Using contracted basis functions and the Lanczos algorithm to compute spectra of flexible Van der Waals dimers

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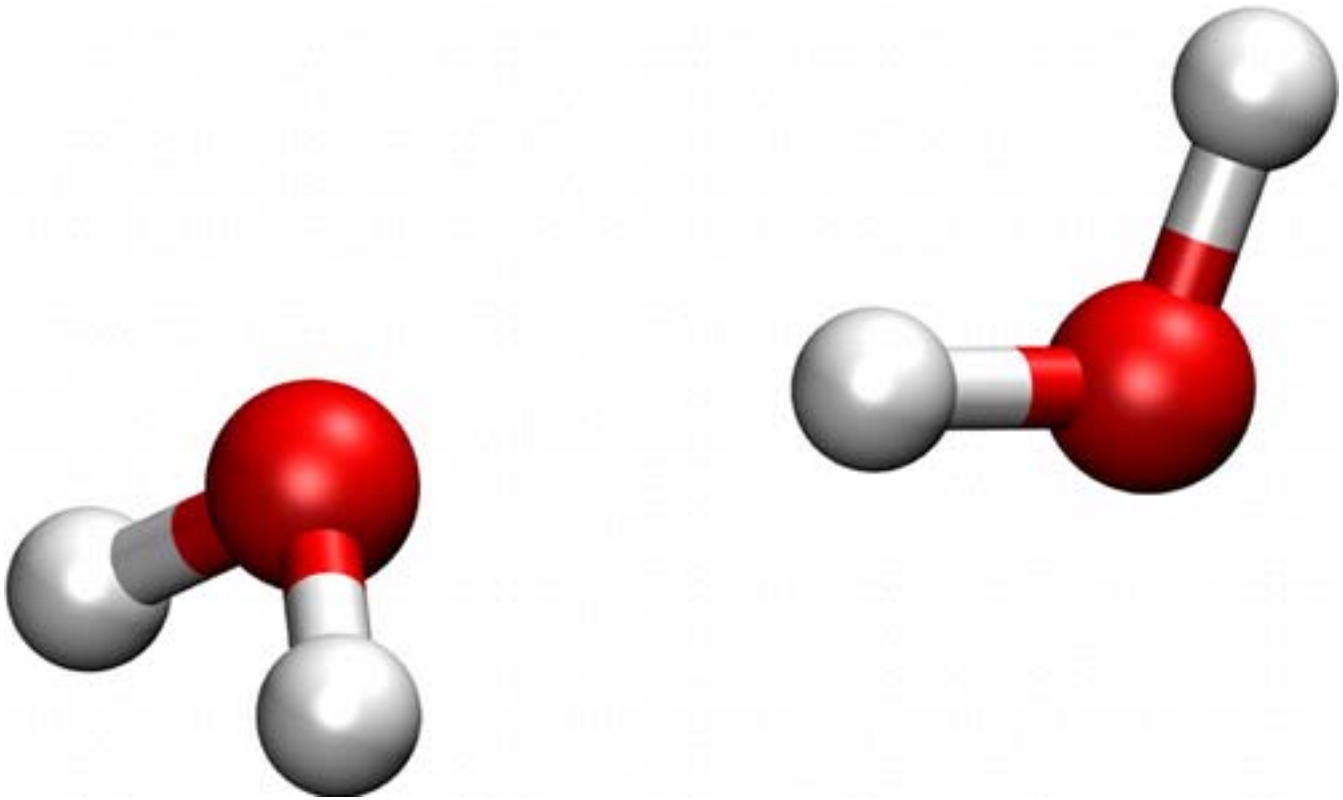
Calculating spectra is useful because it enables spectroscopists to

- predict the position (and intensity) of unobserved transitions
- verify the accuracy of or refine potential energy surfaces
  - extract information about interactions
- assign observed spectra

A new method for computing ro-vibrational spectra that is particularly efficient for Van der Waals clusters

- Clusters consist of stable molecules held together by Van der Waals (VdW) interactions.
- Design a basis that exploits the weakness of coupling between intra- and inter-monomer coordinates, but with which matrix-vector products and hence iterative eigensolvers are efficient.
- Apply it to compute ro-vibrational levels of the water dimer for which a lot of detailed experimental information is available,
  - important for understanding liquid water, solutions, some biological processes

Water dimer



- We do not force the monomers to be rigid.
- Allowing monomers to vibrate is important for some VdW clusters (for which coupling between intra- and inter-monomer coordinates is significant).
- Benchmark for assessing the accuracy of the rigid-monomer approximation.
- Calculating the spectrum of a VdW cluster is difficult because large amplitude motion makes harmonic models poor.

How does one solve the Schroedinger equation ?

- represent wavefunctions with basis functions

$$\psi_n(\mathbf{r}, \boldsymbol{\theta}) = \sum_k c_k^n \quad f_k(\mathbf{r}, \boldsymbol{\theta})$$

- compute eigenvalues and eigenvectors of the Hamiltonian matrix

Fundamental Recipe

$$\hat{K} + \hat{V} \rightarrow \hat{H} \xrightarrow{basis} \mathbf{H} \rightarrow \begin{matrix}\text{eigenvalues,} \\ \text{eigenvectors}\end{matrix} \rightarrow \begin{matrix}\text{energies,} \\ \text{wavefunctions}\end{matrix}$$

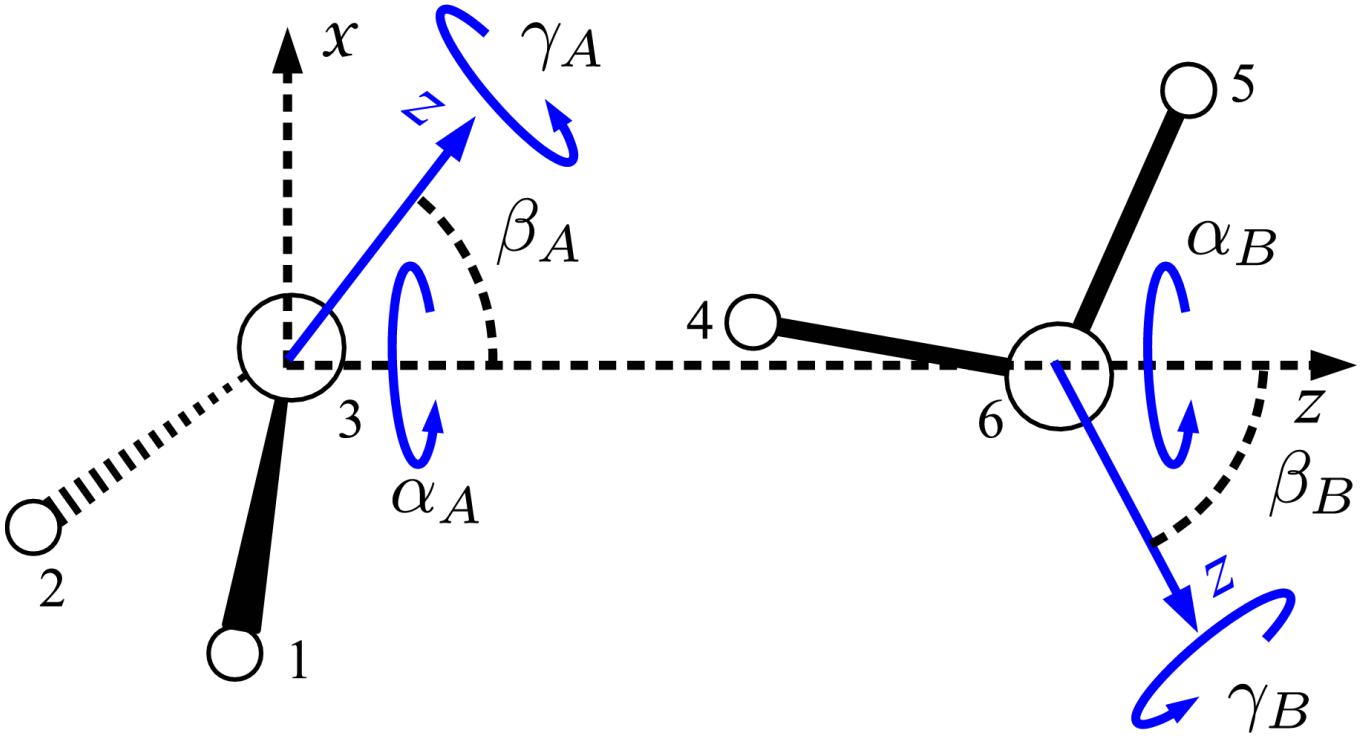
$$\rightarrow \text{Spectrum}$$

We want to be able to deal with large amplitude motion

Normal coordinates are not appropriate for molecules with large amplitude motion.

For VdW clusters, it is best to use inter- and intra-monomer vibrational coordinates.

For water dimer



The intra-monomer coordinates are $q_A = \{R_{1A}, R_{2A}, \theta_A\}$ and $q_B = \{R_{1B}, R_{2B}, \theta_B\}$.
The inter-molecular coordinates are $Q = \{r_0, \alpha_A, \beta_A, \gamma_A, \alpha_B, \beta_B, \gamma_B\}$.
The rotational coordinates are $\{\alpha, \beta\}$.

For a dimer, four frames are used to define the coordinates :

- A space-fixed (SF) frame
- The dimer-fixed frame, whose orientation is specified by the two polar angles, α and β, that orient $\vec{r_0}$ in the SF frame.
- Two monomer-fixed (MF) frames attached to the two monomers and whose orientation is specified by Euler angles.

$$\text{SF frame} \xrightarrow{\alpha,\beta} \text{DF frame} \begin{cases} \xrightarrow{\alpha_A,\beta_A,\gamma_A} \text{MF frame (A)} \\ \xrightarrow{\alpha_B,\beta_B,\gamma_B} \text{MF frame (B)} \end{cases}$$

For water dimer a convenient basis is

$$\chi^{1A}_{n_1}(R_{1A})\chi^{\theta_A}_{n_2}(\theta_A)\chi^{2A}_{n_3}(R_{2A}) \times \chi^{1B}_{n_4}(R_{1B})\chi^{\theta_B}_{n_5}(\theta_B)\chi^{2B}_{n_6}(R_{2B})$$
$$\chi^{r_0}_{n_r}(r_0) \times D^{j_A*}_{m_A,k_A}(\alpha_A,\beta_A,\gamma_A)D^{j_B*}_{m_B,k_B}(\alpha_B,\beta_B,\gamma_B)D^{J*}_{MK}(\alpha,\beta,0)$$

In this basis

- there are simple equations for all matrix elements of angular terms in the kinetic energy operator (KEO)
- singularities in the KEO cause no trouble.

About 10 1-d functions required for each vibrational coordinate.

$\Rightarrow (2J+1) * 10^{3N-6}$ multi-d basis functions required.

This is the curse of dimensionality.

The Hamiltonian matrix is

- too large to calculate
- too large to store in memory
- too large to diagonalise

How large is too large ?

To calculate only the $J = 0$ levels of H_2O, one requires a $\sim 10^3 \times 10^3$ matrix, ~ 0.008 GB

Add a single atom :
to calculate only the $J = 0$ levels of CH_2O, one requires a $\sim 10^6 \times 10^6$ matrix, ~ 8000 GB

For methane, to calculate the $J = 0$ levels, one requires a $\sim 10^9 \times 10^9$ matrix, $\sim 8 \times 10^9$ GB

For water dimer, to calculate the $J = 0$ levels, one requires a $\sim 10^{12} \times 10^{12}$ matrix, $\sim 8 \times 10^{15}$ GB

Diagonalization can be avoided by using iterative methods

- Energy levels, intensities, rate constants, cross sections can be computed from time-independent methods that require only evaluating matrix-vector products
- Matrix-vector products can be done without storing a Hamiltonian matrix or even computing its elements
- Only a few vectors are stored
- Using multi-dimensional quadrature does not significantly increase the cost

Lanczos Algorithm

$$\mathbf{H} = \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} \rightarrow \begin{pmatrix} \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot \end{pmatrix} = \mathbf{T}$$

- Amongst the eigenvalues of $\mathbf{T}$ are eigenvalues of $\mathbf{H}$
- Eigenvectors of $\mathbf{H}$ are obtained from those of $\mathbf{T}$

Despite the advantages of iterative methods, a product basis is too big

Even for $J = 0$, a product basis is too large for water dimer

It would be necessary to use $\sim 10^{12}$ basis functions (8000 GB for one vector) !

When an iterative eigensolver by itself is not enough

Methods that exploit a sum-of-products PES

- Prune the product basis : Halonen and Child, TC and Wang, Poirier, Tannor
- Use optimized 1-d basis functions : MCTDH
- Coupled cluster type methods, Christiansen
- Use a sum-of-products basis that is not a direct product basis : work with Arnaud Leclerc and Phillip Thomas

Methods that exploit a multimode decomposition (ANOVA)

- Prune the product basis using an electronic-structure-theory motivated scheme

When an iterative eigensolver by itself is not enough

Methods designed to use a general potential

- Prune the product basis and use a Smolyak nondirect product quadrature (similar ideas can be used to fit potentials). TC and Avila, Lauvergnat
- Use "simply contracted" basis functions and avoid the need to store the potential on a full grid by storing an intermediate matrix

Kinetic energy operator (KEO)

$$T = T^A(\mathbf{q_A}; \mathbf{p_A}, \mathbf{j_A}) + T^B(\mathbf{q_B}; \mathbf{p_B}, \mathbf{j_B}) + T_{int}(\mathbf{Q}; \mathbf{p_{r_0}}, \mathbf{j_A}, \mathbf{j_B}, \mathbf{J})$$

$$T^A = \frac{1}{2} \begin{pmatrix} \mathbf{p_A^\dagger} & \mathbf{j_A^\dagger} \end{pmatrix} \begin{pmatrix} \mathbf{G(q_A)} & \sigma(\mathbf{q_A}) \\ \sigma^{\mathbf{t}}(\mathbf{q_A}) & \mathbf{\Gamma}(q_A) \end{pmatrix} \begin{pmatrix} \mathbf{p_A} \\ \mathbf{j_A} \end{pmatrix}$$

$$T_{int} = -\frac{1}{2\mu_0} \frac{\partial^2}{\partial r_0^2} + B_0(r_0) \left[\mathbf{J}^2 - \cot\beta \frac{\partial}{\partial \beta} + (\mathbf{j_A} + \mathbf{j_B})^2 - 2(\mathbf{j_A} + \mathbf{j_B}) \cdot \mathbf{J} \right]$$

T^A and T^B are standard triatomic ro-vibrational KEOs, but the rotational coordinates are wrt the DF frame and not a SF frame.

Brocks, van der Avoird, Sutcliffe, Tennyson, Mol. Phys. 50, 1025 (1983)

Any known triatomic KEO can be copied and pasted into the full KEO.

One can use bisector or Eckart axes. One can use Radau or Jacobi vectors. (We use bisector axes and Radau coordinates.)

Well known ro-vibrational triatomic basis sets can be used for the monomer coordinates.

Hamiltonian

$$H = T^A + T^B + T_{int} + V$$

$$V = V^A(q_A) + V^B(q_B) + \Delta V(q_A, q_B, Q)$$

$$H = H_{fast} + T_r^A + T_{cor}^A + T_r^B + T_{cor}^B + T_{int}$$

where

$$H_{fast} = T_v^A + T_v^B + V^A(q_A) + V^B(q_B) + \Delta V(q_A, q_B, Q)$$

The [6+6] adiabatic approach of Leforestier

Leforestier makes a vibrational basis by solving

$$H_{fast}\phi_v(q_A, q_B; Q) = \mathcal{E}(Q)\phi_v(q_A, q_B; Q)$$

and then solving

$$[T_{int} + \tilde{T}_r^A + \tilde{T}_r^B + \mathcal{E}(Q)]\chi_k(Q) = E_k\chi_k(Q) \ ,$$

in a basis

$$L(Q) * D_{MK}^{J*}(\alpha, \beta, 0)$$

where

$$L(Q) = \langle Q|\alpha_0; j_A, k_A, m_A; j_B, k_B, m_B\rangle$$

He uses

$$\tilde{T}_r^A = \frac{1}{2} j_A^\dagger \tilde{\Gamma}_v^A(Q) j_A$$

and

$$\tilde{\Gamma}_v^A \simeq \langle \phi_v(q_A, q_B; Q) | \Gamma(q_A) | \phi_v(q_A, q_B; Q)$$

- The intra-monomer basis functions depend parametrically on **Q**.

Our simply-contracted basis function method

Re-write

$$H = T_{int} + H^A + H^B + \Delta V(q_A, q_B, Q) + T_r^A + T_r^B + T_{cor}^A + T_{cor}^B \ .$$

Solve

$$H^X \phi_{vX} = \mathcal{E}_{vX} \phi_{vX} \quad X = A, B \ .$$

Solve the Schroedinger equation in the basis

$$\phi_{vA}(q_A)\phi_{vB}(q_B)L(Q)\ D_{MK}^{J*}(\alpha, \beta, 0)$$

Matrix elements

$$\langle v'|H|v\rangle$$
$$= \underbrace{\frac{1}{2}j_A^\dagger\langle v'|\Gamma^A|v\rangle j_A}_{T_r^A} + \underbrace{\frac{1}{2}j_A^\dagger\langle v'|\sigma_A^t p_A|v\rangle j_A + \frac{1}{2}j_A^\dagger\langle v'|p_A^\dagger\sigma_A|v\rangle j_A}_{T_{cor}^A}$$
$$+ \underbrace{\frac{1}{2}j_B^\dagger\langle v'|\Gamma^B|v\rangle j_B}_{T_r^B} + \underbrace{\frac{1}{2}j_B^\dagger\langle v'|\sigma_B^t p_B|v\rangle j_B + \frac{1}{2}j_B^\dagger\langle v'|p_B^\dagger\sigma_B|v\rangle j_B}_{T_{cor}^B}$$
$$+ T_{int}\delta_{v',v} + \langle v'|\Delta V(q_A, q_b, Q)|v\rangle + (\mathcal{E}_{v_A} + \mathcal{E}_{v_B})\delta_{v',v}$$

- A diagonal block of $\langle v'|\Delta V(q_A, q_b, Q)|v\rangle$ is a reduced-dimension PES. The required number of blocks depends on the importance of the coupling and the desired accuracy.

Disadvantages of Leforestier's approach

- Inherent approximations
  - Discard T^A_{cor} and T^B_{cor}
  - Because $\phi_v(q_A, q_B; Q)$ depends parametrically on Q, $\langle\phi_v(q_A, q_B; Q)|\Gamma(q_A)|\phi_v(q_A, q_B; Q)$ depends on Q. To avoid this Leforestier makes additional approximations.
  - Non-adiabatic coupling is neglected (Leforestier uses a single $\phi_v(q_A, q_B; Q)$)
- Computational cost
  - Two 3-d "fast" Schroedinger equation must be solved at about a million slow geometries. We solve two 3-d "fast" Schroedinger equations only once.

How do we deal with $\langle v'|\Delta V(q_A, q_b, Q)|v\rangle$

This is critical.

The most obvious approach is,

$$\langle L'|\langle v'|\Delta V(q_A, q_b, Q)|v\rangle L|\rangle$$
$$= \sum_{\alpha}\sum_{\beta} w_\alpha w_\beta L'(Q_\alpha) v'((q_A)_\beta, (q_B)_\beta)\ \Delta V((q_A)_\beta, (q_B)_\beta, Q_\alpha)$$
$$v((q_A)_\beta, (q_B)_\beta) L(Q_\alpha)$$

This requires storing $\Delta V((q_A)_\beta, (q_B)_\beta Q_\alpha)$ which is an array with $\sim 10^{12}$ components.

$\Delta V((q_A)_\beta, (q_B)_\beta Q_\alpha)$ is a 12th order or 12-d tensor.

Instead use the F matrix idea

$$\langle L'|\langle v'|\Delta V(q_A, q_B, Q)|v\rangle|L\rangle$$

$$= \sum_\alpha T_{L',\alpha}\langle v'|\Delta V(q_A, q_B, Q_\alpha)|v\rangle (T^t)_{\alpha,L}$$

$$= \sum_\alpha T_{L',\alpha} F_{v',v;\alpha} (T^t)_{\alpha,L} \ ,$$

where

$$T_{L',\alpha} = \sqrt{w_\alpha} L'(Q_\alpha)$$

- F is a 3rd order or 3d tensor ($3 \ll 12$).
- Owing to the fact that there are very few $|v\rangle$, the memory cost of storing F is small.
- F matrix elements for different α can be computed on different cores.
- The calculation of F is the most time consuming step. On 1024 cores it takes 20 hours (10^6 Q points ; 10^3 q points).

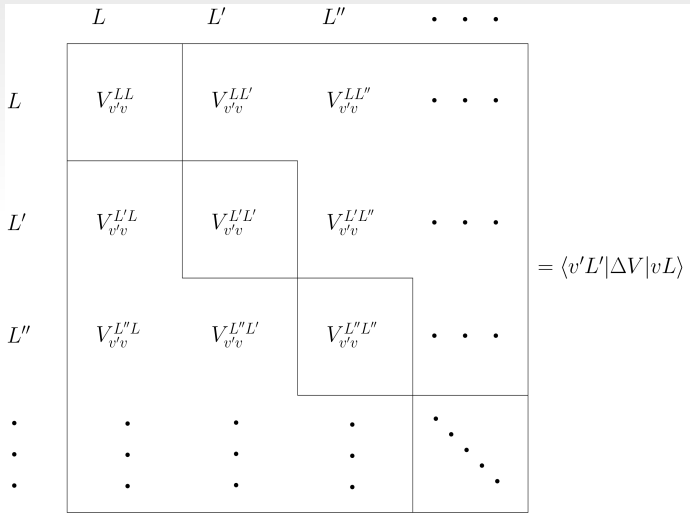
The same sort of idea was used previously for methane and CH_5^+

ΔV matrix : F-matrix method

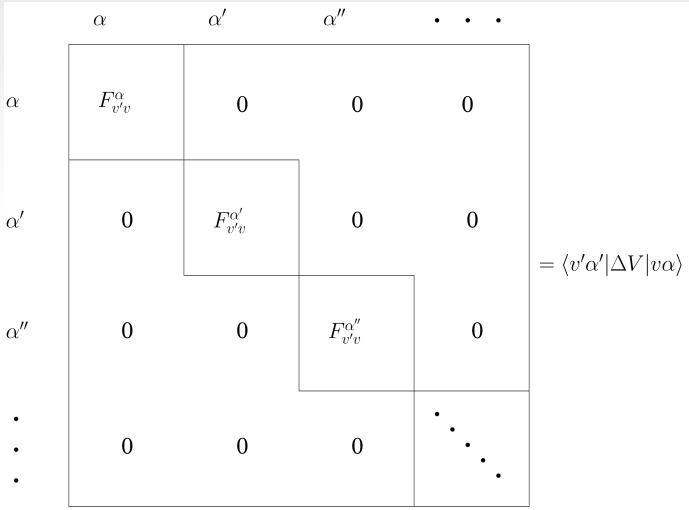
We do not store the ΔV matrix, but store the **F**-matrix.

$$\langle v'L'|\Delta V(\mathbf{q},\mathbf{Q})|vL\rangle = \sum_{\alpha}\langle L'|\alpha\rangle \boxed{\langle v'\alpha|\Delta V(\mathbf{q},\mathbf{Q}_\alpha)|v\alpha\rangle} \langle\alpha|L\rangle$$

$\boxed{F^{(\alpha)}_{v'v}}$



4-index array



3-index array: F-matrix

- 3-index array is much smaller $\dfrac{N_L^2 N_v^2}{N_\alpha N_v^2} = \dfrac{N_L^2}{N_\alpha} \approx$ millions

Water dimer

Three tunneling paths

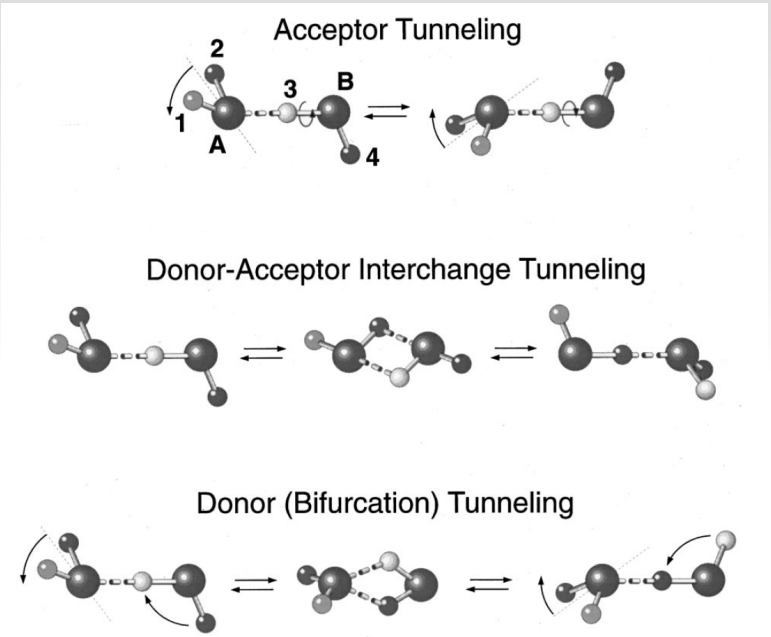
On SAPT-5st PES

ΔV barrier height, Δ tunneling splittings

$\Delta V = 156\ \mathrm{cm}^{-1}, \Delta \approx 10\ \mathrm{cm}^{-1}$

$\Delta V = 185\ \mathrm{cm}^{-1}, \Delta \approx 0.3\ \mathrm{cm}^{-1}$

$\Delta V = 636\ \mathrm{cm}^{-1}, \Delta \approx 0.02\ \mathrm{cm}^{-1}$

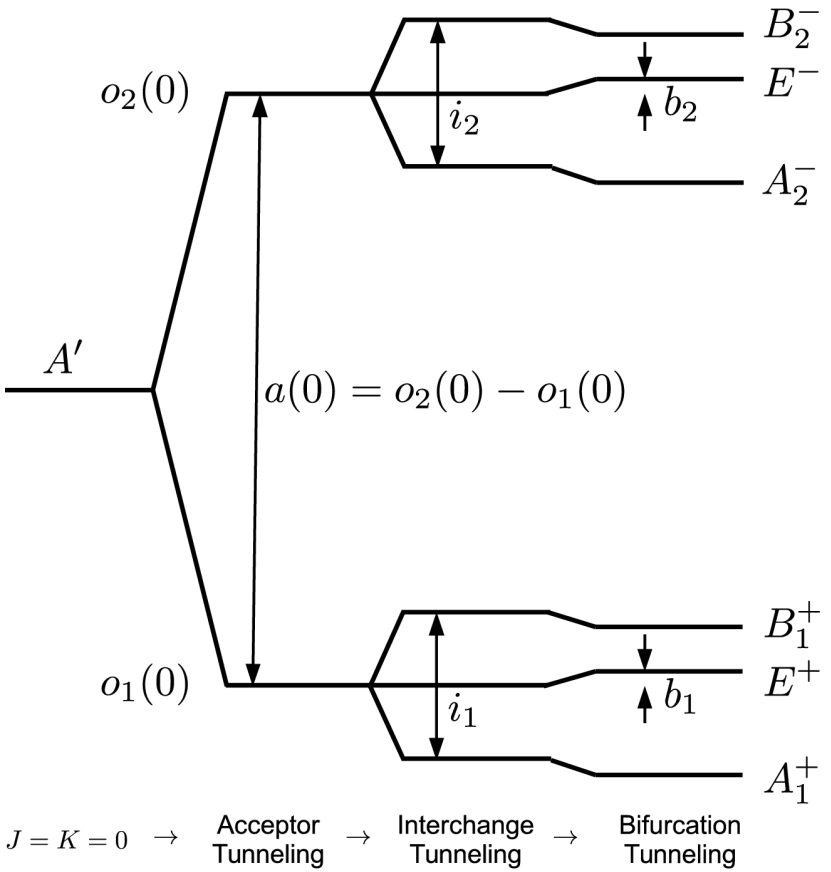


- Only the acceptor tunneling path does not break the H-bond. It therefore has the lowest barrier and the largest splitting.

Figure from Groenenboom, Wormer, van der Avoird, Mas, Bukowski, Szalewicz, JCP, 113, 6702(2000)

Energy level pattern

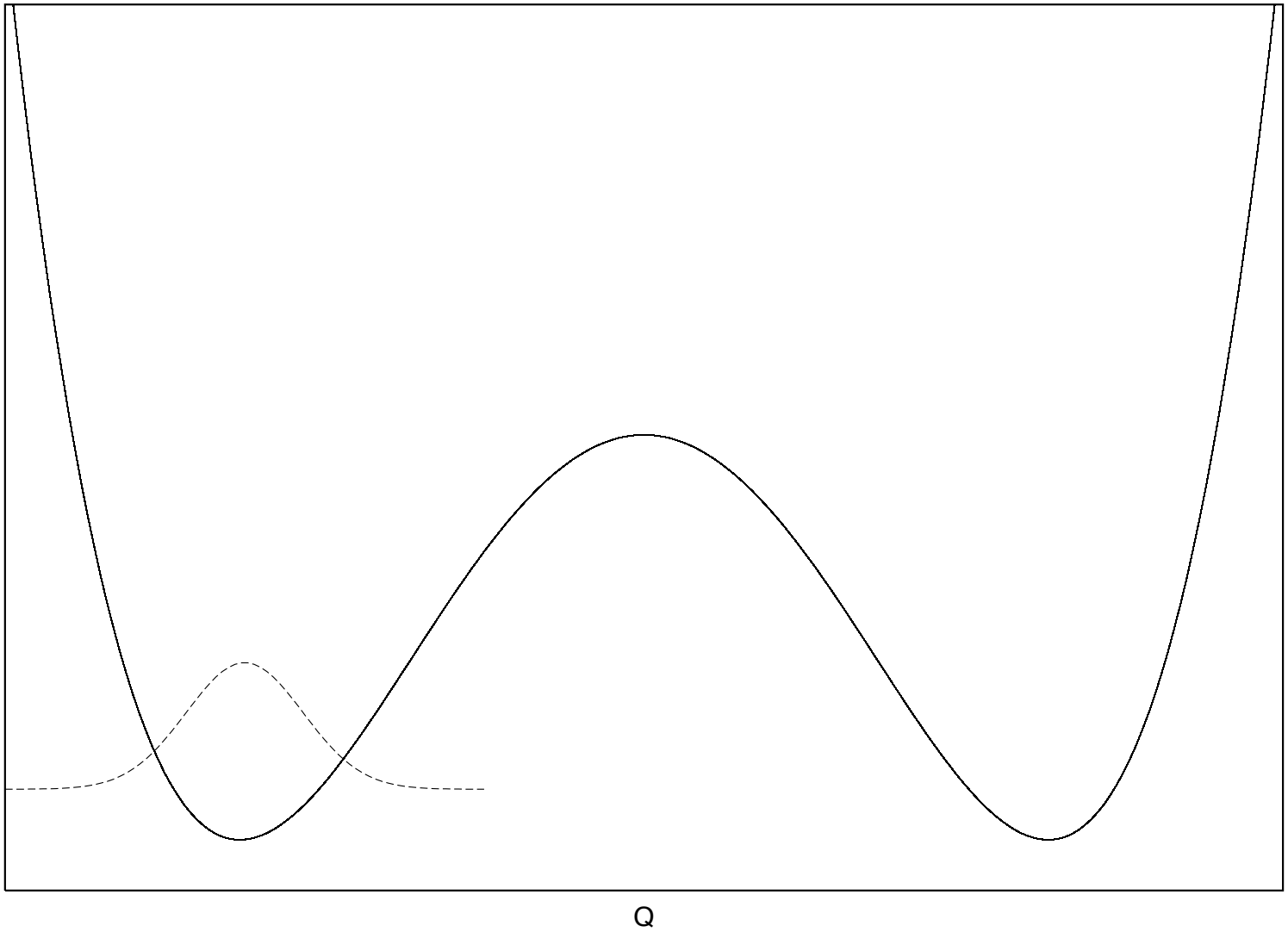
- The appropriate permutation-inversion group is G_{16}
- There are 8 equivalent equilibrium structures
- Tunnelling splits each state into 8 states (6 levels)



Dyke, JCP 66, 492 (1977)

Why are problems with multiple minima difficult ?

Basis functions must have amplitude in all the wells



Convergence errors of E^+ vibrational levels of $(H_2O)_2$ (in cm^{-1})

$N_v \rightarrow$	1	3	10	22	48
$E_{cut} \rightarrow$	1.	1600.	3800.	5400.	7500.
ZPE	10.34	4.63	0.67	0.09	-1108.49
GS	-0.02	0.01	0.00	0.00	0.41
DT	0.29	-0.13	0.02	0.00	62.03
AW	0.26	0.35	0.03	0.01	109.17
AT	0.39	0.23	0.05	0.01	117.18
	1.29	0.09	0.03	0.01	129.69
	-0.11	-0.02	0.05	0.02	143.34
	1.66	0.20	0.05	0.01	171.82
	0.85	0.35	0.07	0.02	189.06

- E^+ levels appear in the triple sub-folk of each vibrational state.
- $N_v = 10$ is the final basis chosen with errors smaller than 0.1 cm^{-1}.

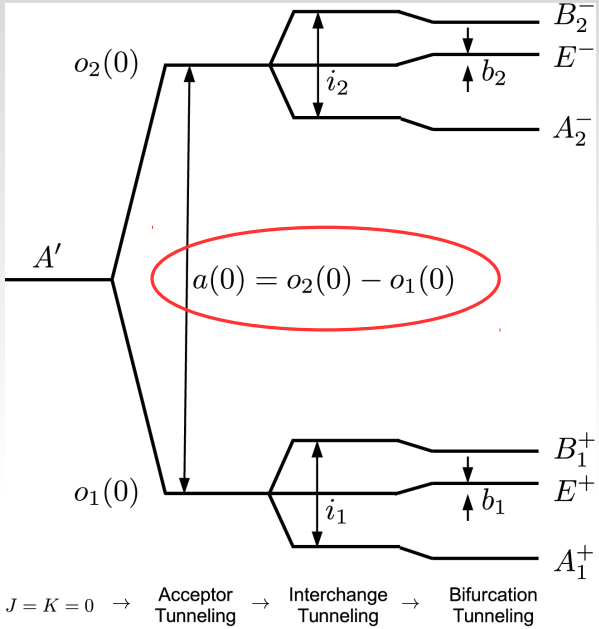
Comparison with the adiabatic results for E^+ levels of $(H_2O)_2$ (in cm^{-1}).

	$N_v = 48$ $E_{cut} = 7500.$	[6+6]D	diff.
ZPE	-1108.49	-1108.27	0.22
GS	0.41	0.26	-0.15
DT	62.03	61.84	-0.19
AW	109.17	109.06	-0.11
AT	117.18	117.43	0.25
	129.69	129.60	-0.09
	143.34	143.30	-0.04
	171.82	171.95	0.13
	189.06	189.32	0.26

- We also computed the DMC ZPE on the PES, -1109(2) cm^{-1} in good agreement with our variational calculation

The most important (largest) tunneling splitting : acceptor tunneling splitting.

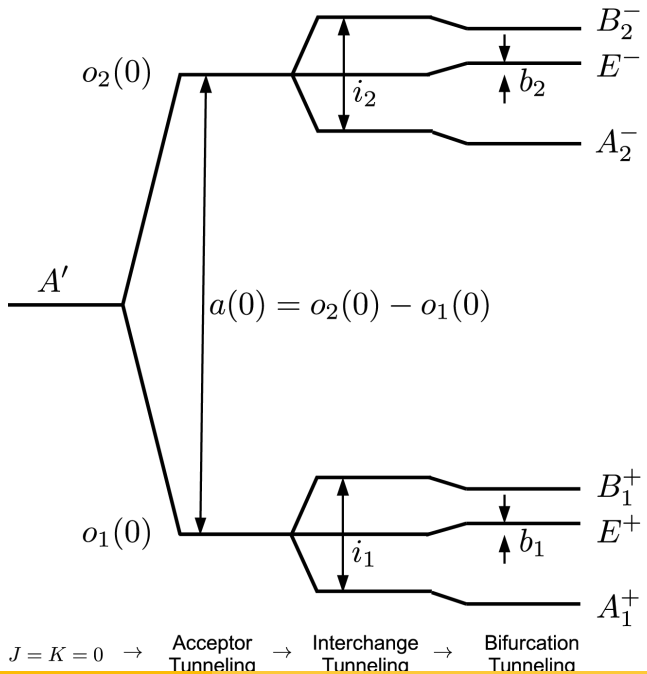
	Obs.	[6+6]D	This work
$a(K=0)$	N.A.	12.75	12.50
$a(K=1)$	N.A.	3.10	2.98
$a(K=0)+a(K=1)$	13.92	15.84	15.48
Cal. $-$ Obs.	0.00	1.92	1.56



- Our acceptor tunneling splitting is 0.4 cm^{-1} less than the [6+6]D result. This reduces the difference between theory and experiment from 1.9 to 1.5 cm^{-1}.

Bifurcation splittings $b_1(K)$ and $b_2(K)$ (in cm^{-1}) .

	Expt.	[6+6]D	This work	CC-pol-8s(6D)
$b_1(0)$	N/A	-0.0490	0.0333	0.0218
$b_1(1)$	N/A	-0.1235	-0.0296	-0.0198
$(\|b_1(0)\| + \|b_1(1)\|)/2$	0.0227	0.0862	0.0314	0.0208
$b_2(0)$	N/A	0.1198	0.0331	0.0216
$b_2(1)$	N/A	0.0521	-0.0360	-0.0255
$(\|b_2(0)\| + \|b_2(1)\|)/2$	0.0249	0.0859	0.0346	0.0236



Conclusion

- A new method for computing ro-vibrational spectra of molecules or clusters whose vibrational coordinates can be divided into inter-monomer and intra-monomer groups
- Does not require using a sum-of-products PES
- Works even for PESs with multiple wells
- Able to cope with large amplitude motion because it does not depend on normal coordinates
- Use both contracted basis functions and a Lanczos eigensolver
- Store a small intermediate matrix to obviate the need to store the potential on a full-d grid
- For H_2O dimer our results agree well with those obtained from a [6+6] adiabatic approach. For HOD dimer differences will be larger

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Because the basis is huge it would be far too costly to form the potential matrix and explicitly multiply the matrix with vectors.

To illustrate the computation of a matrix-vector product consider

$$w_{l'm'} = \sum_{lm} V_{l'm',lm}\ x_{lm}$$

replace

$$\begin{aligned} V_{l'm',lm} &= \int d\theta \int d\phi Y_{l'm'}(\theta,\phi) V(\theta,\phi) Y_{lm}(\theta,\phi) \\ &\approx \sum_{\beta\gamma}\ T^{m'}_{l'\beta}\ Q_{m'\gamma}\ V(\theta_\beta,\phi_\gamma)\ Q_{m\gamma}\ T^{m}_{l\beta} \end{aligned}$$

$$w_{l'm'} = \sum_{lm} \sum_{\beta\gamma} T^{m'}_{l'\beta} \; Q_{m'\gamma} \; V(\theta_\beta, \phi_\gamma) \; Q_{m\gamma} \; T^{m}_{l\beta} \; x_{lm}$$

$$w_{l'm'} = \sum_{\beta} T^{m'}_{l'\beta} \sum_{\gamma} Q_{m'\gamma} \; V(\theta_\beta, \phi_\gamma) \sum_{m} Q_{m\gamma} \sum_{l} T^{m}_{l\beta} \; x_{lm}$$

The largest vector is labelled by the grid indices.