Exact Quantum Dynamics Calculations of Large Dimensional Molecules Using Phase Space Basis Truncation

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I. Introduction
II. Theory
III. The Phase Space Picture
IV. SwitchBLADE
V. Model Systems
VI. Diphosphorous Oxide (3 atoms)
VII. Methyleneimine (5 atoms)
VIII. Acetonitrile (6 atoms)
IX. Benzene (12 atoms)
X. Finals thoughts

Progress…

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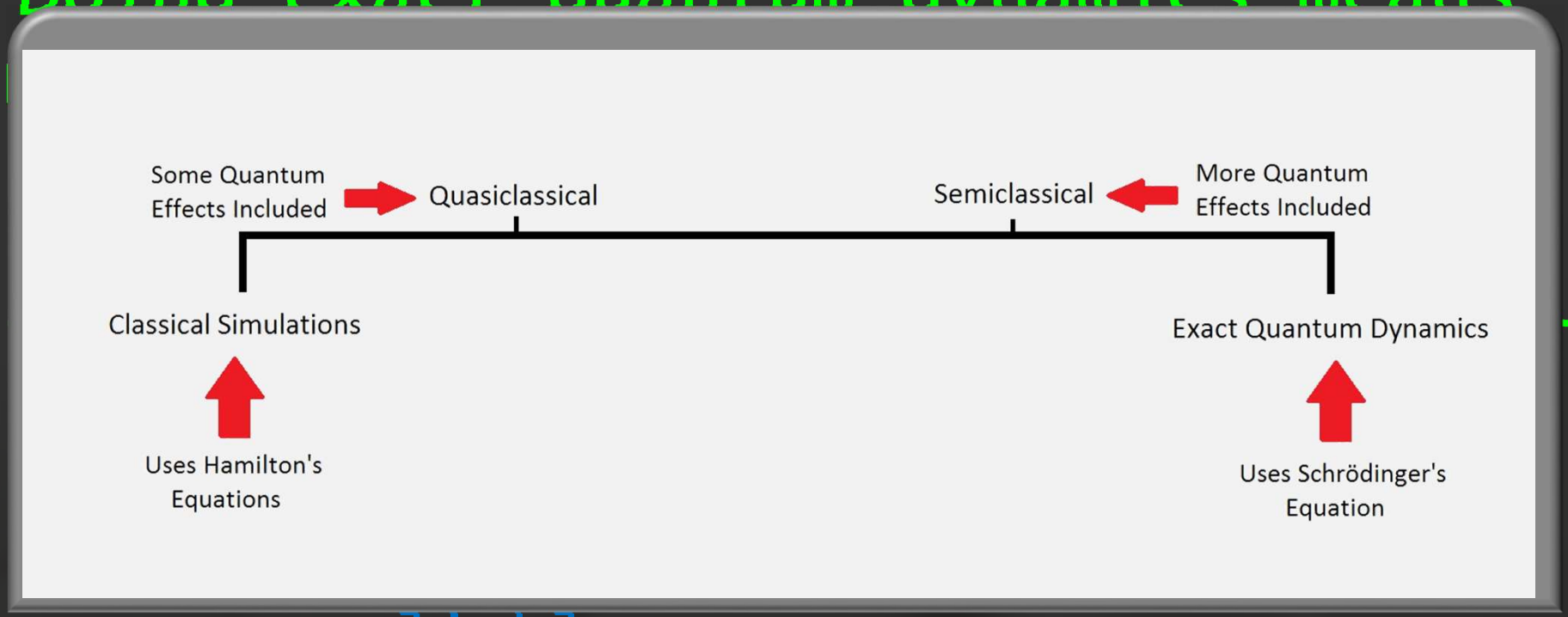
Progress…

What do we mean by exact?

/work/01922/thalvers/intro

"Doing exact quantum dynamics means



>> Reliable Accuracy

Progress…

/work/01922/thalvers/intro

>> Solve The time independent Schrödinger equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

>> Born-Oppenheimer Approximation

>> Bound States

>> Rovibrational Spectroscopy

Progress…

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>> Numerical diagonalization via a basis set expansion

$$\tilde{H}_{mn} = \langle \Phi_m | \hat{H} | \Phi_n \rangle$$

In general, all quantities of interest can be computed from the eigenenergies and eigenfunctions

Progress…

>> Three basic steps to EQD

1. Choice of potential energy
   - >> Ab intio
   - >> DFT
2. Choice of basis set
   - >> Direct product basis set
   - >> Symmetry
   - >> Curse of Dimensionality
3. Choice of diagonalization method
   - >> Direct vs. Iterative

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>> Three basic steps to EQD

1. Choice of potential energy

$$V(x) = Ax\text{^}4 + Bx\text{^}3 + Cx\text{^}2 + Dx$$

2. Choice of basis set

>> Phase space truncated momentum symmetrized Gaussians

>> Correlated energy truncated harmonic oscillator states

3. Choice of diagonalization method

>> Direct diagonalization using Lapack and Scalapack libraries

Progress…

>> Exponential scaling

$$\tilde{H}_{mn} = \langle \Phi_m | \hat{H} | \Phi_n \rangle$$

Direct Product Basis (DPB)

$$|\Phi_{\{I\}}\rangle = |\phi_{n_1}\rangle \otimes |\phi_{n_2}\rangle \otimes \ldots \otimes |\phi_{n_D}\rangle$$

For a DPB, the size of the Hamiltonian matrix grows exponentially with the dimensionality (D) of the system

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>> Basis truncation

N: Total number of basis function used in the Hamiltonian expansion

K: Number of converged states produced by a given calculation

Basis Efficiency: $\epsilon = {}^{K}/_{N}$

Problem specific criterion for increasing the basis efficiency by decreasing N but maintaining K

Progress…

>> Basis truncation

1. Symmetrized Gaussians
   >> Well localized in phase space

Phase Space Truncation:

$$H(q_1, p_1, \cdots, q_D, p_D) \leq E_{\max}$$

2. Harmonic Oscillator
   >> Direct analogy to excitation energy

Energy Truncation: $\sum_{i=1}^{D} \omega_i^{\mu} n_i \leq E_{\max}$

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Progress…

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How do we connect phase space and basis truncation?

Progress…

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>> Wigner-Weyl formalism

Density Operator: $\hat{\rho}_K = \sum_{i=1}^{K} |\Psi_i\rangle\langle\Psi_i|$

Weyl transformation: $\hat{\rho}_K \rightarrow \rho_K(q_1, p_1 \dots q_D, p_D)$

The density operator for a given Hamiltonian defines a Wigner PDF. That PDF defines a phase space volume: $\mathbb{R}_K$

Progress…

>> Wigner-Weyl formalism

Density Operator: $\hat{\rho}_K = \sum_{i=1}^{K} |\Psi_i\rangle\langle\Psi_i|$

Quasi Classical Approximation:

$$\rho_k^{\mathrm{QC}} \approx \Theta[E_{\max} - H(q_1, p_1 \cdots q_D, p_D)]$$

Progress…

/work/01922/thalvers/theory

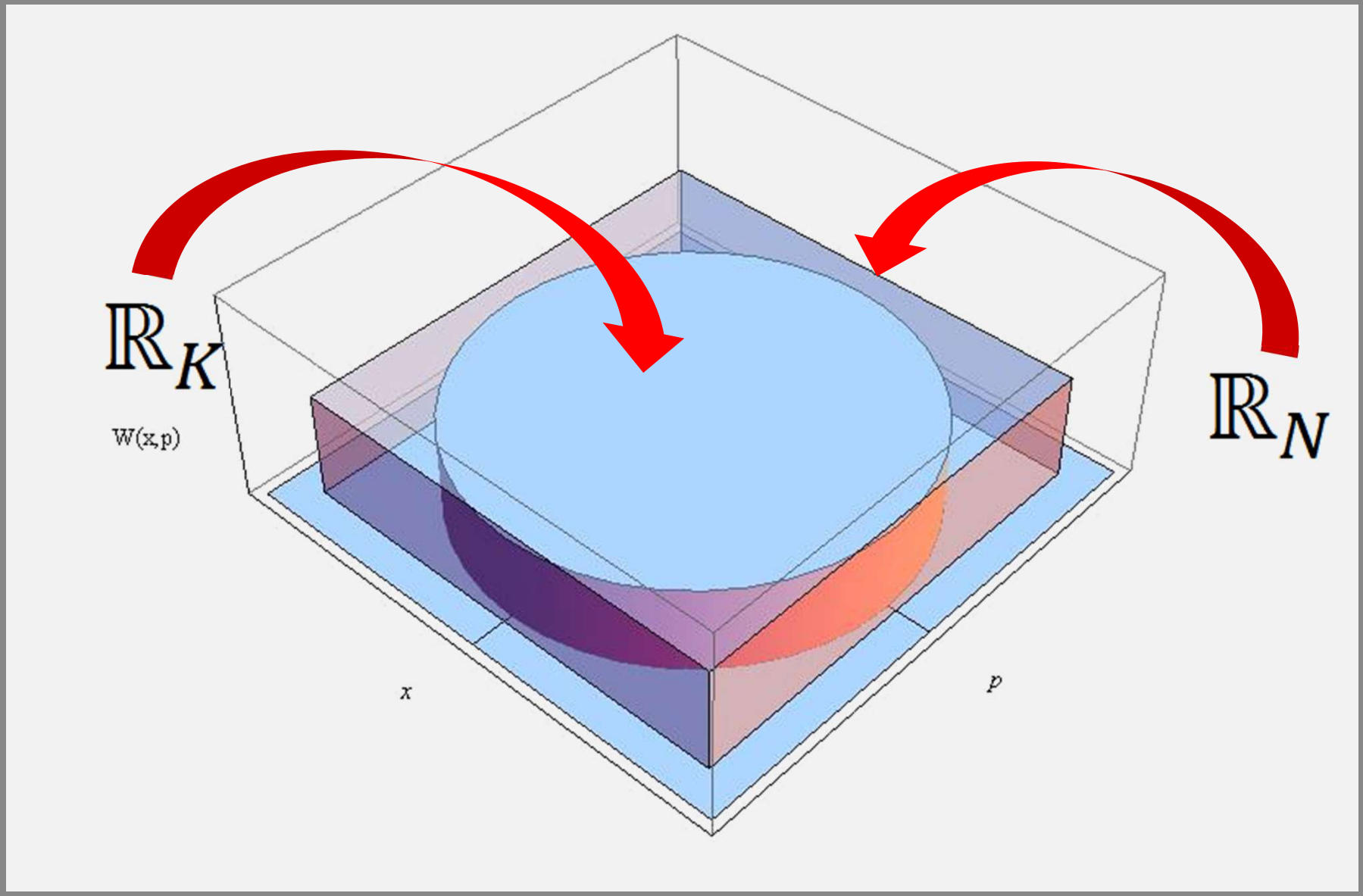
>> Wigner-Weyl formalism

Density Operator: $\hat{\rho}_N = \sum_{j=1}^{N} |\Phi_j\rangle\langle\Phi_j|$

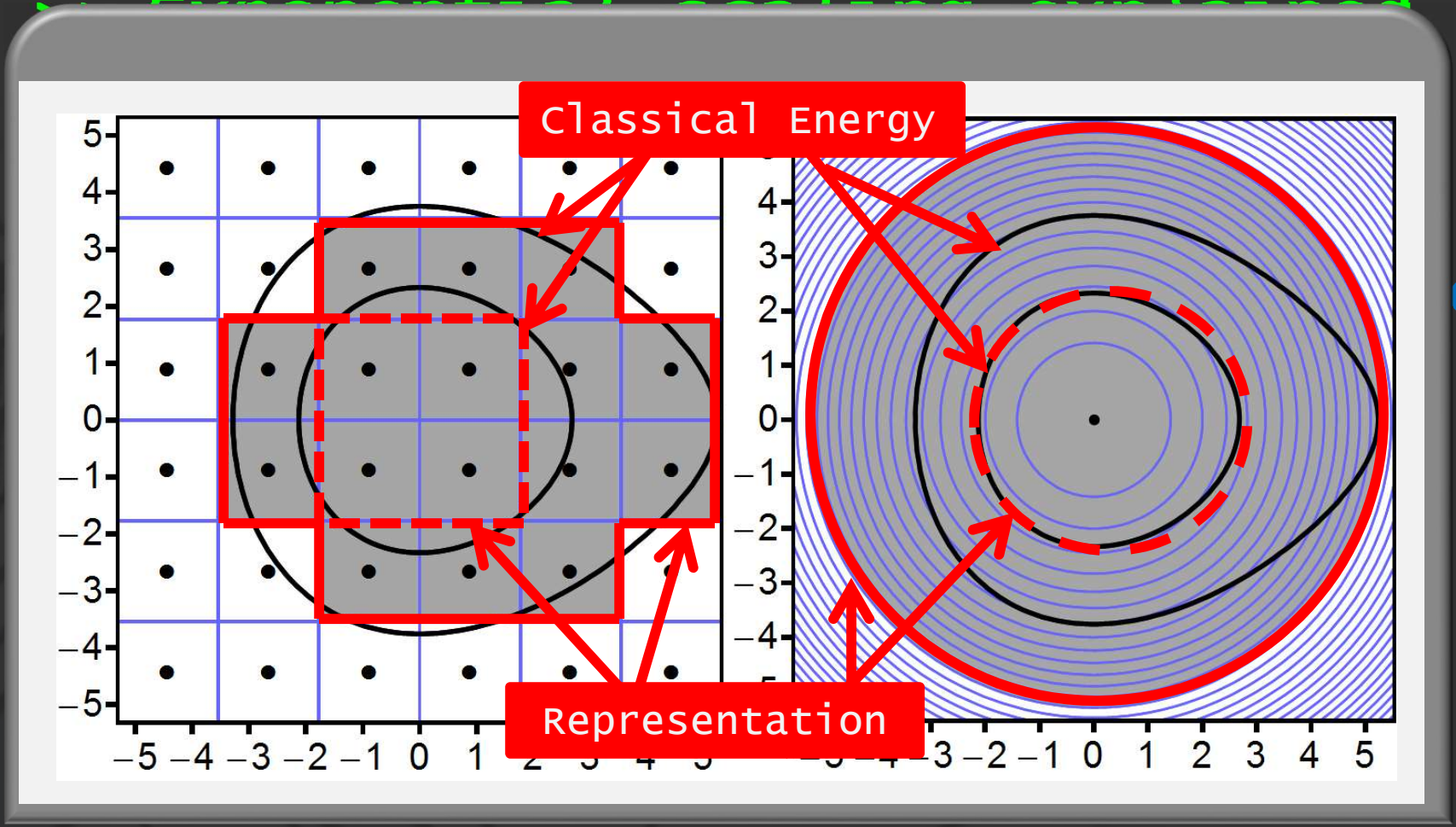
Weyl transformation: $\hat{\rho}_N \rightarrow \rho_N(q_1, p_1 \dots q_D, p_D)$

The density operator for the representational basis defines a Wigner PDF. That PDF defines a phase space volume: $\mathbb{R}_N$

Progress…


$\mathbb{R}_K$
W(x,p)
$\mathbb{R}_N$
x
p

/work/01922/thalvers/theory



Progress…

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How do we design a basis set from localized functions?

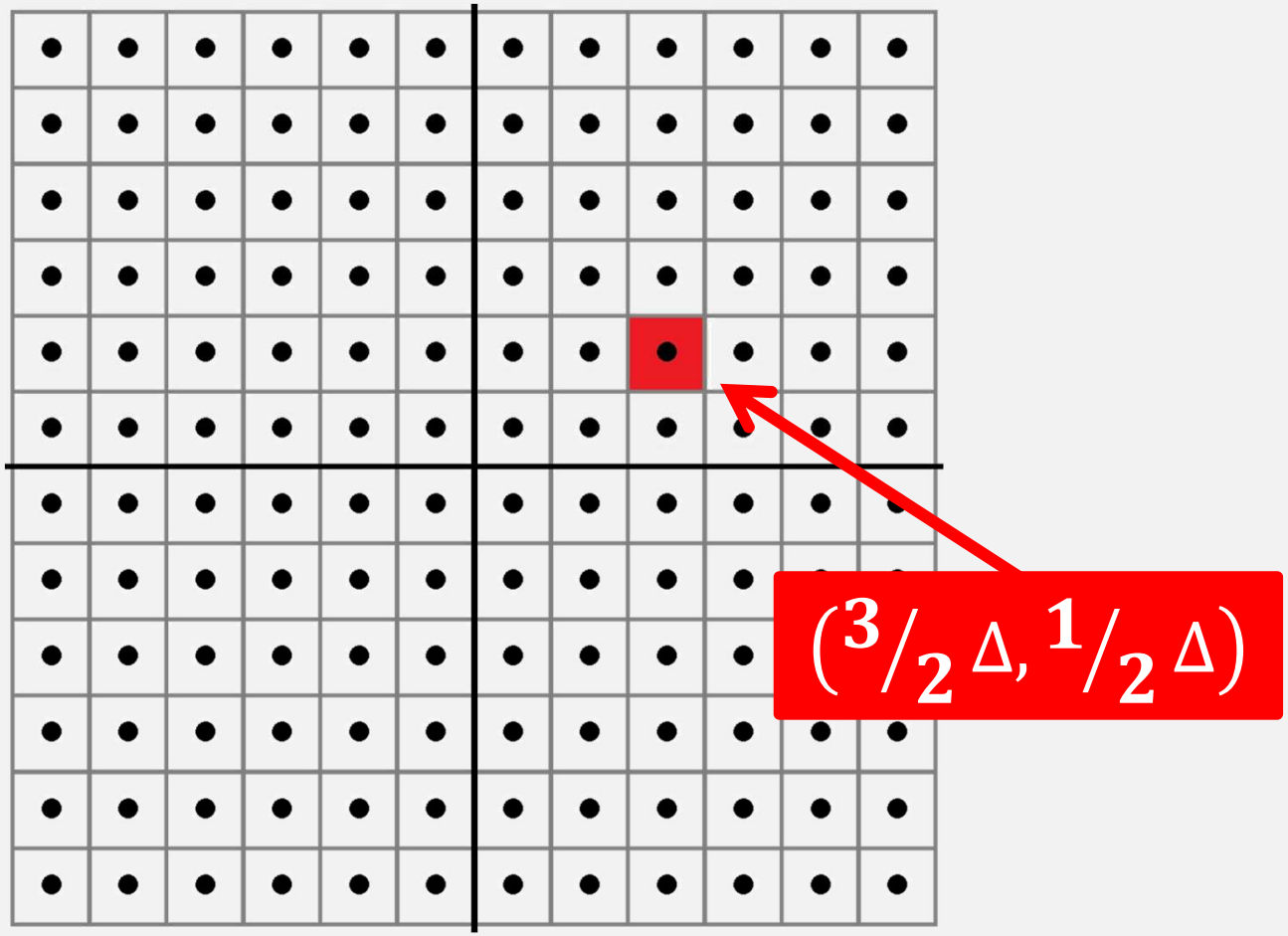
Progress…

>> Phase space wavelets

- >> Generated from some two-parameter function: $f_{mn}(q)$
- >> (m,n) are discretized parameters that result from transformations of the (m=0,n=0) fiducial function: $f_{00}(q)$
- >> Wavelets are (ideally) localized in coordinate and/or Fourier space

Progress…

The Weyl-Heisenberg Lattice



>> Doubly dense Von Neumann lattice

The Von Neumann wavelet used on the Weyl-Heisenberg lattice

$$g_{mn}^{(2)}(q) = \pi^{-1/4} e^{-\frac{1}{2}(q-m\Delta)^2} e^{in\Delta q} e^{-\frac{1}{2}imn\Delta^2}$$

The (2) superscript denotes double density: $\Delta^2 = \pi\hbar$

Progress…

>> Doubly dense Von Neumann lattice

The Von Neumann wavelet used on the Weyl-Heisenberg lattice

$$g_{mn}^{(2)}(q) = \pi^{-1/4} e^{-\frac{1}{2}(q-m\Delta)^2} e^{in\Delta q} e^{-\frac{1}{2}imn\Delta^2}$$

Pros: Collectively local and complete

Cons: Linearly dependent

Progress…

>> Momentum Symmetry

>> Majority of physical systems have momentum symmetry

$$\hat{T} = \sum \frac{1}{2m_i} \hat{p}_i^2$$

>> Create new set from linear combinations of +n and −n critically dense Gaussians

>> This process is many-to-one

/work/01922/thalvers/theory

>> Momentum symmetrized, doubly dense Gaussians

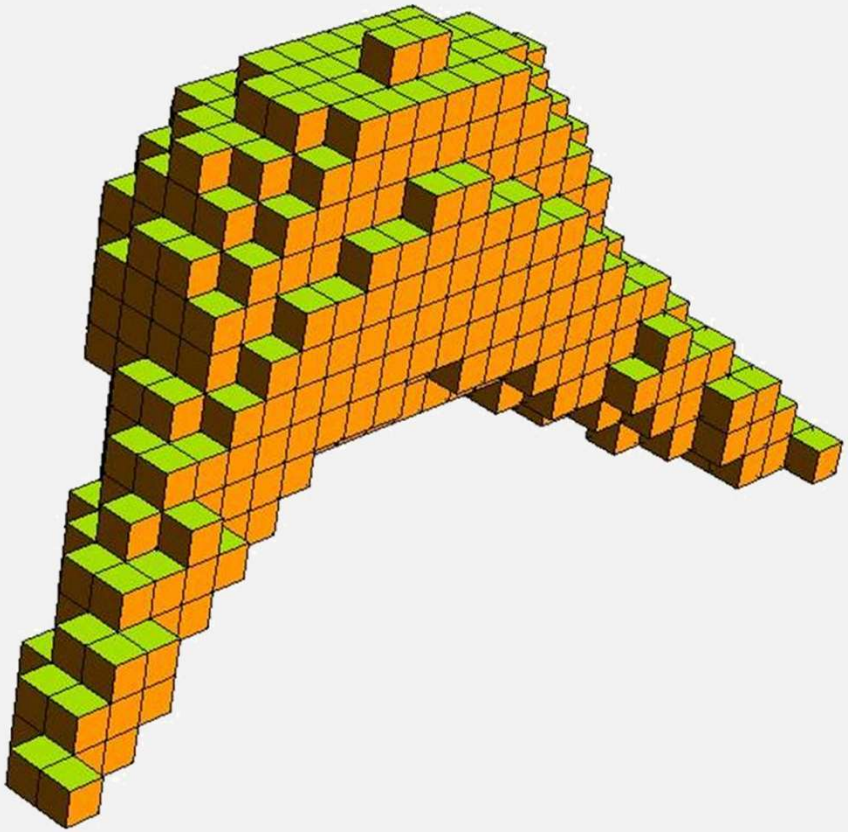
$$\phi_{mn}(q) = \frac{1}{\sqrt{2}}\left[e^{\frac{i\pi}{2}(nm+n+1)}\, g^{(2)}_{mn}(q) + e^{-\frac{i\pi}{2}(nm+n+1)}\, g^{(2)}_{m(-n)}(q)\right]$$

$$\phi_{mn}(q) = \left(\frac{4}{\pi}\right)^{1/4} e^{-\frac{1}{2}\left(q-\sqrt{\pi}\right)^2} \sin\left[n\sqrt{\pi} - \frac{n\pi}{2}(2m+1)\right]$$

Pros: Complete, linearly independent, collectively local

Cons: non-orthogonal?

Progress…



Higher D

>> Start with a Direct Product basis

>> Only keep functions that are inside E_{max}

Defeats exponential scaling

But what about non-localized basis functions?

Progress…

- >> Phase space based energy truncation
  - >> PST has no application to functions that are not localized in phase space
  - >> We can still gain insight from the PSP
  - >> We must look at the Wigner PDF's directly

Progress…

>> Phase space based energy truncation

Harmonic oscillator basis functions are amenable to Energy Truncation:

$$\sum_{i=1}^{D} \omega_i^{\mu} n_i \leq E_{\max}$$

How do we choose the coefficients?

/work/01922/thalvers/theory

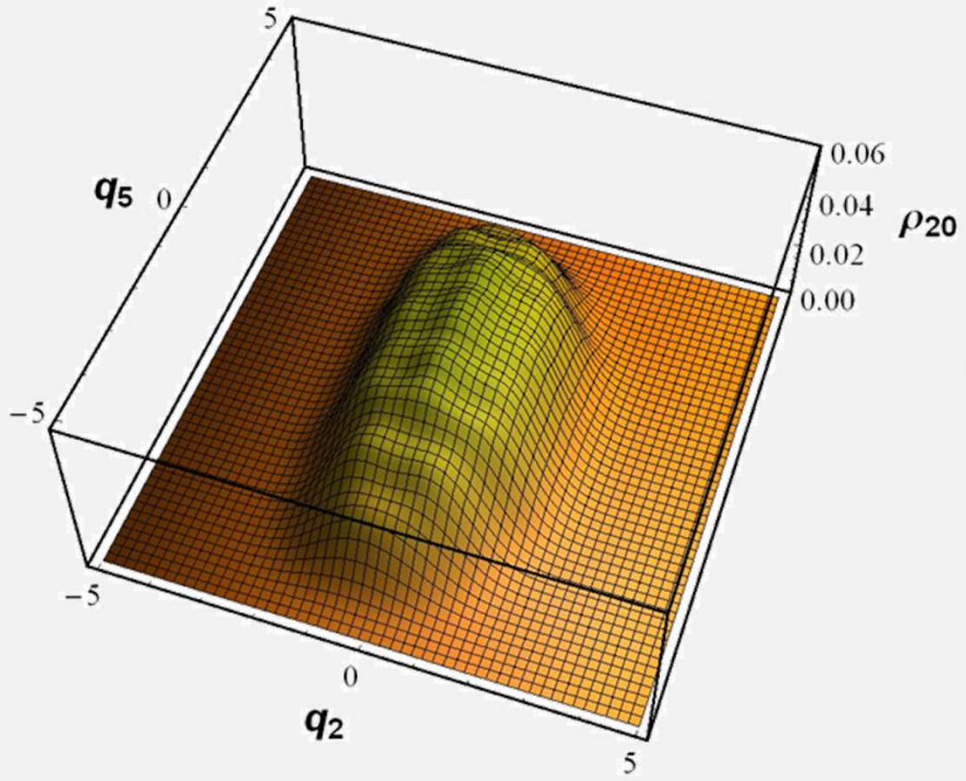
>> Phase space based energy truncation

Two obvious choices:

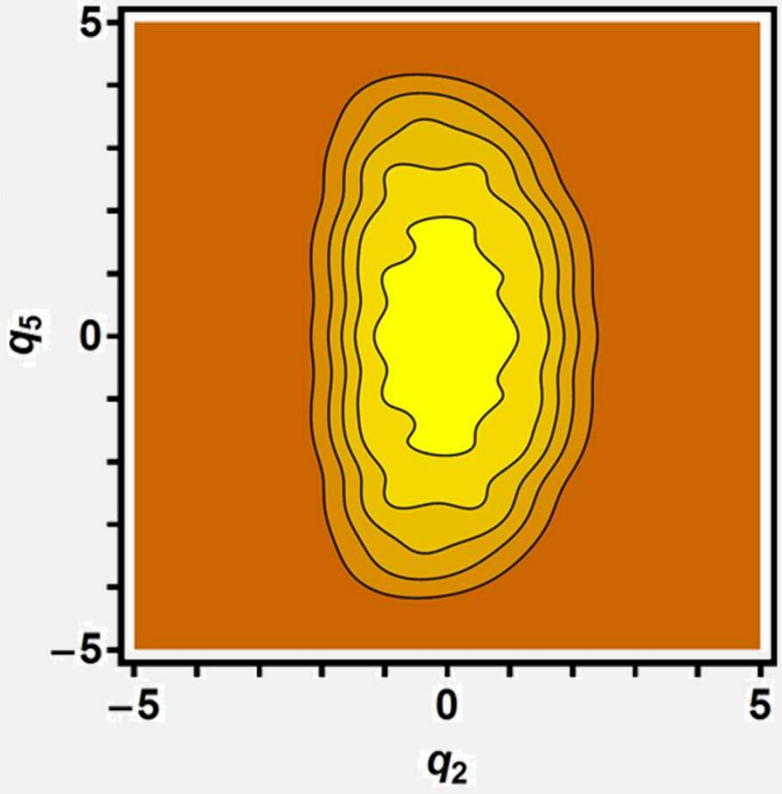
1. Set μ to zero
2. Set μ to one

Progress…

Position Projection of 2D Wigner PDF

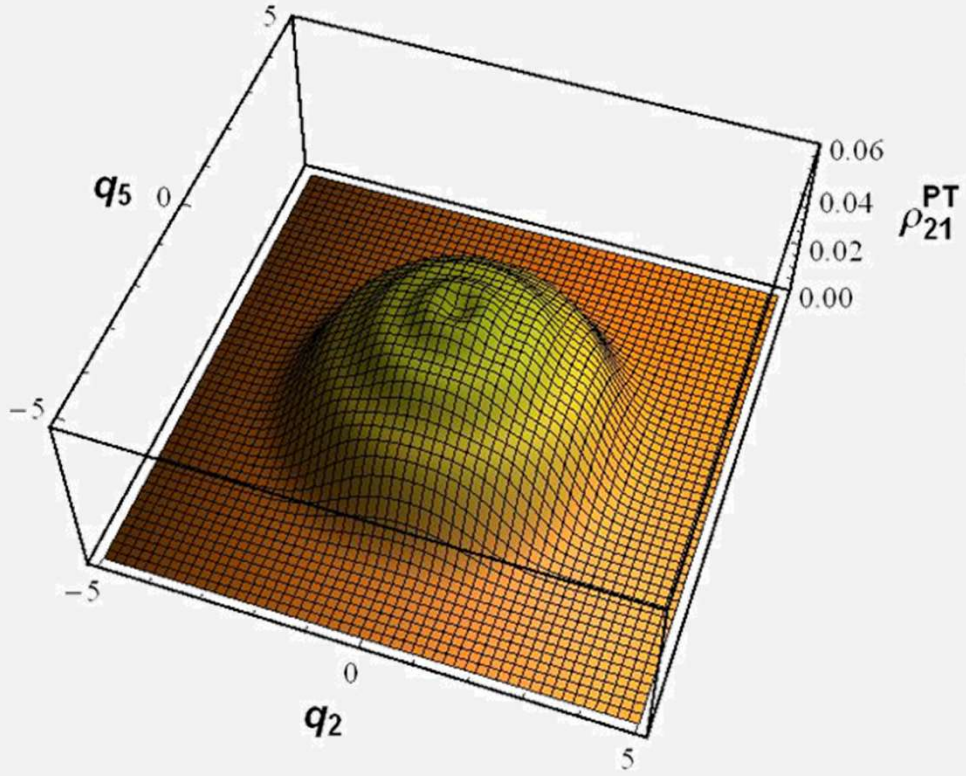


(a)

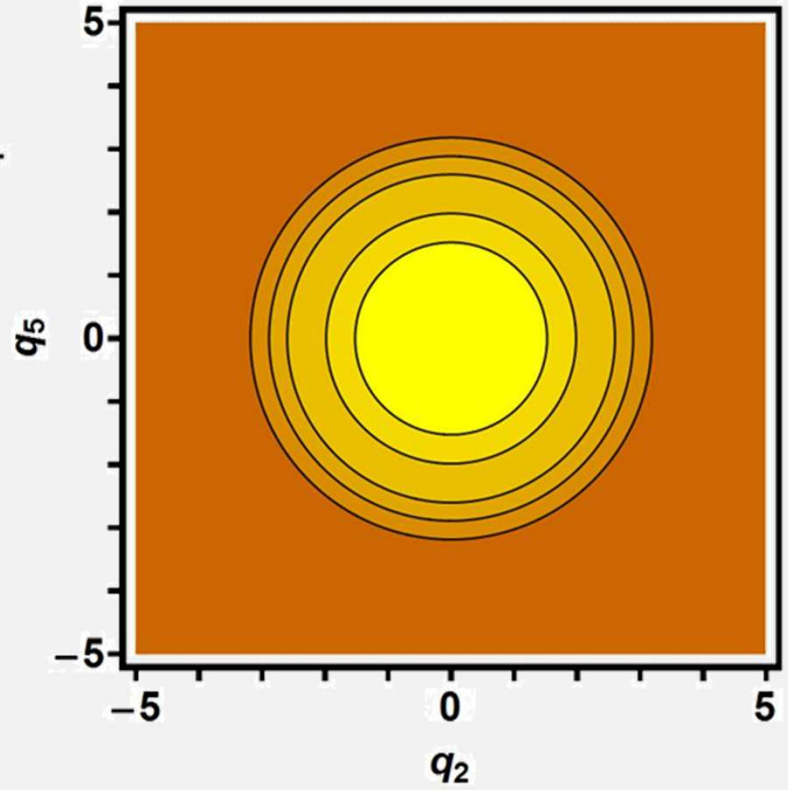


(b)

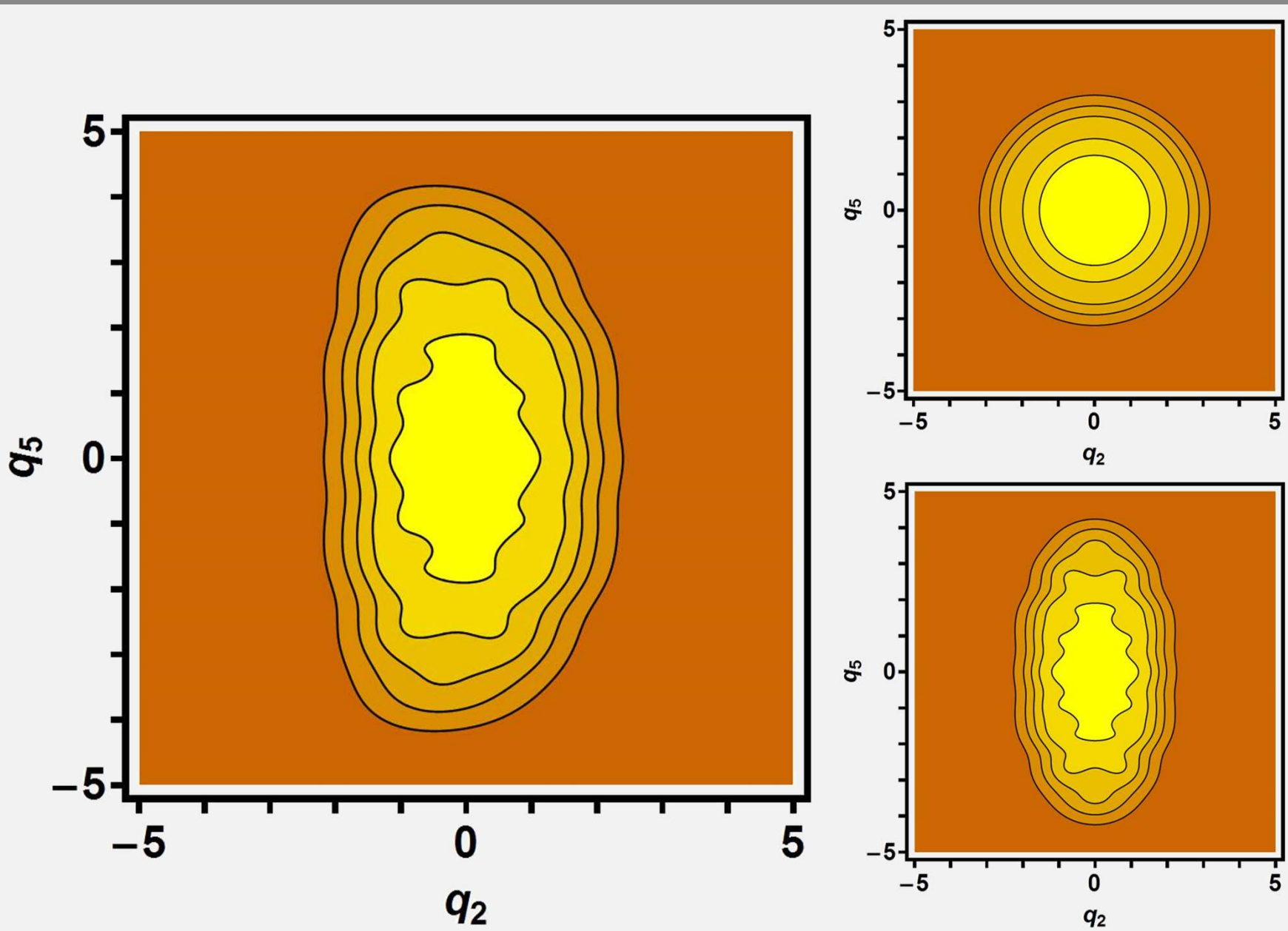
Position Projection of 2D Wigner PDF



(a)



(b)


5
0
−5
q_5
−5
0
5
q_2
5
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−5
q_5
−5
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5
q_2
5
0
−5
q_5
−5
0
5
q_2

/work/01922/thalvers/theory

>> Phase space based energy truncation

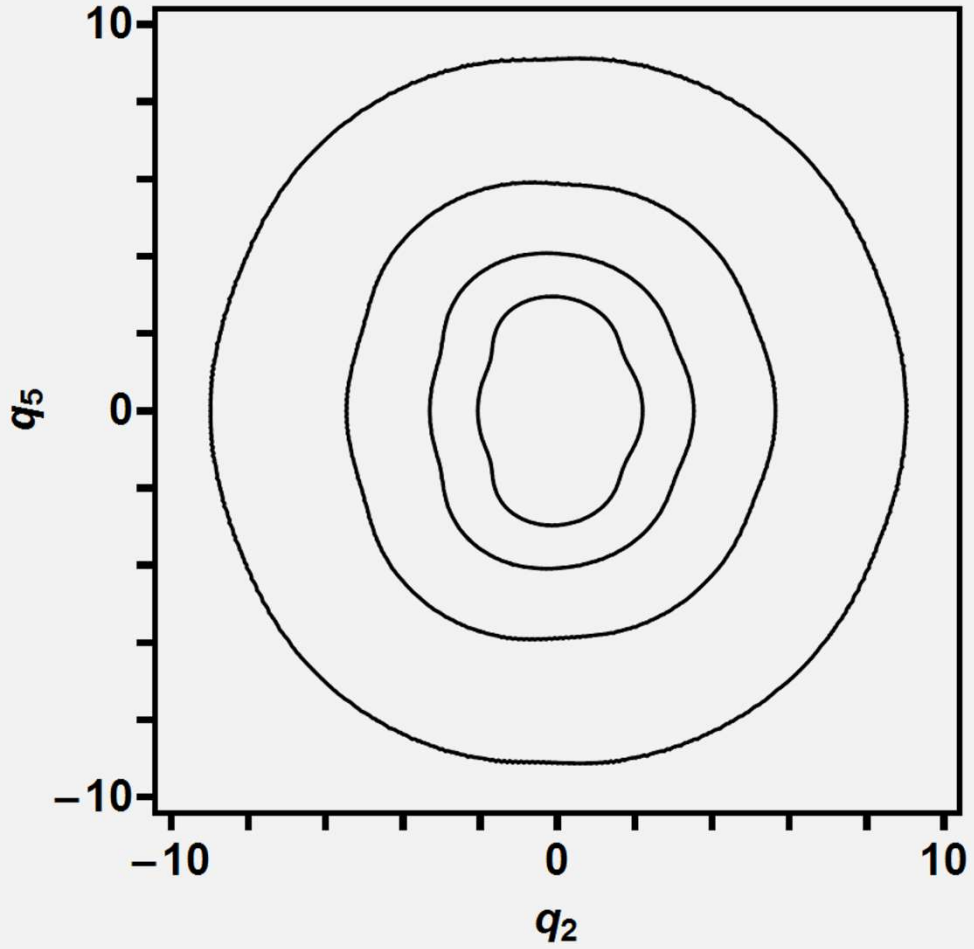
Two obvious choices:

1. Set μ to zero
2. Set μ to one

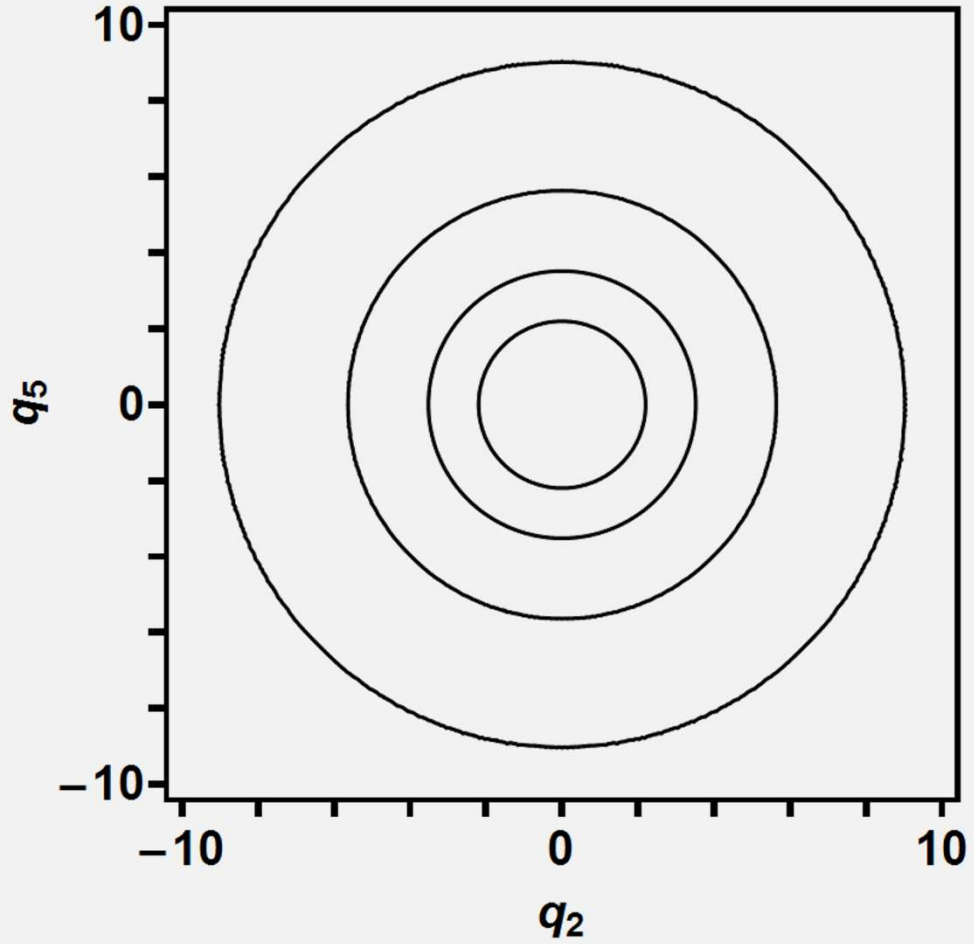
If choice 2 is so much better, why ever choose 1?

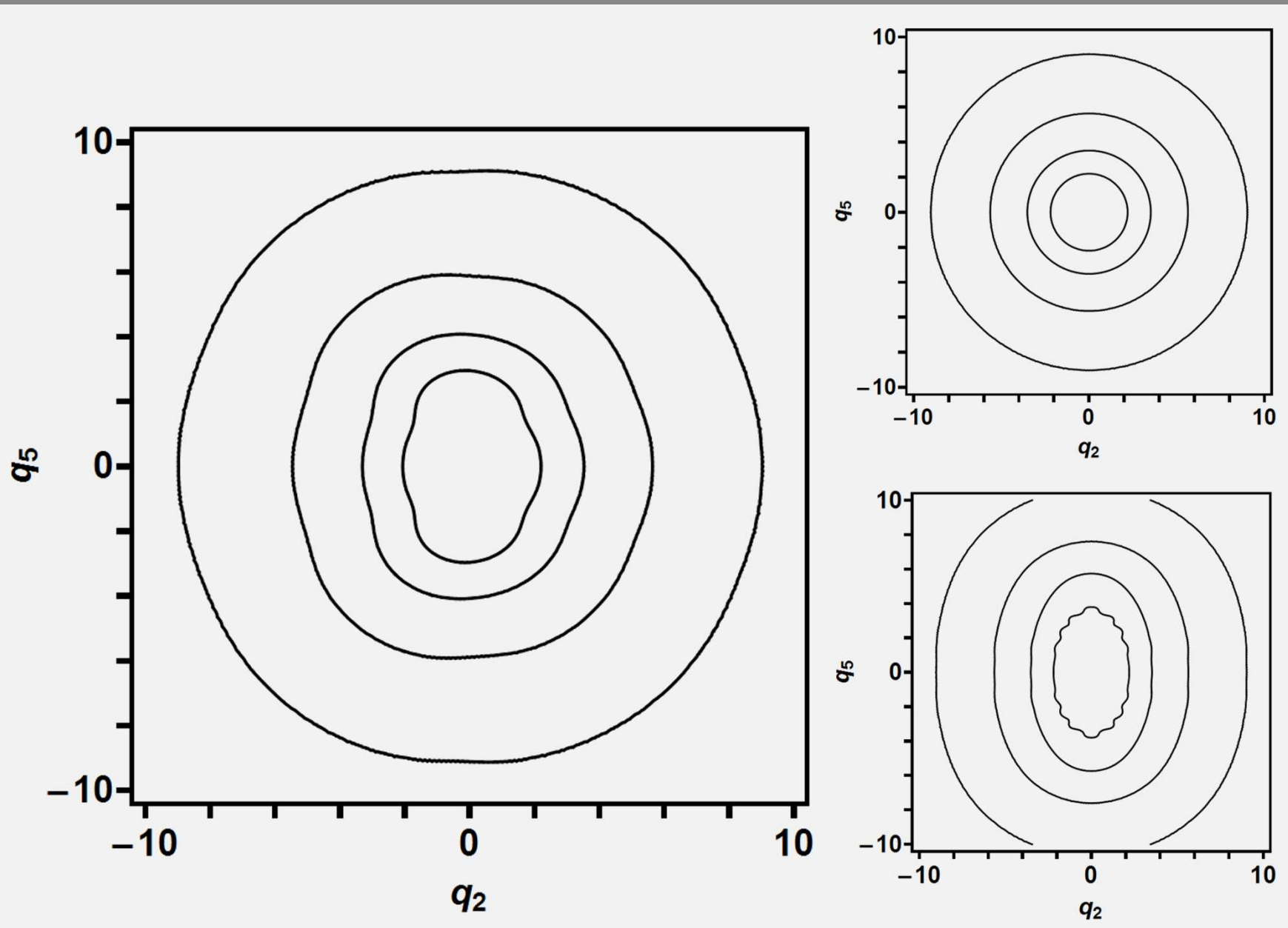
Progress…

Position Projection of 2D Wigner PDF



Position Projection of 2D Wigner PDF




10
0
−10
q_5
−10
0
10
q_2
10
0
−10
q_5
−10
0
10
q_2
10
0
−10
q_5
−10
0
10
q_2

>> Phase space based energy truncation

Two obvious choices:

-> 1. Set μ to zero

2. Set μ to one

Conclusion: For N>>K, low efficiency but high accuracy, choose 1

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>> Phase space based energy truncation

Two obvious choices:

1. Set μ to zero

-> 2. Set μ to one

-> 3. Both

Conclusion: For N~K, high efficiency but low accuracy, choose 2

Progress…

>> Hybrid truncation

- >> If all calculations are analytic then the solutions are variational
- >> The eigenvalues approach the correct solution from above
- >> The lowest lying eigenvalue from any calculation for a given state index is the most correct

Progress…

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	Method			
State	A	B	C	Hybrid
1	E_1^A	E_1^B	E_1^C	E_1^A
2	E_2^A	E_2^B	E_2^C	E_2^A
3	E_3^A	E_3^B	E_3^C	E_3^B
4	E_4^A	E_1^B	E_4^C	E_4^C

$$E_2^A < E_2^B < E_2^C$$

Progress…

>> Hybrid truncation

>> We can combine multiple truncations together

>> Even from different basis sets

>> Choose methods that target different energy ranges

μ = 0.0	μ = 0.5	μ = 1.0
Low energy	Middle energy	High energy

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Progress…

/work/01922/thalvers/SB

SwitchBLADE

>> Switchable Basis set Linear Algebra modules for Dimensionally independent Eignsolves

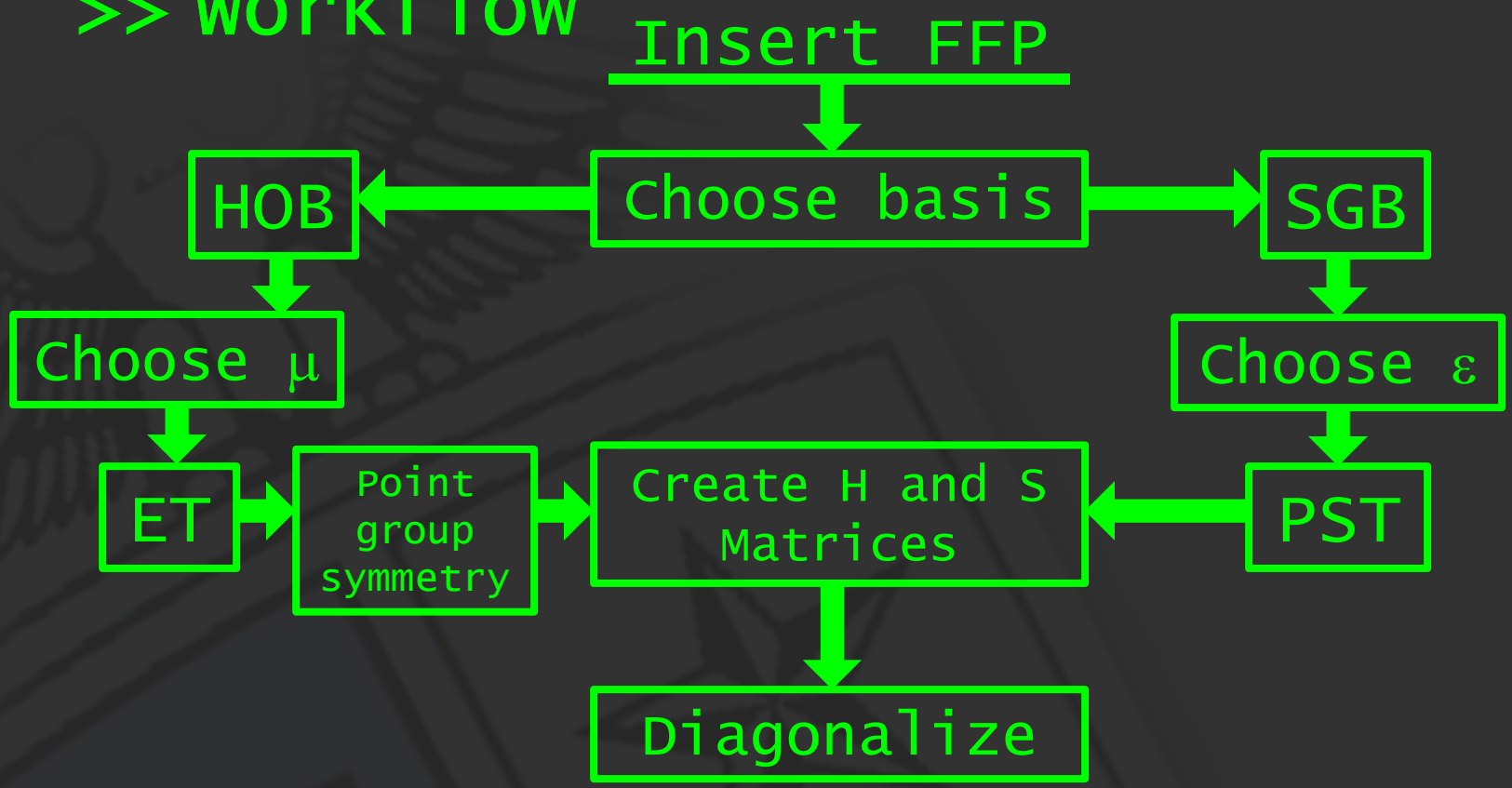
Progress…

/work/01922/thalvers/SB

- >> Features
  - >> Two separate basis sets
    - >> Symmetrized Gaussians
    - >> Harmonic Oscillator
  - >> Dimensionally independent
    - >> Tested from D=2 to D=30
  - >> Highly parallel
    - >> Scales up to 7000+ cores
  - >> Easy to use
    - >> User only needs to provide FFP

Progress…

>> Workflow



Progress…

>> Issues

- >> Accuracy
  - >> only ~2% (~10 cm^{-1})
- >> Potential Energy
  - >> Limited to FFP's
- >> Scaling
  - >> Non-parallel modules

Progress…

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Progress…

/work/01922/thalvers/results

>> Coupled Anharmonic Oscillators

4th order FFP in normal mode coordinates:

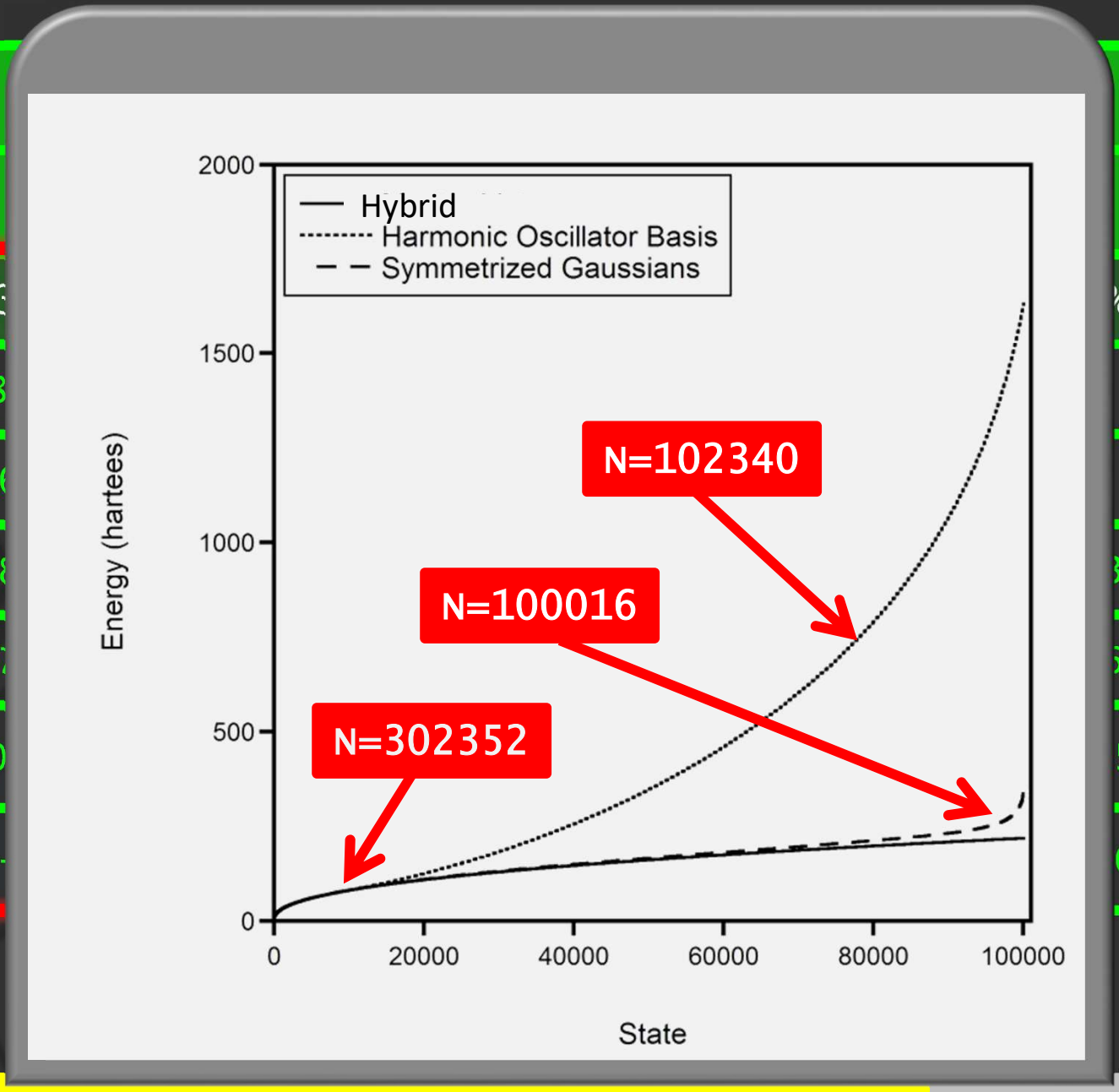
$$H = \sum_i \omega_i (p_i^2 + q_i^2) + \sum_{ijk} \phi_{ijk} q_i q_j q_k + \sum_{ijkl} \phi_{ijkl} q_i q_j q_k q_l$$

$$\omega_i = 1 \; ; \; \forall i \qquad \phi_{ijk} = 0$$

$$\phi_{iiii} = \alpha_i$$
$$\phi_{iijj} = \beta_{ij}$$

Progress…

N			0.06%
~1000	8		31
~3000	16		75
~10000	38		428
~30000	87		1775
~100000	20		4105
~175000	-		25176



Progress…

/work/01922/thalvers/results

>> P_2O (D=3)

4th order FFP in normal mode coordinates:

$$H = \sum_i \omega_i (p_i^2 + q_i^2) + \sum_{ijk} \phi_{ijk} q_i q_j q_k + \sum_{ijkl} \phi_{ijkl} q_i q_j q_k q_l$$

>> 18 potential energy terms

FFP: C. Pouchan, M. Aouni, and D. Bégué, Chem. Phys. Lett. 334, 352(2001)

Progress…

ν_0 = 197 cm^{-1}

ν_{8000} = 1[illegible] cm^{-1}

P_2O: N1=201414, N2=405522		
Accuracy cm^{-1}	K	K/N
150	34252	17%
40	15271	7.6%
15	8869	4.4%
4	2981	1.5%
0.15	33	0.016%

>> All states computed using SG's only

Progress…

/work/01922/thalvers/results

>> CH_2NH (D=9)

4th order FFP in normal mode coordinates:

$$H = \sum_i \omega_i (p_i^2 + q_i^2) + \sum_{ijk} \phi_{ijk} q_i q_j q_k + \sum_{ijkl} \phi_{ijkl} q_i q_j q_k q_l$$

>> 159 potential energy terms

FFP: C. Pouchan, K. Zaki, J. Chem. Phys. 107, 342(1997)

Progress…

ν_0 = 1212 cm^{-1}

ν_{5000} = 7992659 cm^{-1}

CH_2NH: N1=212197, N2=409582		
Accuracy cm^{-1}	K	K/N
150	5242	2.5%
40	1494	0.7%
15	531	0.25%
4	79	0.04%
0.15	4	0.0019%

>> All states computed using SG's only

Progress…

/work/01922/thalvers/results

>> CH_3CN (D=12)

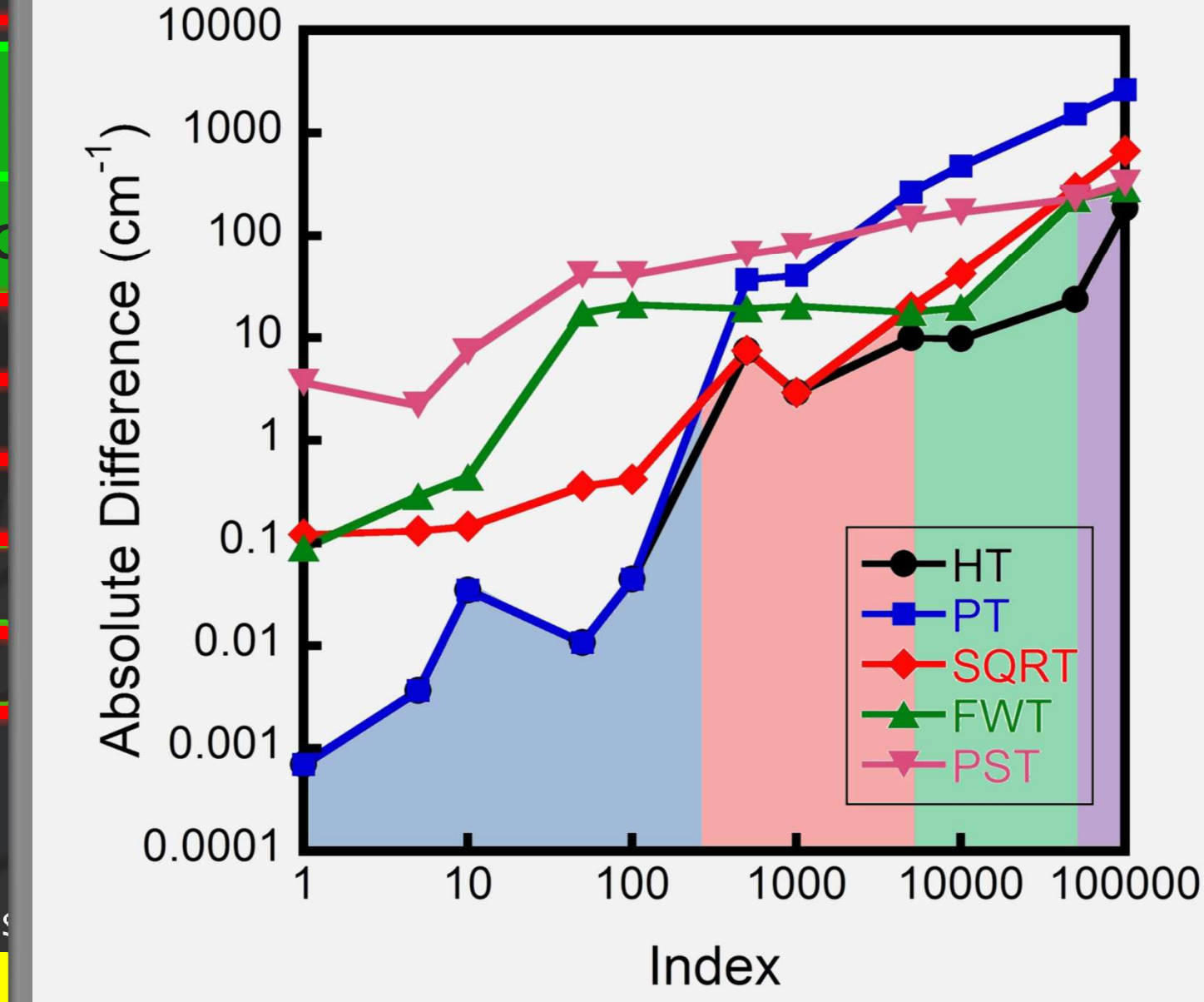
4th order FFP in normal mode coordinates:

$$H = \sum_i \omega_i (p_i^2 + q_i^2) + \sum_{ijk} \phi_{ijk} q_i q_j q_k + \sum_{ijkl} \phi_{ijkl} q_i q_j q_k q_l$$

>> 311 potential energy terms

FFP: D. Bégué, P. Carbonniere, C. Pouchan, J. Phys. Chem. A. 109, 4611(2005)

Progress…


Absolute Difference (cm-1)
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
1
10
100
1000
10000
100000
Index
HT
PT
SQRT
FWT
PST

/work/01922/thalvers/results

>> C_6H_6 (D=30)

4th order FFP in normal mode coordinates:

$$H = \sum_i \omega_i (p_i^2 + q_i^2) + \sum_{ijk} \phi_{ijk} q_i q_j q_k + \sum_{ijkl} \phi_{ijkl} q_i q_j q_k q_l$$

>> 1022 potential energy terms

FFP: A. Willetts, N. C. Handy, W. H. Green, and D. Jayatilaka, J. Chem. Phys. 94, 5608(1990)

Progress…

$\nu_0 = 399\ cm^{-1}$

$\nu_{600000} = 6908\ cm^{-1}$

C_6H_6 Hybrid		
Accuracy cm^{-1}	K	K/N
150	2688280	96%
40	1835631	66%
15	534638	19%
4	316	0.0004%
0.15	0	0.0%

Progress…

>> Symmetry

- >> Benzene has D_{6h} point group symmetry
- >> HOB functions have parity symmetry
- >> Three of the operations transform the basis functions with even/odd parity
- >> Result: 8-Fold reduction in N

Block Sizes for C_6H_6 (μ=0.0)		
Block	D_{6h} Irrep	N
1	$A_{1g} + E_{2g}$	719588
2	$A_{2g} + E_{2g}$	717697
3	$B_{1u} + E_{1u}$	717955
4	$B_{2u} + E_{1u}$	717602
5	$B_{1g} + E_{1g}$	707327
6	$B_{2g} + E_{1g}$	709084
7	$A_{1u} + E_{2u}$	708032
8	$A_{2u} + E_{2u}$	709057
Total	-	5706342

Progress…

Block: B_{2u} + E_{1g}				
Index	Label	Willetts* (cm^{-1})	N~0.7M ν_i (cm^{-1})	N~0.35M $\Delta\nu_i$ (cm^{-1})
1	ν_{18}	1058	1040.98	0.53
2	$\nu_4+\nu_{16}$	1125	1111.178	0.21
3	ν_{15}	1167	1147.751	0.47
4	$\nu_{10}+\nu_{16}$	1273	1260.279	0.59
5	$\nu_{10}+\nu_{16}$	1273	1260.781	0.41
6	ν_{14}	1318	1315.612	0.29
7	$\nu_5+\nu_{16}$	1418	1377.769	0.57
8	ν_{19}	1512	1496.231	0.23
9	$\nu_{10}+\nu_{11}$	1552	1525.564	1.4
10	$\nu_6+\nu_{12}$	1637	1624.036	0.18

*A. Willetts, N. C. Handy, W. H. Green, and D. Jayatilaka, J. Chem. Phys. 94, 5608(1990)

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>> Summary

- >> The phase space picture is an invaluable tool
- >> Black-box EQD software is possible
- >> SwitchBLADE is a robust platform
- >> Hybrid Truncation allows for high accuracy and high efficiency

/work/01922/thalvers/final_thoughts

>> Still more to do

- >> Accuracy improvements
  - >> PSRO's
- >> Generalized Hamiltonians
  - >> Rovibrational states
  - >> Scalable quadrature
- >> Iterative methods
  - >> Better scaling diag routines
  - >> ScalIT

Progress…


>> EOF
>> Questions?
Progress…