

Une surface de potentiel de référence pour $\text{H}_2\text{O}-\text{H}_2 \dots$

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En 5 étapes . . .

- Choix de grilles adaptées
 - ➔ Monte Carlo et « importance sampling »
- Calibration de la PES « rigid-body »
 - ➔ CCSD(T)-R12
- Prise en compte de la modulation de la PES par la dynamique intra-moléculaire
 - ➔ qqs 10^5 calculs CCSD(T) « légers »
- Expansion angulaire et interpolation sur R et sur les coordonnées intra-moléculaires
- Estimateurs de convergence et d'erreur

R12

Pour une revue:

Noga J. and Valiron P., « Explicitly Correlated Coupled Cluster R12 Calculations », *Computational Chemistry: Reviews of Current Trends Vol. 7*, **2002**, 131, edited by J. Leszczynski, World Scientific, Singapore, New Jersey, London, Hong Kong.

R12 theory in a nutshell !

Electron-electron cusp condition (T. Kato, 1975)

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

which implies

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

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)⁻³ for any conventional CI-type expansions
(L+1)⁻⁷ for R12-type methods

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

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

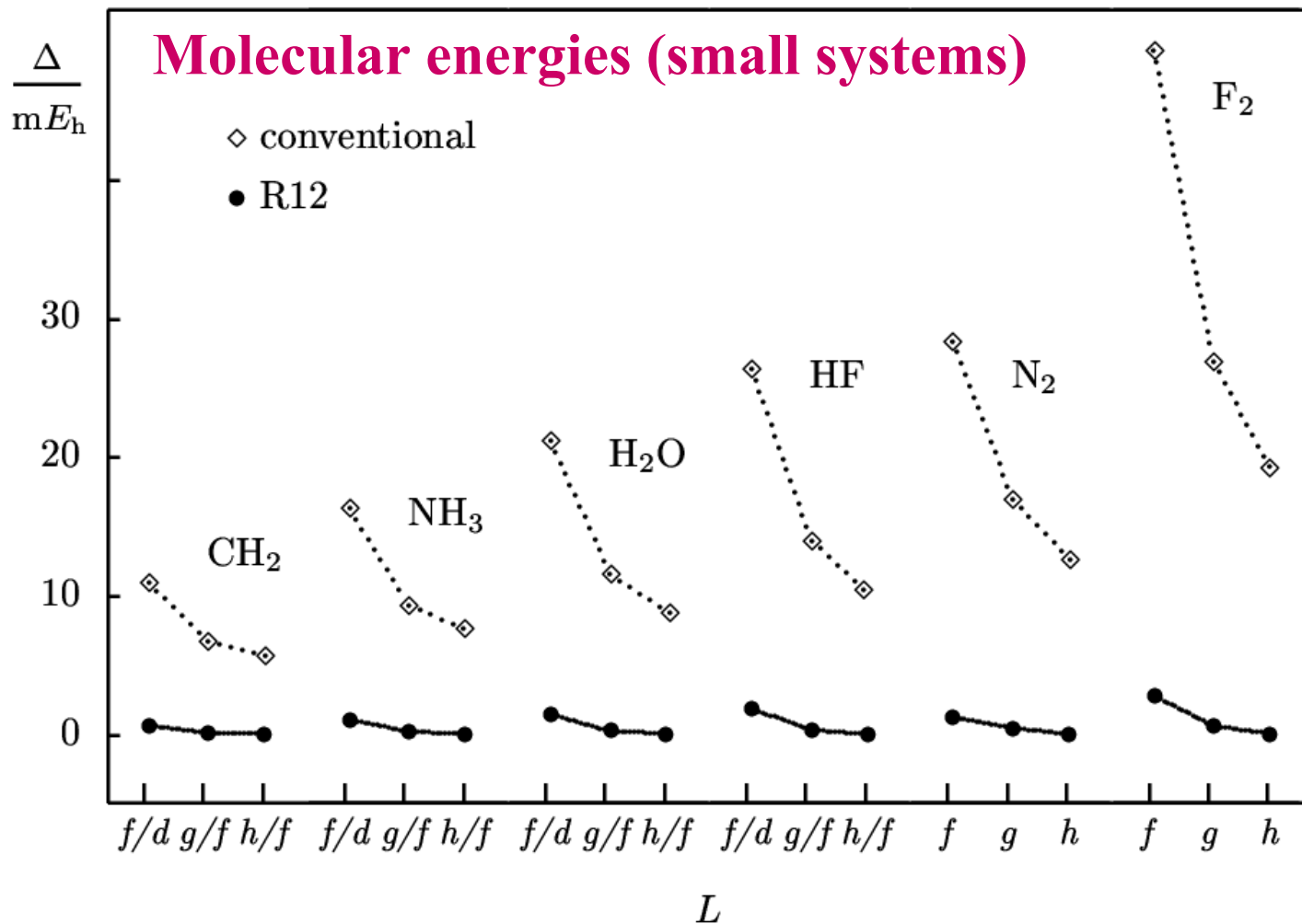
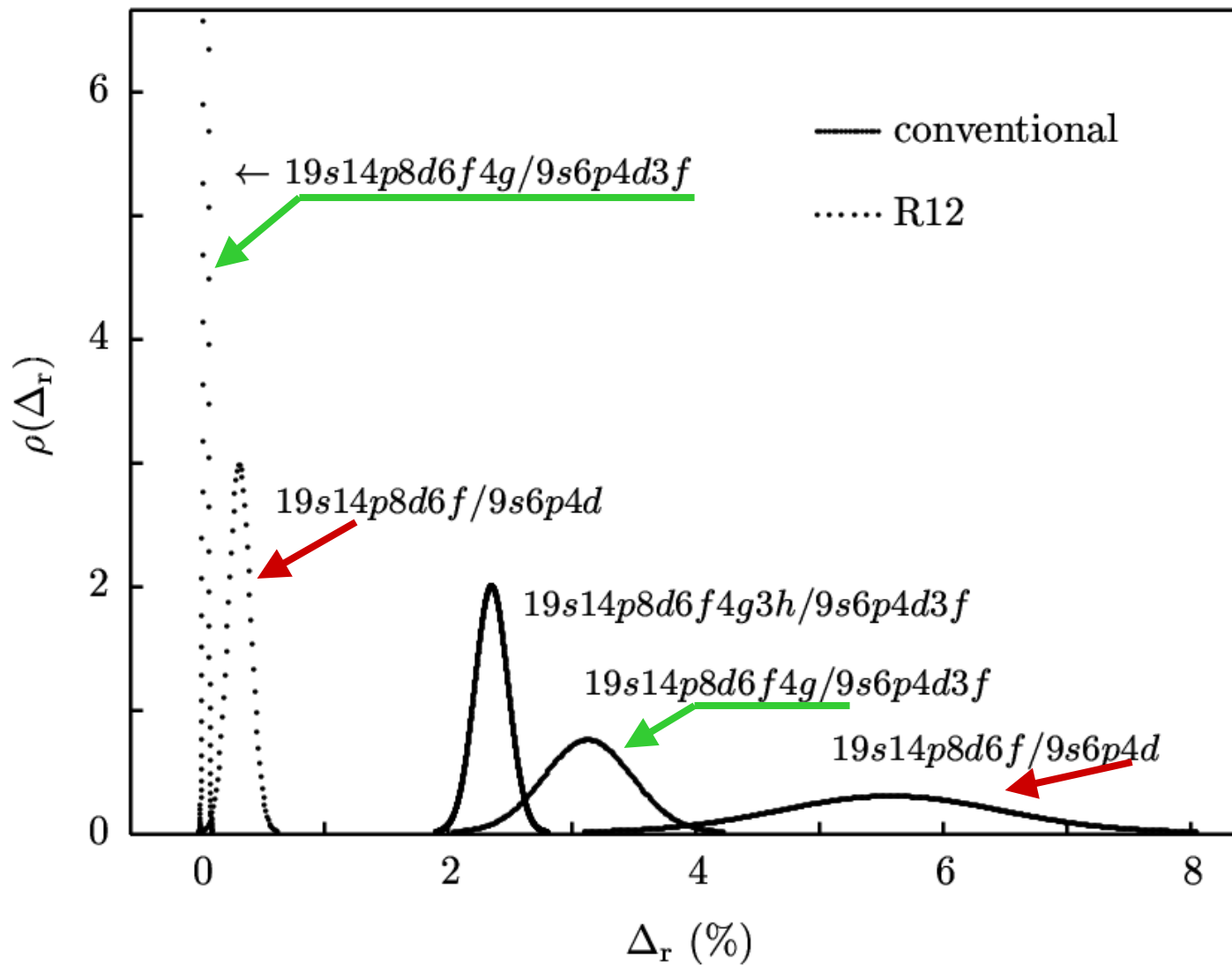


Fig. 2 Errors (Δ) of the CCSD(T)-R12 molecular energies with increasing angular momentum (L) functions included in the basis. Subsets of $9s6p4d3f$ basis for hydrogen and $19s14p8d6f4g3h$ for other atoms were used. The conventional values are approximated by taking the cusp correction contributions from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

Convergence study of molecular energies



Our R12 code supports...

- Closed shell, open shell and ROHF reference
- Approximate triples CCSD(T) and CCSD[T]
- Exact triples CCSDT (*be patient...*)
- Some properties (static multipoles...)

Still lacking support for...

- Gradients
- Multireference coupled cluster or CI
- Excited states
- Non-Born-Oppenheimer couplings

Price to pay for R12...

Large basis sets to fulfill the « standard approximation » for the closure relation of the R12 ansatz:

- saturated s set for H, He, Li and Be;
- saturated $spdf$ sets from B to Ca.

Conventional basis sets need adjustments to fulfill above conditions and might induce numerical instabilities of the R12 amplitudes.

→ *development of « R12 suited » basis sets.*

« Universal » R12 suited basis sets for reliable predictions already available for H, C, N, O...

Valiron P., Kedzuch S. and Noga J., « Avoiding numerical instabilities in R12 calculations through universal R12 consistent basis sets », *Chem. Phys. Lett.*, 2002, accepted.

Noga J. and Valiron P., « Towards universal R12 consistent basis sets », *Collect. Czech. Chem. Commun.*, 2002, soumis.

Premiers résultats R12 pour $\text{H}_2\text{O}-\text{H}_2 \dots$

Plus de 500 géométries déjà calculées mais...

- *40 h CPU par calcul sur SP3 (16 h sur SP4)*
- *70 GO d'espace disque*
- *1 TO d'E/S*

Convergence des calculs coupled cluster explicitement corrélés pour l'interaction H₂-H₂O

Table 8: Monitoring H₂ –H₂O PES (in cm⁻¹)

R	θ	ϕ	θ'	ϕ'	Phillips et al	CCSD(T)-R12 ^a	CCSD(T)-R12 ^b	(T)-[T] ^a
5.0	0	0	0	0	69.6	-12.6	-11.0	0.6
5.0	180	0	180	0	771.9	712.3	713.6	-2.1
6.0	0	0	0	0	-198.4	-220.9	-219.6	0.2
6.0	180	0	180	0	73.48	63.5	65.3	-1.2

^a using the R12-suited basis set truncated to 19s14p8d6f and 9s6p4d for O and H, respectively.

^b using the R12-suited full basis set of 19s14p8d6f4g3h and 9s6p4d3f size for O and H, respectively. These results are expected to be converged better than their difference with previous column, leading to an accuracy of about 1 cm⁻¹ with respect to the basis set.

^c the difference between CCSD[T]-R12 and CCSD(T)-R12 indicates the importance of higher order diagrams towards the full CI, and thus provide an estimator of the method accuracy. Non dynamical and relativistic corrections are not included.

➔ **Précision ~1 cm-1, sans contrepoids, niveau CCSD(T)**

➔ **Convergence comparable hiérarchie full-CI**

Conventions expansion angulaire : c.f. PMG94

Because of rotational invariance, physically meaningful quantities, such as the intermolecular potential, depend only on a smaller number of relative (or body-fixed) angles. In general, one can choose three angles, corresponding to rotation of the system as a whole, in an arbitrary way. A convenient choice does this by fixing the water molecule orientation at $\alpha, \beta, \gamma = 0, 0, 0$ and defining θ, φ and θ', φ' as the collision direction and the H_2 orientation *relative to the water molecule body-fixed axis system*.

In terms of these relative coordinates Eqs. (1)-(2) can be written as

$$V(R, \theta, \varphi, \theta', \varphi') = \sum_{p_1 q_1 p_2 p} v_{p_1 q_1 p_2 p}^{(R)} t_{p_1 q_1 p_2 p}(\theta, \varphi, \theta', \varphi'),$$

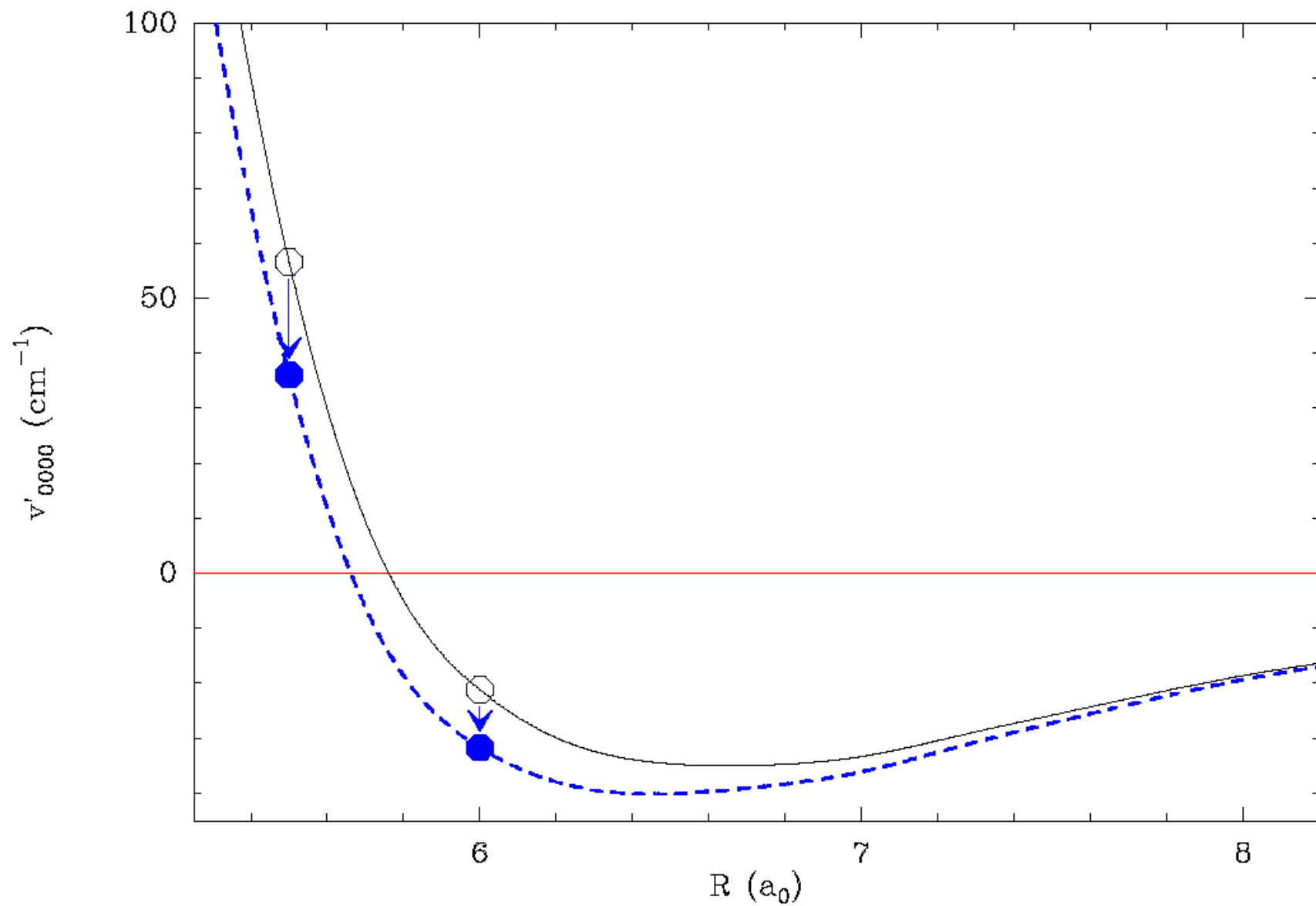
where

$$t_{p_1 q_1 p_2 p}(\theta, \varphi, \theta', \varphi') = (1 + \delta_{q_1 0})^{-1} \sum \begin{bmatrix} p_1 & p_2 & p \\ r_1 & r_2 & r \end{bmatrix} Y_{p_2 r_2}(\theta', \varphi') Y_{p_1 r_1}(\theta, \varphi) [\delta_{q_1 r_1} + (-1)^{p_1 + q_1 + p_2 + p} \delta_{-q_1 r_1}],$$

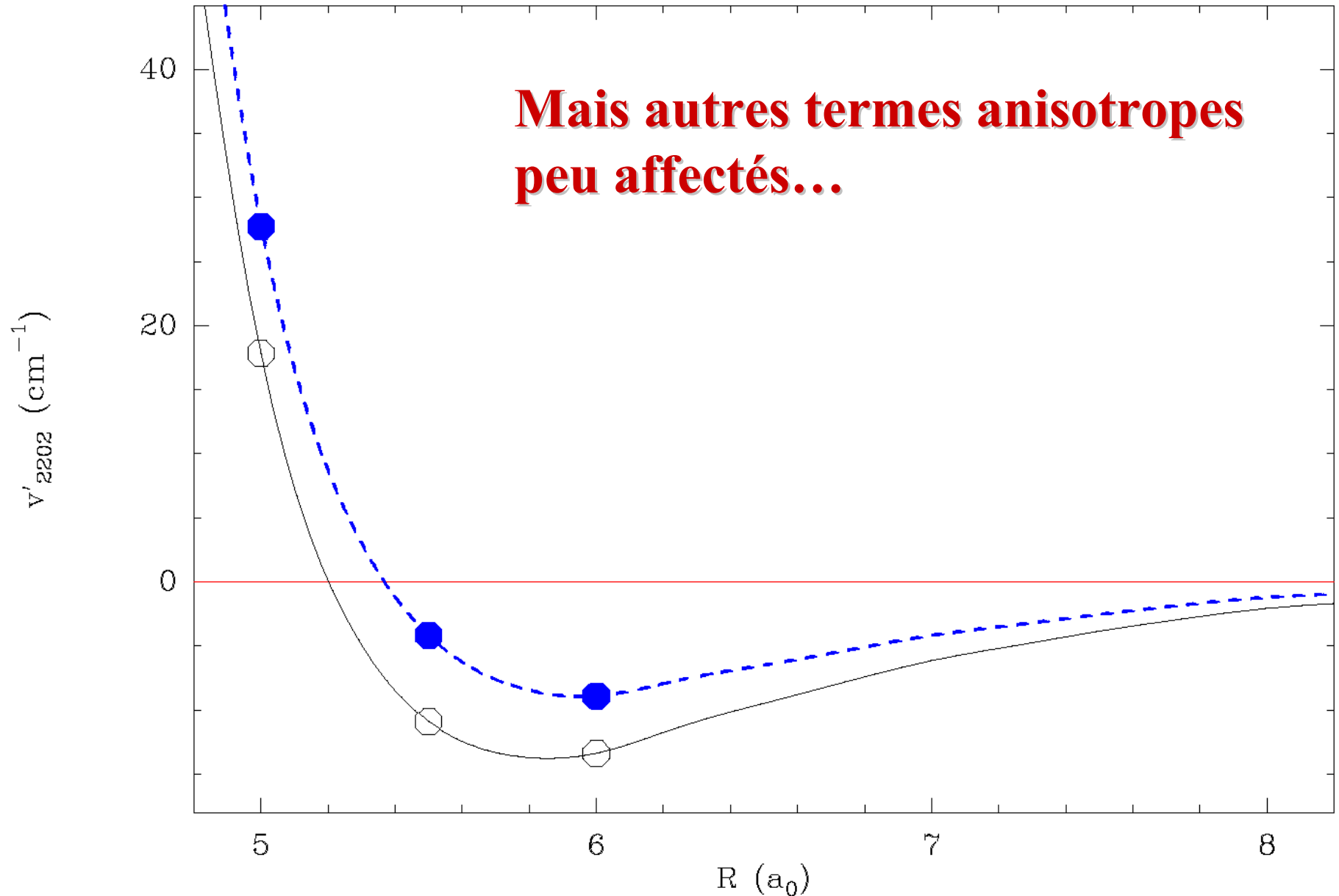
δ_{ij} is a Kronecker delta, equal to one if $i=j$ and to zero otherwise, and the sum is again over r_1, r_2, r .

**Mais normalisation
à $(4\pi)^2$**

Potentiel isotrope fortement modifié



Terme anisotrope le plus affecté : v_{2202}

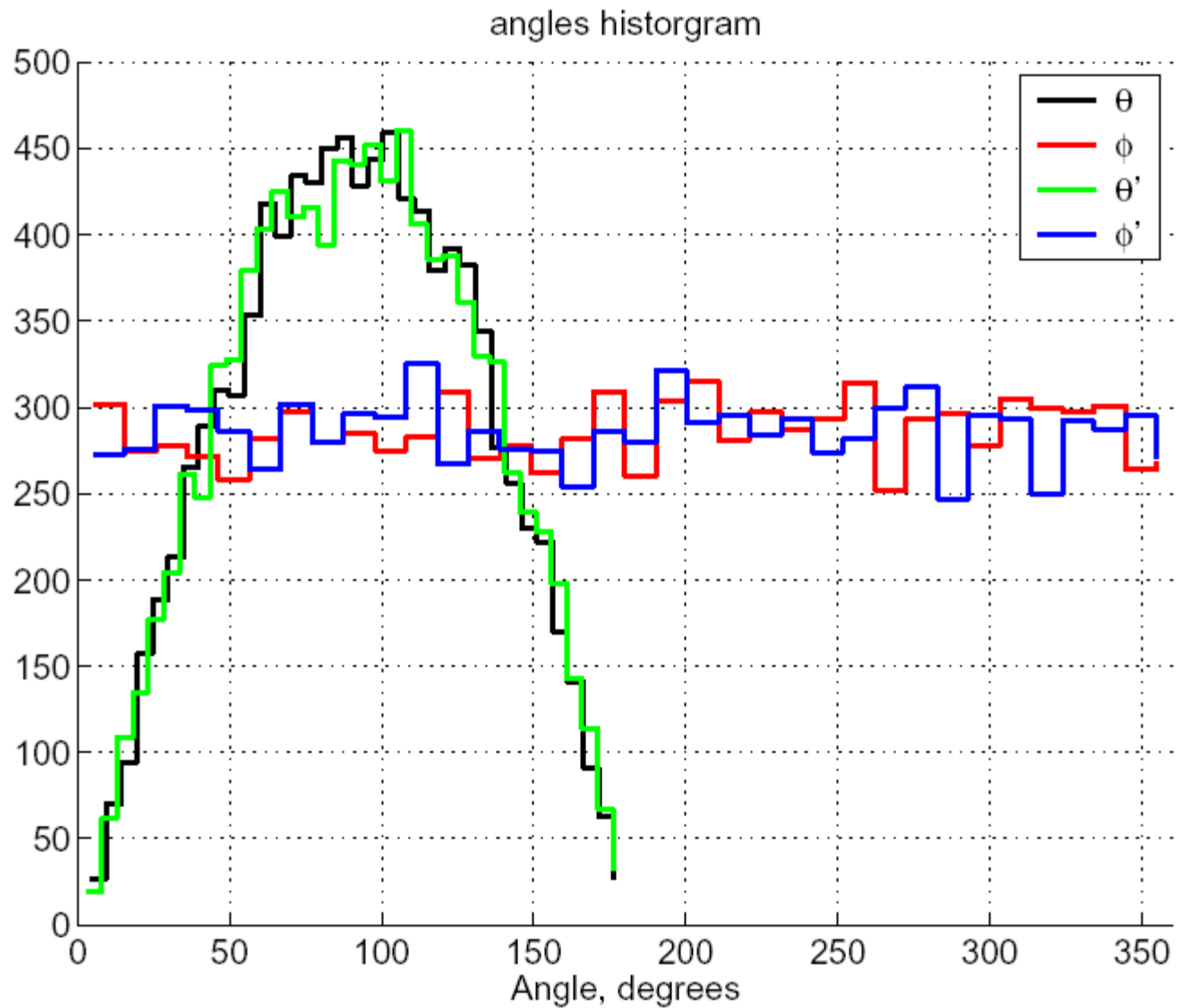


Exploration PES 9-D H₂O-H₂...

Quelle stratégie ?

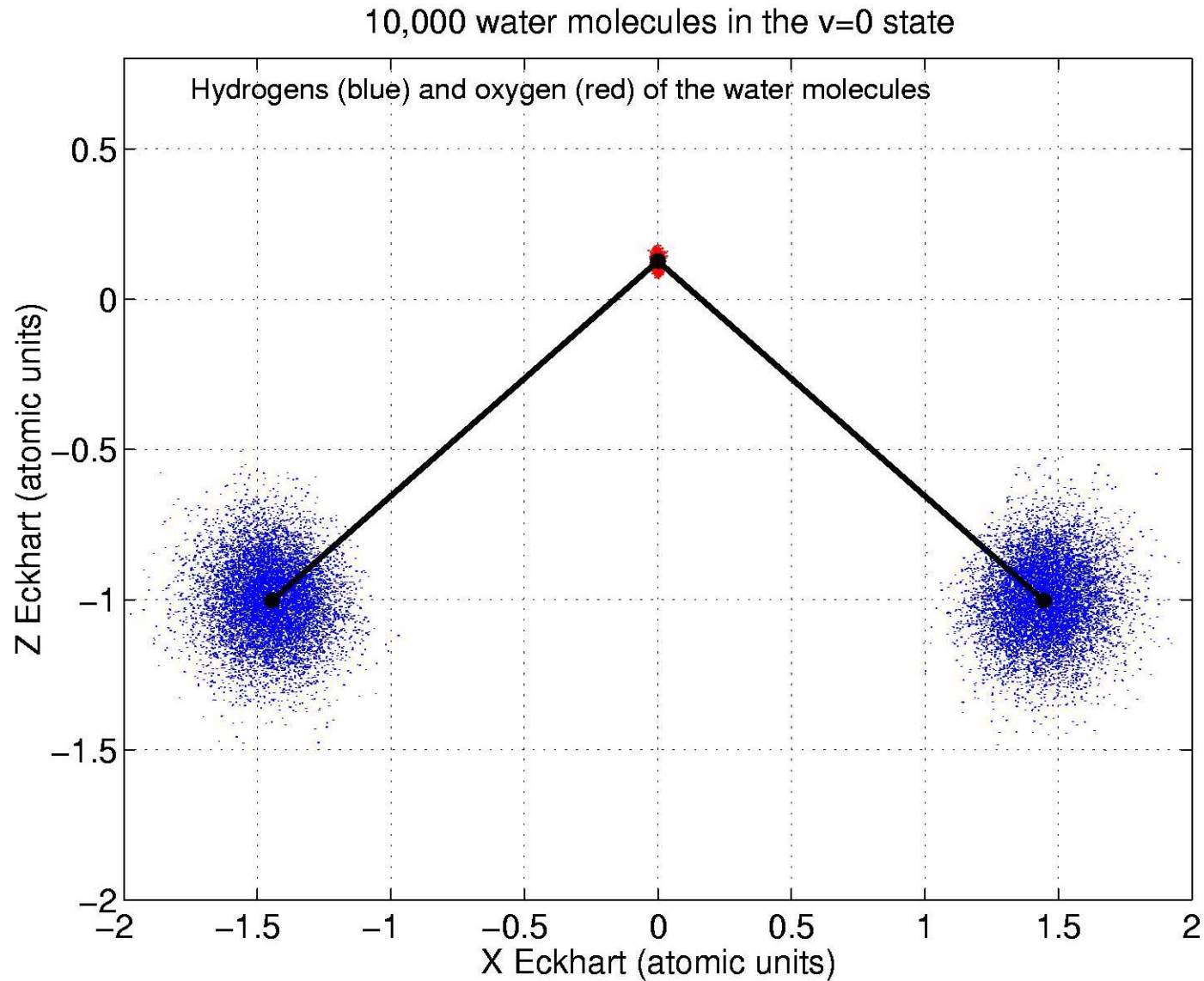
- Grille Monte Carlo 9-D par « importance sampling » sur les fonctions vibrationnelles
- Grille 5-D en référence
- Double contreponds
- Base Aug-CC adaptée (mix DZV et TZV)
- CCSD(T) nécessaire
 - ➔ $\frac{1}{4}$ h par géométrie 5-D ou 9-D

Echantillonnage angulaire

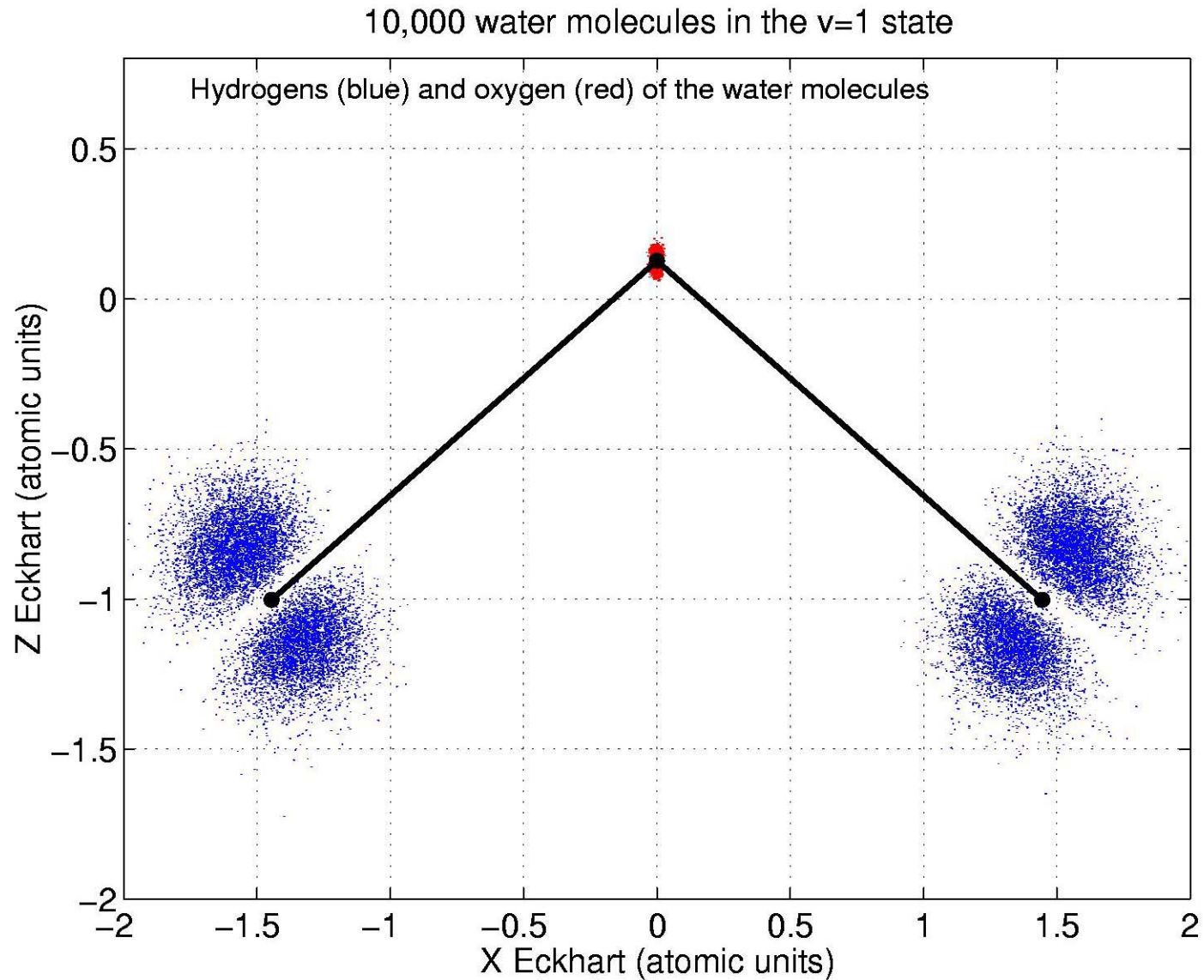


Water in (0,0,0) state

(Importance sampling, wavefunction from J. Tennyson.)

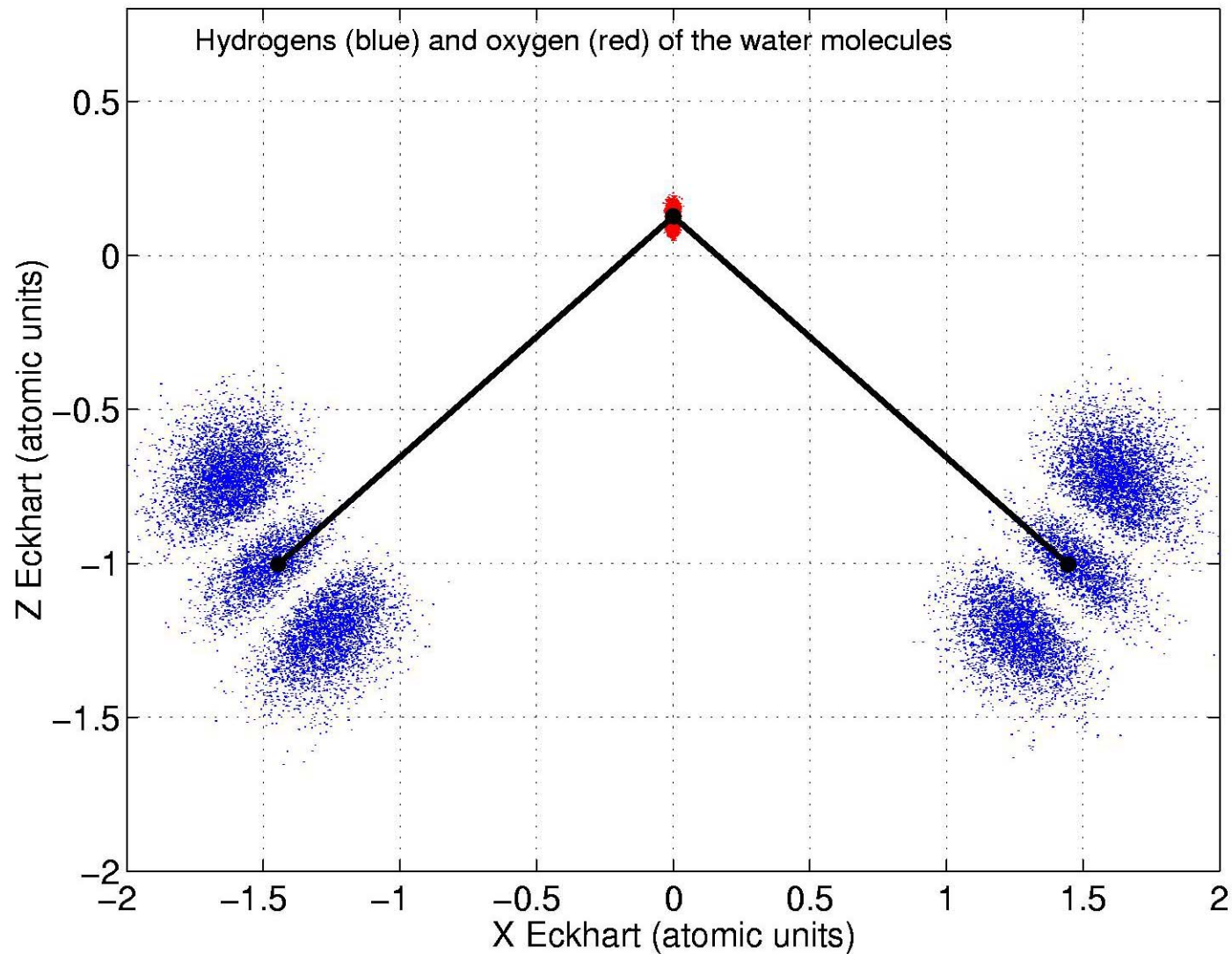


Water in (0,1,0) state



Water in (0,2,0) state

10,000 water molecules in the $v=2$ state



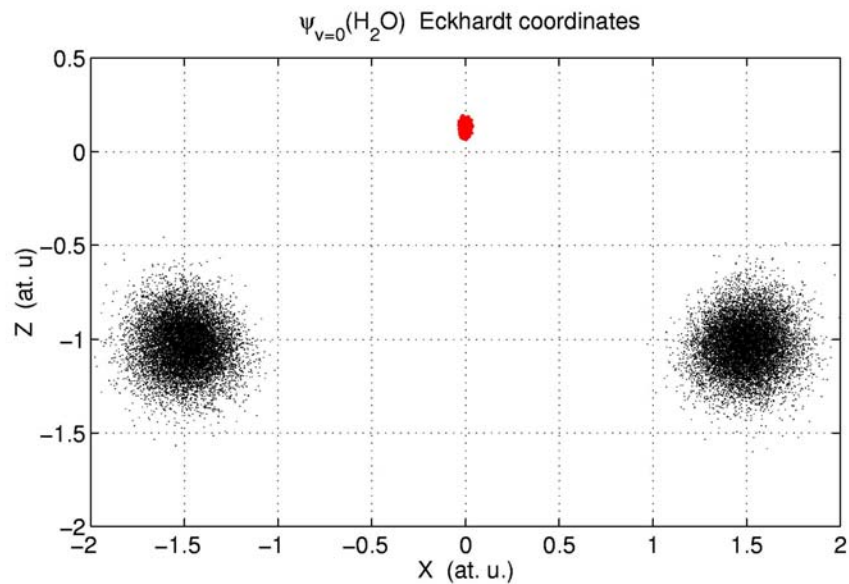
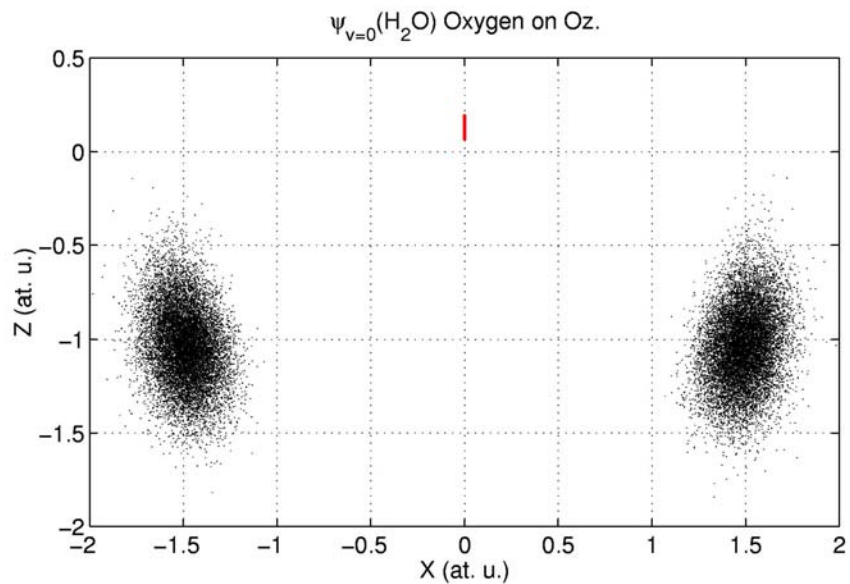
Eckart conditions

Eckart rotation is defined as follows [6]:

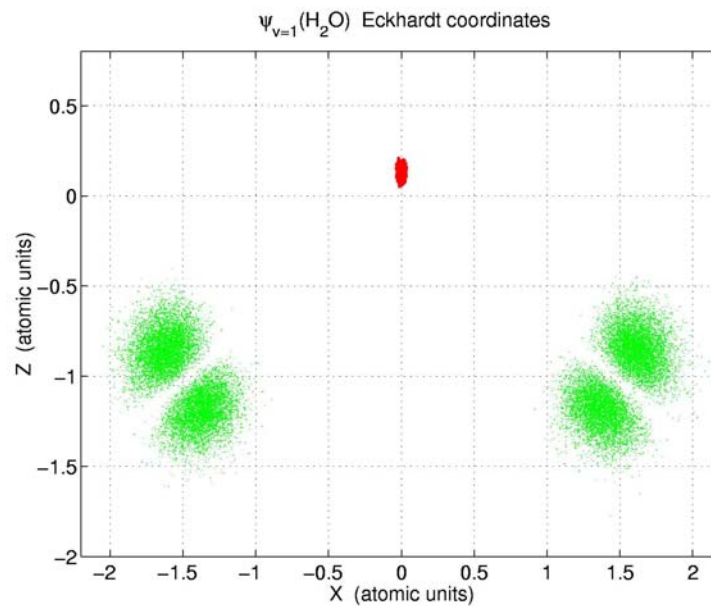
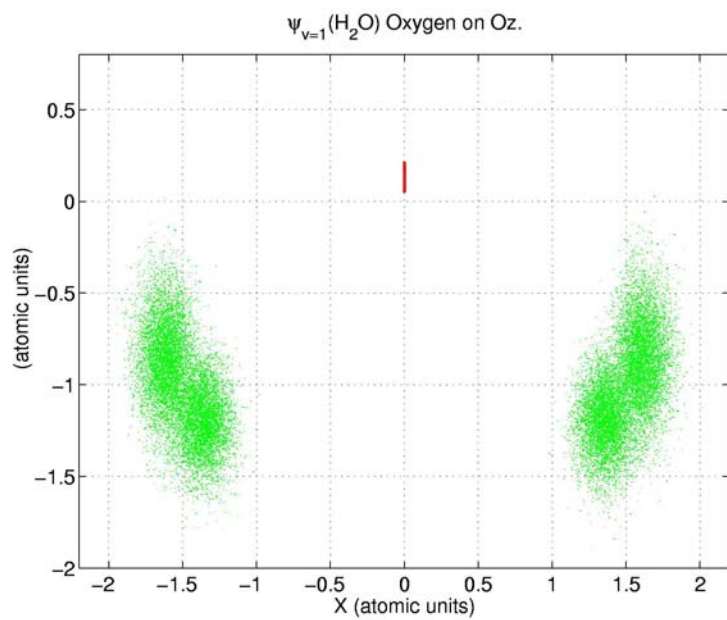
$$\sum_i m_i \mathbf{r}_i^e \times \mathbf{r}_i = 0.$$

[6] P.R. Bunker, *Molecular Symmetry and Spectroscopy*, Academic Press, 1979.

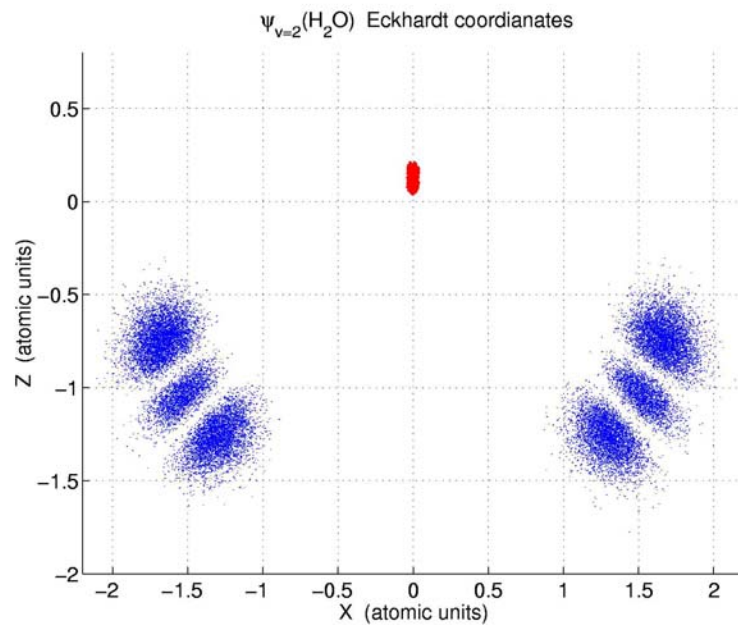
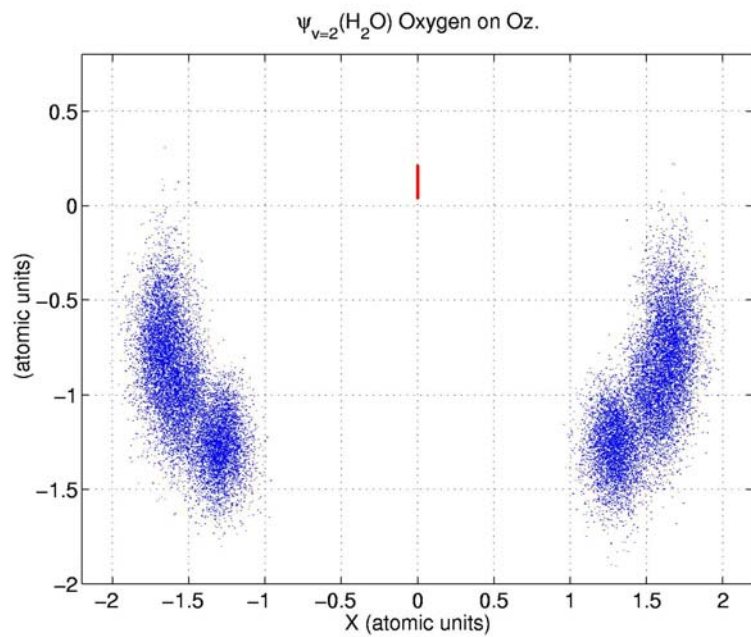
Effect of Eckart conditions for water in (0,0,0) state



Effect of Eckart conditions for water in (0,1,0) state



Effect of Eckart conditions for water in (0,2,0) state



H₂ (v=0)

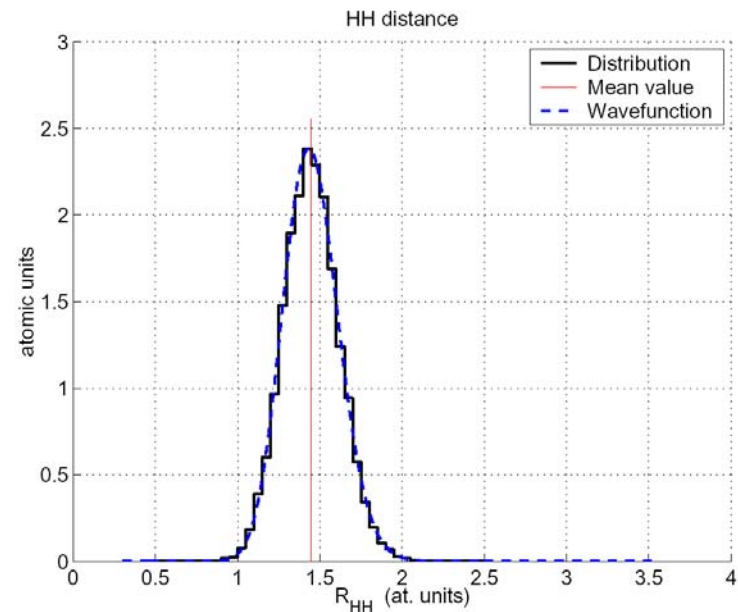
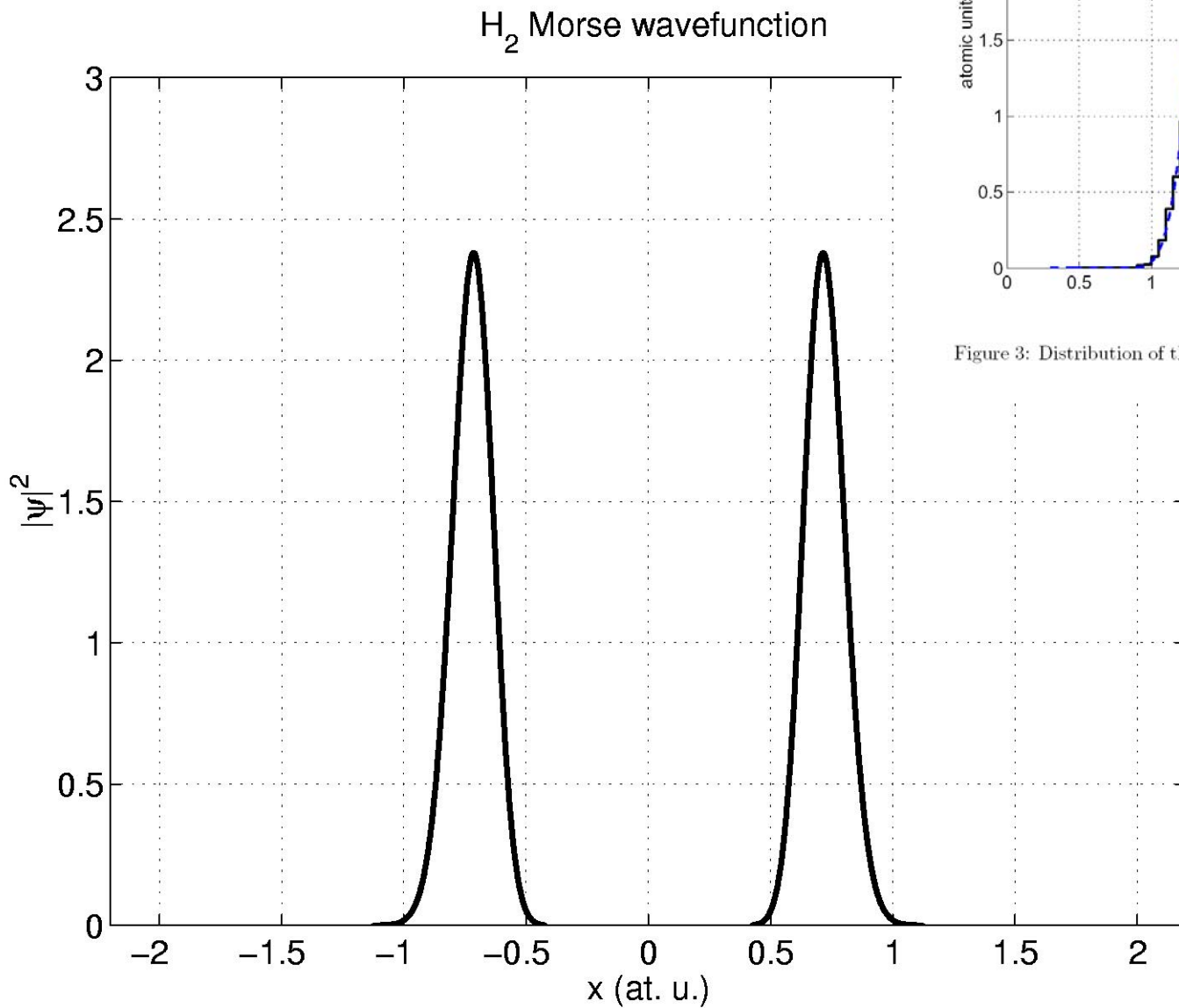


Figure 3: Distribution of the r_{HH} distance, compared to the exact wavefunction

Résultats préliminaires: Moyenne 9-D sur les termes 5-D

- Renforce répulsion / attraction
sur le potentiel isotrope

$$V_{0000} : + 5\% \text{ à } 5 \text{ a.u.}, - 5\% \text{ à } 6 \text{ a.u.}$$

- Affecte tous termes anisotropes

$$V_{1023} \text{ (dip-quad)} \quad +2 \%, \quad +5 \% \text{ à } 5, 6 \text{ a.u.}$$

$$V_{2224} \text{ (quad-quad)} \quad +12 \%, \quad +10 \% \text{ à } 5, 6 \text{ a.u.}$$

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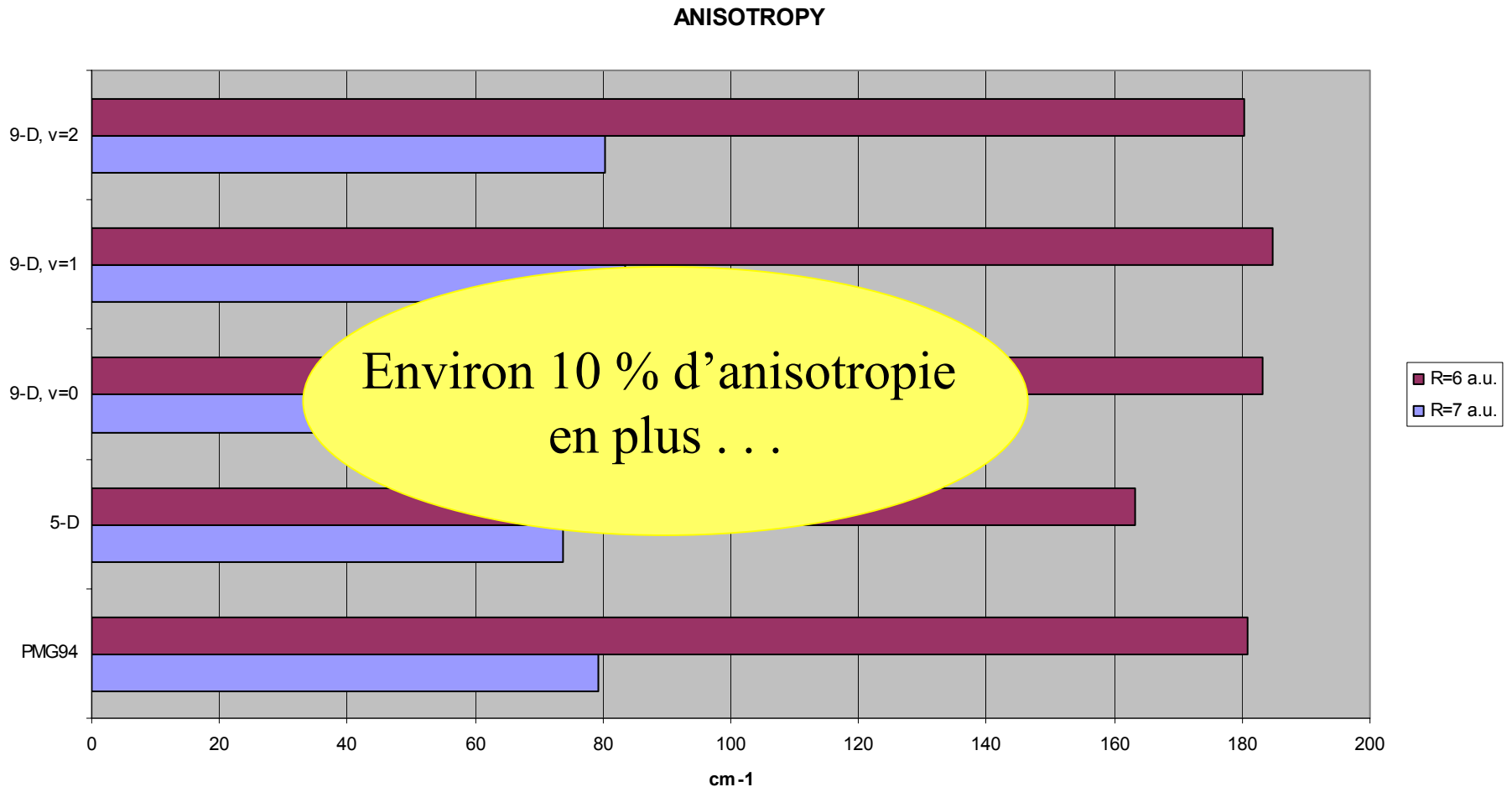
where

$$t_{p_1 q_1 p_2 p}(\theta, \varphi, \theta', \varphi') = (1 + \delta_{q_1 0})^{-1} \sum \begin{bmatrix} p_1 & p_2 & p \\ r_1 & r_2 & r \end{bmatrix} Y_{p_2 r_2}(\theta', \varphi') Y_{p_1 r_1}(\theta, \varphi) [\delta_{q_1 r_1} + (-1)^{p_1 + q_1 + p_2 + p} \delta_{-q_1 r_1}],$$

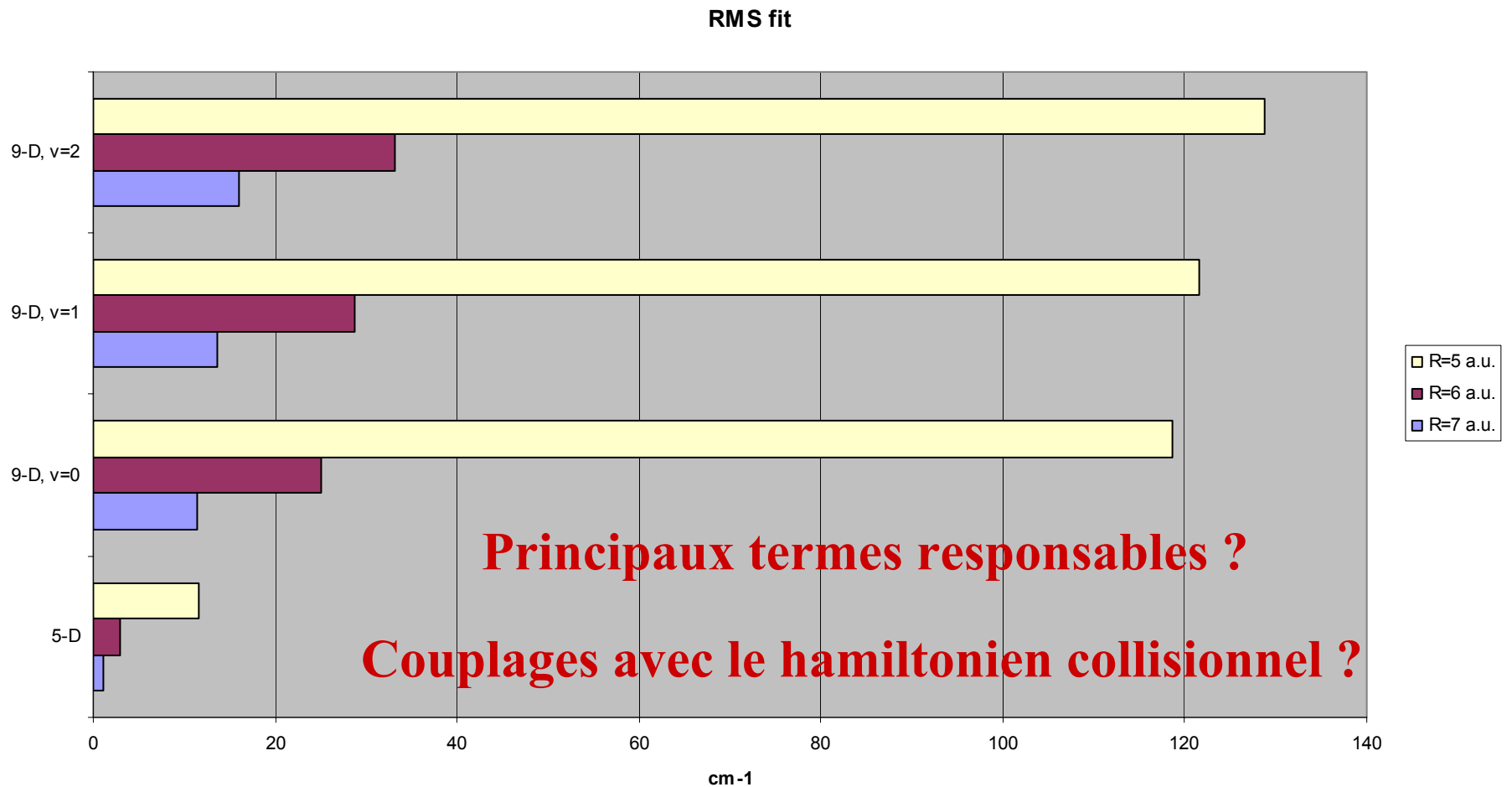
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Anisotropie supplémentaire apportée par la moyenne à 9-D



Modulation du potentiel à 9-D



Conclusions provisoires

- R12 affecte principalement le potentiel isotrope et un petit nombre de termes anisotropes de bas degré
- La moyenne 9-D sur l'expansion rigid-body 5-D affecte tous les termes
 - ➔ refaire calculs collision sur nouvelle expansion rigid-body ???
- Autres conséquences termes 9-D ???

Perspectives

- $\text{H}_2\text{O}-\text{e}^-$ et $\text{H}_2\text{O}-\text{H}$ (démarrage en décembre)
- $\text{HDO}-\text{H}_2$: prise en compte brisure de symétrie via l'échantillonnage 9-D
- Systèmes homologues (H_2S ?)
- NH_3-H_2 : PES 12-D (7 degrés de liberté intra-moléculaires)