

Using the DVR to solve the Schroedinger equation

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How does one solve the Schroedinger equation ?

- represent wavefunctions with basis functions

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

- I'll focus on solving the time-independent Schroedinger equation, but many of the ideas apply also to methods for solving the time-dependent Schroedinger equation,

The discrete variable representation

First, in 1D

$$\hat{H} = \hat{K} + \hat{V}$$

$$\psi_n(x) = \sum_k c_k^n f_k(x)$$

$$(\mathbf{K} + \mathbf{V})\mathbf{C} = \mathbf{C}\mathbf{E}$$

$$(\mathbf{V})_{ij} = \langle f_i | \hat{V} | f_j \rangle; \quad (\mathbf{K})_{ij} = \langle f_i | \hat{K} | f_j \rangle;$$

$$\mathbf{xT} = \mathbf{TX}$$

$$\mathbf{T}^T(\mathbf{K} + \mathbf{V})\mathbf{TU} = \mathbf{U}\mathbf{E}$$

$$(\mathbf{T}^T\mathbf{K}\mathbf{T} + \mathbf{V}^{\text{diag}})\mathbf{U} = \mathbf{U}\mathbf{E}$$

$$\mathbf{T} = \mathbf{T}_1 \otimes \mathbf{T}_2 \otimes \cdots \otimes \mathbf{T}_D$$

Advantages of the direct product DVR approach

- no integrals to compute
- easy to set up the Hamiltonian matrix

The direct product DVR approach has important limitations

- A direct-product Hamiltonian matrix is huge

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$$\Phi_{n_1, n_2, \dots, n_D} = {}^1\phi_{n_1}(q_1) {}^2\phi_{n_2}(q_2) \cdots {}^D\phi_{n_D}(q_D)$$

- About 10 1D functions are required for each vibrational coordinate.
 $\Rightarrow (2J + 1) * 10^{3N-6}$ multi-d basis functions required.
- For some problems a direct product basis is not appropriate

The basis size problem is mitigated 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
- Obviates the need to store a matrix representation of the Hamiltonian
- Even better, Hamiltonian matrix elements are never calculated
- Using multi-dimensional quadrature does not significantly increase the cost

Not good enough

- Iterative methods reduce the memory cost of calculations from $N^2(= (n^D)^2) \rightarrow N(= n^D)$.
- If $D = 6$ and $n = 10$: $8000GB \rightarrow 0.008GB$
- However, if $D = 12$ and $n = 10$
 $8^{15}GB \rightarrow 8000GB$

A direct product basis is also poor whenever the kinetic energy operator (KEO) has important singularities

- Singularities occur when one distinguishes between vibration and rotation by introducing a molecule-fixed frame
- There is a singularity when one coordinate becomes undefined and another has one of its limiting values.
- The simplest example is the H atom : when $\theta = 0$ or π , ϕ is undefined and the KEO is singular.

$$T = \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

To deal with singularities, it is best to use basis functions that are eigenfunctions of a part of the Hamiltonian that includes the singular term

- For example, spherical harmonics. This is an FBR.
- Now the potential matrix is **not** diagonal.
- If the number of coordinates is $\lesssim 5$ and one can exploit symmetry then nondirect product bases can be used without iterative methods (e.g., Chen and Light, J.C.P. 112, 5070 (2000)).

For both the kinetic matrix-vector product in the DVR and the potential matrix-vector product in the FBR, one needs a way of evaluating matrix-vector products, **that does not rely on sparsity**

A 2D FBR potential matrix-vector product example.

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

replace

$$\begin{aligned} V_{l'm',lm} &= \int d\theta \int d\phi Y_{l'm'}(\theta, \phi) V(\theta, \phi) Y_{lm}(\theta, \phi) \\ &\approx \sum_{\beta\gamma} T_{l'\beta}^{m'} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) Q_{m\gamma} T_{l\beta}^m \end{aligned}$$

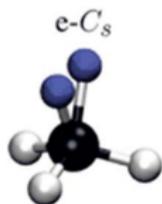
$$w_{l'm'} = \sum_{lm} \sum_{\beta\gamma} T_{l'\beta}^{m'} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) Q_{m\gamma} T_{l\beta}^m x_{lm}$$

$$w_{l'm'} = \sum_{\beta} T_{l'\beta}^{m'} \sum_{\gamma} Q_{m'\gamma} V(\theta_\beta, \phi_\gamma) \sum_m Q_{m\gamma} \sum_l T_{l\beta}^m x_{lm}$$

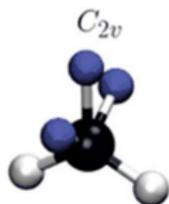
The cost of each sum scales as n^{D+1}

The potential matrix is **not sparse**

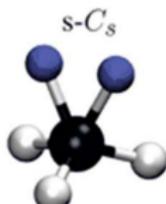
Example of the use of the FBR where singularities are important : ro-vibrational levels of CH_5^+



$$V = 0 \text{ cm}^{-1}$$



$$V = 341 \text{ cm}^{-1}$$



$$V = 29 \text{ cm}^{-1}$$

- CH_5^+ is strongly bound (dissociation energy $\approx 15000 \text{ cm}^{-1}$) but barriers are low and permutation of all the protons is possible. 120 minima are accessible.

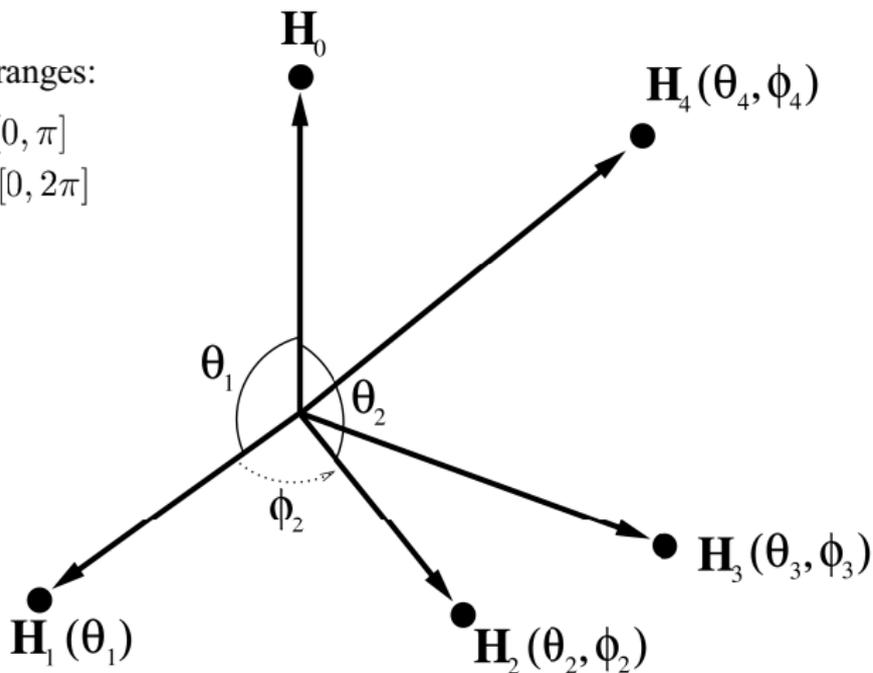
CH_5^+ has 120 wells

7 angles for CH_5^+ : 4 planar angles + 3 dihedral angles

Angle ranges:

$$\theta_i \in [0, \pi]$$

$$\phi_i \in [0, 2\pi]$$



Solve the bend-rotation problem

- The full kinetic energy operator is

$$T = T_{\text{str}} + T_{\text{ben}} + T_{\text{cor}} .$$

- Discard T_{str} ,
- Make a minimized bend potential
- Basis functions :

$$\Theta_{l_1}^{m_1}(\theta_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) Y_{l_3}^{m_3}(\theta_3, \phi_3) Y_{l_4}^{m_4}(\theta_4, \phi_4) D_{JK}^{M*}(\alpha, \beta, \gamma)$$

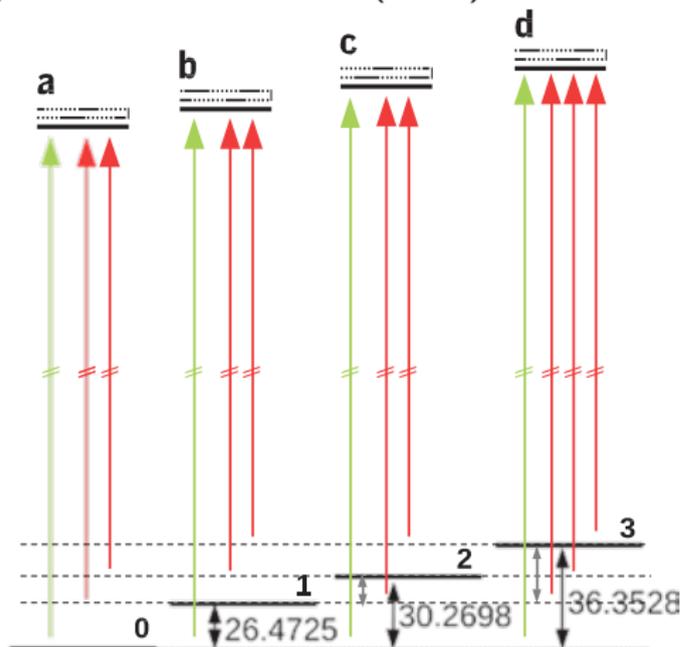
with the constraint

$$m_1 = K - m_2 - m_3 - m_4$$

- For $J = 3$, we use 1020 million basis functions (for one parity).

Experimental ground state combination differences

Asvany et al. reported ground state combination differences (CoDiffs) : Science, 347, 1346(2015).



A possible misassignment

If both parities exist in the trap, there is an assignment that significantly reduces differences between experiment and theory.

Calculated and experimental energy differences.

G_2^-			H_2^-		
ΔE	Expt. Set 1		ΔE	Expt. Set 2	
$J = 0$ (10.9)			$J = 1$ (26.6)		
$J = 2$ 40.9	26.5		$J = 2$ 5.7	39.7	
$J = 1$ 49.5	30.3		$J = 0$ 15.5	47.3	
$J = 2$ 53.5	36.4		$J = 2$ 31.0	51.8	

G_2^+		H_2^+	
ΔE		ΔE	
$J = 1$ (24.2)		$J = 1$ (32.9)	
$J = 2$ 26.8		$J = 2$ 8.1	
$J = 1$ 32.5		$J = 0$ 24.2	
$J = 3$ 37.4		$J = 2$ 25.9	

The key problem is that the basis is too big.

Two strategies

- Do not use basis functions that are products of functions of a single coordinate
- Use basis functions that are products of functions of a single coordinate, but do not keep all possible products.

Contracted basis functions

- Excellent basis functions are obtained by diagonalizing blocks, labelled by DVR indices, of the full Hamiltonian matrix. (Bačić and Light)
- For a triatomic molecule, the Hamiltonian matrix is,

a)

	a_1					a_2			a_3			
	i_1	i_2	i_3	i_4	i_5	i_1	i_2	i_3	i_1	i_2	i_3	i_4
a_1	i_1	i_2	i_3	i_4								
X												
							Y					Z
a_2						i_1	i_2					
							W					
a_3									i_1	i_2	i_3	i_4

Difficult to use for larger molecules

- If there are five angles (e.g. methane), then one must diagonalize many blocks and store many sets of stretch eigenvectors.
- If $n = 10$ and a direct product DVR is used there are 10^5 blocks.
- Some of these can be discarded, but many remain.

Simply contracted functions

Basis functions are selected products of eigenfunctions of reduced-dimension Hamiltonians.

$$H^{(b)} = T_{ben}(\theta, r_e) + V(\theta, r_e).$$

$$X_b(\theta) = \sum_l C_{lb} f_l(\theta)$$

The f_l are primitive FBR or DVR bend basis functions.

$$H^{(s)} = T_{str}(r) + V(\theta_e, r).$$

$$Y_s(r) = \sum_{\alpha} D_{\alpha s} g_{\alpha}(r)$$

The g_{α} are primitive DVR stretch basis functions.

Bramley and Carrington, Wang and Carrington, Yu, Lee and Light

How do we deal with $\langle X_{b'} | \Delta V(r, \theta) | X_b \rangle$

The most obvious approach is,

$$\begin{aligned} & \langle s' b' | \Delta V(r, \theta) | b s \rangle \\ &= \sum_{\alpha} \sum_{\beta} (D^T)_{s', \alpha} (C^T)_{b', \beta} \Delta V(\theta_{\beta}, r_{\alpha}) (C)_{\beta, b} (D)_{\alpha, s} \end{aligned}$$

This requires storing $\Delta V(\theta_{\beta}, r_{\alpha})$ which is an array with $\sim n^D$ components.

When $D = 12$, this makes solving the Schroedinger equation impossible, despite the fact that the basis is small.

Instead use the F matrix idea

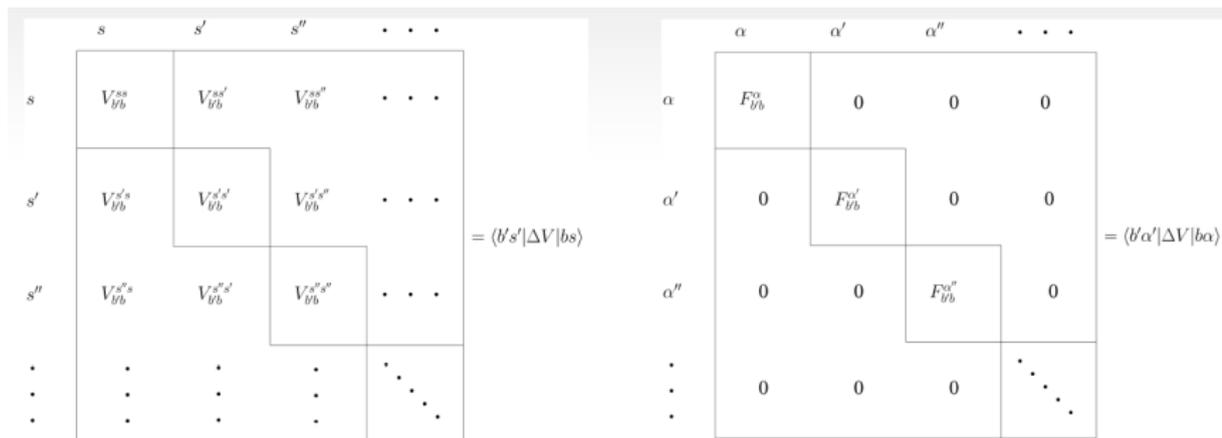
$$\langle s' b' | V(\theta, r) | b s \rangle = \sum_{\alpha} D_{\alpha s'} F_{b' b, \alpha} D_{\alpha s}$$

where

$$F_{b' b, \alpha} = \sum_{\beta} C_{\beta b'} C_{\beta b} \Delta V_{\beta \alpha} .$$

is pre-calculated.

- Owing to the fact that there are very few $|b\rangle$, the memory cost of storing F is small.
- F matrix elements for different α can be computed on different cores.



The DVR is critical

It is imperative that the primitive basis used to solve the stretch problem be a a DVR basis because this makes **F** block diagonal.

- We have used these ideas to compute spectra of hydrogen peroxide, methane, vinylidene, CH_5^+ , and water dimer
- John Light used them to compute spectra of hydrogen peroxide and formaldehyde.

Instead of using contracted basis functions one can prune a direct product basis.

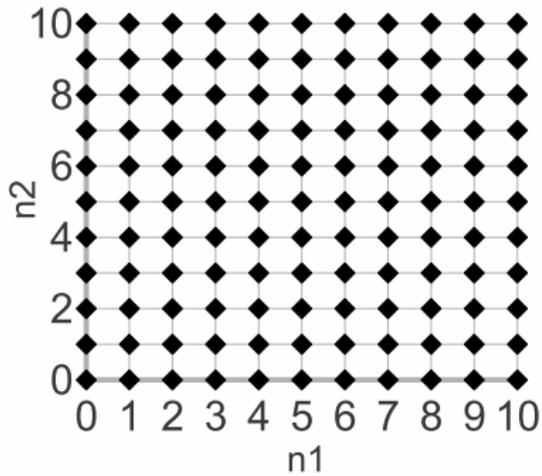
It is possible to use products of 1D functions

$$\Phi_{n_1, n_2, \dots, n_D} = {}^1\phi_{n_1}(q_1) {}^2\phi_{n_2}(q_2) \cdots {}^D\phi_{n_D}(q_D)$$

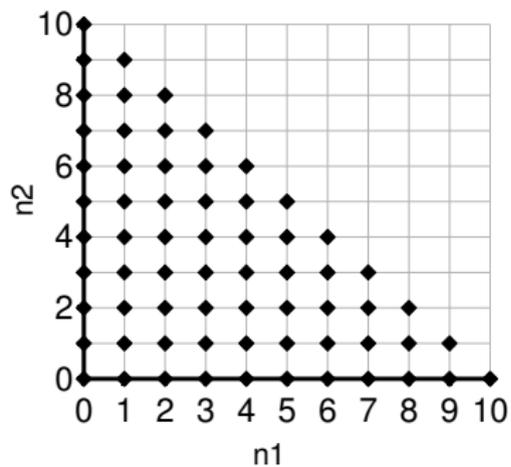
without using ALL the functions in a direct product basis.

This is done by removing functions, usually at the outside of the basis.

Full basis for a 2D problem



Pruned basis for the 2D problem



What 1D functions? Which products are retained?

- Harmonic oscillator functions

- Electronic-structure inspired ideas that retain functions with a limited number of non-zero quantum numbers (Bowman et al.)

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$$n_1 + \cdots + n_D \leq b$$

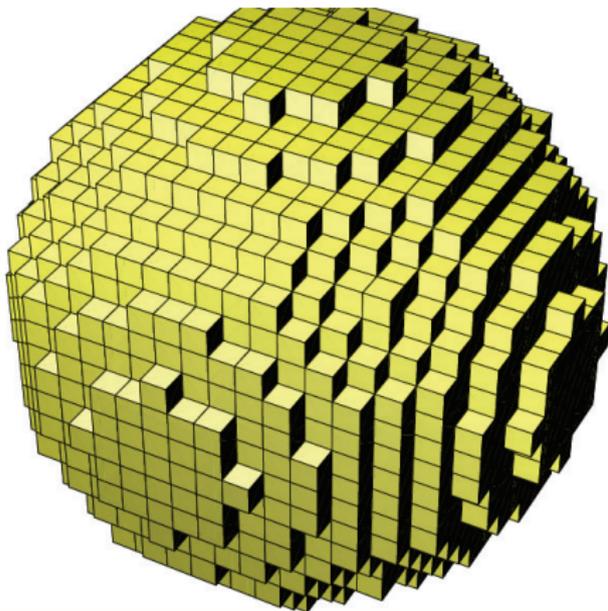
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$$g(n_1) + \cdots + g(n_D) \leq b ,$$

- DVR functions

- Retain DVR functions centered about points with potential values less than a threshold

- SD functions made by (nearly) simultaneously diagonalizing both x and p .
 - Retain SD functions with the smallest diagonal Hamiltonian elements.
- Phase-space localized (PSL) functions
 - Retain PSL functions centered about points with Hamiltonian values less than a threshold (Poirier et al.)



Pruning an harmonic oscillator basis

- If one simply removes basis functions for which

$$\sum_c n_c > b$$

the number of retained functions is

$$\frac{(D + b)!}{D!b!}$$

- For a 7-atom problem with $b = 15$

one vector : 4×10^{17} [3×10^9 GB] \rightarrow 8×10^7 [0.6 GB]

- Can be used in conjunction with a nondirect product Smolyak based quadrature

Some pruning schemes are compatible with sequential summation.

$$n_1 + n_2 + n_3 \leq b \Rightarrow n_1^{\max} = b - n_2 - n_3$$

$$n_2 + n_3 \leq b \Rightarrow n_2^{\max} = b - n_3$$

$$\sum_{n_3}^b \sum_{n_2}^{n_2^{\max}(n_3)} \sum_{n_1}^{n_1^{\max}(n_3, n_2)} A_{n_1 n_1} B_{n_2 n_2} C_{n_3 n_3} v_{n_1 n_2 n_3}$$

can be replaced by

$$\sum_{n_3}^b C_{n_3 n_3} \sum_{n_2}^{n_2^{\max}(n_3)} B_{n_2 n_2} \sum_{n_1}^{n_1^{\max}(n_3, n_2)} A_{n_1 n_1} v_{n_1 n_2 n_3}$$

-

$$g^1(n_1) + \dots + g^D(n_D) \leq b ,$$

with $g^c(n_c)$ designed to include only basis functions coupled by terms in the potential that depend on a small sub-set of the coordinates (cf. Multimode (Bowman))

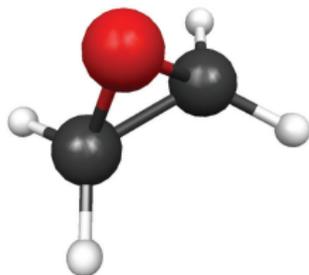
- Retain the basis functions for which c_n^{sum} is large.

$$c_n^{sum} = \sum_{m=1}^{10} |U_{nm}|$$

U is the matrix of eigenvectors.

Ethylene Oxide (7 atoms)

Quartic force field from D. Bégué et al., J. Chem. Phys. **127**
164115 (2007).



Ethylene Oxide (7 atoms)

TABLE I. The lowest 25 calculated vibrational energies of ethylene oxide.

Eigenvectors	$n_1 + n_2 + \dots n_{15} < 9$	
990, 148	1, 307, 504	Difference
12461.481	12461.485	-0.004
13254.165	13254.248	-0.083
13283.438	13283.463	-0.026
13339.808	13339.815	-0.007
13478.684	13478.726	-0.042
13582.716	13582.763	-0.047
13585.169	13585.208	-0.040
13607.271	13607.284	-0.014
13609.505	13609.523	-0.018
13732.318	13732.329	-0.011
13928.911	13928.897	0.015
13956.747	13956.757	-0.010
14048.800	14049.077	-0.277
14072.623	14072.730	-0.107
14102.577	14102.635	-0.058
14131.859	14131.923	-0.063
14156.575	14156.581	-0.006
14216.389	14216.287	0.102
14267.014	14267.188	-0.174
14293.804	14293.891	-0.087

Conclusion

- A direct product DVR calculation is easy if
 - The KEO has no important singularities
 - The total number of basis functions is less than about 50'000
- A good way to deal with angular singularities is to use an FBR for angles (and a DVR for stretches)
- To deal with the basis size problem one may
 - Contract the basis. Contraction is facilitated by using a DVR.
 - Use iterative methods. Wherever possible it is important to do sums sequentially.
 - Prune the primitive basis.
- Combining these ideas it is now possible to compute accurate solutions for problems with seven and maybe more atoms.

Thanks to Joel Bowman for sending us his CH_5^+ potential.

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