values.



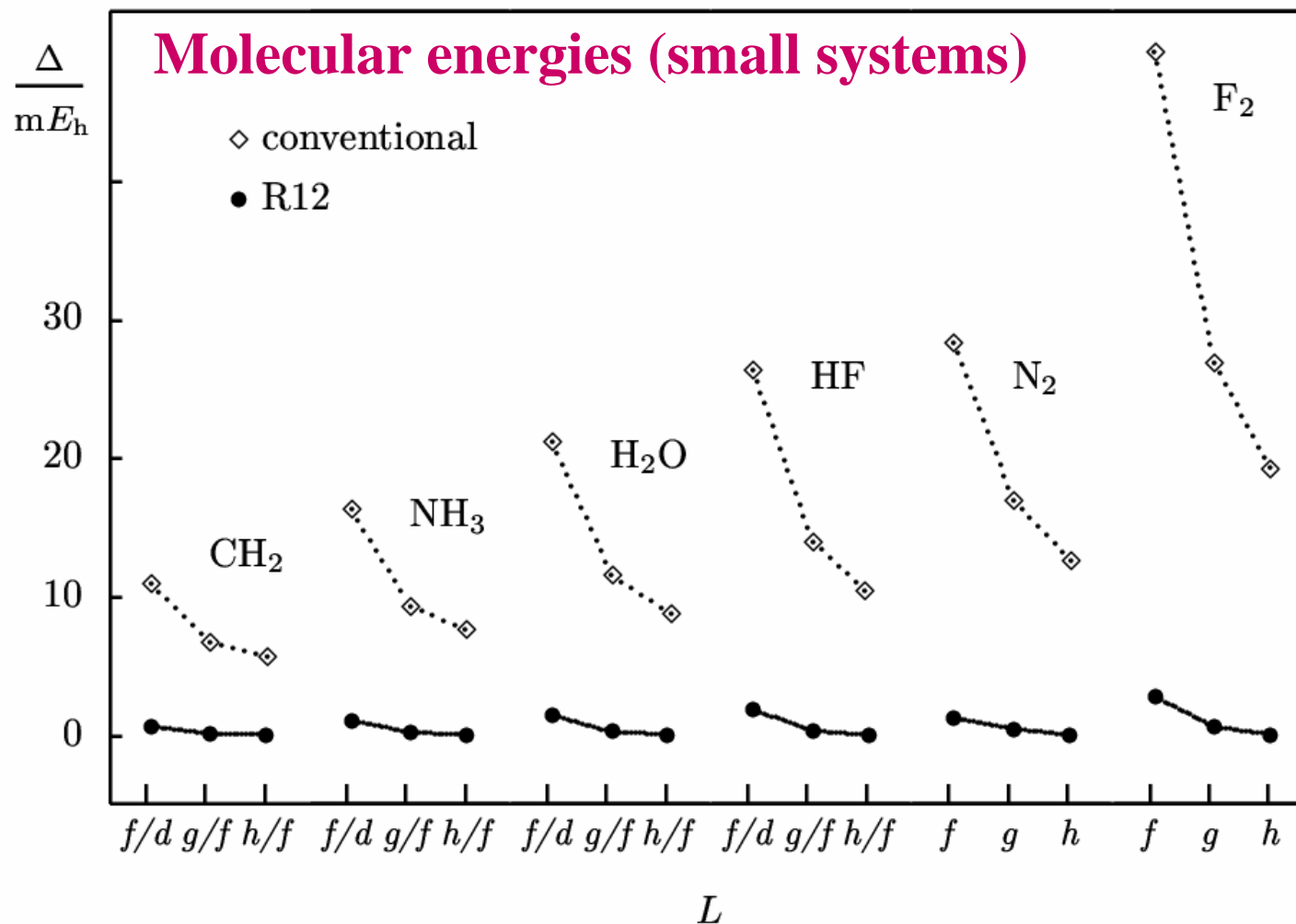
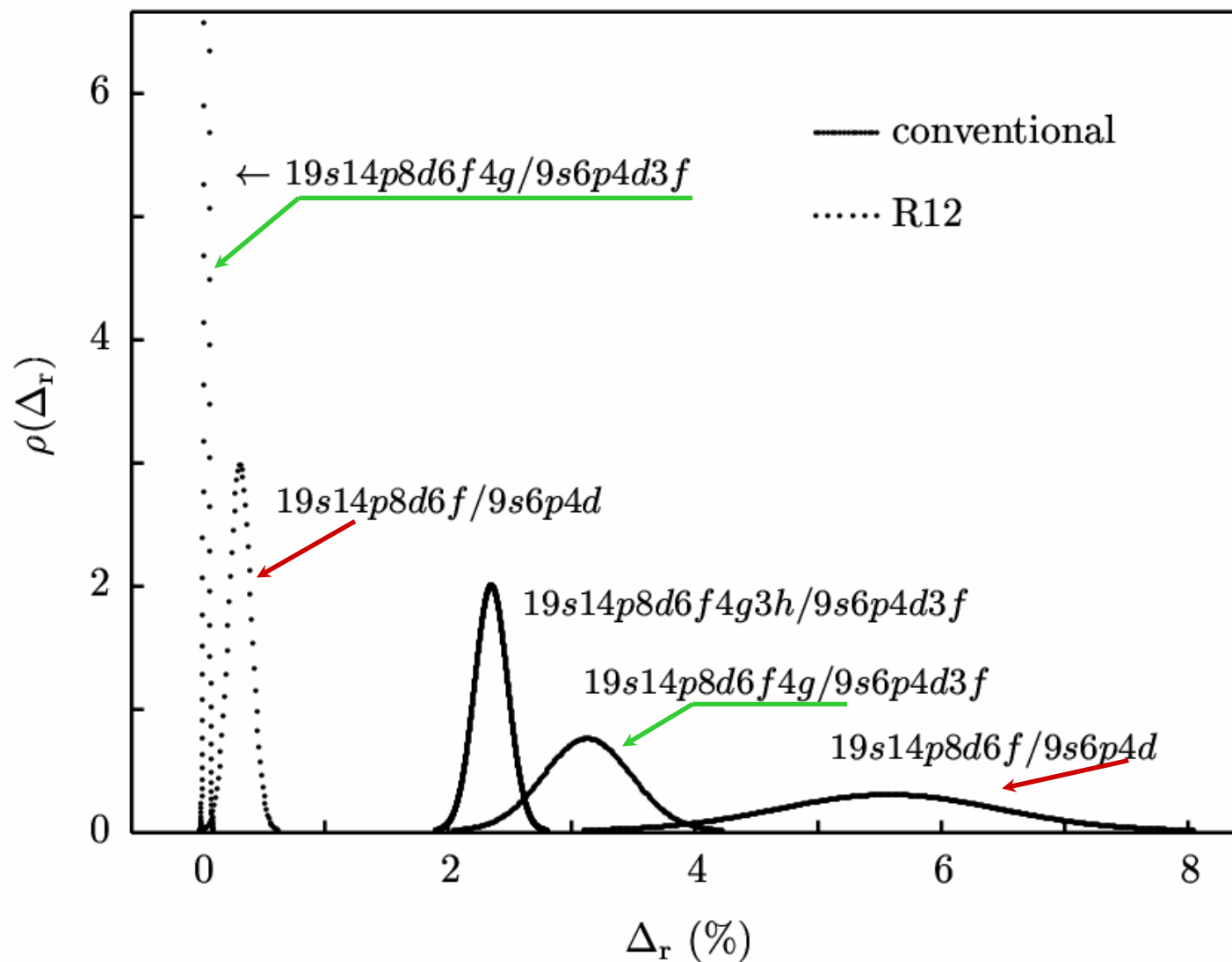
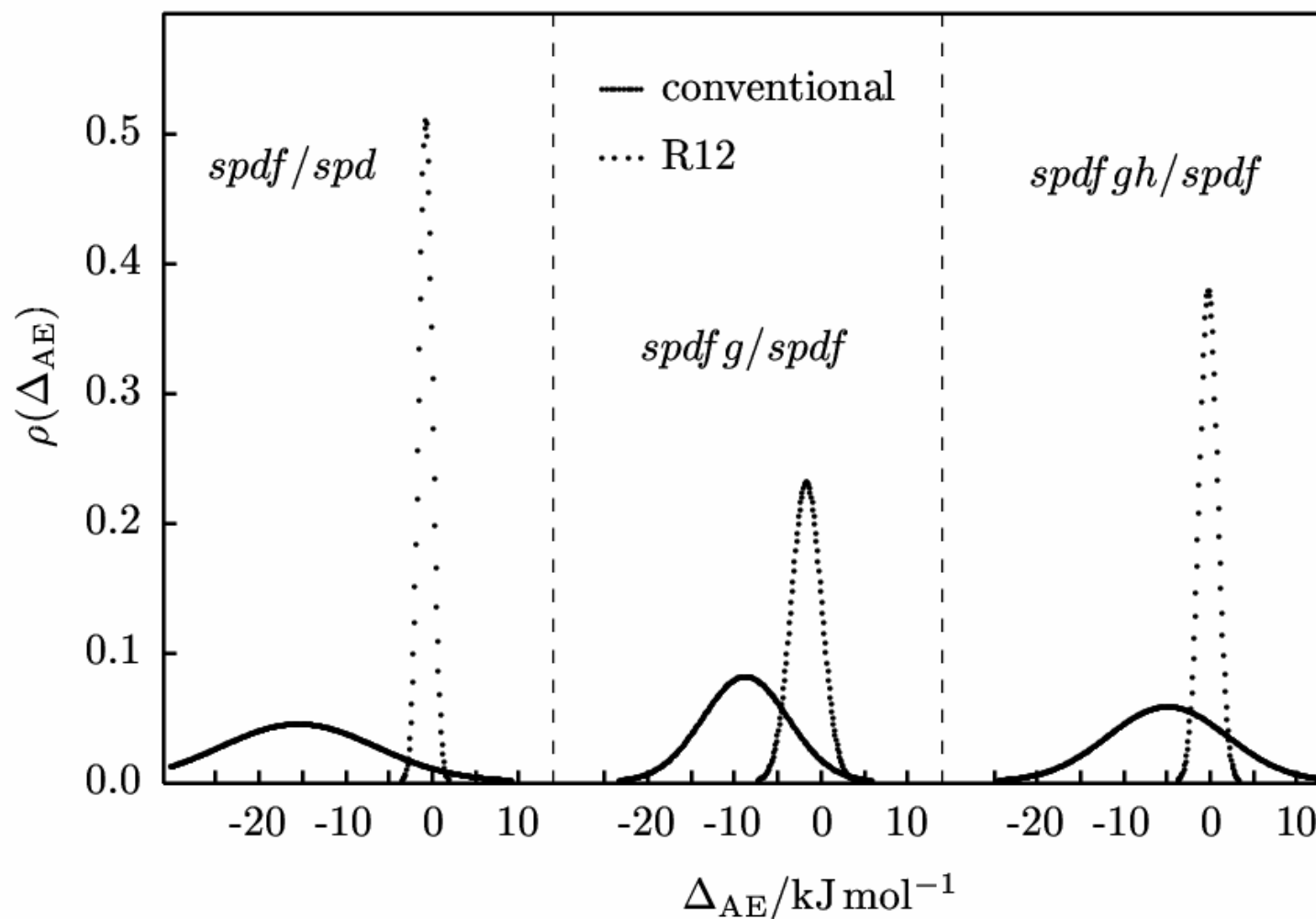


Fig. 2 Errors ( $\Delta$ ) of the CCSD(T)-R12 molecular energies with increasing angular momentum ( $L$ ) functions included in the basis. Subsets of  $9s6p4d3f$  basis for hydrogen and  $19s14p8d6f4g3h$  for other atoms were used. The conventional values are approximated by taking the cusp correction contributions from MBPT(2)-R12. For details see the text.

## Convergence study of molecular energies



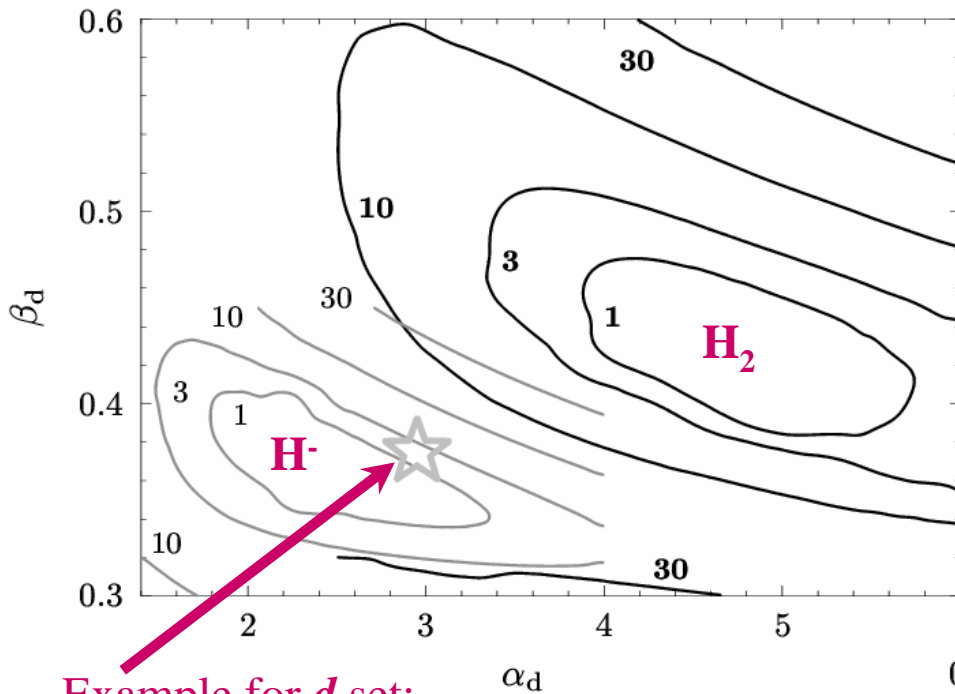
## Atomization energies: comparison to experiment



→ R12 uncertainties are dominated by **method limitations** at CCSD(T) level

# Some references for R12

- ✓ CC-R12 theory review by J. Noga, W. Klopper and W. Kutzelnigg in *Recent advances in coupled cluster methods*, Ed. by Rodney J. Barlett, World Scientific 1997.
- ✓ Open shell developments and **error estimators**: J. Noga and P. Valiron, 2000, *CPL* **324**, 166; J. Noga, P. Valiron and W. Klopper, 2001, *JCP* **115**, 2022.
- ✓ Progress review by J. Noga and P. Valiron, 2002, *Computational Chemistry: Reviews of current trends*, Vol. 7, Ed. by J. Leszczynski, World Scientific, p 131.

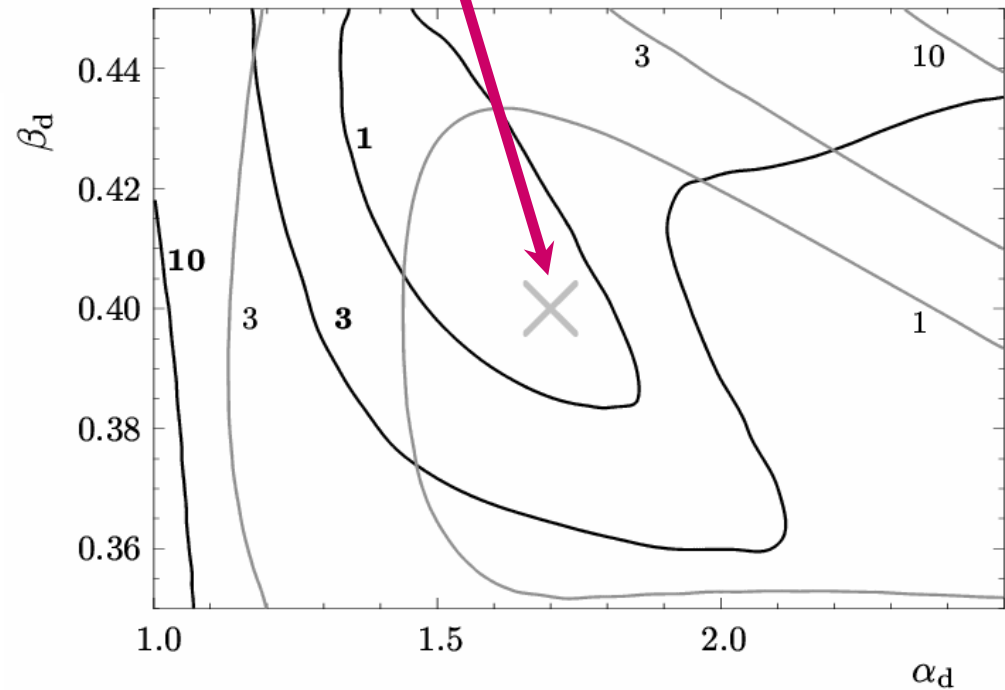


R12 suited basis set:  
 optimal  $d$  and  $f$  sets for *both*  
 $H_2$  and  $H^-$  *within*  $1 \mu E_h$ .  
 Outperforms aug-cc-pV5Z (80  
 AO's) with only 68 AO's.

Example for  $d$  set:

Conventional parent basis for H  
 (aug-cc-pV5Z quality).  
 Optimal exponent parameters  
 for  $H_2$  and  $H^-$  differ.

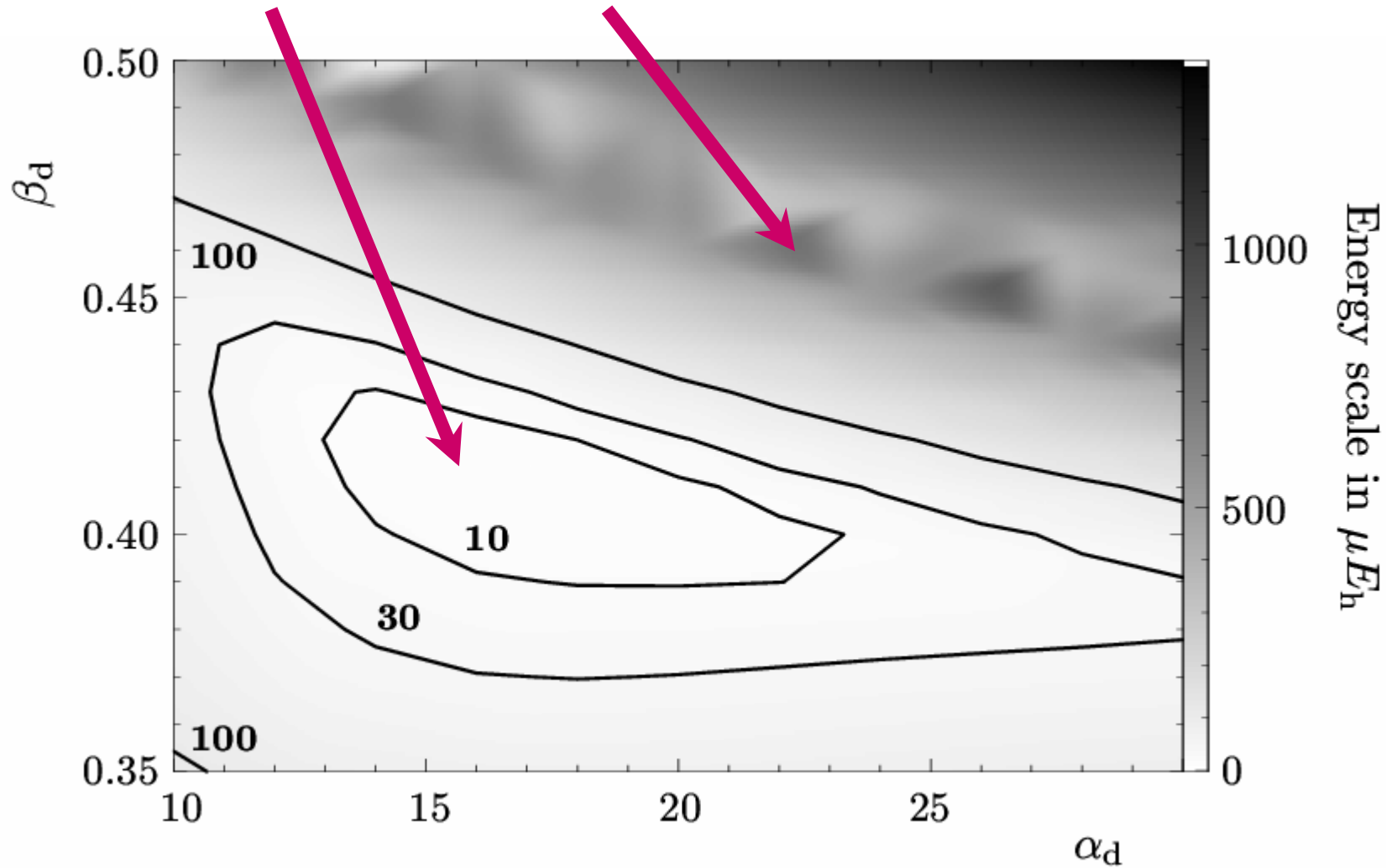
Example for  $d$  set:



# Hydrogen set

# Carbon set : Optimizing $d$ set for C-

Energy map and instability domains within the required  $spdf$  set

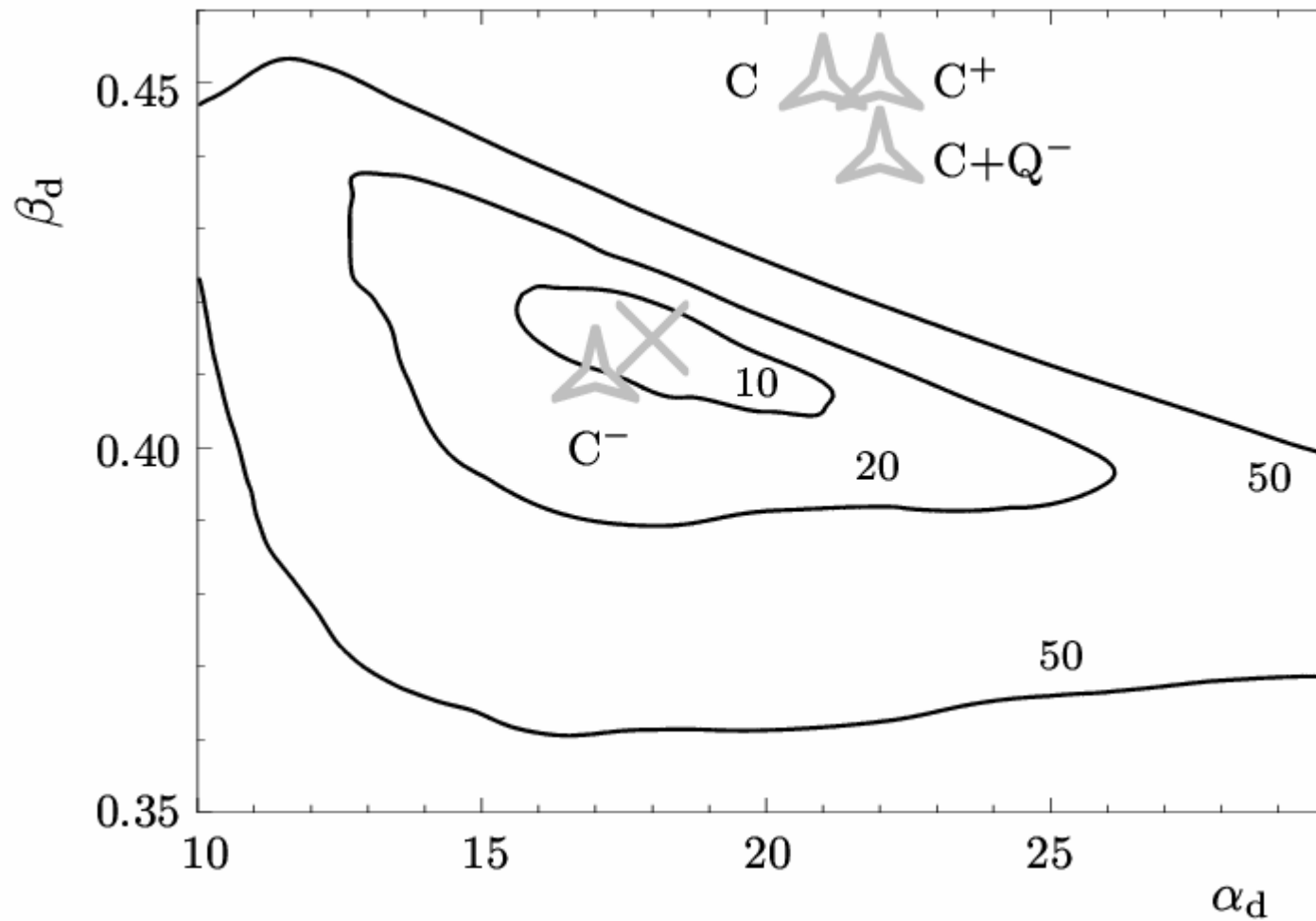


# « Maximum error map » for Carbon.

Optimal  $d$  and  $f$  sets within  $10 \mu E_h$  for C, C+Q, C<sup>+</sup>, C<sup>-</sup>.

Vastly outperforms aug-cc-pCV5Z (181 AO's) with only 141 AO's.

Example for  $d$  set



# Bases R12 disponibles ?

- H , He
- Li, Be, B, C, N, O, F, Ne
- Possible pour Na à Ar (trouver un esclave !)  
→ *Le soufre serait utile...*
- Limitations au delà pour satisfaire à la “standard approximation”...

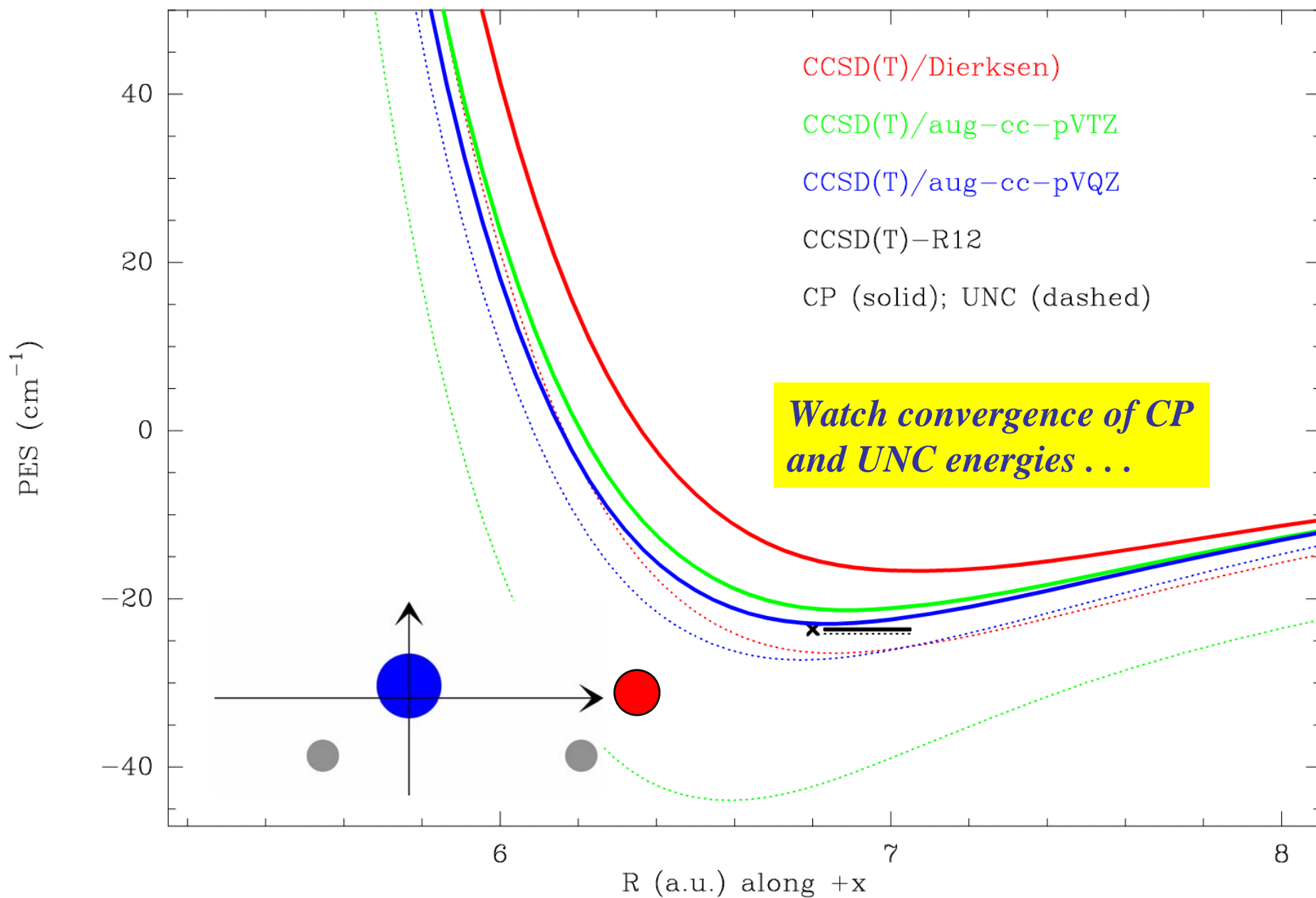


# Ammonia-Helium: illustration of convergence issues

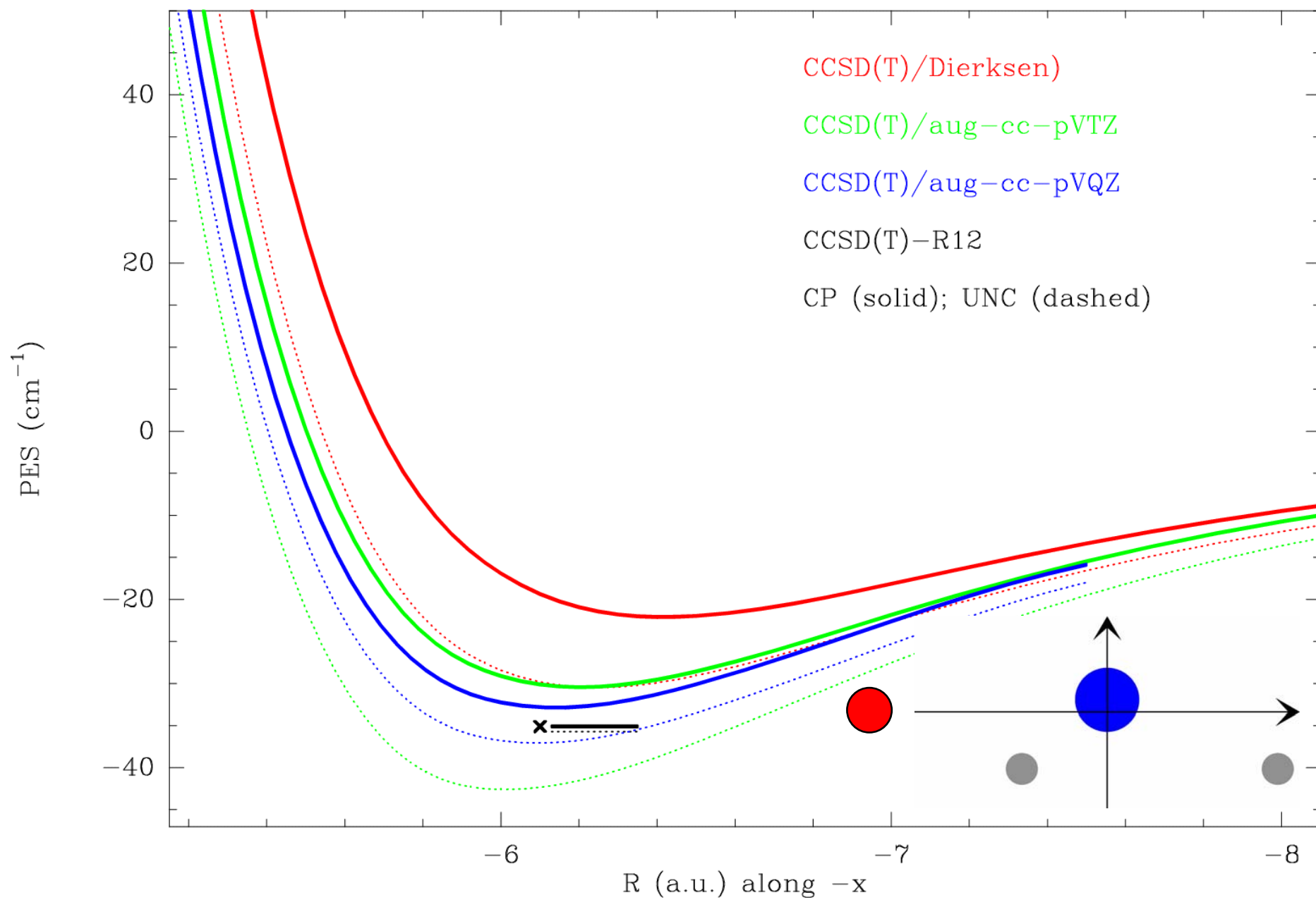
28 octobre 2003

Bratislava, P. Valiron

# Ammonia — Helium



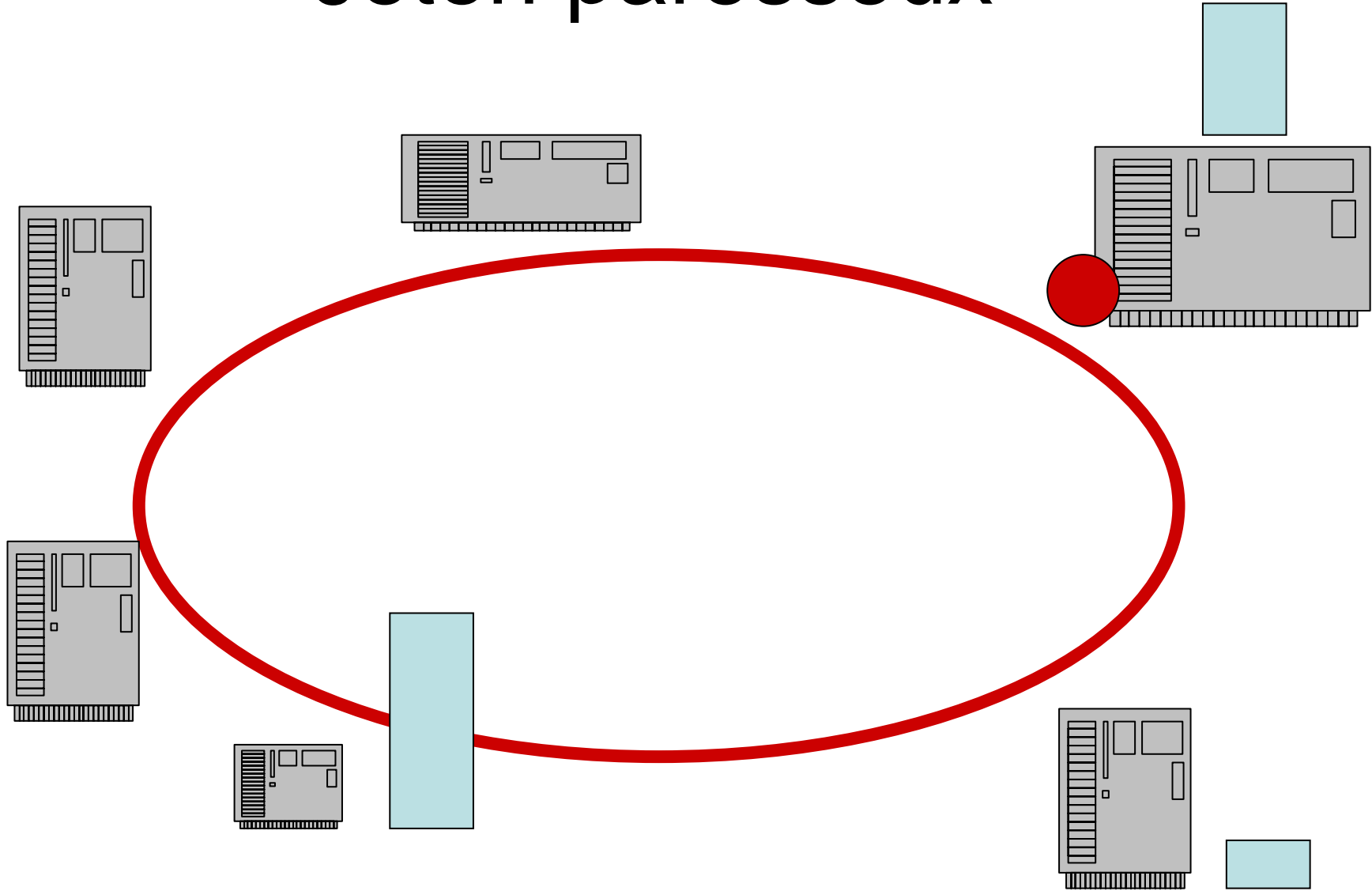
# Ammonia — Helium



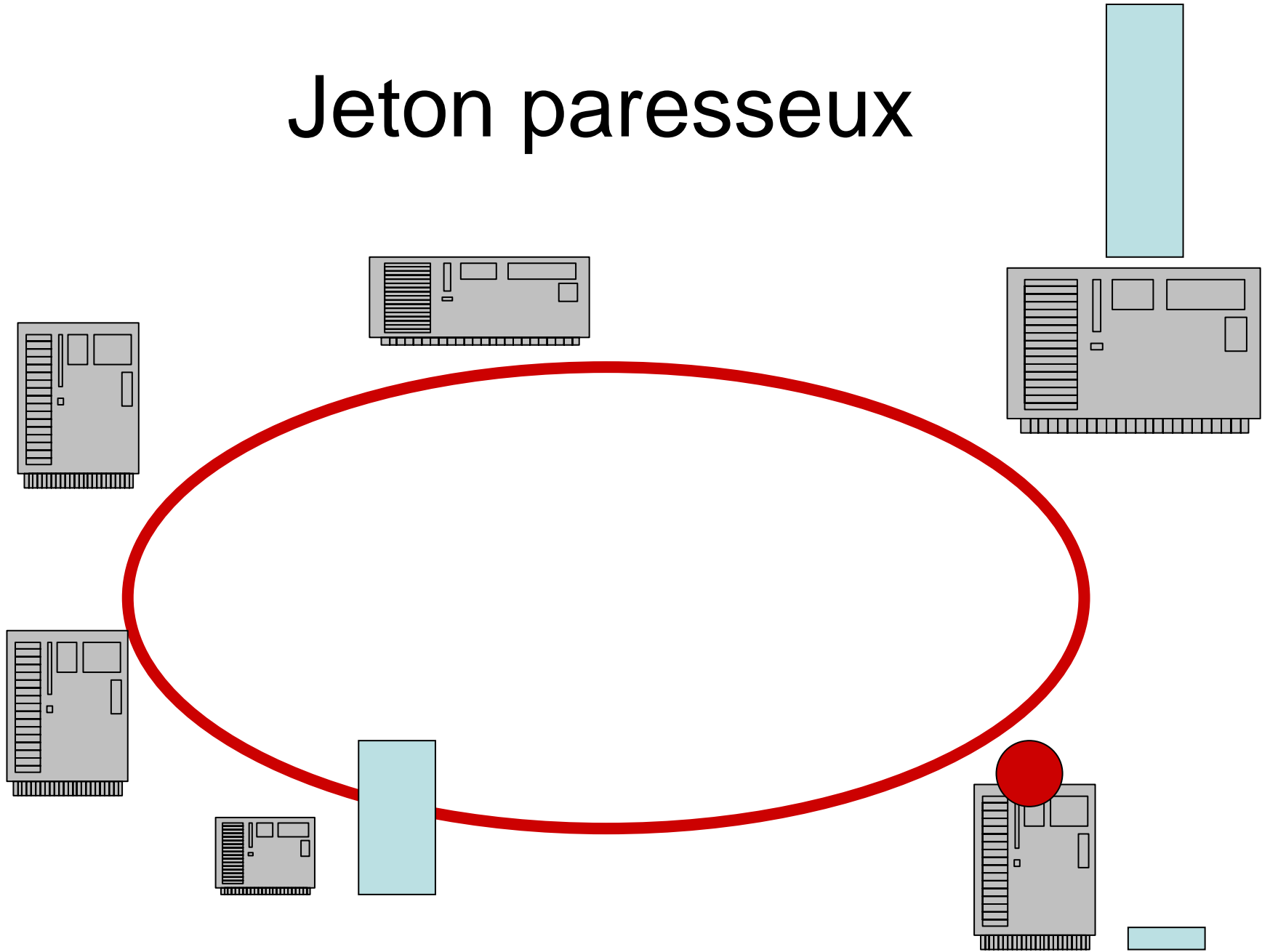
# DIRCCR12-OS

- Un code de production CCSD(T) avec ou sans R12, référence RHF / UHF / ROHF
  - Implémentation “directe” très performante si  $O^2 < N$ 
    - OK pour tous systèmes “astro” accessibles aujourd’hui avec les bases R12.
    - Plus de 500 Mflops/proc sur zahir
  - Parallélisme MPI **très robuste et très portable**
    - Fortran “à la vanille” avec un zeste de C, compatible gcc+g77
    - Supporte une architecture **hétérogène**
      - Maître 64 bits, esclaves 32/64bits, petits et grands indiens...
    - Découverte auto-adaptative des espaces de travail
    - Equilibrage dynamique auto-adaptatif de toutes les boucles parallèles par circulation paresseuse d’un jeton
      - sans dépendance à la latence du réseau
      - quasiment sans communication
- Le code pourrait tourner efficacement entre Paris et Helsinki !!!!

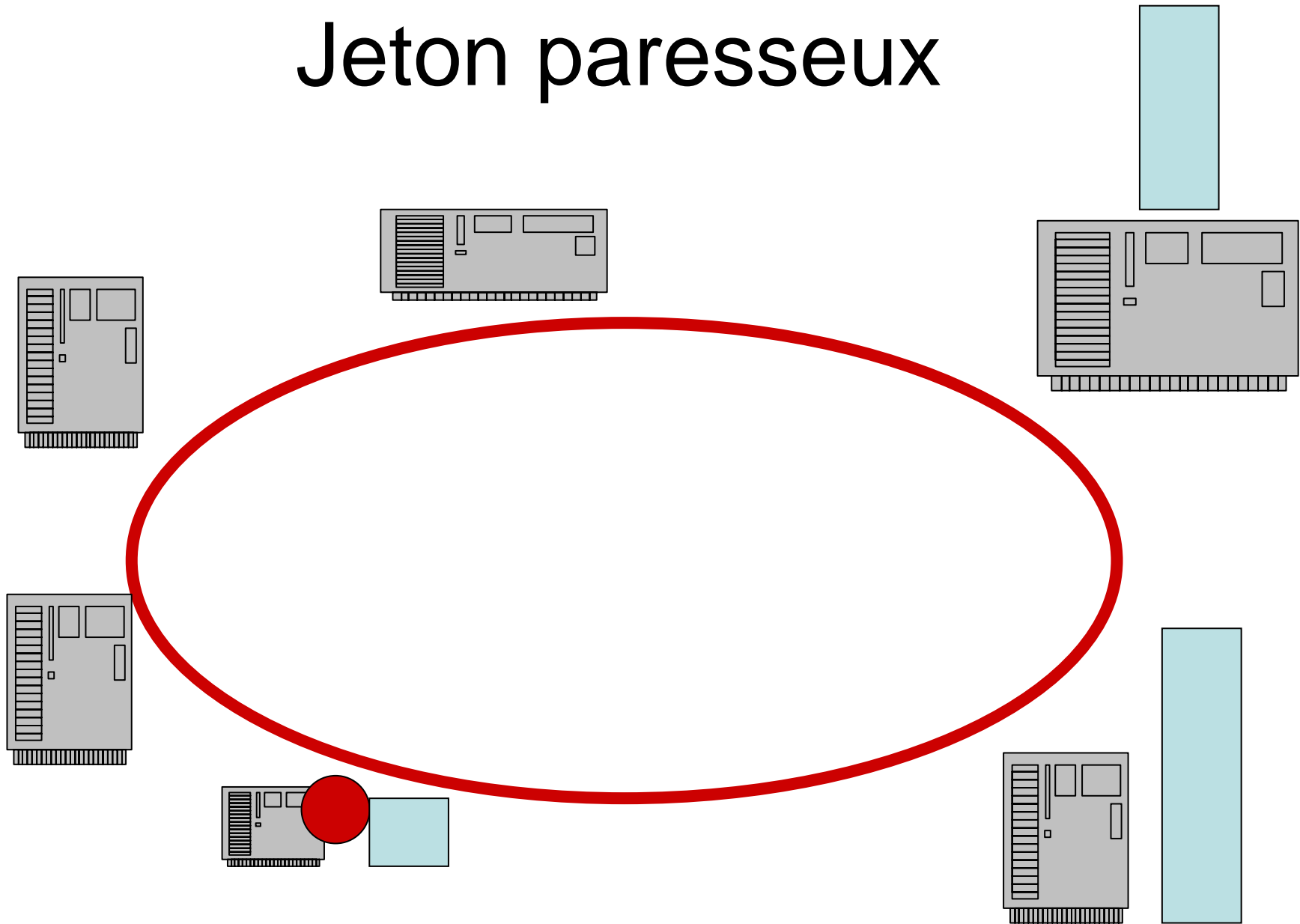
# Jeton paresseux



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# Jeton paresseux

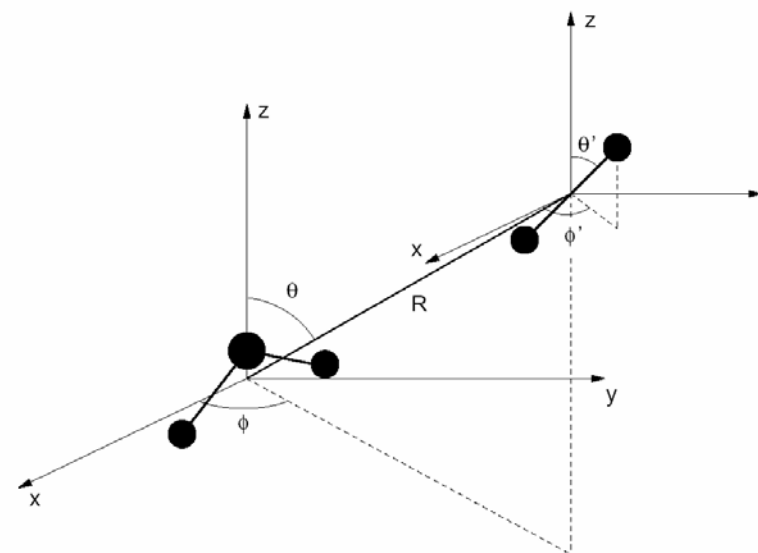
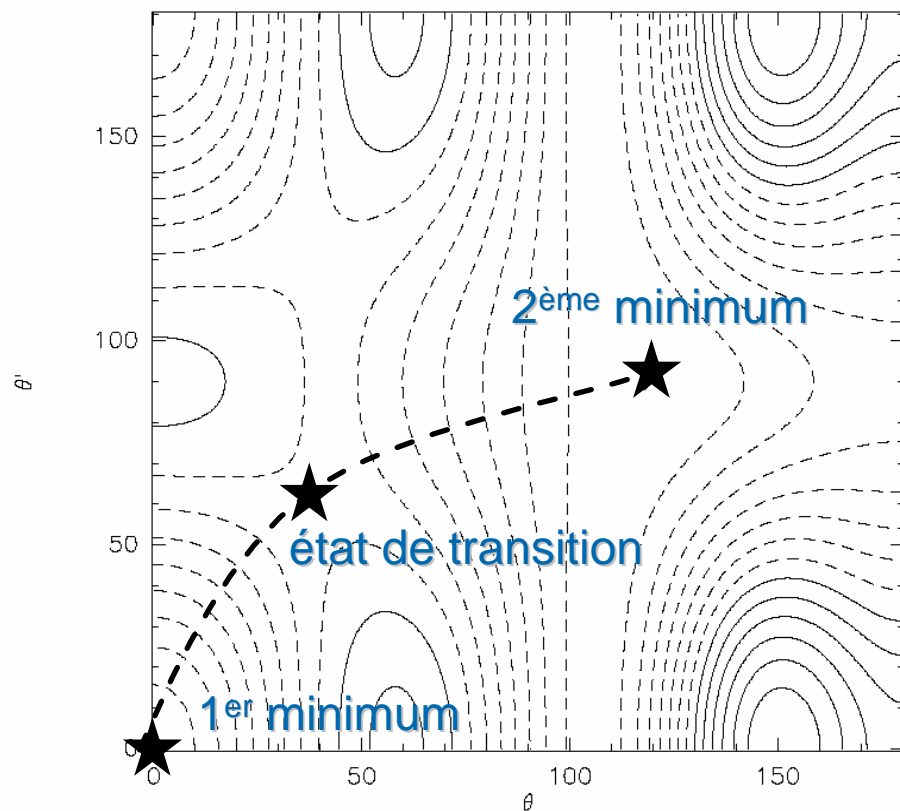


# Quid des surfaces de potentiel?

- Multidimensionnelles  
Ex: H<sub>2</sub>O-H<sub>2</sub>  
5-D si molécules rigides,  
9-D si molécules déformables
- Problèmes d'échantillonnage et d'expansion angulaire en vue des calculs de collision.



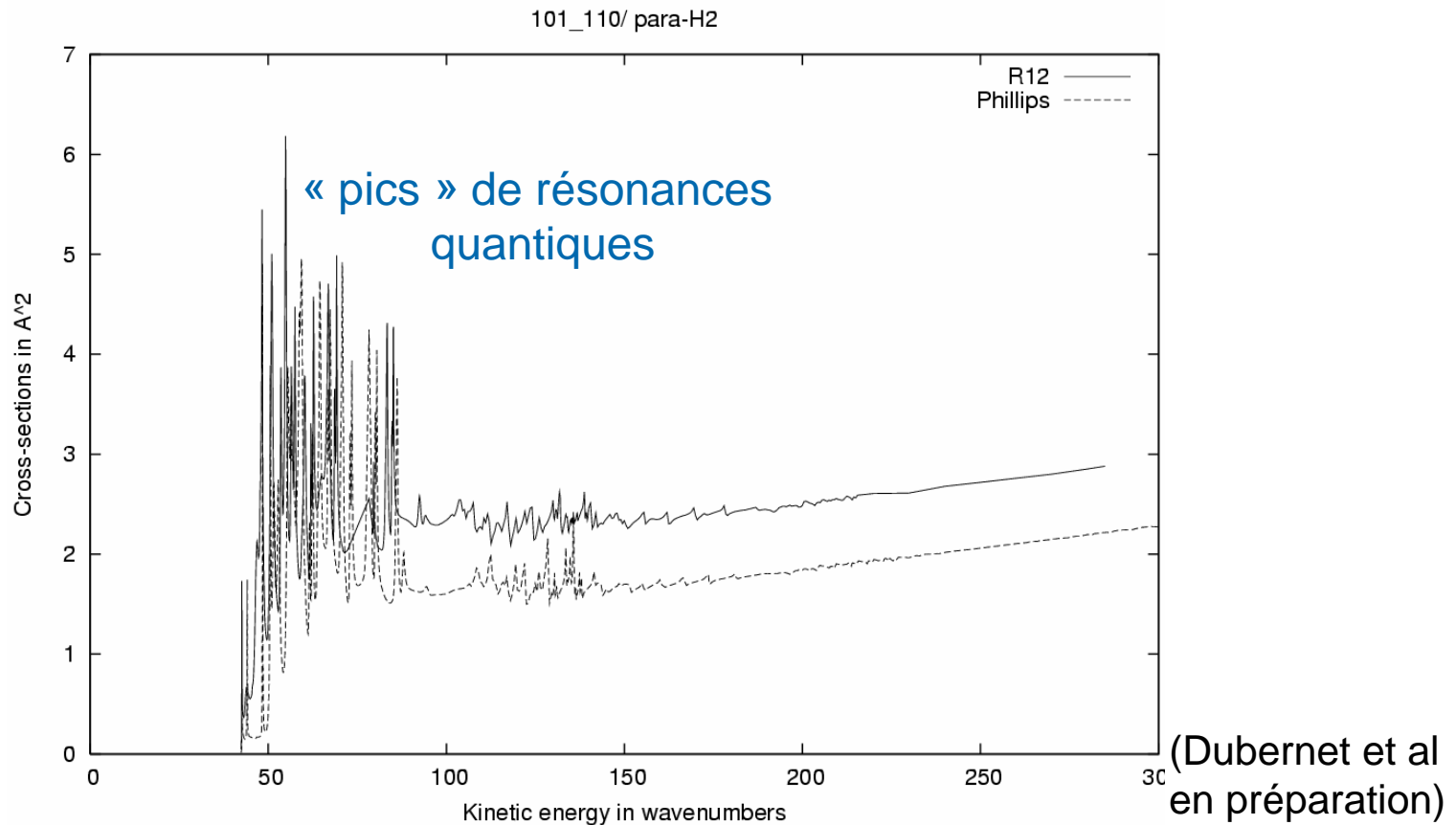
# La surface de potentiel $\text{H}_2\text{O}-\text{H}_2$



(Valiron et al., en préparation)

*La surface de potentiel est l'ingrédient clef pour décrire la dynamique collisionnelle.*

# Les collisions H<sub>2</sub>O-H<sub>2</sub>



*Les calculs des taux de collision sont très sensibles à la topologie de la surface d'énergie potentielle.*

# Ugly details of PES angular expansion

$$V(R, \theta, \phi, \theta', \phi') = \sum v_{l_1 m_1 l_2 l}(R) \bar{t}_{l_1 m_1 l_2 l}(\theta, \phi, \theta', \phi'), \quad (1)$$

where  $\bar{t}_{l_1 m_1 l_2 l}(\theta, \phi, \theta', \phi')$  is the normalized spherical tensor:

$$\begin{aligned} \bar{t}_{l_1 m_1 l_2 l}(\theta, \phi, \theta', \phi') &= \alpha_{l_1 m_1 l_2 l} (1 + \delta_{m_1 0})^{-1} \sum \begin{pmatrix} l_1 & l_2 & l \\ r_1 & r_2 & r \end{pmatrix} Y_{l_2 r_2}(\theta', \phi') Y_{l r}(\theta, \phi) \\ &\times \left[ \delta_{m_1 r_1} + (-1)^{l_1 + m_1 + l_2 + l} \delta_{-m_1 r_1} \right], \end{aligned} \quad (2)$$

with the normalization factor [23]:

$$\alpha_{l_1 m_1 l_2 l} = \left[ 2(1 + \delta_{m_1 0})^{-1} (2l_1 + 1)^{-1} \delta_{l_1 l'_1} \delta_{m_1 m'_1} \delta_{l_2 l'_2} \delta_{l l'} \right]^{-1/2}. \quad (3)$$

# Error estimator for a random sampling

The error on least square fit coefficient is given by

$$e_{\alpha_i} = \alpha_i - \beta_i = S_{ij}^{-1} \langle g_j | R^{th} \rangle_N$$

For any random sampling all nodes are equivalent and the weight ( $w_k$ ) is uniform over the whole surface  $w_k = \tau/N = \int d\vec{r}/N$ . The Montecarlo theorem gives a statistical estimate of the random quadratures  $\langle g_i | R^{th} \rangle_N$ .

We show in the appendix that

$$e_i \sim \sqrt{\frac{\tau}{N}}^{rms} \|S^{-1}\| (1 - \rho(n, N))^{-1/2}$$

with

$$\rho(n, N) = \frac{(|\|S^{-1}\| n - 1|)}{N} < 1$$

Where the  $S^{-1}$  matrix norm is chosen as it's maximum eigenvalue :

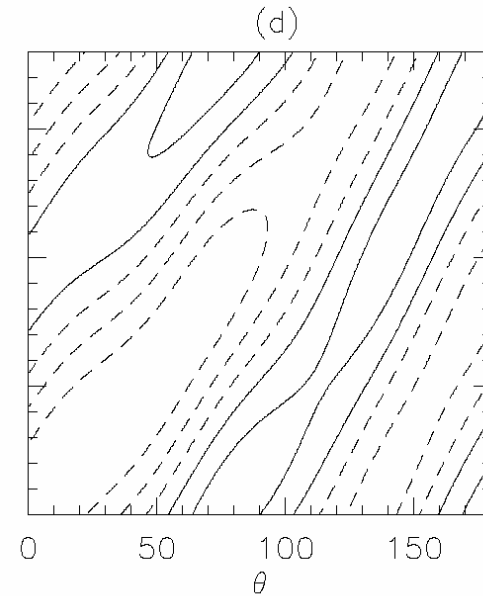
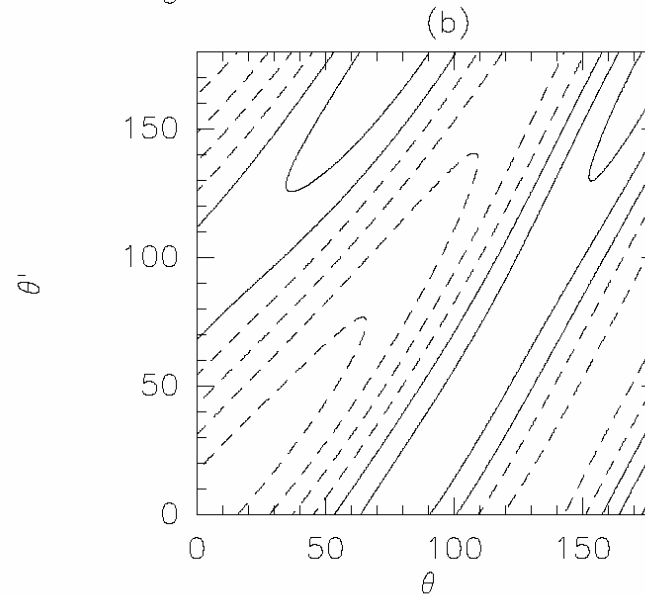
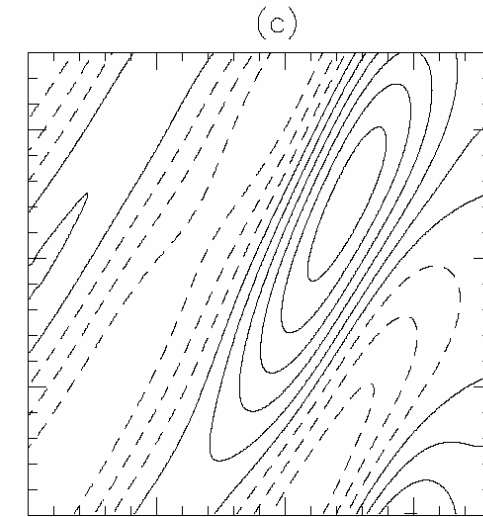
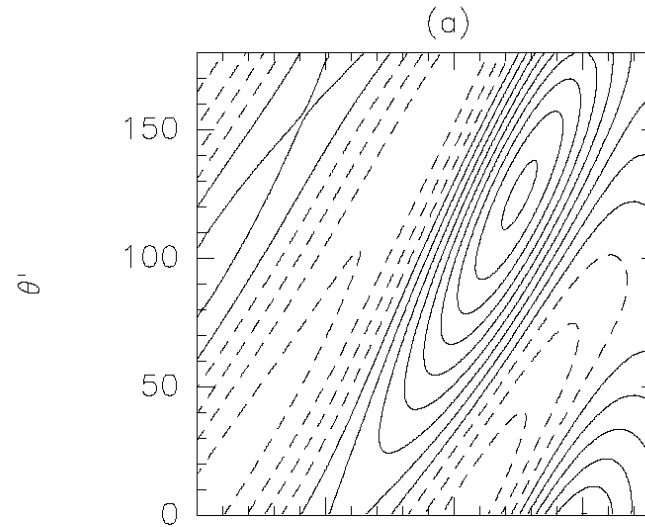
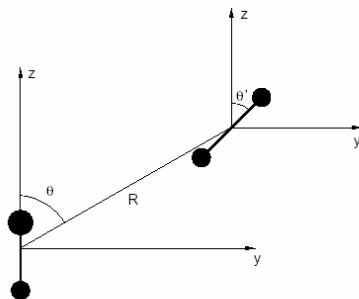
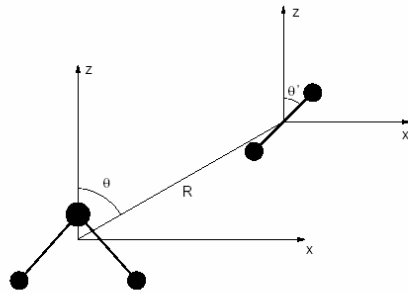
$$\|S^{-1}\| = \text{Max}_i |\lambda_i|$$

***C. Rist, A. Faure et P. Valiron, in preparation***

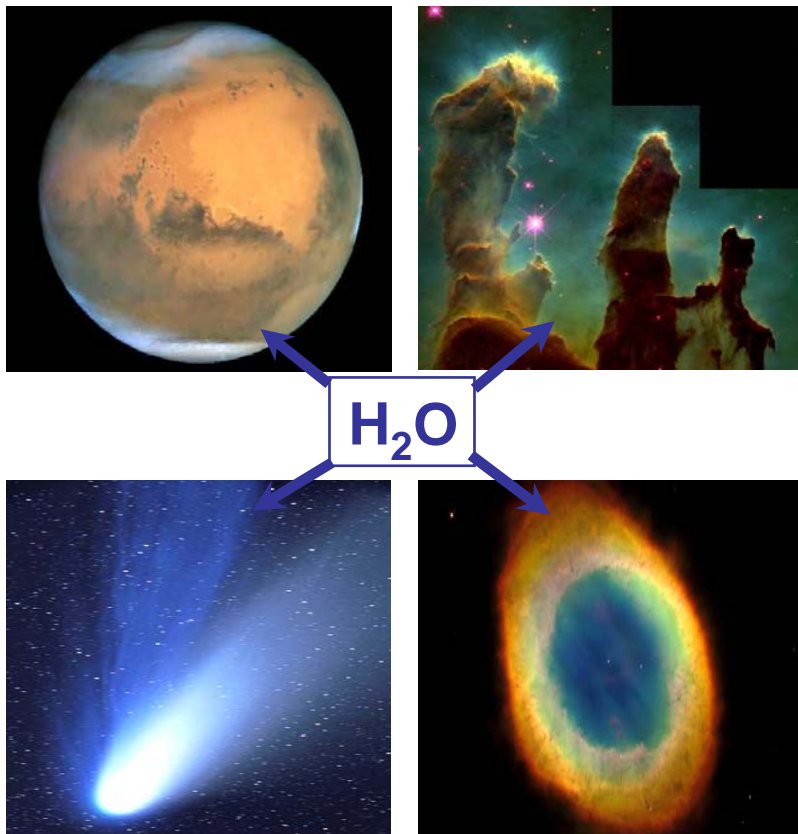
# Illustration of possible instabilities in the angular expansion

Converged (present work)

Poorly converged (PMG94)



# Ubiquitous Water in the Universe



## $H_2O$ , HDO



## HDO ?



### A challenge for molecular physics

- WANTED: accurate excitation rate coefficients for  $H_2O$  and HDO with  $H_2$ ,  $H$ ,  $e^-$ .
- R12 reference calculations for  $cm^{-1}$  accuracy.
- Excitation of  $H_2O$  bending and 9-D effects: a reference benchmark

Noga J., Valiron P., « Explicitly Correlated Coupled Cluster R12 Calculations », *Computational Chemistry: Reviews of Current Trends Vol. 7*, 2002, 131.

# A computational challenge for modeling 9-D intra-molecular effects

- 9-D Monte Carlo importance sampling to include 9-D effects as *corrections* over the accurate 5-D reference surface.
- ~ 500 000 géométries,
- ~ 200 000 CPU hours on our experimental PC grid.



Action Concertée Incitative  
[ACI]  
Globalisation des Ressources  
Informatiques et des Données  
[GRID]



Prospective en matière de  
codes de collision,

Marie-Lise Dubernet-Tuckey