Computing (ro-)vibrational spectra: beyond direct product basis sets

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Direct product basis set

$$N = n^D; \quad 10 < n < 100$$

Matrix size $> 10^6$

Two options:

- (1) Use direct product basis but calculate observables without diagonalisation
  - Lanczos
  - Filter diagonalisation
- (2) Better basis set

(1) ⇒ 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 the matrix

- Only a few vectors are stored.

- Four-atom systems have been studied using these methods for more than a decade.

- Five-atom (direct product basis) systems are not possible.

To go beyond four atoms we must use better basis sets

Two obvious strategies:

- (i) Contracted basis functions

- (ii) Pruned direct product basis sets

Contracted basis functions

- Contracted basis functions are eigenfunctions of reduced-dimension Hamiltonians

- Key: coupling is included into the basis functions.

- Break coordinates into groups and solve sub-problems

For the bend problem we use spherical harmonic type primitive basis functions, $f_l(\theta)$.

For the stretch problem we use DVR primitive basis functions, $g_\alpha(r)$.

There are two types of contracted basis sets

(1) Adiabatic contracted functions

- Contract the bend basis for every DVR stretch point

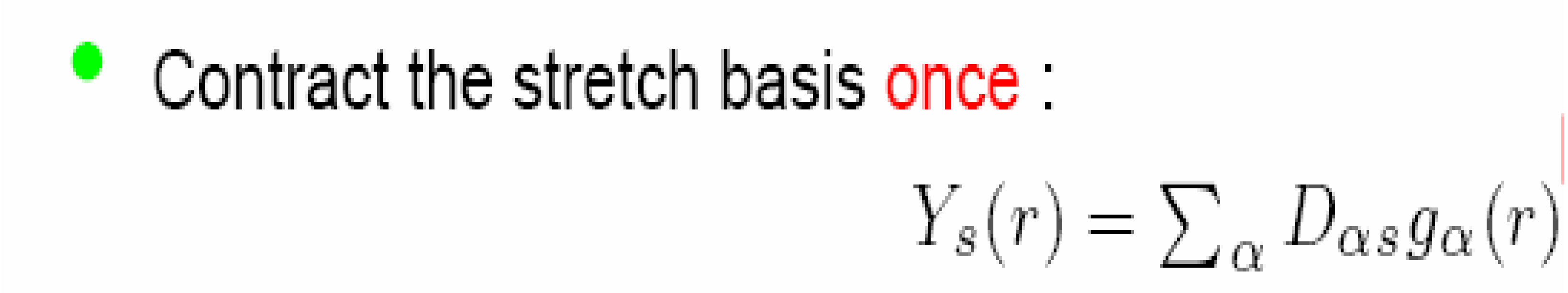
$$H = T_{ben}(\theta, r) + T_{str}(r) + V(\theta, r)$$

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

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

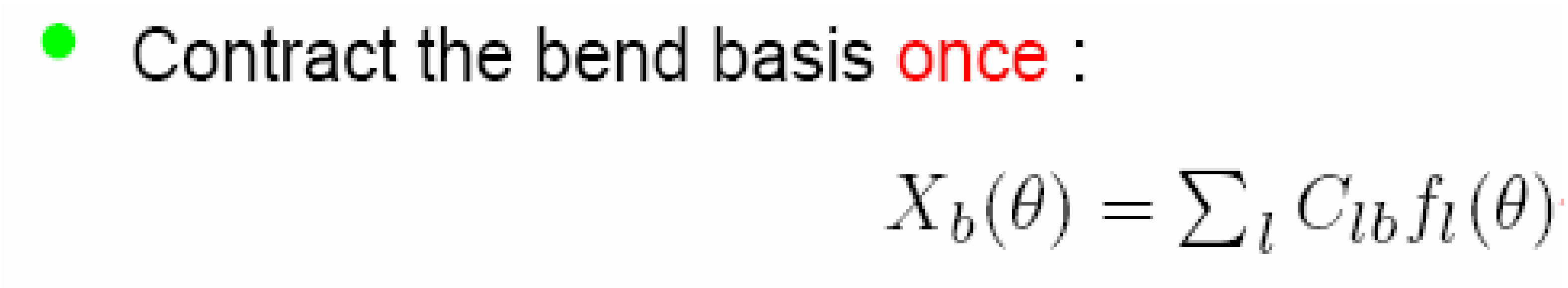
- Bacic, Light, Bowman (direct diagonalisation)
- Friesner, Leforestier Carrington (Lanczos)

(2) Simply contracted basis functions



- Contract the stretch basis once :

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



- Contract the bend basis once :

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

Carter and Handy (direct diagonalisation)
Carrington, Yu (Lanczos)

$$H = T_{ben}(\theta, r) + T_{str}(r) + V(\theta, r)$$

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

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

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

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

$$H = H^b + H^s + \Delta T + \Delta V$$

Using contracted basis functions with an iterative methods is not simple:

- Contracted matrix-vector products may be more costly than direct-product matrix-vector products

- The most obvious way to do matrix-vector products for the coupling terms is

contracted vector → product vector → apply coupling → contracted vector

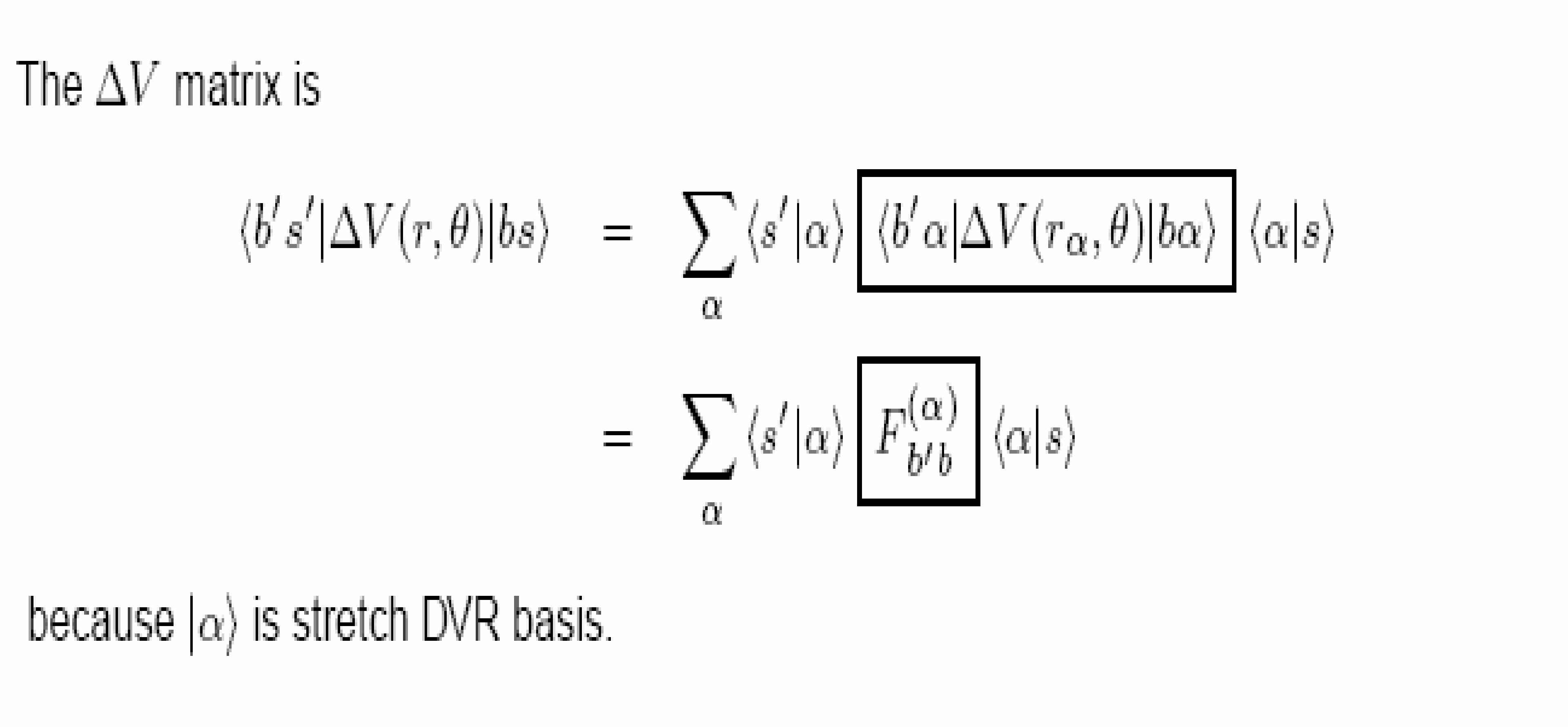
which entails storing a large vector

We solve the bend and stretch problems with the Lanczos algorithm (computing both eigenvalues and eigenvectors).

For our purposes simply contracted functions are better than adiabatic contracted functions because

- Matrix-vector products are less expensive
- There are far fewer reduced dimension eigenproblems to solve. To use adiabatic contracted functions for methane it would be necessary to solve the 5D bend problem thousands of times. Using simply contracted functions it is solved once. It would be impossible to store the adiabatic contracted bend functions.

A good way to do the ΔV matrix-vector product



The ΔV matrix is

$$\begin{aligned}\langle b' s' | \Delta V(r,\theta) | bs \rangle &= \sum_{\alpha} \langle s' | \alpha \rangle \boxed{\langle b' \alpha | \Delta V(r_\alpha,\theta) | b\alpha \rangle} \langle \alpha | s \rangle \\ &= \sum_{\alpha} \langle s' | \alpha \rangle \boxed{F^{(\alpha)}_{b'b}} \langle \alpha | s \rangle\end{aligned}$$

because $|\alpha\rangle$ is stretch DVR basis.

The ΔV matrix is

$$\begin{aligned}\langle b' s' | \Delta V(r,\theta) | b s\rangle &= \sum_{\alpha} \langle s'|\alpha\rangle \boxed{\langle b'\alpha|\Delta V(r_\alpha,\theta)|b\alpha\rangle} \langle\alpha|s\rangle \\ &= \sum_{\alpha} \langle s'|\alpha\rangle \boxed{F^{(\alpha)}_{b'b}} \langle\alpha|s\rangle\end{aligned}$$

where an $\mathbf{F}$ matrix is defined.

$$\begin{array}{c|cccc|}
 & (\alpha) & (\alpha') & (\alpha'') & \cdots \\
\hline
(\alpha) & F^{(\alpha)}_{b'b} & 0 & 0 & 0 \\
(\alpha') & 0 & F^{(\alpha')}_{b'b} & 0 & 0 \\
(\alpha'') & 0 & 0 & F^{(\alpha'')}_{b'b} & 0 \\
\vdots & 0 & 0 & 0 & \ddots \\
\hline
\end{array} = \langle b'\alpha'|\Delta V|b\alpha\rangle$$

$$\begin{array}{c|cccc|}
 & s & s' & s'' & \cdots \\
\hline
s & V_{b'b}^{ss} & V_{b'b}^{ss'} & V_{b'b}^{ss''} & \cdots \\
s' & V_{b'b}^{s's} & V_{b'b}^{s's'} & V_{b'b}^{s's''} & \cdots \\
s'' & V_{b'b}^{s''s} & V_{b'b}^{s''s'} & V_{b'b}^{s''s''} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots \\
\hline
\end{array} = \langle b's'|\Delta V|bs\rangle$$

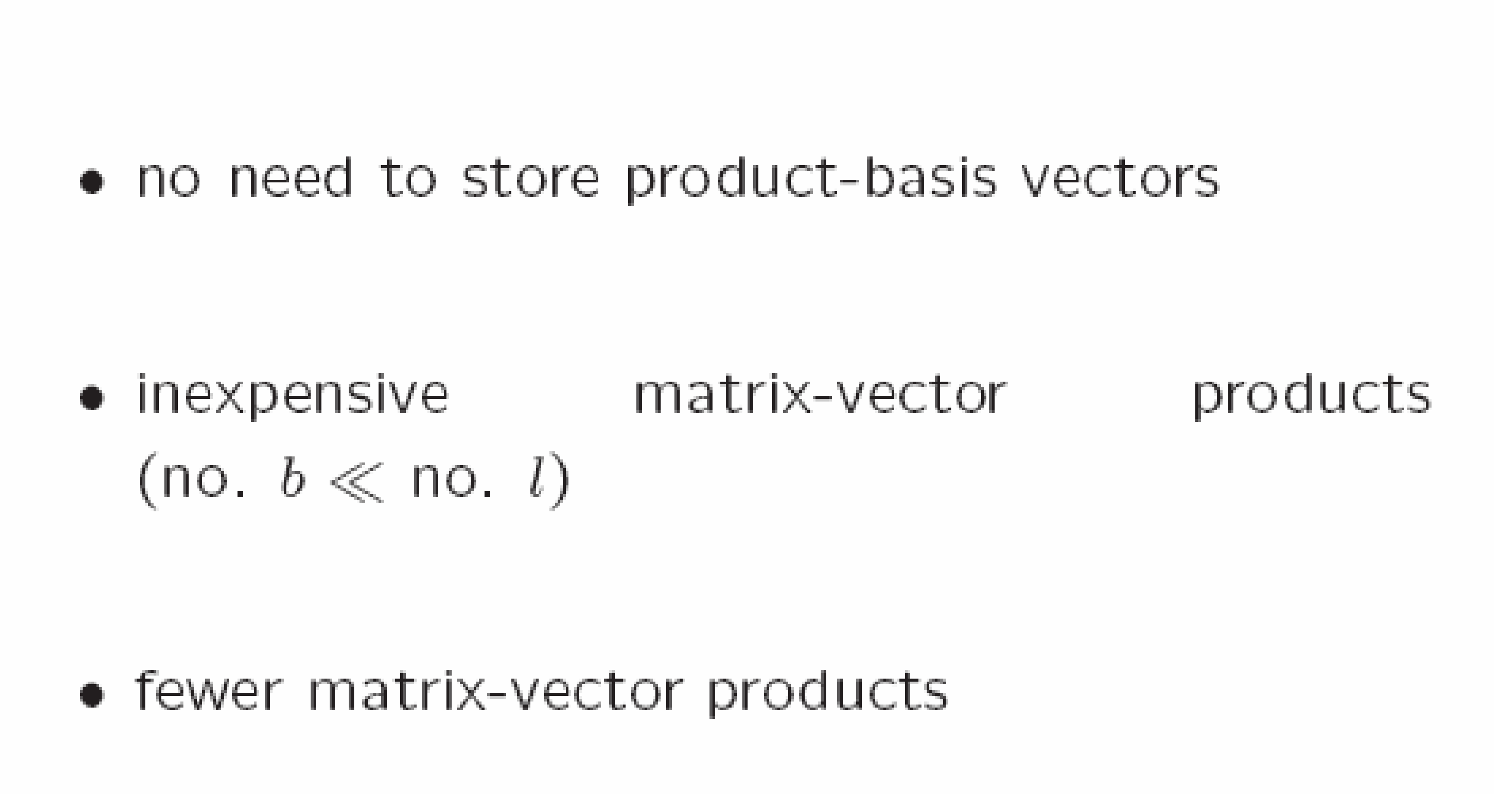
- The ΔV matrix-vector product is

$$u'^{(K)}_{b's'} = \sum_{bs} \langle b'^{(K)} s' | \Delta V | b^{(K)} s \rangle u^{(K)}_{bs}$$

- It is best done in three steps

$$\begin{aligned}
u^{(1)(K)}_{b\alpha} &= \sum_{s} D_{\alpha s} u^{(K)}_{bs} \\
u^{(2)(K)}_{b'\alpha} &= \sum_{b} F^{(K,\alpha)}_{b'b} u^{(1)(K)}_{b\alpha} \\
u'^{(K)}_{b's'} &= \sum_{\alpha} D_{\alpha s'} u^{(2)(K)}_{b'\alpha}
\end{aligned}$$

Advantages of the simply-contracted basis Lanczos combination



- no need to store product-basis vectors
- inexpensive matrix-vector products (no. $b \ll$ no. l)
- fewer matrix-vector products

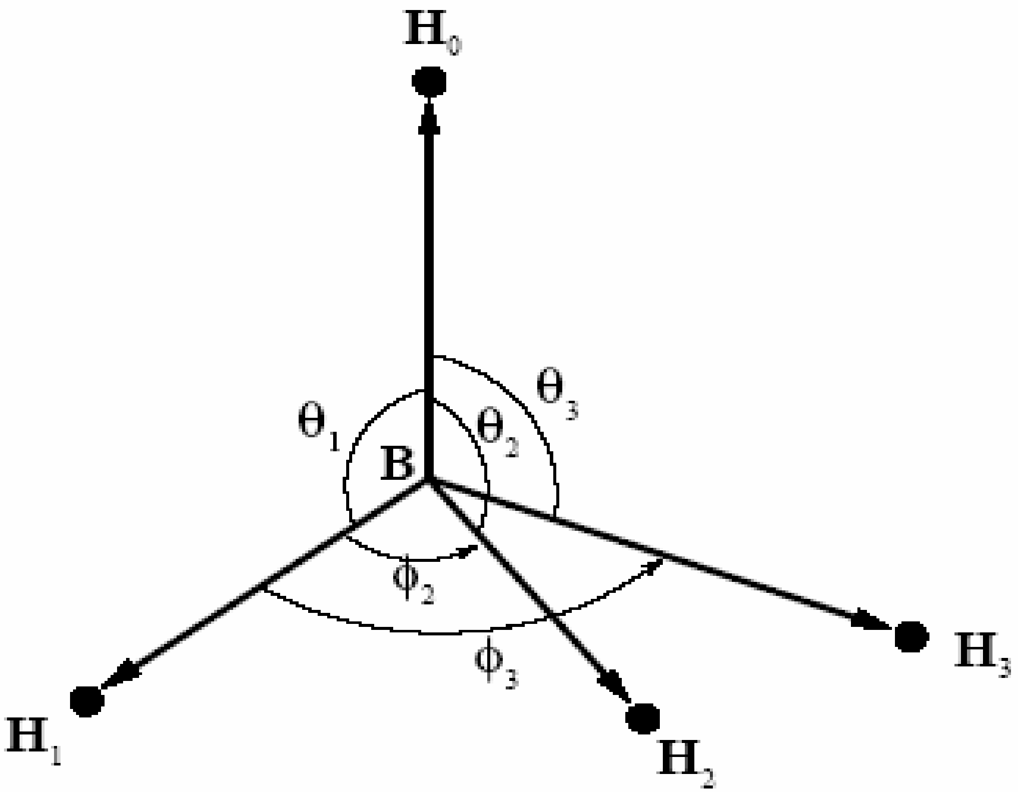
Results

The $J = 0$ calculation for H_2O_2 is 10 times cheaper than using the product basis approach J. Chem. Phys. 117 6923 (2002).

CH_4 $J = 0$
J. Chem. Phys. 119, 101-117 (2003).

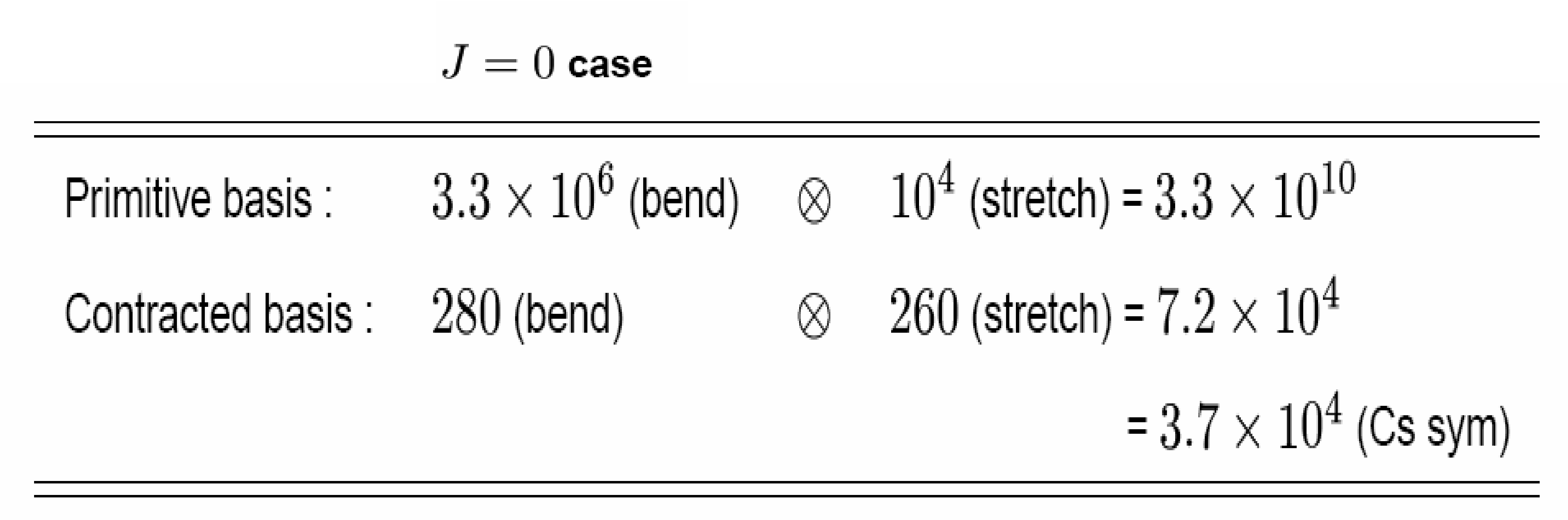
CH_4 $J > 0$
J. Chem. Phys. 121, 2937-2954 (2004).

Radau vectors and polyspherical coordinates for CH_4.



B is the canonical point. Carbon atom is not shown.
The range of angles: $(\theta_1, \theta_2, \theta_3) \in [0, \pi]$; $(\phi_2, \phi_3) \in [0, 2\pi]$

For J=0 and J=1 basis size reduced by factor of 10^6



$J = 0$ **case**

Primitive basis :	3.3×10^6 (bend)	$\otimes$	10^4 (stretch) = 3.3×10^{10}
Contracted basis :	280 (bend)	$\otimes$	260 (stretch) = 7.2×10^4
			= 3.7×10^4 (Cs sym)

$J = 1$ case

Primitive basis : 1×10^7 (bend) $\otimes$ 10^4 (stretch) = 1.0×10^{11}

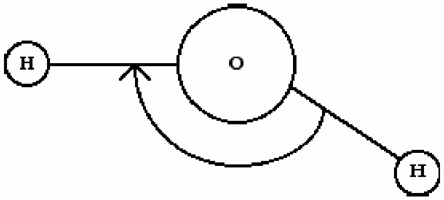
Contracted basis : 246×3 (bend) $\otimes$ 260 (stretch) = 1.9×10^4
= 9.6×10^4 (Cs sym)

Parts of the contracted-basis Lanczos approach are similar to MCTDH

- Memory cost is reduced by storing matrices in the contracted bend basis (cf. storing the mean field matrices in MCTDH).
- Basis size is reduced by contraction (cf. “mode combination” in MCTDH)
- When we use PODVR for the stretches no DVR approximation is made for the 1-D separable parts (cf. CDVR)

Prune a direct product basis:

E.g.



Direct product basis functions are

$$\Phi_{kj} = {}^1\phi_k(r_1)\ {}^2\phi_j(r_2)\ .$$

$$k, j = 0, \cdots 10$$

Some of these functions are unnecessary. Remove them from the basis.

Build and prune is itself not new

- Carter and Handy use 1-d e'functions to form a basis which is pruned
  - spectra
- It is common (Colbert and Miller?) to remove DVR functions
  - scattering calculation
- Bowman and co-workers prune a vibrational CI basis

We choose our 1-d functions differently
— to facilitate truncation.

Standard 1-d basis options

EF basis

$$H = {}^1H + {}^2H + {}^3H + {}^4H + V_{couple}$$

$${}^1H({}^1\phi_k(q_1)) = {}^1E_k({}^1\phi_k(q_1))$$

DVR basis

$$\delta_\beta(q_1) = \sum_k (T^t)_{\beta,k}({}^1\phi_k(q_1))$$

where

$$\mathbf{Q_1 T = T \Lambda}$$

Which basis functions should be discarded?

- EF bases usually truncated on the basis of zeroth-order energies
- DVR bases usually truncated on the basis of potential values at DVR points

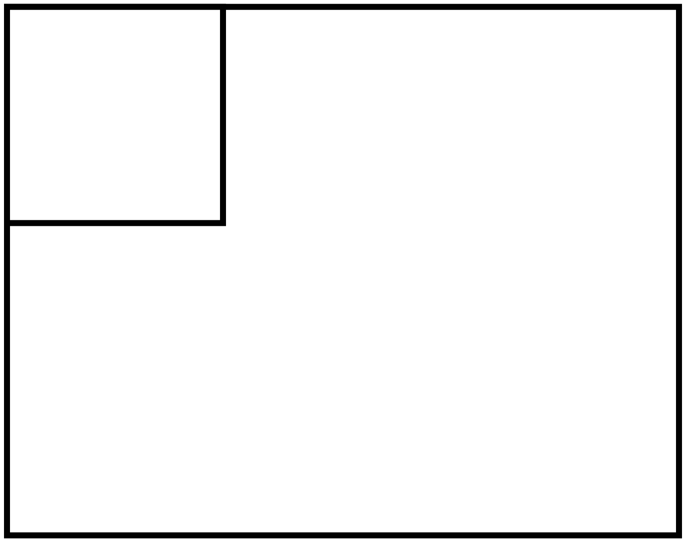
We truncate on the basis of diagonal matrix elements of the full Hamiltonian matrix.

Basis functions are sorted so that

$$H_{ii} > H_{jj} \quad if \quad i > j$$

How should one choose the 1-d functions?

Q. When is it true that e'values of the top left corner of a matrix are close to e'values of the entire matrix



A. When matrix elements H_{ij} decrease as $|i - j|$ increases, i.e., matrix elements closest to the diagonal are the largest.

I denote such a matrix as nearly diagonal

Is the EF matrix nearly diagonal?

It is V_{couple} that limits its near diagonality

Is the DVR matrix nearly diagonal?

H_{ij} decreases as $|i-j|$ increases but the 1-d kinetic energy matrix is full and this limits the near diagonality of the DVR matrix.

We want 1-d functions that give us a more truncateable Hamiltonian matrix.

1-d basis functions that are better than both EF and DVR 1-d functions

We use orthogonal basis functions that make both q_c and ${}^cH$ as diagonal as possible.

q_c nearly diagonal $\rightarrow$ V_{couple} nearly diagonal

This basis nearly diagonalises V_{couple} and $\sum_c {}^cH$ and therefore $H = \sum_c {}^cH + V_{couple}$

The new 1-d basis functions are obtained using a simultaneous diagonalisation (SD) algorithm.

We apply SD to (α_c $\mathbf{q}_{\mathbf{c}\phi}$) and ${}^{\mathbf{c}}\mathbf{H}_{\phi}$.

This means find ${}^{\mathbf{c}}\mathbf{U}$ such that

$$\sum_i \sum_{j \neq i} (({}^{\mathbf{c}}\mathbf{U})^t \ \alpha_c \, \mathbf{q}_{\mathbf{c}\boldsymbol{\Phi}} \ {}^{\mathbf{c}}\mathbf{U})^2_{ij} + \sum_i \sum_{j \neq i} (({}^{\mathbf{c}}\mathbf{U})^t \ {}^{\mathbf{q}_c}\mathbf{H}_{\boldsymbol{\Phi}} \ {}^{\mathbf{c}}\mathbf{U})^2_{ij}$$

is minimised.

${}^{\mathbf{c}}\mathbf{U}$ is a product of Jacobi rotation matrices.

A 1-D SD function is

$${}^c\theta_a(q_1) = \sum_k ({}^cU^t)_{a,k}({}^c\phi_k(q_c)) \ .$$

α_c determines the relative diagonality of q_c and ${}^cH$.

$\alpha_c = 0 \rightarrow$ EF basis. All contributions to off-diagonal elements are from V_{couple}

$\alpha_c = large \rightarrow$ DVR basis. All contributions to off-diagonal elements are from $\sum_c {}^cH$.

We choose α_c to minimise contributions to important off-diagonal elements from both V_{couple} and $\sum_c {}^cH$.

Truncating the basis

If the number of coordinates < 8 we compute all the diagonal matrix elements and discard functions associated with large diagonal elements.

If the the number of coordinates > 8 it is better not to compute all the diagonal elements. Instead

$$H = H_1(q_1, \cdots, q_{D/2}) + H_2(q_{D/2+1}, \cdots, q_D) + H_{coup}$$

Compute diagonal elements for H_1 and truncate a basis for H_1

Compute diagonal elements for H_2 and truncate a basis for H_2

Recombine and truncate

How to choose α?

We do not choose α to make the entire H matrix as nearly diagonal as possible but to reduce the coupling between the retained and discarded basis functions.

Define

$$\Delta_{tot} = \sum_{i}^{N_R} (\lambda_i^\alpha - E_i)$$

N_R = number of retained basis functions

λ_i^α = ith e'value of $H_\alpha^{N_R}$

E_i = ith e'value of the untruncated matrix

$$\Delta_{tot} = tr(H_\alpha^{N_R}) - \sum_i^{N_R} E_i$$

the smaller the trace is, the better are the e'values computed from $H_\alpha^{N_R}$

Choose α to minimise the trace. This reduces the total or average error.

To find the best α we need not compute off-diagonal matrix elements. Only diagonal matrix elements are required and these are also needed for sorting the basis functions.

As the trace is minimised the e'values of $H_{\alpha}^{N_R}$ approach the lowest e'values of the entire H matrix and the matrix that represents H in the basis corresponding to the value of α that minimizes the trace becomes nearly block diagonal.

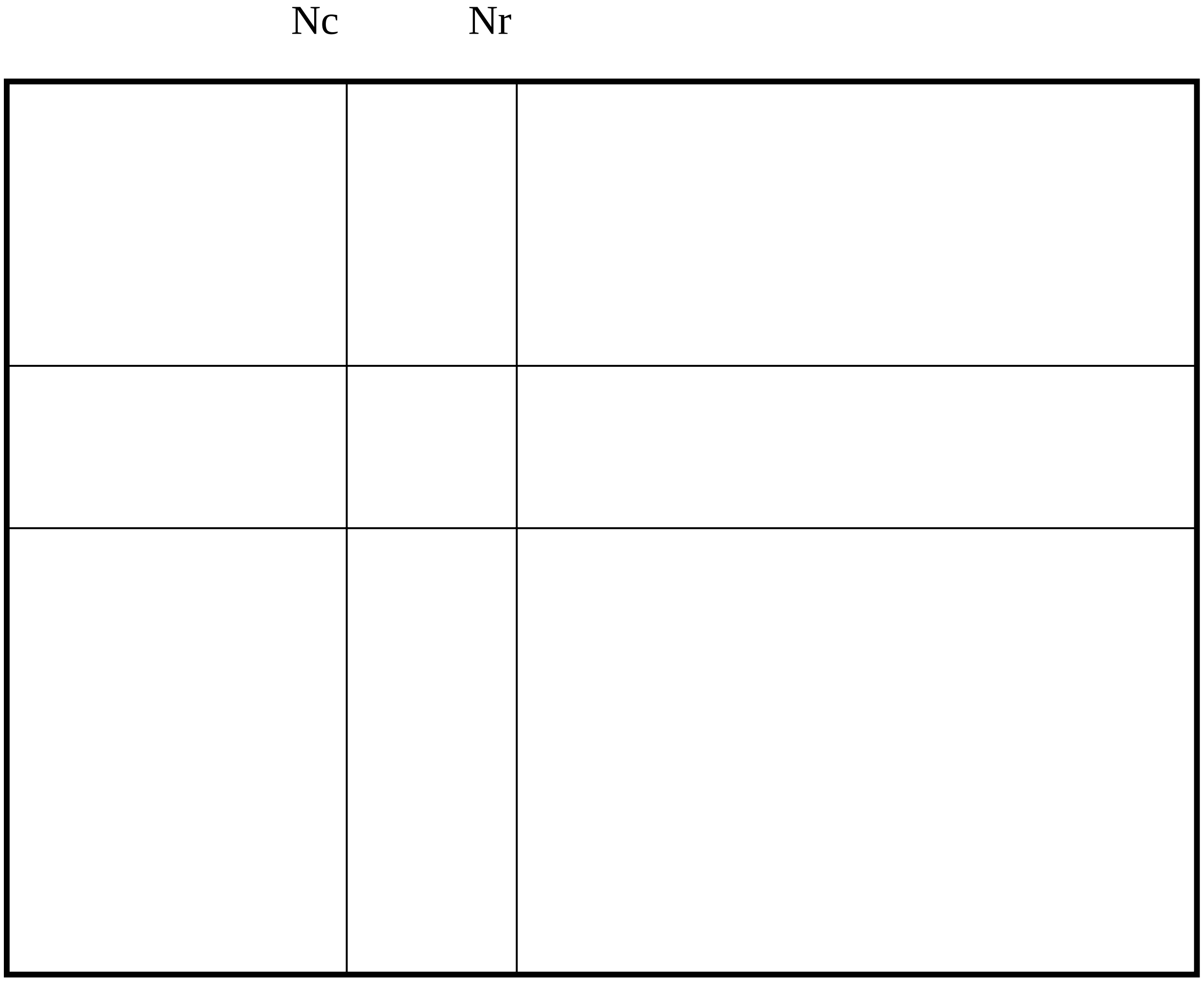
Use perturbation theory

The basis is chosen to make the Hamiltonian nearly diagonal (largest elements close to the diagonal) and to reduce matrix elements that couple retained and discarded functions.

Perturbation theory should work well.

We have used second order Van Vleck perturbation theory with both the SD and the EF matrices.

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_{\mathrm{R}} & \mathbf{H}_{\mathrm{A}} \\ \mathbf{H}_{\mathrm{A}} & \mathbf{H}_{\mathrm{U}} \end{pmatrix}$$


Nc
Nr

Some Results

$$H = H_0 + H_{coup} \ .$$

$$H_0 = \sum_{c=1}^{D} (p_c^2)/2 + \sum_{c=1}^{D/2} (x_c^2)/2 + \sum_{c=D/2+1}^{D} (x_c^2)/7 \ .$$

We have done calculations with $D = 6, 8$, and 16.

For each value of D half the modes are of frequency one, while the other half are of a frequency slightly greater than 1/2.

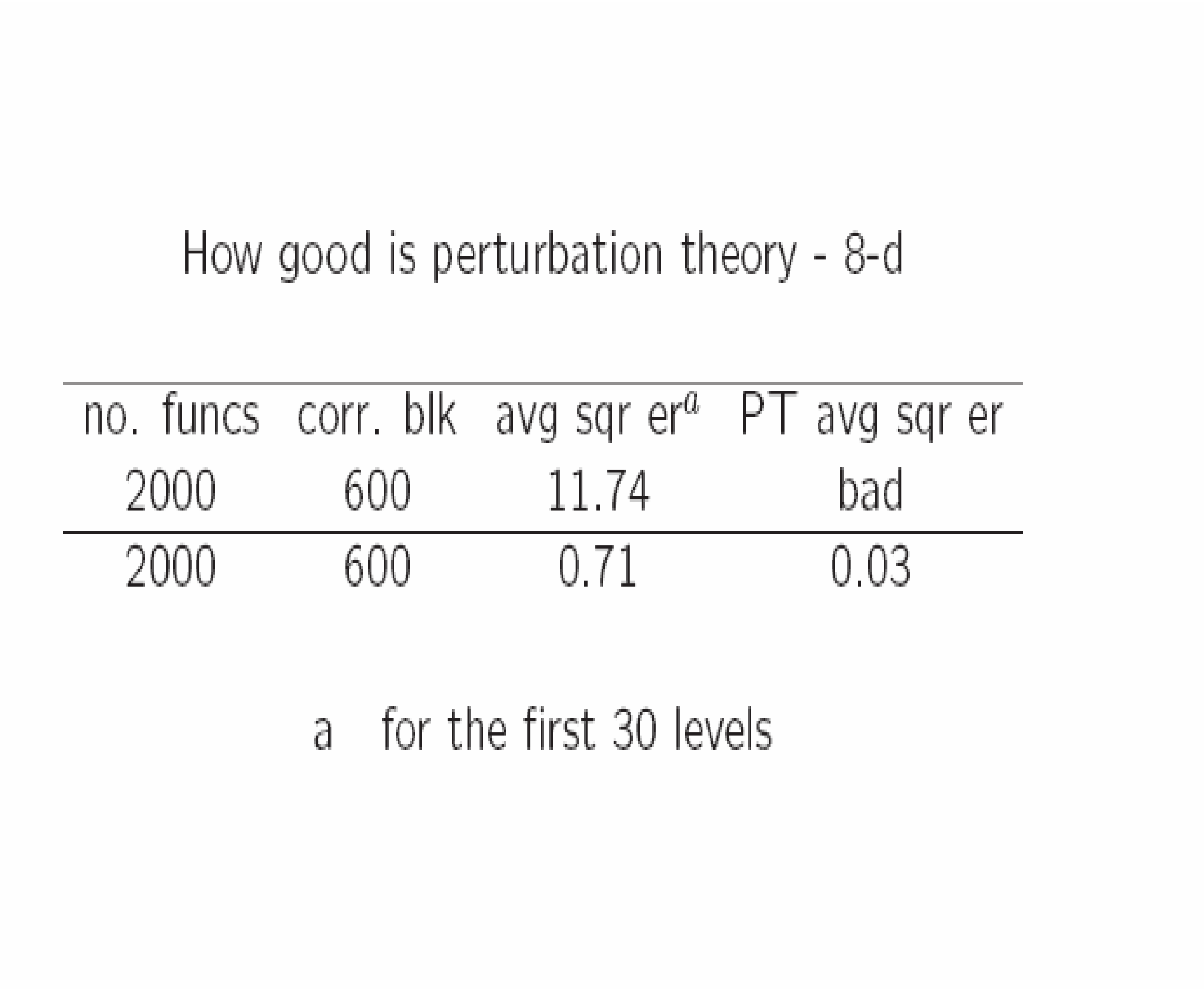
$$H_{coup} = a(x_1^2 x_2^2 + x_1^2 x_3^2 + \ldots + x_2^2 x_3^2 + \ldots)$$

Energy levels of 16-D Hamiltonian

Eigenfunction Basis			SD-Basis			
10000 EF	40000 EF	80000 EF	4000 SD	8000 SD	40000 SD	4k(SD)-80k(EF)
9.222(1)	9.151(?)	9.100(?)	8.893	8.885	8.882^a	-0.207
11.129(8)	10.682(?)	10.658(?)	10.403(8)	10.367(8)	10.183(8)	-0.255
11.495(8)	10.804(?)	10.794(?)	10.642(8)	10.471(8)	10.347(8)	-0.152
13.384(7)	12.719(?)	12.367(?)	11.689(7)	11.544(7)	11.322(7)	-0.678
13.404(1)	12.721(?)	12.451(?)	11.837	11.758	11.488	-0.614
13.464(5)	12.796(?)	12.628(?)	12.067(5)	11.891(5)	11.812(5)	-0.561

- All of the 4'000-SD levels are below their 80'000-SD counterparts. To do the 80'000- EF calculation we use Lanczos. The 4'000-SD diagonalisation is done in a few minutes on a PC.

- DMC ground state is 8.883 ± 0.002



How good is perturbation theory - 8-d

	no. funcs	corr. blk	avg sqr er[a]	PT avg sqr er
EF	2000	600	11.74	bad
SD	2000	600	0.71	0.03

a for the first 30 levels

Another Hamiltonian

- Easily computable numerically exact energy levels
- Kinetic coupling

$$H(\mathbf{q}) = \sum_{k}^{D} \frac{-1}{2} \frac{\partial^2}{\partial q_k^2} + \sum_{k}^{D} (c_2 q_k^2 + c_3 q_k^3 + c_4 q_k^4)$$

We have done calculations with $D = 4, 8, 16$.

Numerically exact energy levels can easily be comuted by solving a 1-D problem (there is no coupling).

$$\mathbf{q} = \mathbf{M}\mathbf{x}$$

The transformation matrix is $\mathbf{M} = c\mathbf{T}$

$\mathbf{M}$ is not orthogonal but

c is a constant chosen to make $|M| = 1$ (so that the volume element of integrals is unity).

$\mathbf{T}$

$$T = \begin{bmatrix} 1 & a & a & a & a & a \\ a & 1 & a & a & a & a \\ a & a & 1 & a & a & a \\ a & a & a & 1 & a & a \\ a & a & a & a & 1 & a \\ a & a & a & a & a & 1 \end{bmatrix}$$

- A good way to make Hamiltonians to test methods for solving the Schroedinger equation:
- Exact levels are known
- Bound states and not resonances
- East to choose coefficients to get a molecule-like potential

In terms of the the $\mathbf{x}$ coordinates the potential is messy and strongly coupled.

For example for $D = 16$ the tetralinear terms fill 16 pages!

For 8-D we use $a = 0.02$.

For 16-D we use $a = 0.005$

Even if a is very small, $H(x)$ is strongly coupled because there are many coupling terms and because many q_k^n terms contribute to each coupling term.

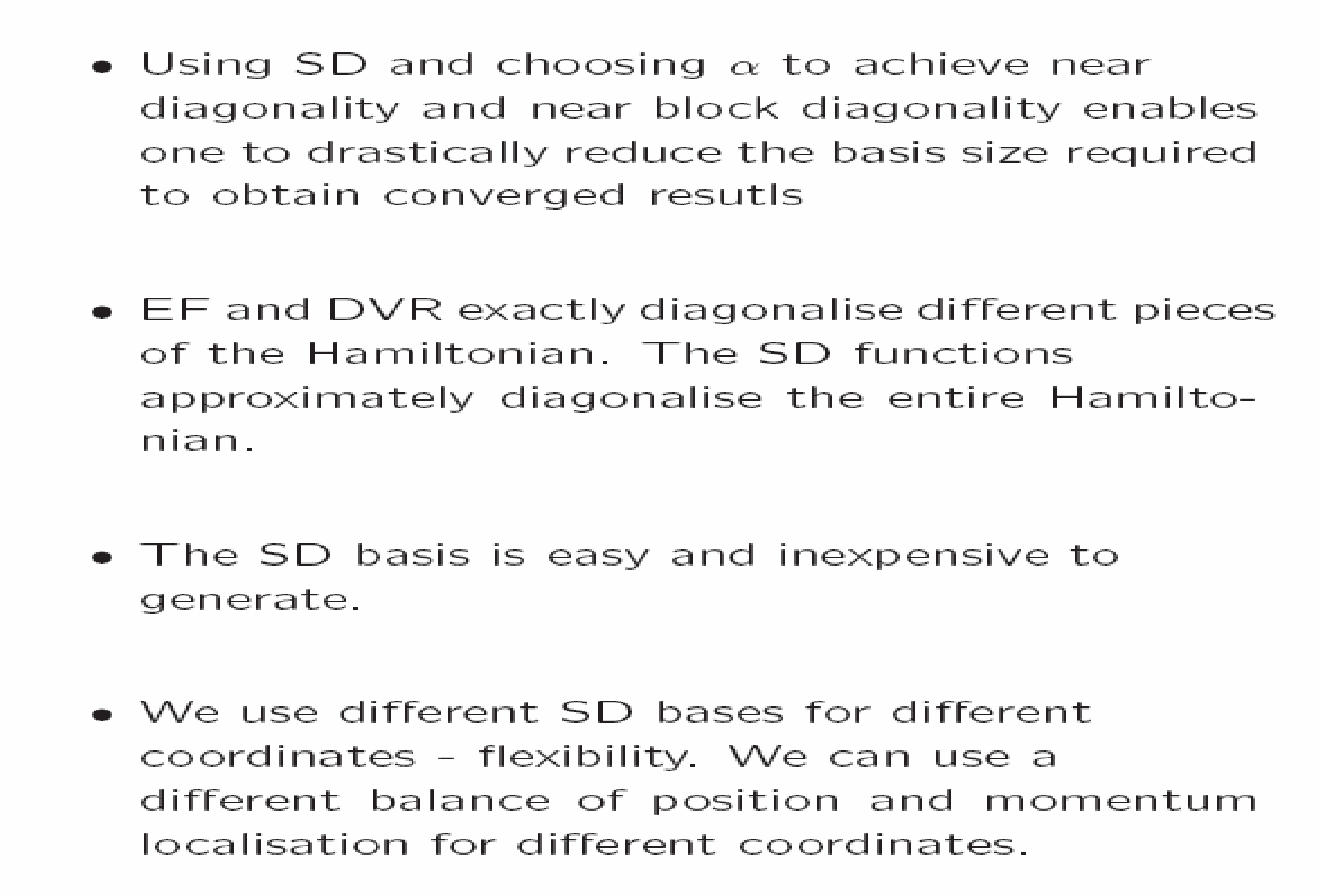
8-D Results

Basis type	Basis size	States to within 0.1 without/with perturbation theory	States to within 1.0 (without perturbation theory)
EF	40’000	0/0	5360
SD	40’000	7/518	8135

16-D Results

Basis type	Basis size	States to within 0.1 without/with perturbation theory	States to within 1.0 (without perturbation theory)
EF	6’000	0	883
SD	6’000	1	1688

Advantages of SD basis functions



- Using SD and choosing α to achieve near diagonality and near block diagonality enables one to drastically reduce the basis size required to obtain converged resutls

- EF and DVR exactly diagonalise different pieces of the Hamiltonian. The SD functions approximately diagonalise the entire Hamiltonian.

- The SD basis is easy and inexpensive to generate.

- We use different SD bases for different coordinates - flexibility. We can use a different balance of position and momentum localisation for different coordinates.

- The same procedure is used for all coordinates and all molecules (there is no restriction to Cartesian coordinates or orthogonal coordinates).

- We have computed converged levels for a 16-d Hamiltonian

- So far we exploit the sum of products form of the potential.

- These ideas work well even if coordinates cannot be separated into weakly coupled groups.

- For 8-d we need 2'000 SD functions to converge 30 levels. For 16-d we need 4'000 SD functions to converge 30 levels
  → roughly linear scaling.

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