Flexible Potential Energy Surface from Iterative Calculations of Rovibrationals Molecular States

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Mathematical Methods for Ab Initio Quantum Chemistry

October, 20th Nice

Outline

I - Ab initio methodogy and specificity of $(H_2O)_2$

II - Iterative Pseudo spectral scheme

III - Non-Linear Fitting of a Flexible PES for $(H_2O)_2$

I-Why a Flexible Potential Energy Surface

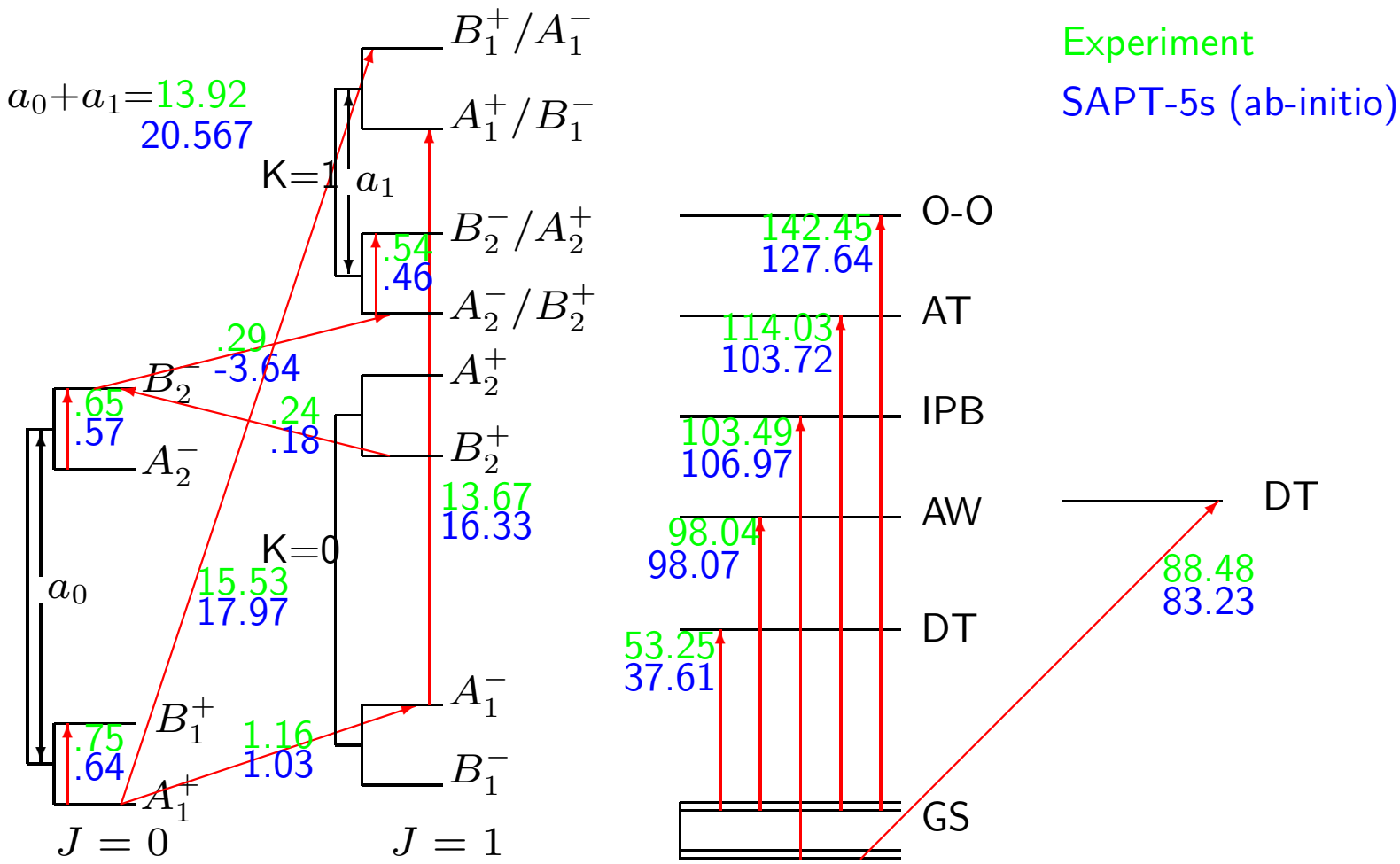
- an accurate description of the potential energy surface of water cluster

$$
\begin{aligned}
V(M_1, M_2, \ldots M_N) &= \sum_{\alpha} V^{(1)}(M_\alpha) + \sum_{\alpha<\beta} V^{(2)}(M_\alpha, M_\beta) \\
&+ \sum_{\alpha<\beta<\gamma} V^{(3)}(M_\alpha, M_\beta, M_\gamma) + \ldots + V_{pol}(M_1, M_2, \ldots M_N)
\end{aligned}
$$

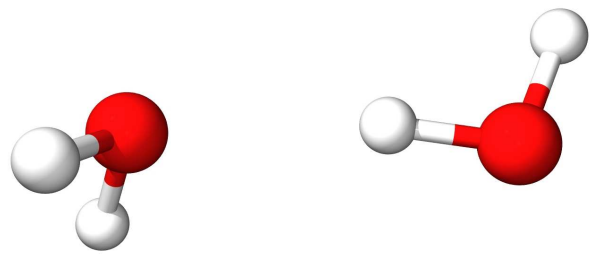
represents a real challenge for chemists $\longrightarrow$ simulate properties of liquid water

- a accurate PES should reproduce well tunnelings effect experimentaly observed in molecular beams

I-Experiment vs Ab-initio



I-Ab-Initio Method -1-



- **Supermolecular approach** :

$$V^{(2)}(M_A, M_B) = V(M_A, M_B) - V^{(1)}(M_A) - V^{(1)}(M_B)$$

  - conceptualy easy
  - expensive calculations with high theory level (CCSD(T)) and very large basis set to reproduce properties of hydrogen bonding (TZ2P(f,d)+diff)
  - problems of BSSE

I-Ab-Initio Method -2-

- **SAPT approach** :

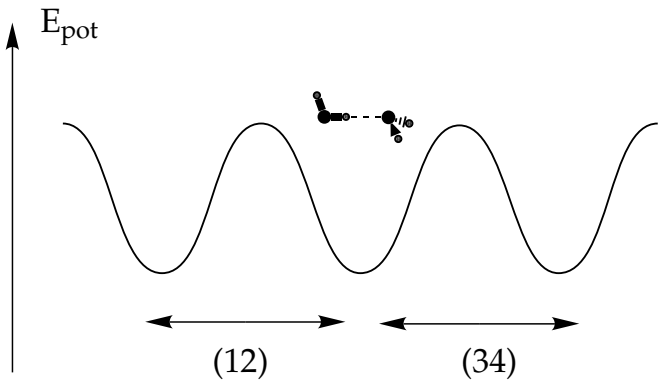
$$
\begin{aligned}
E_{int}^{(n)} &= \langle \psi_0 | \hat{\mathbf{H}}_{int} | \Psi_{n-1} \rangle \\
|\Psi_n\rangle &= |\psi_0\rangle + \sum_{k \neq 0} \frac{|\psi_k\rangle\langle\psi_k|}{(E_k - E_0)} (\Delta E_n - \hat{\mathbf{H}}_{int}) \hat{\mathbf{A}} |\Psi_{n-1}\rangle
\end{aligned}
$$

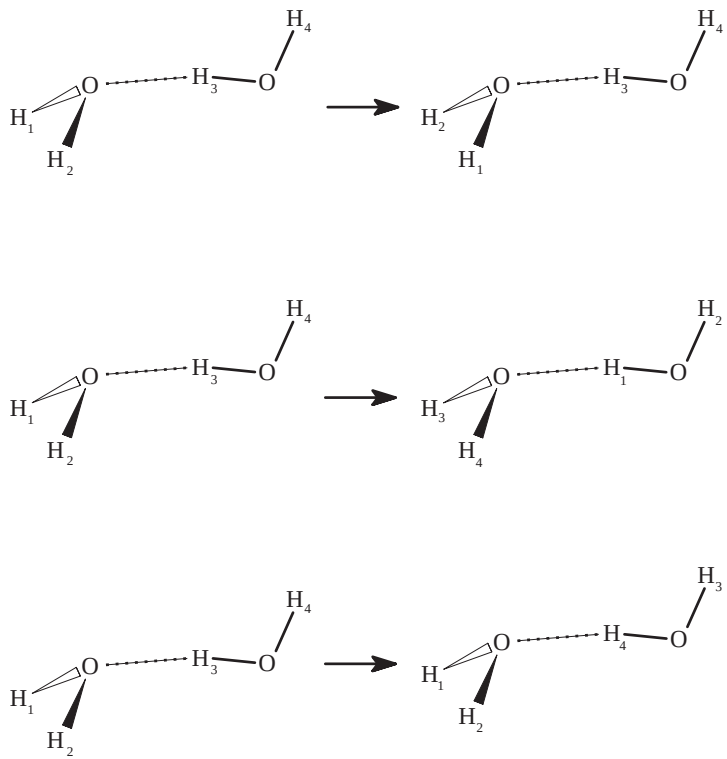
  - Perturbative method which the monomer electronic function $\Psi(M_\alpha)$ to calculate the fundamental intermolecular interaction
  - as only $\Psi(M_\alpha)$, we can use a higher level of theory as in supermolecular approach
  - no problems of BSSE
  - but possible poor convergence of the interaction energy

I-Specificity of the PES of Water Dimer

Water dimer is a very floppy molecule with large amplitude motions

- a 180° rotation of each monomer around its symmetry axis;
- exchange of the two monomers





I-Permutation Inversion Group

Feasible Permutation-Inversion operations introduced by Longuet-Higgins, Hougen :

$$O_{G_{16}} \in \left\{ \begin{array}{ccccc} E & (12) & (12)(34) & (13)(24)(56) & (1324)(56) \\ & (34) & & (14)(23)(56) & (1423)(56) \end{array} \right\} \otimes \{E, E^*\}$$

Permution inversion group

$$G_{16} = \left\{ G_2^{(a)} \otimes G_2^{(b)} \circledS G_2^{(ab)} \right\} \otimes \mathcal{E}$$

- isomorphic to the point group D_{4h}
- use the irreductible representation of the point group to label the symetry of each level

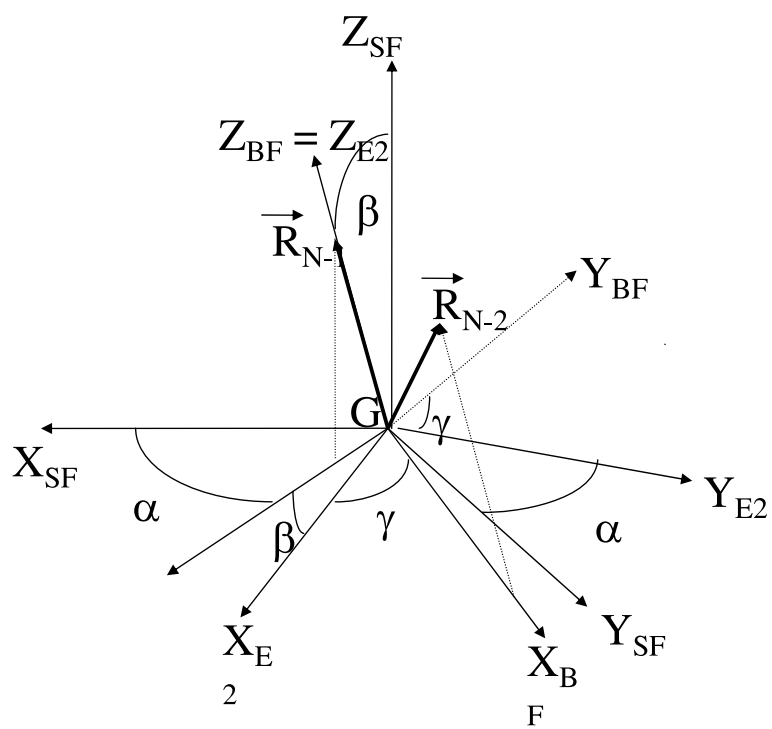
$$\Gamma \in \left\{ A_1^+, A_2^+, B_2^+, E^+, A_1^-, A_2^-, B_2^-, E^- \right\}$$

II-Collisional approach

Utilization of Jacobi coordinates to correctly describe large amplitude motions with $\left\{\vec{R}_i; i = 1 \ldots N-1\right\}$ for a system of N atoms

(Iung & Gatti Quant.Chem.**106**,130(2006))

- $\left\{R_i^{(BF)} = R_i^{(SF)}, i = 1 \ldots N-1\right\}$
- $\left\{\theta_i^{(BF)}, i = 1 \ldots N-2\right\}$
- $\left\{\varphi_i^{(BF)}, i = 1 \ldots N-3\right\}$

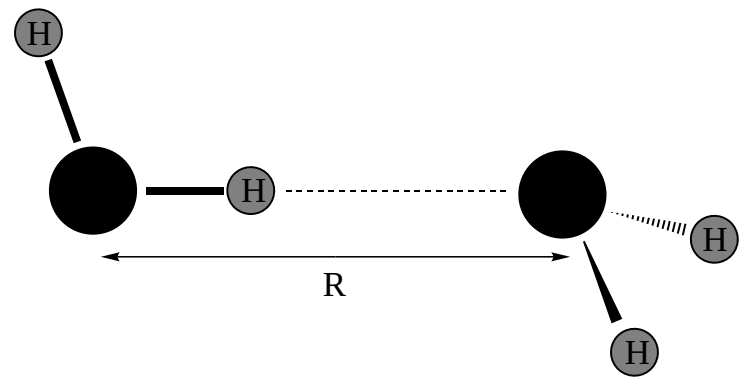


II-Rigid Hamiltinian operator

(Brocks,van der Avoird, Sutcliffe & Tennyson Mol.Phys.**50**,507(2003))

(Gatti & Iung Theo.Comp.Chem.**2**(4),1025(1983))

$$\begin{aligned}\mathbf{H} &= -\frac{\hbar^2}{2\mu_{AB}}\frac{\partial^2}{\partial\mathcal{R}^2} + \mathbf{H}_{rot}^{(A)} + \mathbf{H}_{rot}^{(B)} \\ &+ \mathbf{V}(\mathcal{R}, \mathbf{\Omega}^{(A)}, \mathbf{\Omega}^{(B)}) \\ &+ \frac{1}{2\mu_{AB}R^2}\left\{\mathbf{J}^2 + \mathbf{j}^2 - 2\mathbf{j}.\mathbf{J}\right\}\end{aligned}$$



- $\mathbf{H}_{rot}^{(\alpha)}$ and $\mathbf{j}_{(\alpha)}$: rotational Hamiltonian and angular momentum of monomer α,
- $\mathbf{j} = \mathbf{j}_A + \mathbf{j}_B$: coupled rotational angular momentum,
- $\mathbf{\Omega}^{(\alpha)} \equiv (\varphi^{(\alpha)}, \theta^{(\alpha)}, \chi^{(\alpha)})$: Orientation of monomer α in BF$^{(\alpha)}$

II-Choice of Basis Set

Basic Operation for iterative methods requires to evaluate $\hat{\mathbf{H}}\Psi$

$$\text{where } \hat{\mathbf{H}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}$$

Duality of the wavefunction

- Spectral, in a basis set $\{\varphi_n(\mathbf{Q})\}$;

$$\Psi(Q) = \sum_n c_n \varphi_n(\mathbf{Q})$$

- Grid representation $\{Q_p\}$;

$$\psi_p \equiv \Psi(Q_p)$$

grid representation could be expressed in term of collocation matrix $R_{pn} = \varphi_n(Q_p)$

$$\psi = \mathbf{Rc}$$

II-Choice of spectral representation

spectral representation is choosen such that $\hat{\mathbf{T}}$ is analytic

$$\hat{\mathbf{T}}\varphi_n(\mathbf{Q}) = \sum_m C_{mn}\varphi_m(\mathbf{Q}) \tag{1}$$

if we can use spectral representation defined by orthogonal polynomial

$$\begin{aligned} \varphi_n(Q) &= \sqrt{W(Q)}\mathcal{P}_n(Q) \\ \int \varphi_n(Q)\varphi_m(Q)dQ &= \int \mathcal{P}_n(Q)\sqrt{W(Q)}\mathcal{P}_m(Q)dQ = \delta_{nm} \end{aligned}$$

there exist related Gaussian quadrature which justifies the diagonal approximation of any local operator $V(Q)$

$$\int \varphi_n(\mathbf{Q})V(\mathbf{Q})\varphi_m(\mathbf{Q}) \simeq \sum_p \varphi_n(\mathbf{Q}_p)\Omega_p V(\mathbf{Q}_p)\varphi_m(\mathbf{Q}_p) \tag{2}$$

For $(H_2O)_2$ the total spectral basis set is $\mathcal{B}_R \otimes \mathcal{B}^A_{ang} \otimes \mathcal{B}^B_{ang} \otimes \mathcal{B}^{AB}_{ang}$

II-Radial Basis Set

$$\hat{\mathbf{T}}_R = -\frac{\hbar^2}{2\mu_{AB}}\frac{\partial^2}{\partial R^2}$$

- Primitive basis $S_n(R) = \sqrt{\frac{2}{L}}\sin\frac{n\pi(R-R_{min})}{L}$
- Equidistant grid $R_p = R_{min} + p.\Delta R$
- Contraction of both bases by diagonalization

$$\hat{\mathbf{T}} + V_{eff}(R) \rightarrow \varphi_m$$

- Diagonalization the position operator $\hat{\mathbf{R}}$ gives the reduced grid (PODVR method)

II-Partial angular basis set

The Wigner functions

$$\langle \phi, \theta, \chi | jk\omega \rangle = \sqrt{\frac{2j+1}{8\pi^2}} D^{j*}_{\omega k}(\phi, \theta, \chi) = \sqrt{\frac{2j+1}{8\pi^2}} e^{i\omega\chi} d^j_{\omega k}(\cos\theta) e^{ik\phi}$$

lead to an analytical expression of the rotational hamiltonian

$$\begin{aligned} \hat{\mathbf{T}}_{rot} |jk\omega\rangle &= \left\{ \frac{1}{2}(B_x + B_y)(j(j+1) - k^2) + B_z k^2 \right\} |jk\omega\rangle \\ &+ \frac{1}{4}(B_x - B_y) F^+_{jk} |j, k+2, \omega\rangle \\ &+ \frac{1}{4}(B_x - B_y) F^-_{jk} |j, k-2, \omega\rangle \end{aligned}$$

where $F^{\pm}_{jk} = [j(j+1) - k(k \pm 1)]^{1/2} [j(j+1) - (k \pm 1)(k \pm 2)]^{1/2}$

II-Total angular basis set

1. Spectral angular basis set

   - $\mathcal{B}_{unc} = \{|j_A, k_A, \omega_A\rangle\} \otimes \{|j_B, k_B, \omega_B\rangle\} \otimes \{|J, \Omega, M\rangle\}$

   - $\mathcal{B}_{cpl} = \{|j_A j_B k_A k_B; j\Omega\rangle |J, \Omega, M\rangle\}$

   - $\mathcal{B}_{sym}^{(\Gamma)} = \{|\nu; \Gamma\rangle, \nu = 1, N_\Gamma\}$

$$|\nu; \Gamma\rangle = \sum_i c_{i\nu}^{(\Gamma)} |\xi_i, \Omega\rangle \qquad \left\{ \begin{array}{lcl} |\xi_1, \Omega\rangle & = & |j_A j_B k_A k_B; j\Omega\rangle \\ |\xi_2, \Omega\rangle & = & |j_B j_A k_B k_A; j\bar{\Omega}\rangle \\ |\xi_3, \Omega\rangle & = & |j_A j_B \bar{k}_A \bar{k}_B; j\bar{\Omega}\rangle \\ |\xi_4, \Omega\rangle & = & |j_B j_A \bar{k}_B \bar{k}_A; j\Omega\rangle \end{array} \right.$$

2. Angular grid basis set associated to intercoordinates

$\{\varphi_p, \chi_q^A, \chi_r^B, \theta_s^A, \theta_t^B, R_i\}$ avec $\varphi = \varphi_A - \varphi_B$

II-PSSH scheme

Split Hamiltonian

$$\hat{\mathbf{H}} = \hat{\mathbf{T}}_R + \hat{\mathbf{H}}_{AB} + \hat{\mathbf{H}}_{cc} + \hat{\mathbf{V}}$$

Pseudo spectral scheme to evaluate $V\Psi$ from angular spectral representation

$$|\Psi^{JM\Gamma}\rangle = \sum_{\nu\Omega p} \Psi^{JM\Gamma}_{\nu\Omega p} |\nu, \Gamma\rangle \otimes |J\Omega M\rangle \otimes |R_p\rangle$$

- Transformation to the grid $\{\psi_q\}$ (with collocation matrix of Gauss-Legendre for $d^j_{\omega k}(\cos\theta)$ and FFT for $e^{ik\varphi}$ and $e^{i\omega\chi}$)
- Acting the diagonal potential $\psi_q \to V(Q_q)\psi_q$
- Back transform to the spectral representation of Ψ by inverse transformation

II-Lanczos Scheme

From a vector $|u_0>$ one recursively produce Krylov space $\mathcal{K} = \{u_n\}_{n=0}^{N}$

$$\beta_{n+1}|u_{n+1}\rangle = \left\{\hat{\mathbf{H}} - \alpha_n\right\}|u_n\rangle - \beta_n|u_{n-1}\rangle$$

$$\begin{cases} \alpha_n = \langle u_n|\hat{\mathbf{H}}|u_n\rangle \\ \beta_n = \langle u_{n+1}|\hat{\mathbf{H}}|u_n\rangle \end{cases}$$

in which $\mathbf{H}$ is tridiagonal

$$\mathbf{H} = \begin{pmatrix} \alpha_0 & \beta_1 & & & \\ \beta_1 & \alpha_1 & \beta_2 & & 0 \\ & \ddots & \ddots & \ddots & \\ 0 & & \ddots & \ddots & \ddots \end{pmatrix}$$

without reorthogonalization

II-Properties of this algorithm

- Conserves the symmetry of the seed vector $|u_0>$
- Converges first the low density part of the spectrum

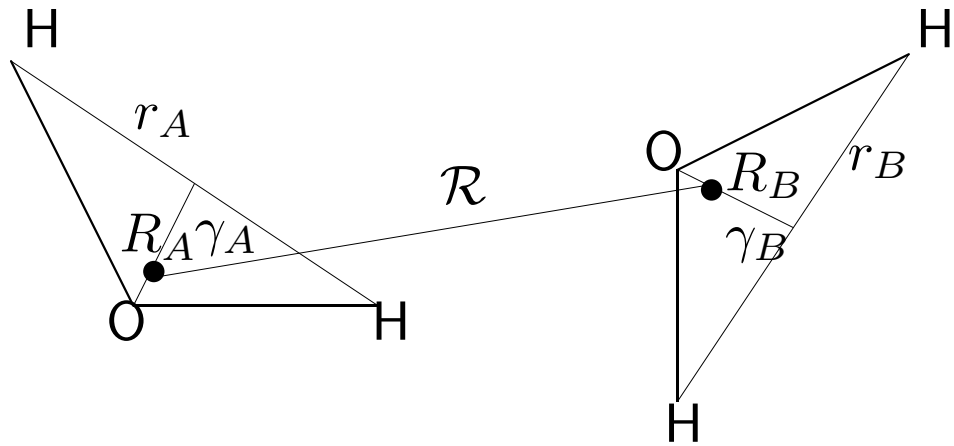
$$convergence \propto \frac{|\lambda_{i+1} - \lambda_i|}{|\lambda_{max} - \lambda_{min}|}$$

- Diagonalization of $\mathbf{T}$ matrix (QL $O(N^2)$) gives eigenvalues and a modification of the algorithm allows one to discard spurious eigenvalues from the error norm

$$\sigma_\alpha = ||(\mathbf{H} - E_\alpha)\Psi_\alpha|| = \beta_N \langle u_N | \Psi_\alpha \rangle$$

- Molecular basis set size ranges from 10^5 to 2×10^6

III-Flexible Hamiltonian



$$\mathbf{H} = -\frac{\hbar^2}{2\mu_{AB}}\frac{\partial^2}{\partial\mathcal{R}^2} + \mathbf{T}_{VR}^{(A)} + \mathbf{T}_{VR}^{(B)} + \mathbf{V}(\mathbf{q}^A, \mathbf{q}^B, \mathcal{R}, \mathbf{\Omega}^A, \mathbf{\Omega}^B)$$

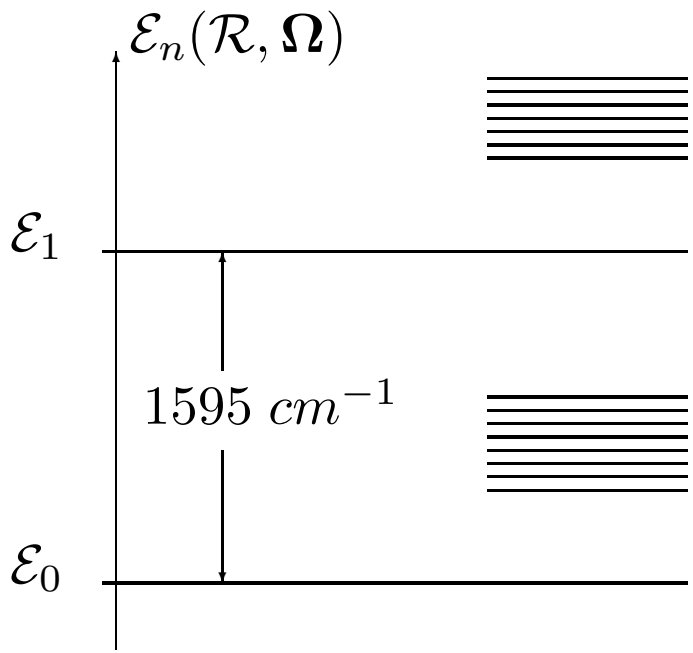
$$+\frac{1}{2\mu_{AB}\mathcal{R}^2}\left\{\mathbf{J}^2 + \mathbf{j}^2 - 2\mathbf{j}.\mathbf{J}\right\} \qquad \mathbf{q}^\alpha = (R_\alpha, r_\alpha, \theta_\alpha)$$

$$\mathbf{T}_{VR}^{(\alpha)} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R_\alpha^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial r_\alpha^2} + \frac{\hat{\ell}_\alpha^2}{2mr_\alpha^2} + \frac{1}{2\mu R_\alpha^2}\left\{\hat{\mathrm{j}}_\alpha^2 + \hat{\ell}_\alpha^2 - 2\hat{\vec{\mathrm{j}}}_\alpha.\hat{\vec{\ell}}_\alpha\right\}$$

Gatti et al., J.Chem.Phys.**108**,8804(1998); **111**,7236(1999)

Leforestier, Gatti, Fellers, Saykally , J.Chem.Phys.**117**,8710(2002)

III-(6+6)d Adiabatic Decoupling between slow $(\mathcal{R}, \mathbf{\Omega})$ and fast $(\mathbf{q}^A, \mathbf{q}^B)$ coordinates



$$\mathbf{H} = \mathbf{H}_{intra}(\mathcal{R}, \mathbf{\Omega}) + \mathbf{T}_{inter}$$

$$\mathbf{H}_{intra} = \mathbf{T}_V^A + \mathbf{T}_V^B + \mathbf{V}(\mathbf{q}^A, \mathbf{q}^B; \mathcal{R}, \mathbf{\Omega})$$

$$\mathbf{H}_{intra}(\mathcal{R}, \mathbf{\Omega})\Phi_{\mathbf{n}_A\mathbf{n}_B}(\mathbf{q}^A, \mathbf{q}^B; \mathcal{R}, \mathbf{\Omega}) = \mathcal{E}_{\mathbf{n}_A\mathbf{n}_B}(\mathcal{R}, \mathbf{\Omega})\Phi_{\mathbf{n}_A\mathbf{n}_B}(\mathbf{q}^A, \mathbf{q}^B; \mathcal{R}, \mathbf{\Omega})$$

Flexible calculation recast into a rigid one using the ground adiabatic potential $\mathcal{E}_0(\mathcal{R}, \mathbf{\Omega}) \longrightarrow V_{ad}$

but the monomers rotational constants depend now on the intermolecular geometry $(\mathcal{R}, \mathbf{\Omega})$ (FC type approximation)

III-Flexible PES

$$
\begin{aligned}
V(\mathbf{q}^A, \mathbf{q}^B, \mathcal{R}, \mathbf{\Omega}^A, \mathbf{\Omega}^B) &= V^{(1)}_{H_2O}(\mathbf{q}^A) + V^{(1)}_{H_2O}(\mathbf{q}^B) \\
&+ V^{(2)}(\mathbf{q}^A, \mathbf{q}^B, \mathcal{R}, \mathbf{\Omega}^A, \mathbf{\Omega}^B)
\end{aligned}
$$

V_{H_2O} : Polyansky, Jensen & Tennyson, J.Chem.Phys.**105**,6490(1996)

Functional form of the 2 body term

Matsuoka, Clementi & Yoshimine, J.Chem.Phys.**64**,1351(1976)

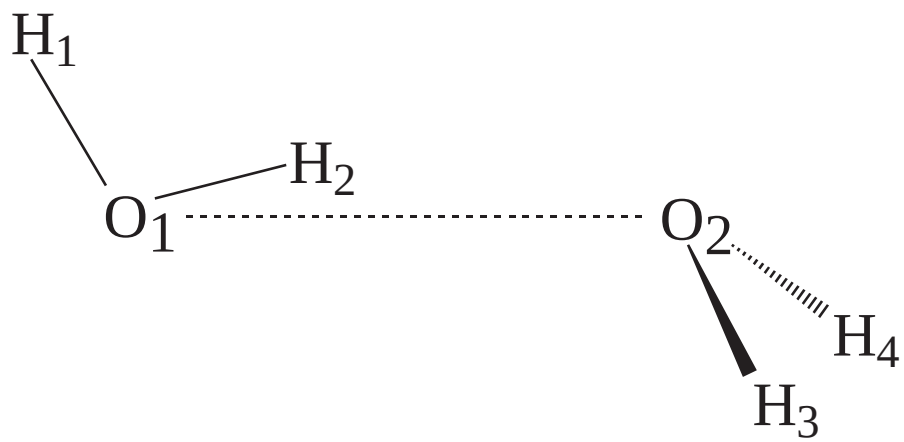
$$
\begin{aligned}
V'_{MCY} &= \sum_{charged\ sites}^{\neq molecules} \frac{q_i q_j}{R_{ij}} + A_{HH} \sum e^{-\beta_{HH} R_{HH}} \\
&+ A_{OO} e^{-\beta_{OO} R_{OO}} \\
&+ A_{OH} \sum e^{-\beta_{OH} R_{OH}} \\
&- A_{V_S H} \sum e^{-\beta_{V_S H} R_{V_S H}}
\end{aligned}
$$

which depends on 11 parameters

III-Ab initio Data

- Ab initio geometry:

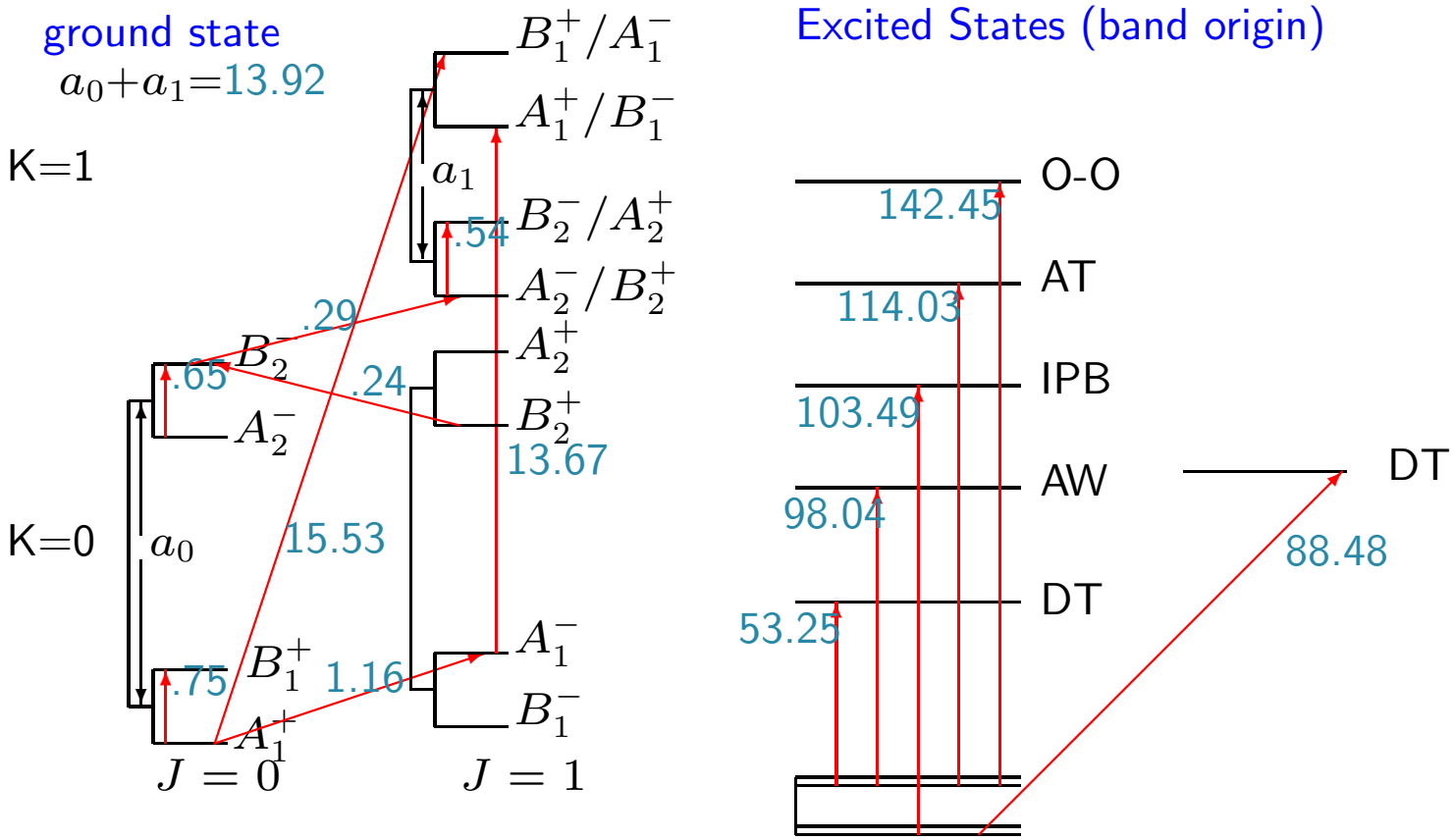
D_e	21 kJ.mol^{-1}
$O_1H_1[D]$	0.9581 Å
$O_1H_2[D]$	0.9663 Å
$O_2H_3[A]$	0.9597 Å
$O_2H_4[A]$	0.9597 Å
O_2H_2	1.9485 Å
$\widehat{H_1O_1H_2}$	104.45
$\widehat{H_3O_2H_4}$	104.58
$\widehat{O_1H_2O_2}$	172.92
$\widehat{H_3O_2O_1}$	110.50



- Rigid EPS of spectroscopic quality SAPT-5s

Tschumper, Leininger, Hoffman, Valeev, Schaeffer, Quack, J.Chem.Phys.**116**,690(2002)
Mas, Bukowski, Szalewicz, Gronenboom, Wormer & van der Avoird, J.Chem.Phys.**113**,6687(2000)

III-Experimental Data



Zwart, ter Muelen, Meerts & Coudert, J.Mol.Spec.**147**,27(1991) Braly, Liu, Brown, Keutsch, Fellers & Saykally, J.Chem.Phys.**112**,10314(2000)

III-Heuristic Optimization of the PES

Define new potential from

$$V^{(2)}(\mathbf{q}^A, \mathbf{q}^B, \mathcal{R}, \mathbf{\Omega}^A, \mathbf{\Omega}^B; \mathbf{p}^{ref} + \delta\mathbf{p})$$

where $\delta p_k = \eta_k . \Delta p_k$ $\qquad$ η is a random number

$$\begin{array}{ccc} \left| D_e^{(rigid)} - D_e^{(Sapt5s)} \right| & < & \epsilon^{(rigid)} \\ \left| D_e^{(flex)} - D_e^{(Ref)} \right| & < & \epsilon^{(flex)} \\ \left| Eq.Geom.^{(flex)} - Eq.Geom.^{(Ref)} \right| & < & \boldsymbol{\epsilon}^{(Geom.)} \\ rms(V_{rigid} - V_{Sapt5s}) & < & \epsilon^{(rms)} \end{array}$$

$$rms = \left\{ \frac{1}{N} \sum_{n=1}^{N} \left(V_{Sapt5s}(\mathbf{Q}_n) - V_{rigid}(\mathbf{Q_n}) \right)^2 \times \exp\left(-\beta \left(V_{Sapt5s}(\mathbf{Q_n}) - \mathbf{V}_{\mathbf{Sapt5s}}^{(\mathbf{min})} \right) \right) \right\}^{\frac{1}{2}}$$

If all these criteria are met continue with . . .

III-Non Linear Fitting

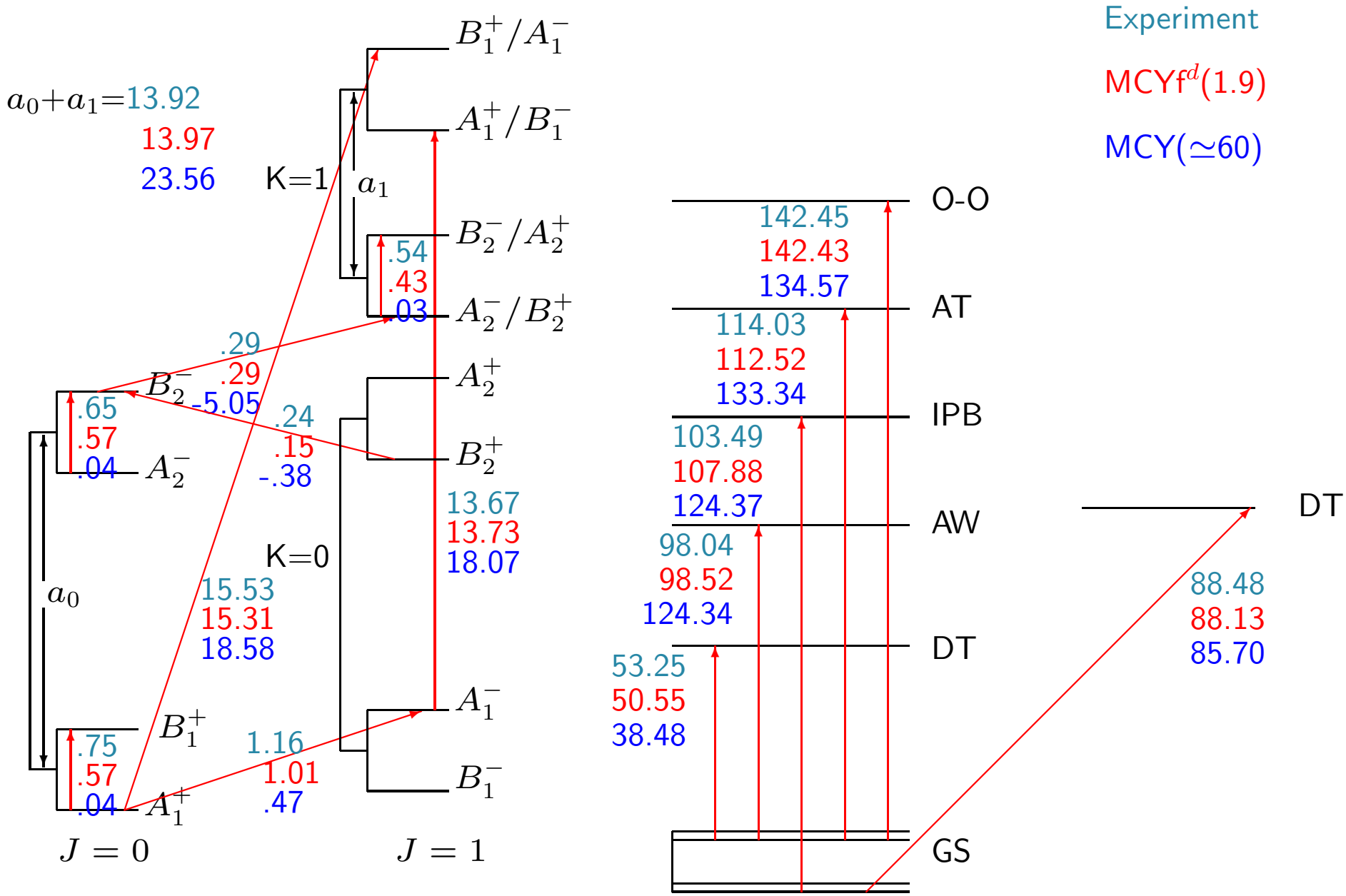
- Minimize the error function

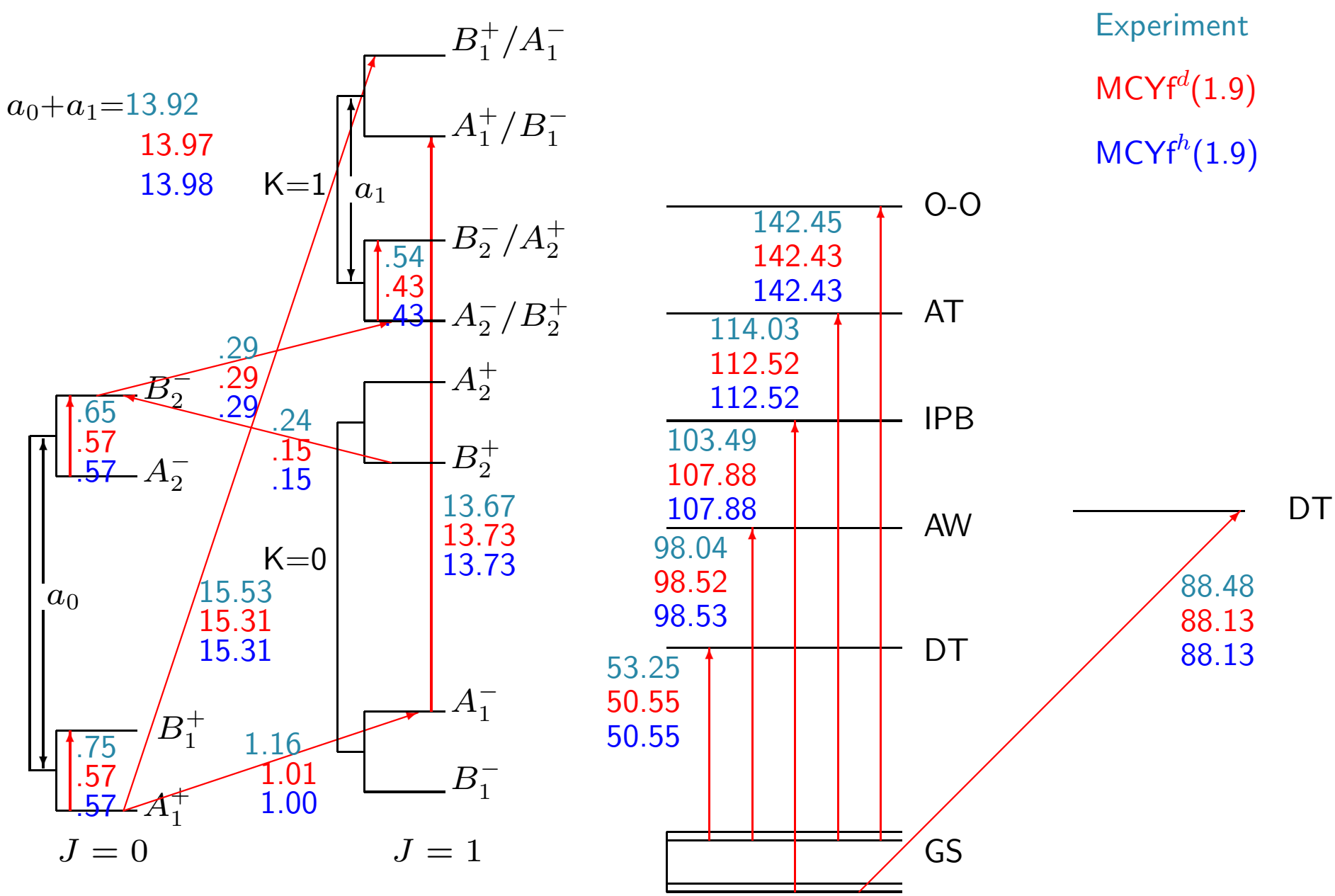
$$\chi^2 = \sum_t^{Transitions} \left\{ \frac{\Delta E_t^{obs} - \Delta E_t^{calc}}{\sigma_t} \right\}^2 + \sum_g^{Geom.Data} \left\{ \frac{G_g^{ref} - G_g^{calc}}{\sigma_g} \right\}^2$$

with non-linear Levenberg-Marquardt $\longrightarrow$ set of parameters $\{p_1, p_2 \ldots p_P\}$

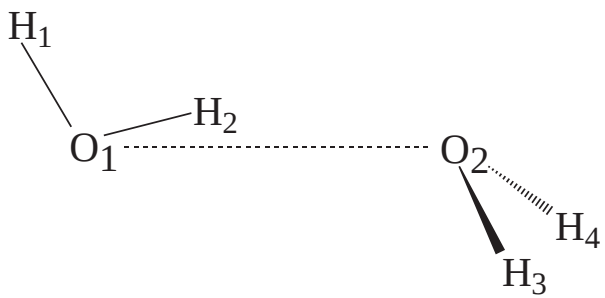
- use Hellmann-Feynmann theorem

$$\frac{\partial E_n^{calc}}{\partial p_q} = \langle \Psi_n | \frac{\partial V(\mathbf{p})}{\partial p_q} | \Psi_n \rangle$$


Experiment
MCYf^d(1.9)
MCY(≃60)
a_0+a_1=13.92
13.97
23.56
K=1
a_1
B_1^+/A_1^-
A_1^+/B_1^-
B_2^-/A_2^+
A_2^-/B_2^+
.54
.43
.03
.29
.29
-5.05
B_2^-
.65
.57
.04
A_2^-
.24
.15
-.38
A_2^+
B_2^+
13.67
13.73
18.07
K=0
a_0
15.53
15.31
18.58
B_1^+
.75
.57
.04
A_1^+
1.16
1.01
.47
A_1^-
B_1^-
$J = 0$
$J = 1$
O-O
142.45
142.43
134.57
AT
114.03
112.52
133.34
IPB
103.49
107.88
124.37
AW
98.04
98.52
124.34
DT
53.25
50.55
38.48
GS
DT
88.48
88.13
85.70


Experiment
MCYf^d(1.9)
MCYf^h(1.9)
a_0+a_1=13.92
13.97
13.98
K=1
a_1
B_1^+/A_1^-
A_1^+/B_1^-
B_2^-/A_2^+
A_2^-/B_2^+
.54
.43
.43
.29
.29
.29
B_2^-
.65
.57
.57
A_2^-
.24
.15
.15
A_2^+
B_2^+
13.67
13.73
13.73
K=0
a_0
15.53
15.31
15.31
B_1^+
.75
.57
.57
A_1^+
1.16
1.01
1.00
A_1^-
B_1^-
$J=0$
$J=1$
O-O
142.45
142.43
142.43
AT
114.03
112.52
112.52
IPB
103.49
107.88
107.88
AW
98.04
98.52
98.53
DT
53.25
50.55
50.55
GS
DT
88.48
88.13
88.13

Equilibrium geometry



	ab initio	MCYf^d	MCYf^h
D_e	1755 cm^{-1}	1760	1760
O_1—H_1	0.958 Å	0.959	0.959
O_1—H_2	0.966 Å	0.968	0.968
O_2—H_3	0.960 Å	0.964	0.964
O_2—H_2	1.948 Å	1.879	1.879
$\widehat{H_1O_1H_2}$	104.45	102.89	102.89
$\widehat{H_3O_2H_4}$	104.58	102.69	102.69
$\widehat{O_1H_2O_2}$	172.92	166.49	166.49
$\widehat{H_3O_2O_1}$	110.50	106.26	106.26

III-Thermodynamic Analysis

- Equation of state for a real gas

$$\frac{p}{kT} = n + B(T)n^2 + C(T)n^3 + \dots$$

- Computation of the quantum SVC with a PSSH scheme

$$\begin{aligned} B(T) &= -\frac{\mathcal{N}}{2V}\frac{\lambda_A^3\lambda_B^3}{Q_A(T)Q_B(T)}\mathrm{Tr}\left[e^{-\beta\mathbf{H}_{AB}} - e^{-\beta\mathbf{H}^o_{AB}}\right] \\ &\propto \iint\left\{1 - e^{-\beta\mathbf{V}_{AB}}\left[1 + \frac{\beta^2}{12}\mathbf{H}^o_{AB}\mathbf{V}_{AB}\right]\right\} d\mathbf{r}_A d\mathbf{r}_B d\mathbf{\Omega}_A d\mathbf{\Omega}_B \end{aligned}$$

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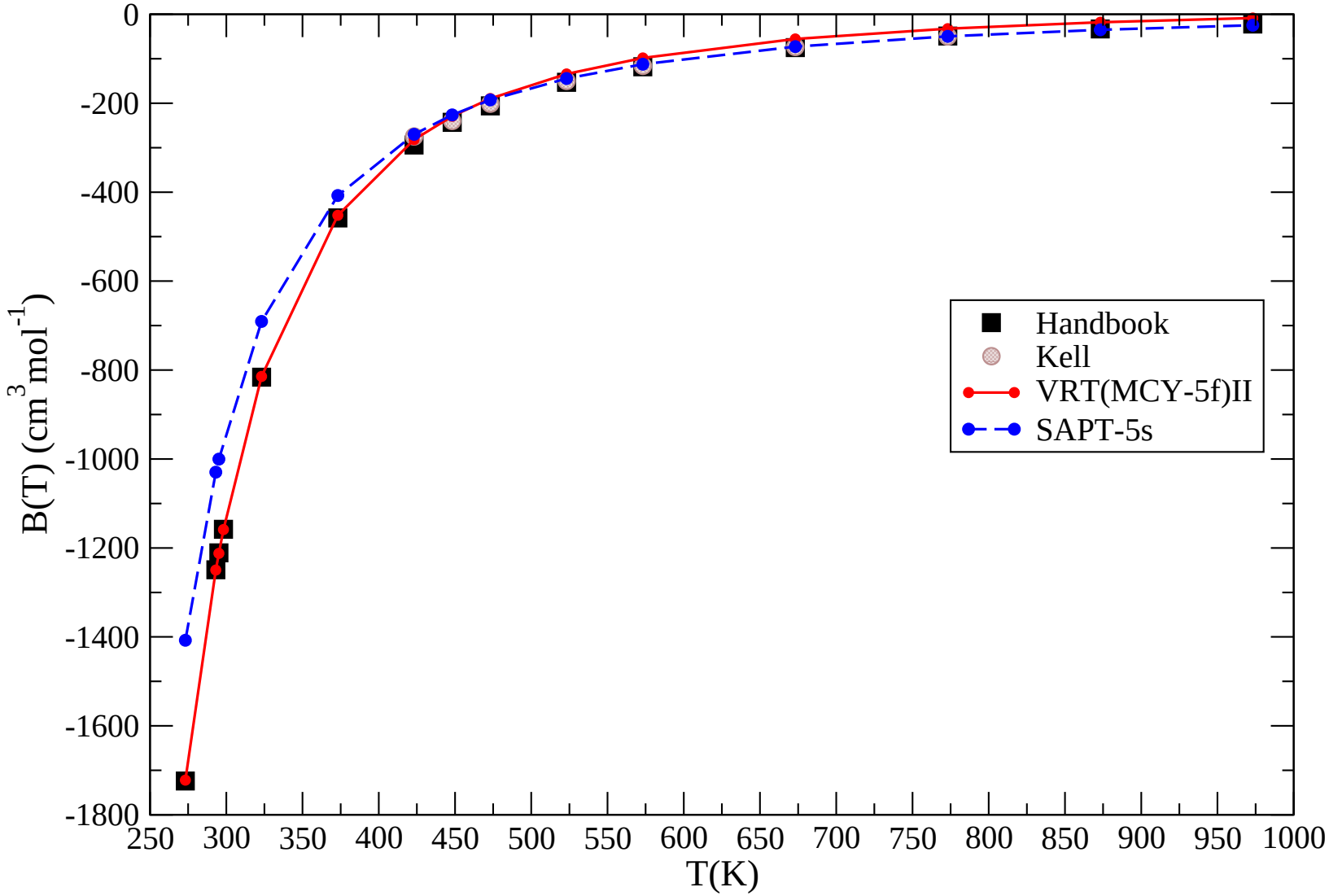
Second Coefficient du Viriel



Future directions

- Improve the PES with a more elaborated two-body functional form
- Fit an explicit polarizability two-body term
- Improve the iterative calculation of bounded states with a preconditioning of the basis set

Acknowledgement

- Claude Leforestier (LSDSMS Montpellier II)
- Fabien Gatti and Christophe Iung (LSDSMS Montpellier II)
- R.J. Saykally (Departement of Chemistry, Berkeley-California)
- David Benoit (Theory group – SFB 569, Ulm Germany)