Sampling general distributions with quasi-regular grids: Applications to the calculations of vibrational spectra

Vladimir Mandelshtam, University of California, Irvine

Motivation

· Albeit numerically often most simple and convenient, the algorithms based on using direct-product grids scale exponentially with the dimensionality (the curse of dimensionality)

· Given a (multidimensional, localized, and normalized) distribution function P(x), the following integral can be computed by the Monte Carlo method:

$$\int P(x)f(x)dx \approx \frac{1}{N}\sum_{n=1}^{N} f(x_n) \qquad \text{with } x_n \text{ sampled randomly from } P(x_n)$$

However, the error scales as $\sim 1/\sqrt{N}$ which may seem to be too slow (at least comparing with quadrature methods in low dimensionality, subject to the latter being feasible)

→ Low-discrepancy Quasi-random sequences; quasi-Monte Carlo (the error often scales as $\sim 1/N$)

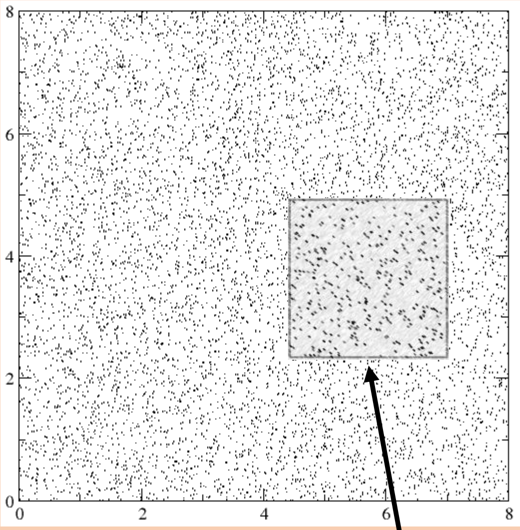
· Generating training sets (e.g., for fitting potential energy surfaces).
The challenge then is to sample all important regions of the configuration space in a least-redundant fashion.

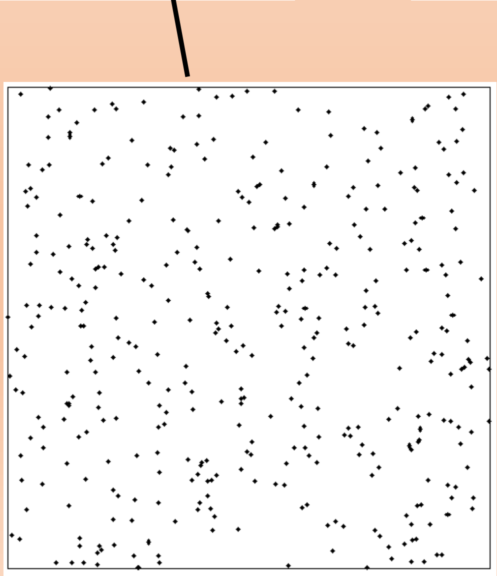
· Constructing an efficient localized basis set (e.g., a Gaussian basis) to solve the Schrödinger equation (SE). One of the outstanding problems is to generate a compact grid that would approximate uniformly all the solutions of the SE in a specific energy range (An optimal grid is expected to be non-uniform and non-direct-product).

Algorithms to generate efficient, i.e., both least-redundant and non-direct-product grids are desirable

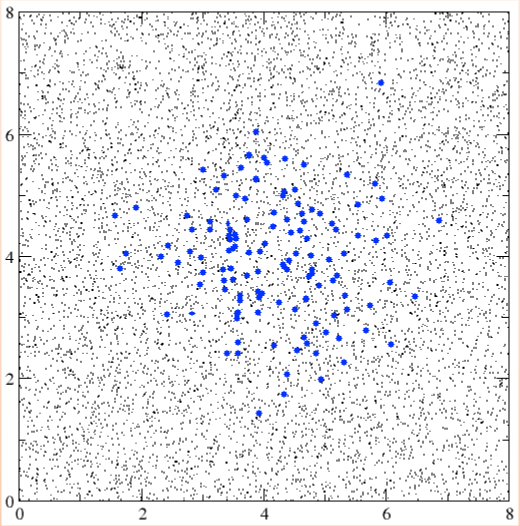
Example: Sampling a general distribution P(x) using a pseudo-random sequence

Pseudo-random uniform



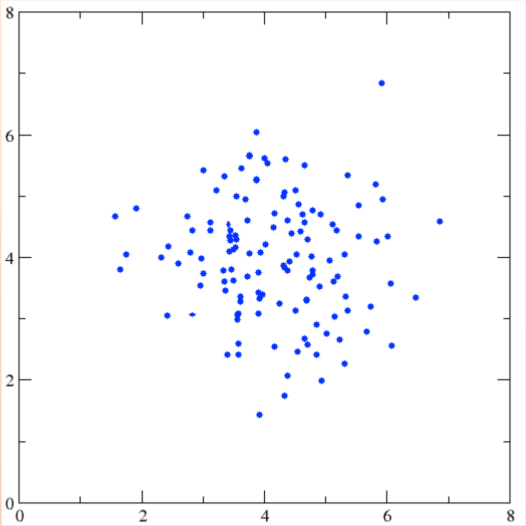


Rejection: accept if $\frac{P(x)}{Pmax} > \eta$ with $\eta \in [0;1]$



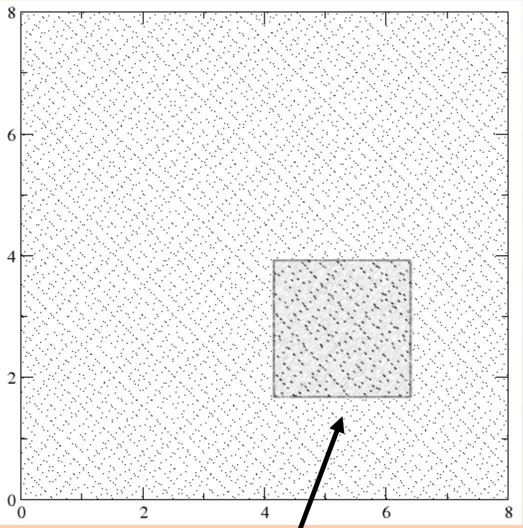
Normal distribution

$P(x) \sim \exp(-x^2/2)$

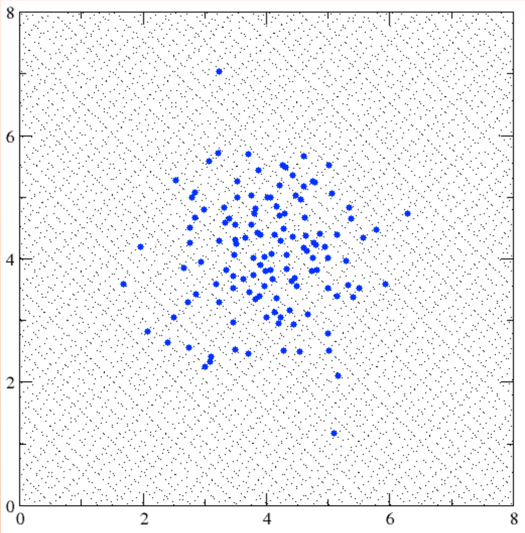


Sampling normal distribution using pseudo-random sequence and rejection method

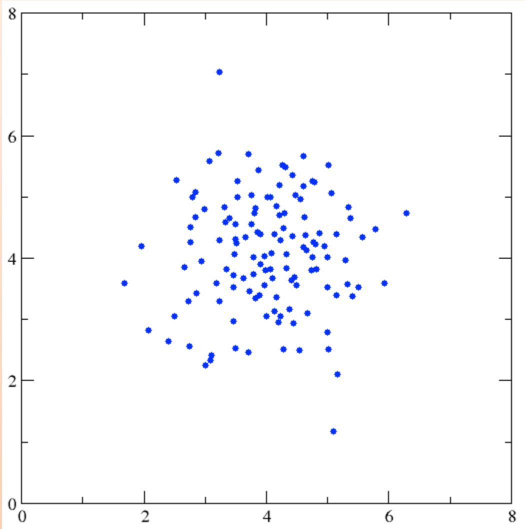
Uniform Quasi-random
(Sobol sequence)

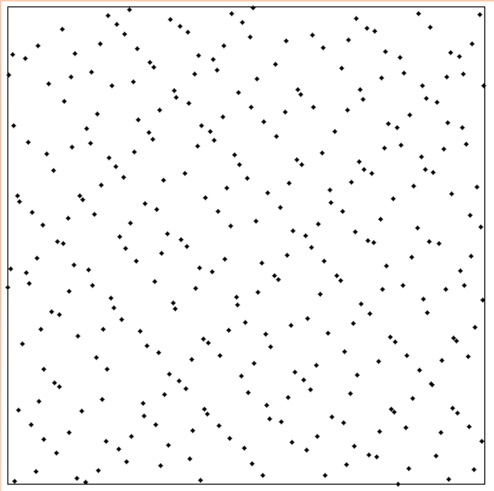


Rejection: accept if
$\frac{P(x)}{Pmax} > \eta$ with $\eta \in [0;1]$



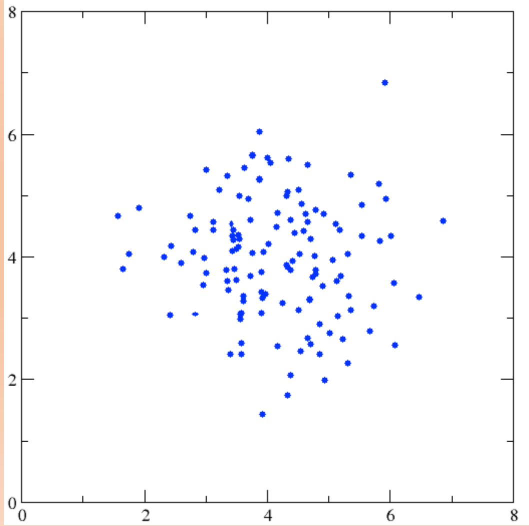
Normal distribution





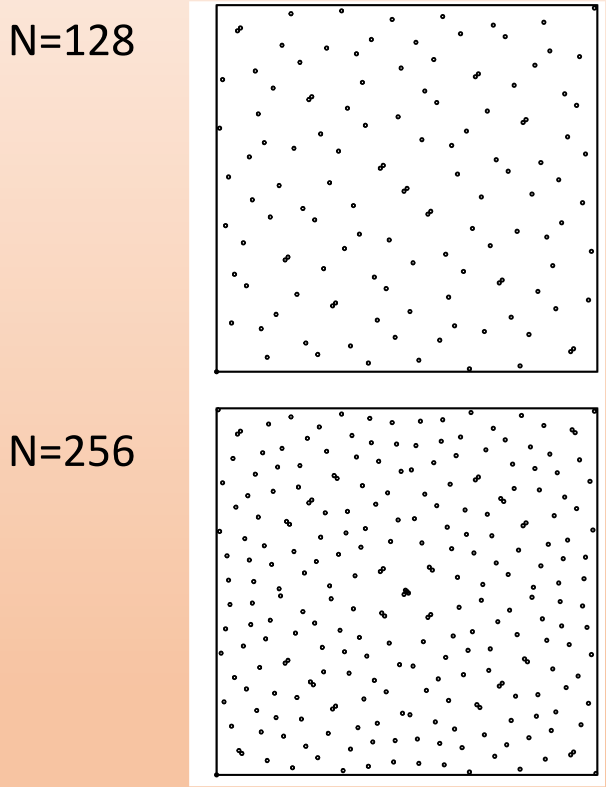
Uniform quasi-random + rejection: the local uniformity is destroyed (broken teeth)

Uniform pseudo-random + rejection



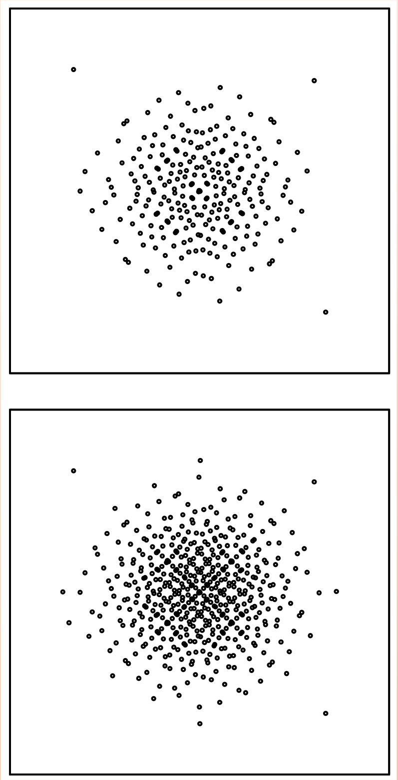
A much better method using a uniform low-discrepancy sequence to sample a product distribution, $P(x_1, \ldots, x_d) = P_1(x_1) \times \ldots \times P_1(x_d)$.

Uniform quasi-random (Sobol) sequence



Using inverse Cumulative Distribution Function: all points will be preserved together with their local uniformity property

Normal distribution



Sandra Brown

Brown, Georgescu & VM, “Self-consistent phonons revisited. II. A general and efficient method for computing free energies and vibrational spectra of molecules and clusters JCP 2013”

$\int P(x) f(x) dx \approx \frac{1}{N} \sum_{n=1}^{N} f(x_n)$ with error $\sim \frac{1}{N}$ for d ~ 10^3 (when none of the quadrature methods are feasible)

The bad news is that a low-discrepancy sequence, as defined for the uniform distribution, is straightforward to transform to a multidimensional distribution $P(x)$ only for special cases (e.g., when $P(x)$ is a product of 1D distributions, $P(x_1, \dots, x_d) = P_1(x_1) \times \dots \times P_1(x_d)$, and the rejection method in conjunction with a low-discrepancy sequence is not appealing.

Can we do better?

Non-uniform quasi - regular grid?

Quasi-regular grid

Shane Flynn and VM (JCP 2019, JCTC 2021).

Given a general (normalized) *d*-dimensional distribution function *P(x)*, consider points {$\mathbf{x}_i$} *(i=1, … , N)* and a purely repulsive homogeneous pair potential:

$$u(x_i, x_j) = [\sigma(x_i)/\, x_{ij}]^{\gamma} \qquad \text{(e.g. } \gamma = 9 + d \text{)}$$

with the position-dependent parameter $\sigma(x_i) = \mathrm{c}\,[\mathrm{N}P(x_i)]^{-1/d}$ and $c = c_0/\int P(x)dx$

The quasi-regular points {$\mathbf{x}_i$} are then obtained by minimizing the energy functional:

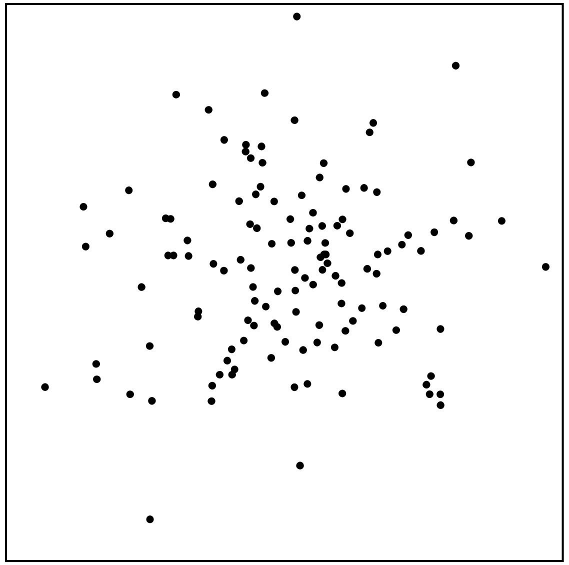
$$U(x_1, \dots, x_N) = \sum_{i \neq j} \sum_{j} u(x_i, x_j) \;\rightarrow min$$

$$U(x_1, \dots, x_N) = \; c^{\gamma} \sum_{i \neq j} \sum_{j} [P(x_i)]^{-1/d}/\, x_{ij}]^{\gamma} \rightarrow min$$

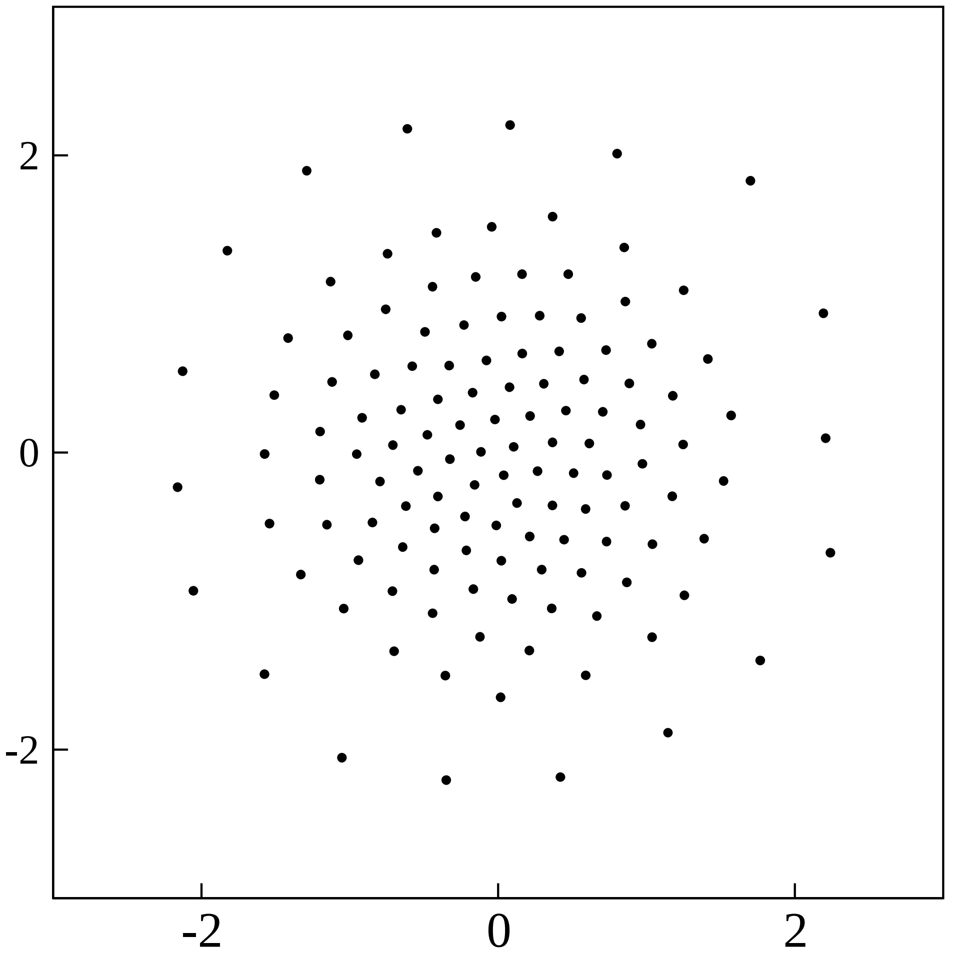
We do not need to know the constant c and hence we can use unnormalized *P(x)*!

Normal distribution (*N*=128)

Random



Assessing the regularity and consistency of a grid sampled from a given distribution *P(r)*

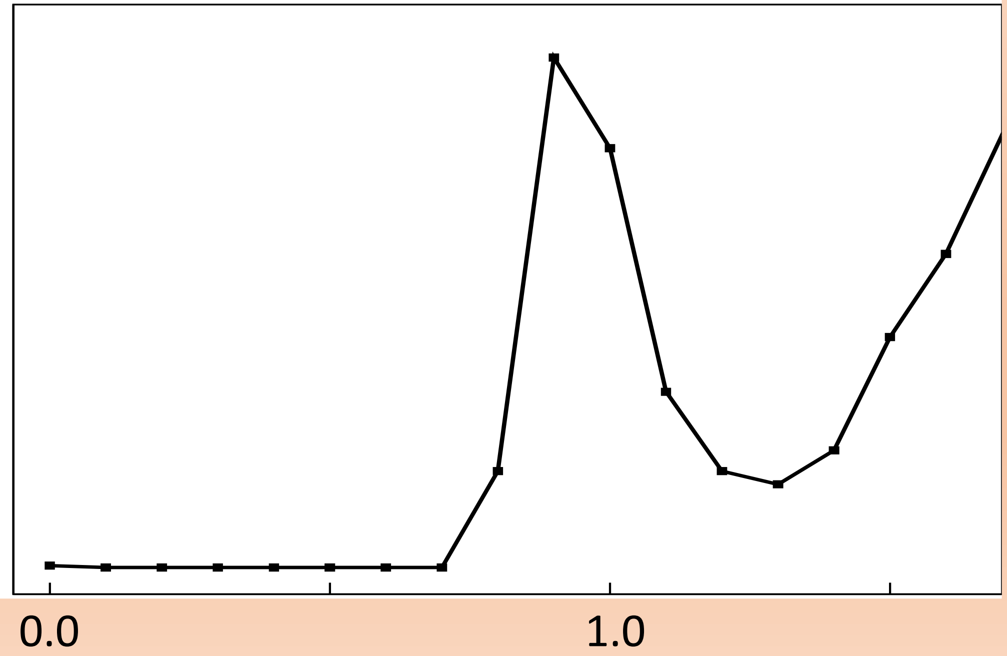


The pair distances are expected to scale as $\sim[P(r)]^{-1/d}$

Scaled radial pair correlation function:

$$g_{sc}(r) = g\left(\frac{r}{\sigma(r)}\right) = g\{r[P(r)]^{1/d}\}$$

where $g(r)$ is the standard radial pair correlation function.



Calculating vibrational molecular spectra using distributed Gaussian basis.

Davis & Heller (J. Comput. Phys. 1979)

Hamilton & Light. (J. Chem. Phys. 1986)

Bacic & Light. (J. Chem. Phys. 1986, 1987, 1988)

Garashchuk & Light (J. Chem. Phys. 2001)

Poirier & Light. (J. Chem. Phys. 2000)

Manzhos & Carrington (J. Chem. Phys. 2016)

Calculating eigenenergies and eigenfunctions of a d-dimensional Hamiltonian using a distributed Gaussian basis in Cartesian coordinates

Hamiltonian (mass-scaled Cartesian coordinates): $\widehat{H} = -\frac{1}{2}\Delta + V(\mathbf{r})$

Gaussian basis: $\Phi_i(\mathbf{r}) := (2\alpha_i/\pi)^{d/4} \exp\left(-\alpha_i|\mathbf{r}-\mathbf{r}_i|^2\right)$ (i=1, …, N)

Product of two Gaussians is aGaussian

$$\Phi_i(\mathbf{r})\Phi_j(\mathbf{r}) = \mathbf{S}_{ij}\left(\frac{\alpha_i+\alpha_j}{\pi}\right)^{d/2} \exp\left[-(\alpha_i+\alpha_j)(\mathbf{r}-\bar{\mathbf{r}}_{ij})^2\right]$$

The kinetic energy and overlap matrices are analytic:

$$\mathbf{T}_{ij} := -\frac{1}{2}\langle\Phi_i|\nabla^2|\Phi_j\rangle \qquad \mathbf{S}_{ij} := \langle\Phi_i|\Phi_j\rangle$$

Potential energy matrix elements are computed by sparse Gauss-Hermit quadratures:

$$\begin{aligned}\mathbf{V}_{ij} &:= \int_{\mathbb{R}^d} d\mathbf{r}\ \Phi_i(\mathbf{r})\Phi_j(\mathbf{r})V'(\mathbf{r}) \\ &= \mathbf{S}_{ij}\left(\frac{\alpha_i+\alpha_j}{\pi}\right)^{d/2}\int_{\mathbb{R}^d} d\mathbf{r}\ V'(\mathbf{r})\ \exp\left[-(\alpha_i+\alpha_j)(\mathbf{r}-\bar{\mathbf{r}}_{ij})^2\right]\end{aligned}$$

Generalized eigenvalue problem: $(\mathbf{T}+\mathbf{V}-E_k\mathbf{S})\Psi_k = 0$

JOURNAL OF CHEMICAL PHYSICS VOLUME 114, NUMBER 9

Quasirandom distributed Gaussian bases for bound problems

Sophya Garashchuk and John C. Light
James Franck Institute, University of Chicago, Chicago, Illinois 60637

(Received 13 June 2000; accepted 18 December 2000)

We introduce quasirandom distributed Gaussian bases (QDGB) that are well suited for bound problems. The positions of the basis functions are chosen quasirandomly while their widths and density are functions of the potential. The basis function overlap and kinetic energy matrix elements are analytical. The potential energy matrix elements are accurately evaluated using few-point quadratures, since the Gaussian basis functions are localized. The resulting QDGB can be easily constructed and is shown to be accurate and efficient for eigenvalue calculation for several multidimensional model vibrational problems. As more demanding examples, we used a 2D QDGB-DVR basis to calculate the lowest 400 or so energy levels of the water molecule for zero total angular momentum to sub-wave-number precision. Finally, the lower levels of Ar_3 and Ne_3 were calculated using a symmetrized QDGB. The QDGB was shown to be accurate with a small basis. [DOI: 10.1063/1.1348022]

Given a potential energy V(r), how to distribute Gaussians?

$$\Phi_i(\mathbf{r}) := (2\alpha_i/\pi)^{d/4} \exp\left(-\alpha_i|\mathbf{r}-\mathbf{r}_i|^2\right) \qquad (i=1, \ldots, N)$$

Gaussian centers r_i (i=1,… N) are sampled from distribution $P(r_i)$
From a semiclassical argument for d=1 we expect an optimal distribution to be

$P(r_i)=[E_{cut}-V(r_i)]^{-1/2}$ (E_{cut} is an adjusting parameter)

Therefore, for a general d (Bill Pourier, 2004) we should have $P(r_i)=[E_{cut}-V(r_i)]^{-\gamma}$ with $\gamma = \frac{d}{2}$

Garaschuk & Light (JCP 2001): use quasi-random + rejection method

Assuming **quasi-regular** basis, the distances should scale as $\sim [P(r_i)]^{-1/d}$
and hence the inverse widths should scale as $\alpha_i \sim [P(r_i)]^{2/d}$

Gaussian (inverse) widths $\alpha_i = \alpha_0 * (dist_i)^{-2}$

$dist_i$ = the distance between r_i and its nearest neighbor; $\alpha_0 \sim 1$ is an adjusting parameter

Sampling the 2D Morse potential

$$\mathbf{V}(x,y) = D\left[\left(e^{-a_x x} - 1\right)^2 + \left(e^{-a_y y} - 1\right)^2\right]$$

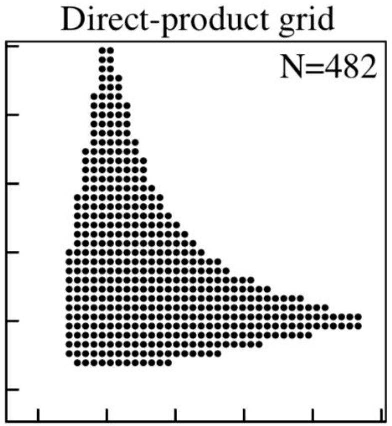
Following Garashchuk & Light JCP 2001

$$P(\mathbf{x}) := \frac{E_{\text{cut}} + \Delta - \mathbf{V}(\mathbf{x})}{\int d\mathbf{x}\ \left[E_{\text{cut}} + \Delta - \mathbf{V}(\mathbf{x})\right]}$$

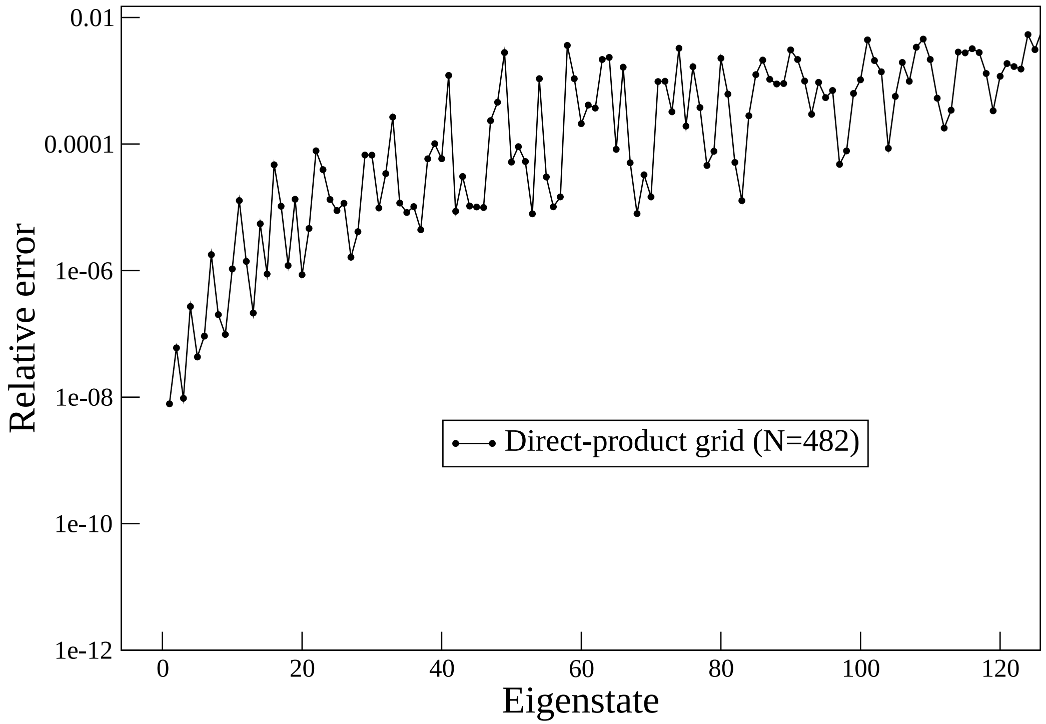
Flynn & VM (JCP 2019)

2D Morse potential.

$$\mathbf{V}(x,y) = D\left[\left(e^{-a_x x} - 1\right)^2 + \left(e^{-a_y y} - 1\right)^2\right]$$

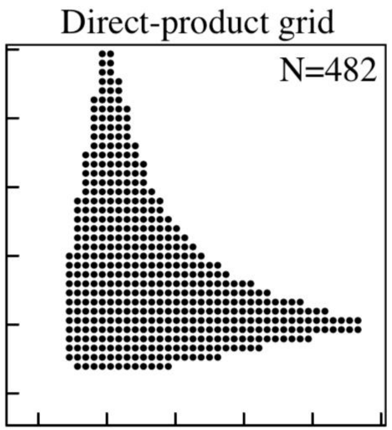


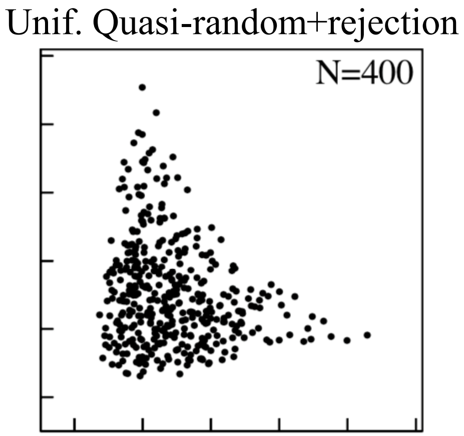
Garashchuk & Light JCP 2001



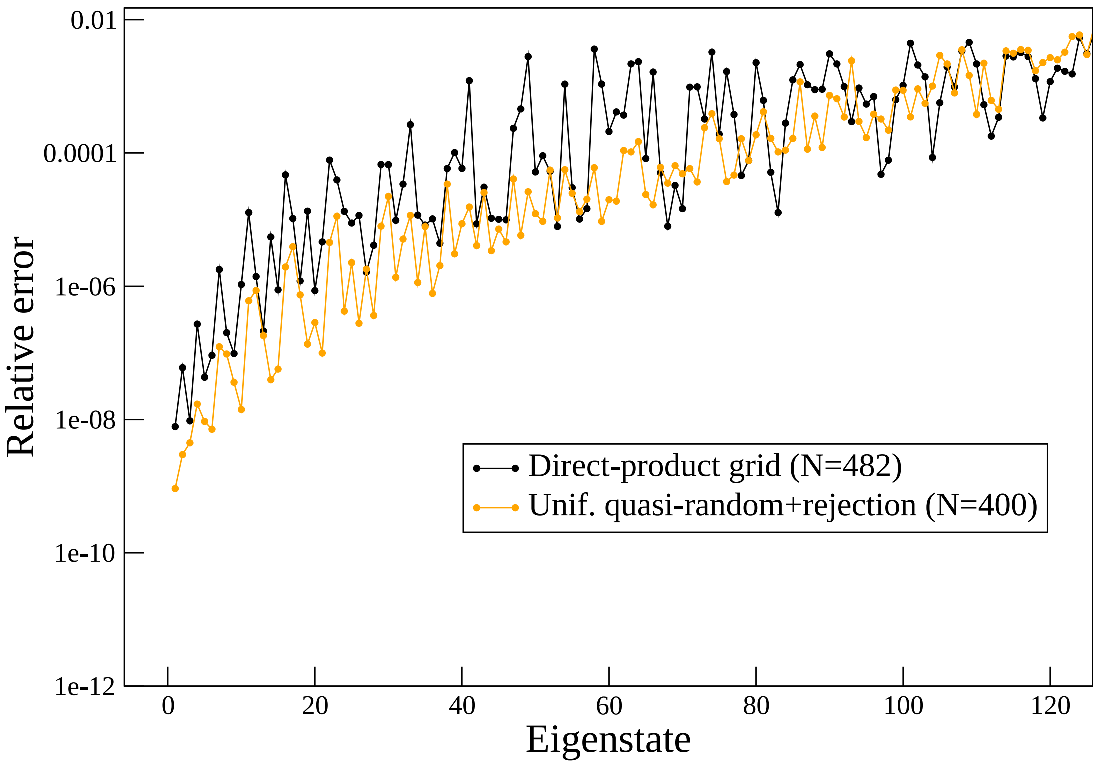
2D Morse potential.

$$\mathbf{V}(x,y) = D\left[\left(e^{-a_x x}-1\right)^2+\left(e^{-a_y y}-1\right)^2\right]$$



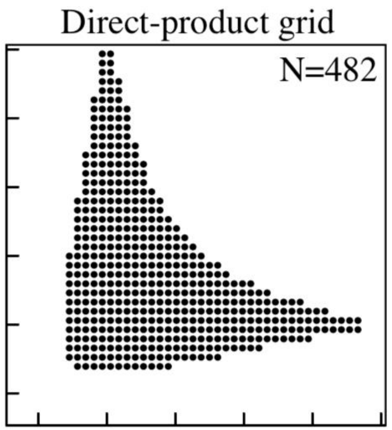


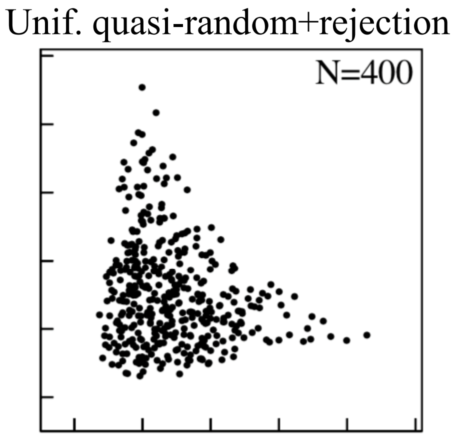
Garashchuk & Light JCP 2001

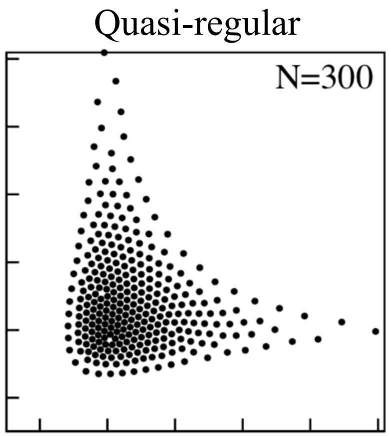


2D Morse potential.

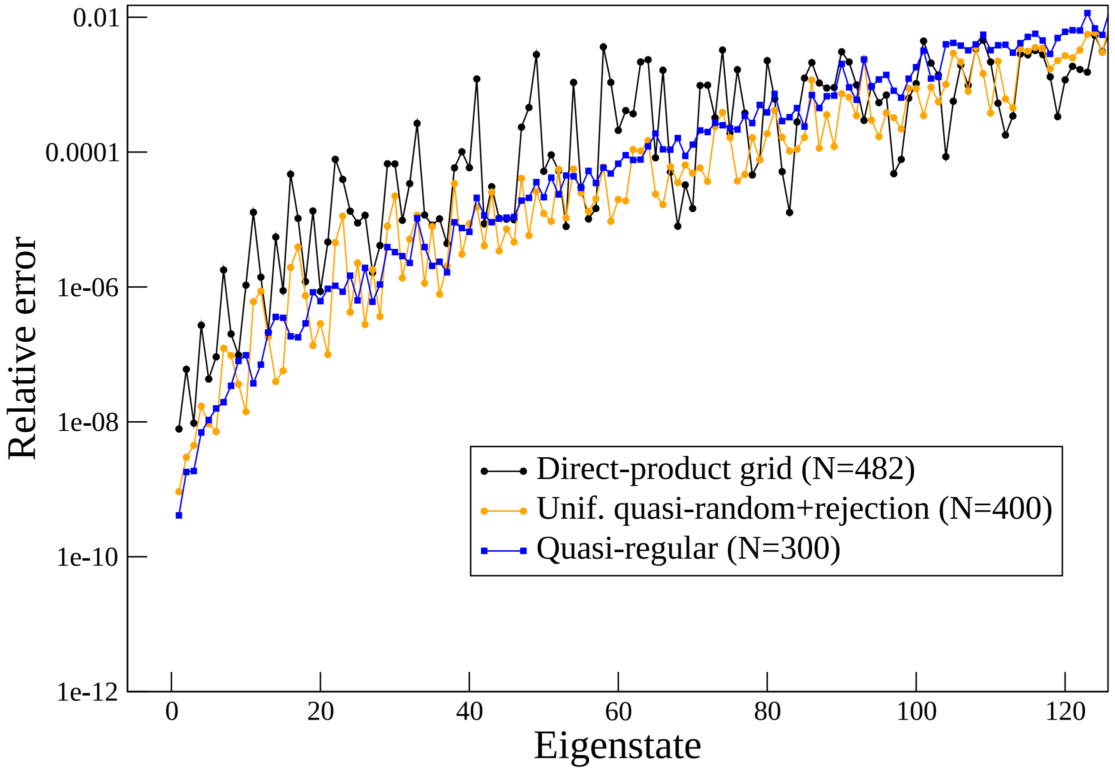
$$\mathbf{V}(x,y) = D\left[\left(e^{-a_x x}-1\right)^2+\left(e^{-a_y y}-1\right)^2\right]$$


Direct-product grid


Unif. quasi-random+rejection

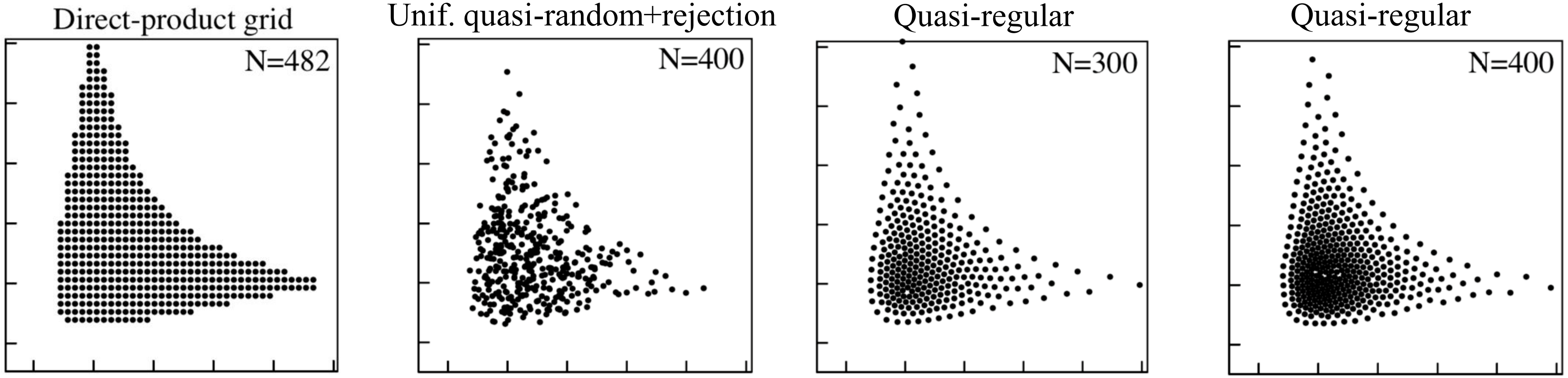

Quasi-regular

Flynn & VM (JCP2019)



2D Morse potential.

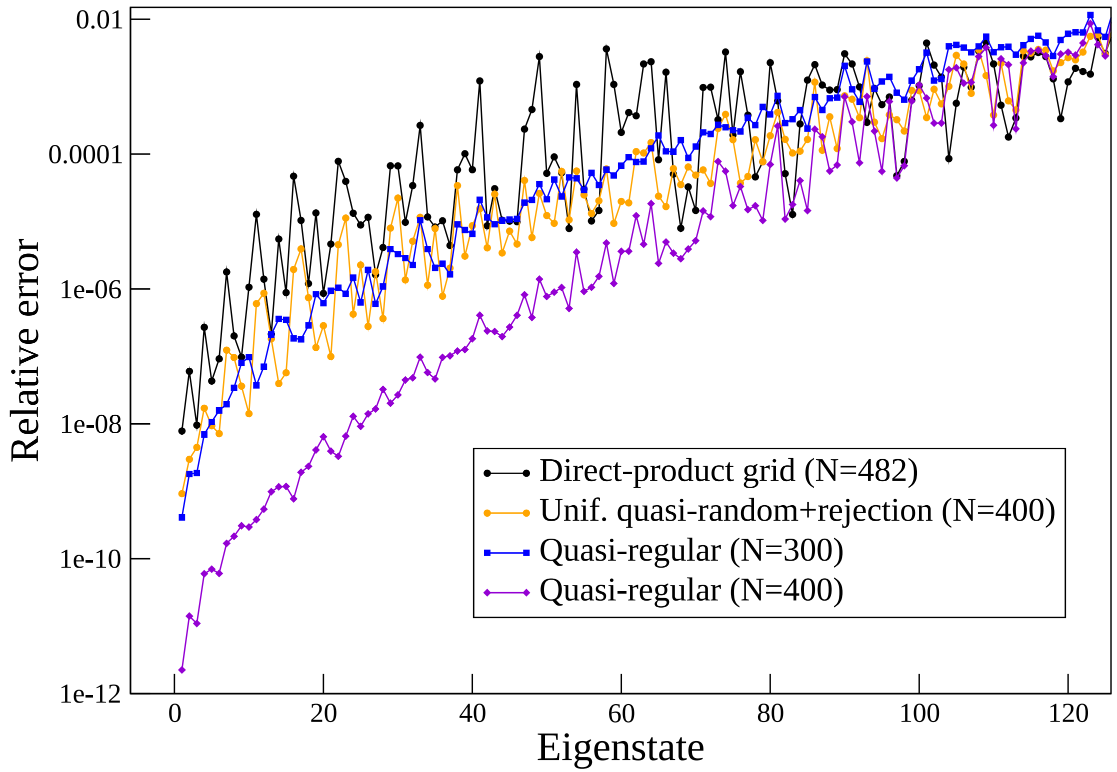
$$\mathbf{V}(x,y) = D\left[\left(e^{-a_x x}-1\right)^2+\left(e^{-a_y y}-1\right)^2\right]$$


Direct-product grid

Unif. quasi-random+rejection

Quasi-regular

Quasi-regular

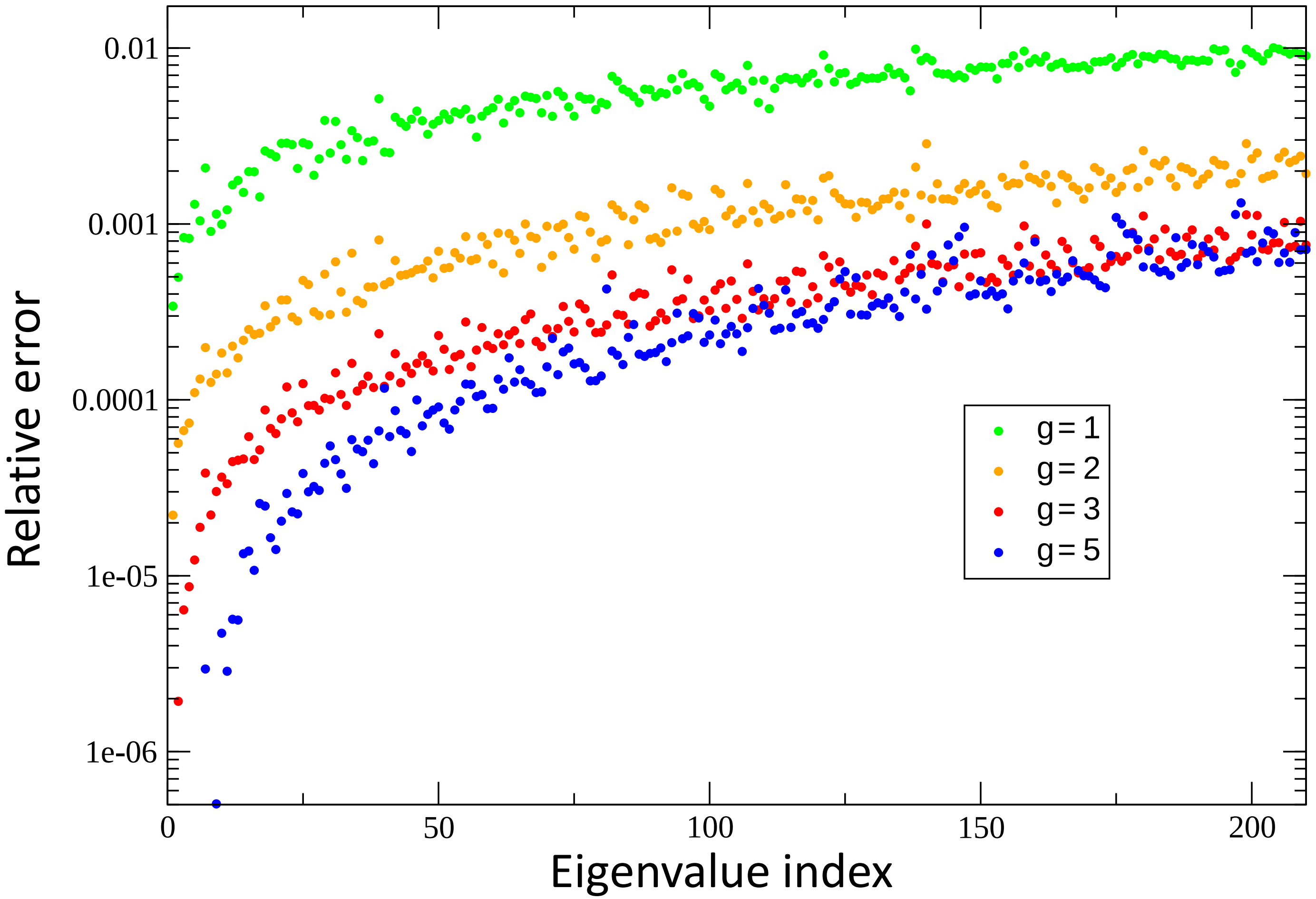


Flynn & VM (JCP 2019)

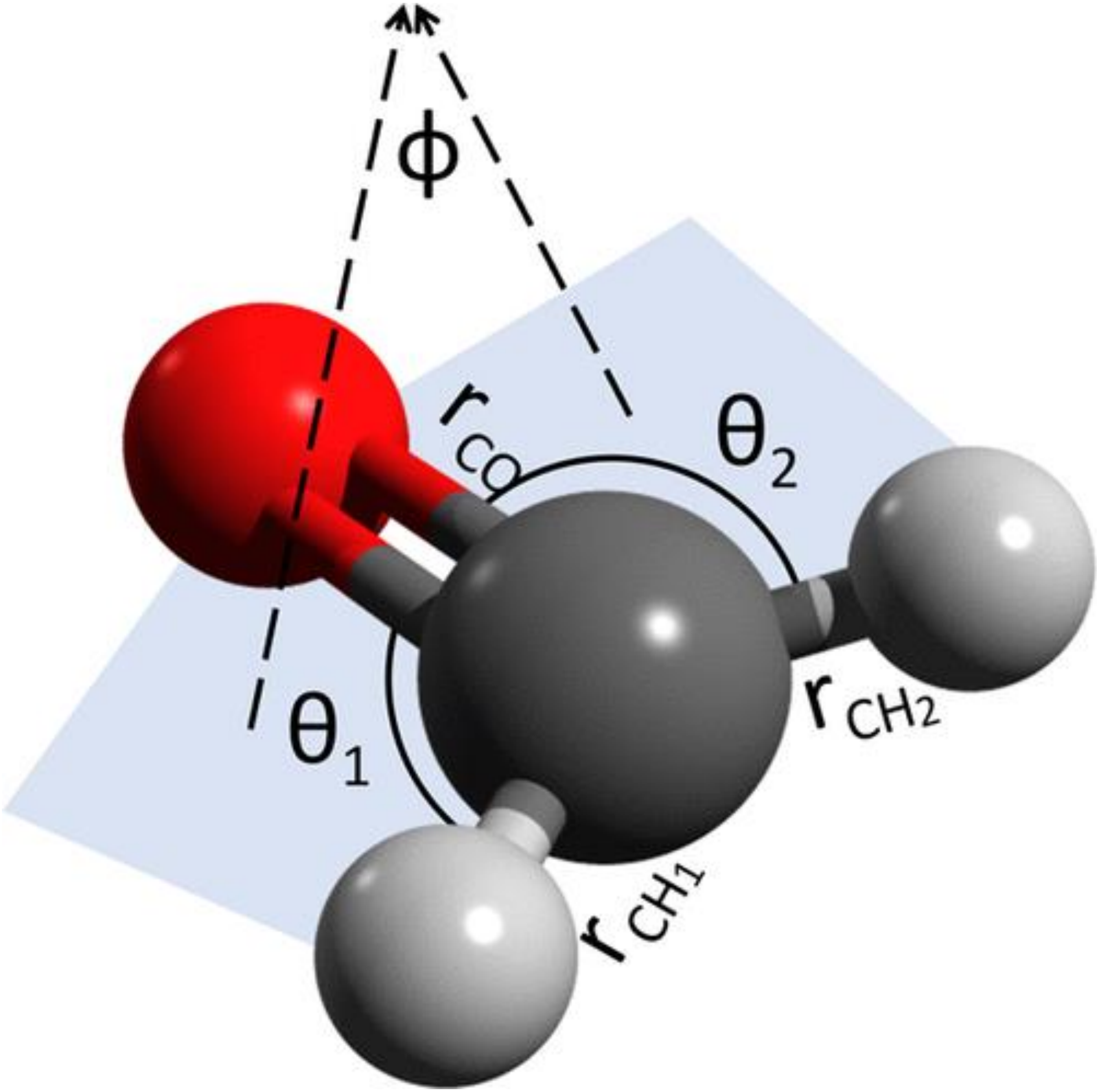
6D Morse oscillator

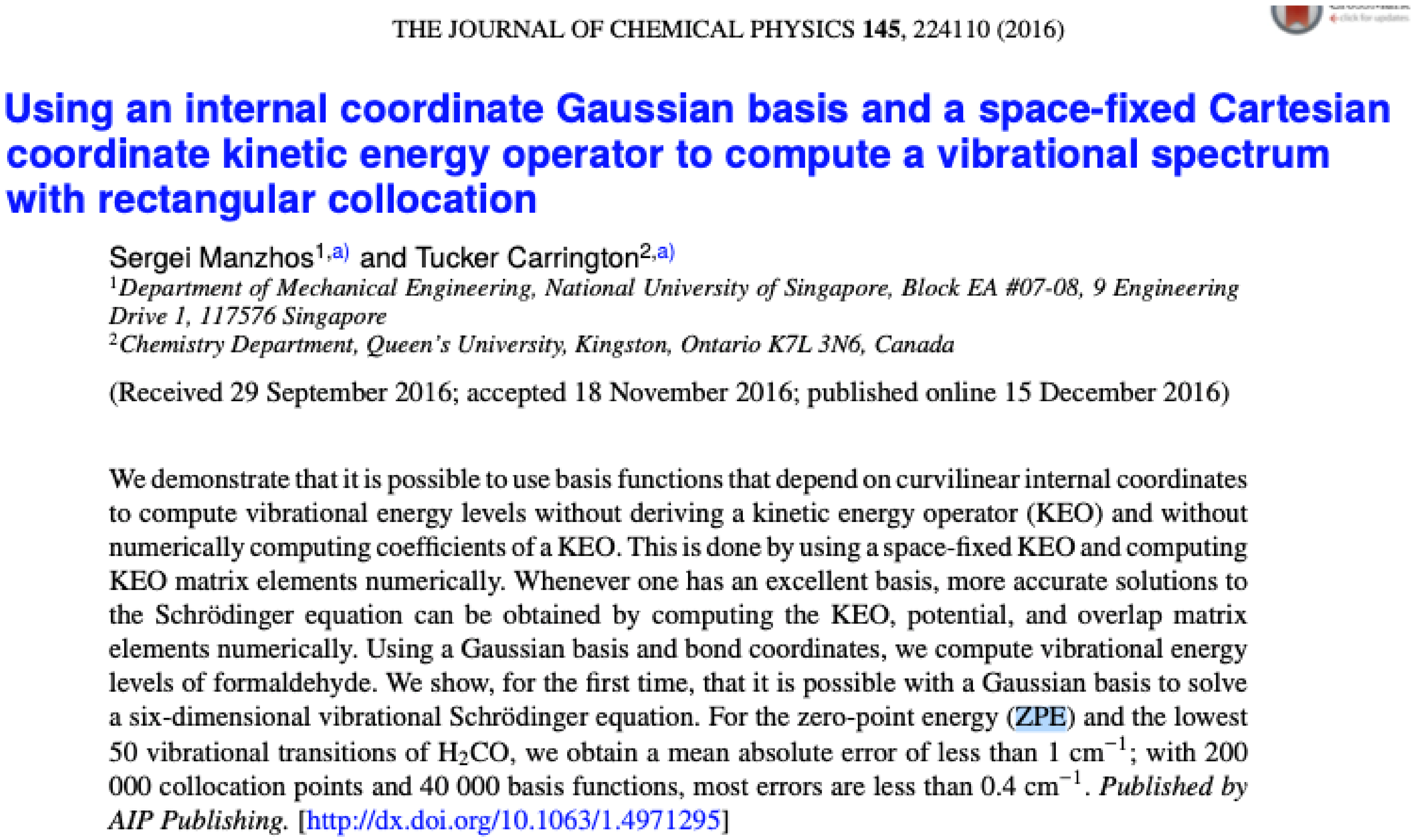
Distributed Gaussian basis using N=8,000
Recall: using semiclassical argument we expect the optimal distribution for a d-dimensional case to be

$$P(r_i)=[E_{cut}-V(r_i)]^{-\gamma} \quad \text{with} \quad \gamma = \frac{d}{2} = 3$$



Calculating vibrational energies of a K-atom molecule using a rotationally and translationally invariant (Gaussian?) basis: we cannot use Cartesian coordinates





THE JOURNAL OF CHEMICAL PHYSICS **145**, 224110 (2016)

Using an internal coordinate Gaussian basis and a space-fixed Cartesian coordinate kinetic energy operator to compute a vibrational spectrum with rectangular collocation

Sergei Manzhos[1,a)] and Tucker Carrington[2,a)]
[1]*Department of Mechanical Engineering, National University of Singapore, Block EA #07-08, 9 Engineering Drive 1, 117576 Singapore*
[2]*Chemistry Department, Queen's University, Kingston, Ontario K7L 3N6, Canada*

(Received 29 September 2016; accepted 18 November 2016; published online 15 December 2016)

We demonstrate that it is possible to use basis functions that depend on curvilinear internal coordinates to compute vibrational energy levels without deriving a kinetic energy operator (KEO) and without numerically computing coefficients of a KEO. This is done by using a space-fixed KEO and computing KEO matrix elements numerically. Whenever one has an excellent basis, more accurate solutions to the Schrödinger equation can be obtained by computing the KEO, potential, and overlap matrix elements numerically. Using a Gaussian basis and bond coordinates, we compute vibrational energy levels of formaldehyde. We show, for the first time, that it is possible with a Gaussian basis to solve a six-dimensional vibrational Schrödinger equation. For the zero-point energy (ZPE) and the lowest 50 vibrational transitions of H_2CO, we obtain a mean absolute error of less than 1 cm^{-1}; with 200 000 collocation points and 40 000 basis functions, most errors are less than 0.4 cm^{-1}. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4971295]

Molecular spectra calculations using internal coordinates, distributed Gaussian basis, and the collocation method

Molecular Hamiltonian (**r** are internal coordinates): $\hat{H} = \hat{T} + V(\mathbf{r})$

Expand the wavefunction in a Gaussian basis using internal coordinates:

$$\Psi(\mathbf{r}) = \sum_{i=1}^{N} \mathbf{c}_i \Phi_i(\mathbf{r}) \qquad \boldsymbol{\Phi}_i(\mathbf{r}) := \exp[-\|\mathbf{r}-\mathbf{r}^{(i)}\|^2_{\boldsymbol{\alpha}^{(i)}}] \; (i = 1, \ldots, N)$$

The Schrödinger equation at the collocation points $\mathbf{r}^{(j)}$: $(\hat{H} - E)\Psi(\mathbf{r}^{(j)}) = 0$

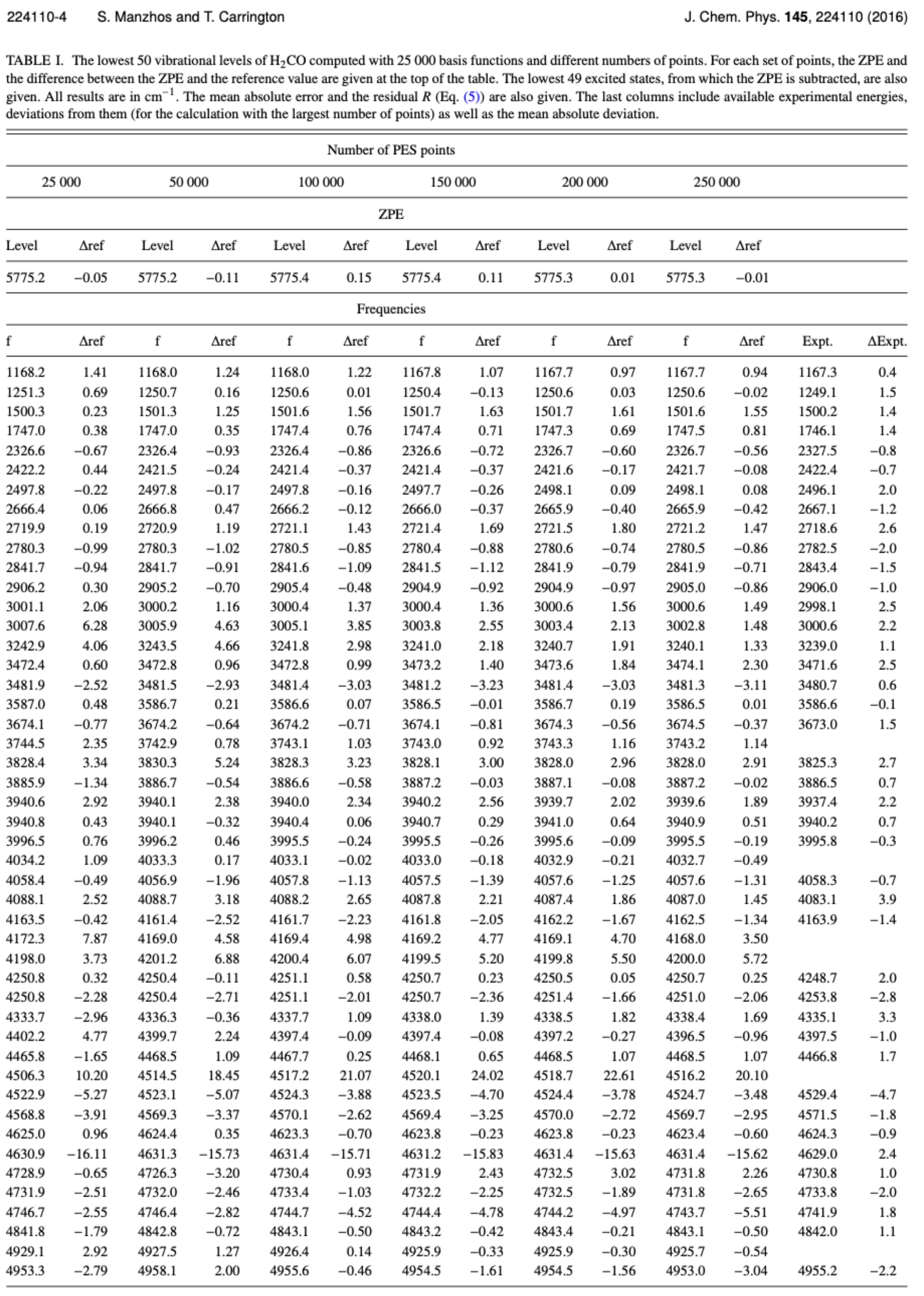
Kinetic energy can be expressed in Cartesian Coordinates and evaluated numerically by finite difference

$$\hat{T} = -\sum_{i=1}^{3N_{\text{atoms}}} -\frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial \mathbf{x}_i^2}$$

We need to solve the generalized eigenvalue problem

$$(\mathbf{H} - E\mathbf{S})\mathbf{c} = 0 \qquad \mathbf{S}_{ji} := \Phi_i(\mathbf{r}^{(j)}); \;\; \mathbf{H}_{ji} := \hat{H}\Phi_i(\mathbf{r}^{(j)})$$

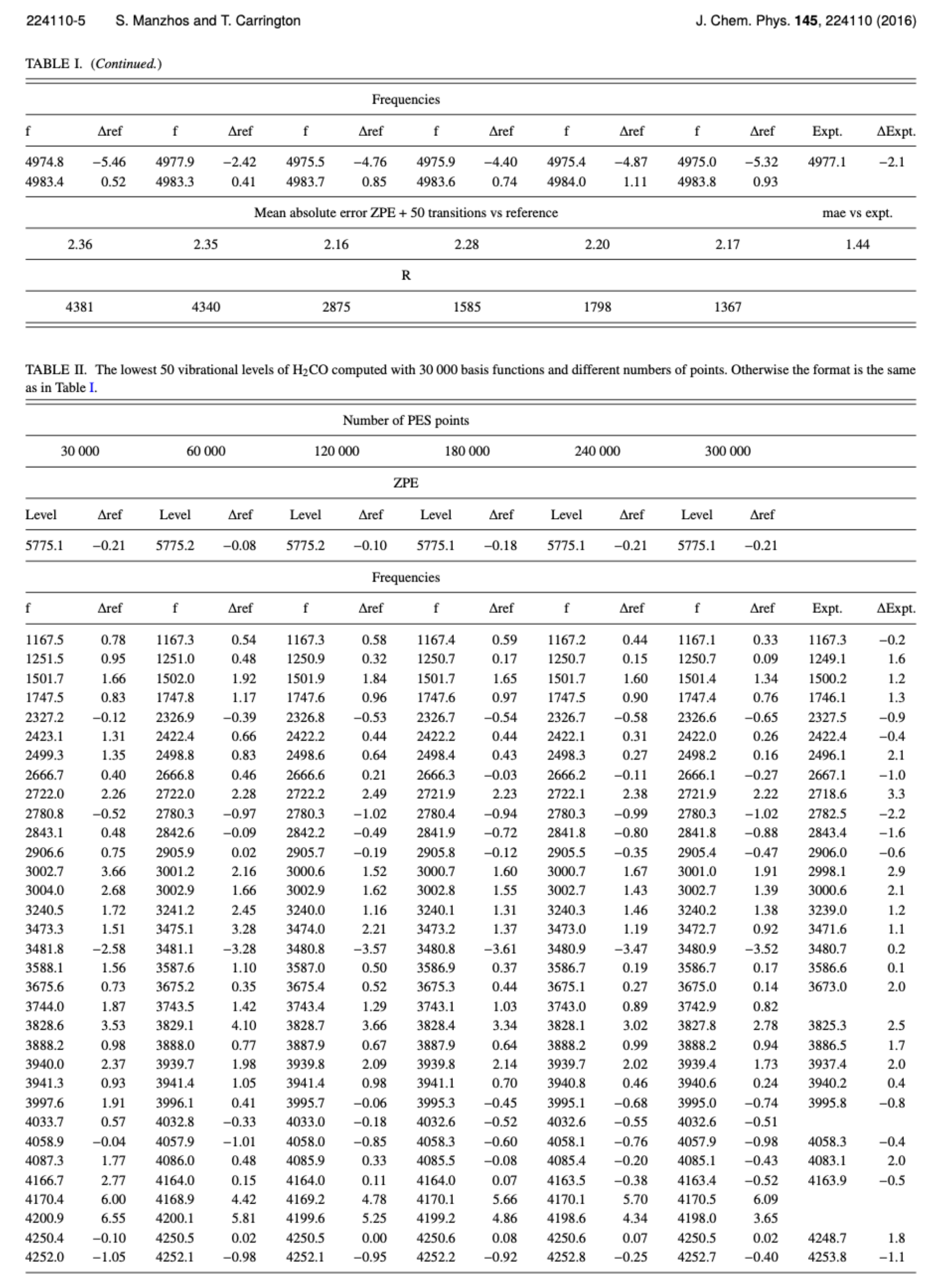
Manzhos & Carrington (JCP 2016): Using **quasi-random+rejection** Gaussian bases with N = 25 000, 39 000, 40 000



224110-4 S. Manzhos and T. Carrington J. Chem. Phys. **145**, 224110 (2016)

TABLE I. The lowest 50 vibrational levels of H_2CO computed with 25 000 basis functions and different numbers of points. For each set of points, the ZPE and the difference between the ZPE and the reference value are given at the top of the table. The lowest 49 excited states, from which the ZPE is subtracted, are also given. All results are in cm^{-1}. The mean absolute error and the residual R (Eq. (5)) are also given. The last columns include available experimental energies, deviations from them (for the calculation with the largest number of points) as well as the mean absolute deviation.

Number of PES points													
25 000		50 000		100 000		150 000		200 000		250 000			
ZPE													
Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref		
5775.2	−0.05	5775.2	−0.11	5775.4	0.15	5775.4	0.11	5775.3	0.01	5775.3	−0.01		
Frequencies													
f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	Expt.	ΔExpt.
1168.2	1.41	1168.0	1.24	1168.0	1.22	1167.8	1.07	1167.7	0.97	1167.7	0.94	1167.3	0.4
1251.3	0.69	1250.7	0.16	1250.6	0.01	1250.4	−0.13	1250.6	0.03	1250.6	−0.02	1249.1	1.5
1500.3	0.23	1501.3	1.25	1501.6	1.56	1501.7	1.63	1501.7	1.61	1501.6	1.55	1500.2	1.4
1747.0	0.38	1747.0	0.35	1747.4	0.76	1747.4	0.71	1747.3	0.69	1747.5	0.81	1746.1	1.4
2326.6	−0.67	2326.4	−0.93	2326.4	−0.86	2326.6	−0.72	2326.7	−0.60	2326.7	−0.56	2327.5	−0.8
2422.2	0.44	2421.5	−0.24	2421.4	−0.37	2421.4	−0.37	2421.6	−0.17	2421.7	−0.08	2422.4	−0.7
2497.8	−0.22	2497.8	−0.17	2497.8	−0.16	2497.7	−0.26	2498.1	0.09	2498.1	0.08	2496.1	2.0
2666.4	0.06	2666.8	0.47	2666.2	−0.12	2666.0	−0.37	2665.9	−0.40	2665.9	−0.42	2667.1	−1.2
2719.9	0.19	2720.9	1.19	2721.1	1.43	2721.4	1.69	2721.5	1.80	2721.2	1.47	2718.6	2.6
2780.3	−0.99	2780.3	−1.02	2780.5	−0.85	2780.4	−0.88	2780.6	−0.74	2780.5	−0.86	2782.5	−2.0
2841.7	−0.94	2841.7	−0.91	2841.6	−1.09	2841.5	−1.12	2841.9	−0.79	2841.9	−0.71	2843.4	−1.5
2906.2	0.30	2905.2	−0.70	2905.4	−0.48	2904.9	−0.92	2904.9	−0.97	2905.0	−0.86	2906.0	−1.0
3001.1	2.06	3000.2	1.16	3000.4	1.37	3000.4	1.36	3000.6	1.56	3000.6	1.49	2998.1	2.5
3007.6	6.28	3005.9	4.63	3005.1	3.85	3003.8	2.55	3003.4	2.13	3002.8	1.48	3000.6	2.2
3242.9	4.06	3243.5	4.66	3241.8	2.98	3241.0	2.18	3240.7	1.91	3240.1	1.33	3239.0	1.1
3472.4	0.60	3472.8	0.96	3472.8	0.99	3473.2	1.40	3473.6	1.84	3474.1	2.30	3471.6	2.5
3481.9	−2.52	3481.5	−2.93	3481.4	−3.03	3481.2	−3.23	3481.4	−3.03	3481.3	−3.11	3480.7	0.6
3587.0	0.48	3586.7	0.21	3586.6	0.07	3586.5	−0.01	3586.7	0.19	3586.5	0.01	3586.6	−0.1
3674.1	−0.77	3674.2	−0.64	3674.2	−0.71	3674.1	−0.81	3674.3	−0.56	3674.5	−0.37	3673.0	1.5
3744.5	2.35	3742.9	0.78	3743.1	1.03	3743.0	0.92	3743.3	1.16	3743.2	1.14		
3828.4	3.34	3830.3	5.24	3828.3	3.23	3828.1	3.00	3828.0	2.96	3828.0	2.91	3825.3	2.7
3885.9	−1.34	3886.7	−0.54	3886.6	−0.58	3887.2	−0.03	3887.1	−0.08	3887.2	−0.02	3886.5	0.7
3940.6	2.92	3940.1	2.38	3940.0	2.34	3940.2	2.56	3939.7	2.02	3939.6	1.89	3937.4	2.2
3940.8	0.43	3940.1	−0.32	3940.4	0.06	3940.7	0.29	3941.0	0.64	3940.9	0.51	3940.2	0.7
3996.5	0.76	3996.2	0.46	3995.5	−0.24	3995.5	−0.26	3995.6	−0.09	3995.5	−0.19	3995.8	−0.3
4034.2	1.09	4033.3	0.17	4033.1	−0.02	4033.0	−0.18	4032.9	−0.21	4032.7	−0.49		
4058.4	−0.49	4056.9	−1.96	4057.8	−1.13	4057.5	−1.39	4057.6	−1.25	4057.6	−1.31	4058.3	−0.7
4088.1	2.52	4088.7	3.18	4088.2	2.65	4087.8	2.21	4087.4	1.86	4087.0	1.45	4083.1	3.9
4163.5	−0.42	4161.4	−2.52	4161.7	−2.23	4161.8	−2.05	4162.2	−1.67	4162.5	−1.34	4163.9	−1.4
4172.3	7.87	4169.0	4.58	4169.4	4.98	4169.2	4.77	4169.1	4.70	4168.0	3.50		
4198.0	3.73	4201.2	6.88	4200.4	6.07	4199.5	5.20	4199.8	5.50	4200.0	5.72		
4250.8	0.32	4250.4	−0.11	4251.1	0.58	4250.7	0.23	4250.5	0.05	4250.7	0.25	4248.7	2.0
4250.8	−2.28	4250.4	−2.71	4251.1	−2.01	4250.7	−2.36	4251.4	−1.66	4251.0	−2.06	4253.8	−2.8
4333.7	−2.96	4336.3	−0.36	4337.7	1.09	4338.0	1.39	4338.5	1.82	4338.4	1.69	4335.1	3.3
4402.2	4.77	4399.7	2.24	4397.4	−0.09	4397.4	−0.08	4397.2	−0.27	4396.5	−0.96	4397.5	−1.0
4465.8	−1.65	4468.5	1.09	4467.7	0.25	4468.1	0.65	4468.5	1.07	4468.5	1.07	4466.8	1.7
4506.3	10.20	4514.5	18.45	4517.2	21.07	4520.1	24.02	4518.7	22.61	4516.2	20.10		
4522.9	−5.27	4523.1	−5.07	4524.3	−3.88	4523.5	−4.70	4524.4	−3.78	4524.7	−3.48	4529.4	−4.7
4568.8	−3.91	4569.3	−3.37	4570.1	−2.62	4569.4	−3.25	4570.0	−2.72	4569.7	−2.95	4571.5	−1.8
4625.0	0.96	4624.4	0.35	4623.3	−0.70	4623.8	−0.23	4623.8	−0.23	4623.4	−0.60	4624.3	−0.9
4630.9	−16.11	4631.3	−15.73	4631.4	−15.71	4631.2	−15.83	4631.4	−15.63	4631.4	−15.62	4629.0	2.4
4728.9	−0.65	4726.3	−3.20	4730.4	0.93	4731.9	2.43	4732.5	3.02	4731.8	2.26	4730.8	1.0
4731.9	−2.51	4732.0	−2.46	4733.4	−1.03	4732.2	−2.25	4732.5	−1.89	4731.8	−2.65	4733.8	−2.0
4746.7	−2.55	4746.4	−2.82	4744.7	−4.52	4744.4	−4.78	4744.2	−4.97	4743.7	−5.51	4741.9	1.8
4841.8	−1.79	4842.8	−0.72	4843.1	−0.50	4843.2	−0.42	4843.4	−0.21	4843.1	−0.50	4842.0	1.1
4929.1	2.92	4927.5	1.27	4926.4	0.14	4925.9	−0.33	4925.9	−0.30	4925.7	−0.54		
4953.3	−2.79	4958.1	2.00	4955.6	−0.46	4954.5	−1.61	4954.5	−1.56	4953.0	−3.04	4955.2	−2.2



224110-5 S. Manzhos and T. Carrington J. Chem. Phys. **145**, 224110 (2016)

TABLE I. (*Continued.*)

Frequencies													
f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	Expt.	ΔExpt.
4974.8	−5.46	4977.9	−2.42	4975.5	−4.76	4975.9	−4.40	4975.4	−4.87	4975.0	−5.32	4977.1	−2.1
4983.4	0.52	4983.3	0.41	4983.7	0.85	4983.6	0.74	4984.0	1.11	4983.8	0.93		
Mean absolute error ZPE + 50 transitions vs reference												mae vs expt.	
2.36		2.35		2.16		2.28		2.20		2.17		1.44	
R													
4381		4340		2875		1585		1798		1367			

TABLE II. The lowest 50 vibrational levels of H_2CO computed with 30 000 basis functions and different numbers of points. Otherwise the format is the same as in Table I.

Number of PES points													
30 000		60 000		120 000		180 000		240 000		300 000			
ZPE													
Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref	Level	Δref		
5775.1	−0.21	5775.2	−0.08	5775.2	−0.10	5775.1	−0.18	5775.1	−0.21	5775.1	−0.21		
Frequencies													
f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	f	Δref	Expt.	ΔExpt.
1167.5	0.78	1167.3	0.54	1167.3	0.58	1167.4	0.59	1167.2	0.44	1167.1	0.33	1167.3	−0.2
1251.5	0.95	1251.0	0.48	1250.9	0.32	1250.7	0.17	1250.7	0.15	1250.7	0.09	1249.1	1.6
1501.7	1.66	1502.0	1.92	1501.9	1.84	1501.7	1.65	1501.7	1.60	1501.4	1.34	1500.2	1.2
1747.5	0.83	1747.8	1.17	1747.6	0.96	1747.6	0.97	1747.5	0.90	1747.4	0.76	1746.1	1.3
2327.2	−0.12	2326.9	−0.39	2326.8	−0.53	2326.7	−0.54	2326.7	−0.58	2326.6	−0.65	2327.5	−0.9
2423.1	1.31	2422.4	0.66	2422.2	0.44	2422.2	0.44	2422.1	0.31	2422.0	0.26	2422.4	−0.4
2499.3	1.35	2498.8	0.83	2498.6	0.64	2498.4	0.43	2498.3	0.27	2498.2	0.16	2496.1	2.1
2666.7	0.40	2666.8	0.46	2666.6	0.21	2666.3	−0.03	2666.2	−0.11	2666.1	−0.27	2667.1	−1.0
2722.0	2.26	2722.0	2.28	2722.2	2.49	2721.9	2.23	2722.1	2.38	2721.9	2.22	2718.6	3.3
2780.8	−0.52	2780.3	−0.97	2780.3	−1.02	2780.4	−0.94	2780.3	−0.99	2780.3	−1.02	2782.5	−2.2
2843.1	0.48	2842.6	−0.09	2842.2	−0.49	2841.9	−0.72	2841.8	−0.80	2841.8	−0.88	2843.4	−1.6
2906.6	0.75	2905.9	0.02	2905.7	−0.19	2905.8	−0.12	2905.5	−0.35	2905.4	−0.47	2906.0	−0.6
3002.7	3.66	3001.2	2.16	3000.6	1.52	3000.7	1.60	3000.7	1.67	3001.0	1.91	2998.1	2.9
3004.0	2.68	3002.9	1.66	3002.9	1.62	3002.8	1.55	3002.7	1.43	3002.7	1.39	3000.6	2.1
3240.5	1.72	3241.2	2.45	3240.0	1.16	3240.1	1.31	3240.3	1.46	3240.2	1.38	3239.0	1.2
3473.3	1.51	3475.1	3.28	3474.0	2.21	3473.2	1.37	3473.0	1.19	3472.7	0.92	3471.6	1.1
3481.8	−2.58	3481.1	−3.28	3480.8	−3.57	3480.8	−3.61	3480.9	−3.47	3480.9	−3.52	3480.7	0.2
3588.1	1.56	3587.6	1.10	3587.0	0.50	3586.9	0.37	3586.7	0.19	3586.7	0.17	3586.6	0.1
3675.6	0.73	3675.2	0.35	3675.4	0.52	3675.3	0.44	3675.1	0.27	3675.0	0.14	3673.0	2.0
3744.0	1.87	3743.5	1.42	3743.4	1.29	3743.1	1.03	3743.0	0.89	3742.9	0.82		
3828.6	3.53	3829.1	4.10	3828.7	3.66	3828.4	3.34	3828.1	3.02	3827.8	2.78	3825.3	2.5
3888.2	0.98	3888.0	0.77	3887.9	0.67	3887.9	0.64	3888.2	0.99	3888.2	0.94	3886.5	1.7
3940.0	2.37	3939.7	1.98	3939.8	2.09	3939.8	2.14	3939.7	2.02	3939.4	1.73	3937.4	2.0
3941.3	0.93	3941.4	1.05	3941.4	0.98	3941.1	0.70	3940.8	0.46	3940.6	0.24	3940.2	0.4
3997.6	1.91	3996.1	0.41	3995.7	−0.06	3995.3	−0.45	3995.1	−0.68	3995.0	−0.74	3995.8	−0.8
4033.7	0.57	4032.8	−0.33	4033.0	−0.18	4032.6	−0.52	4032.6	−0.55	4032.6	−0.51		
4058.9	−0.04	4057.9	−1.01	4058.0	−0.85	4058.3	−0.60	4058.1	−0.76	4057.9	−0.98	4058.3	−0.4
4087.3	1.77	4086.0	0.48	4085.9	0.33	4085.5	−0.08	4085.4	−0.20	4085.1	−0.43	4083.1	2.0
4166.7	2.77	4164.0	0.15	4164.0	0.11	4164.0	0.07	4163.5	−0.38	4163.4	−0.52	4163.9	−0.5
4170.4	6.00	4168.9	4.42	4169.2	4.78	4170.1	5.66	4170.1	5.70	4170.5	6.09		
4200.9	6.55	4200.1	5.81	4199.6	5.25	4199.2	4.86	4198.6	4.34	4198.0	3.65		
4250.4	−0.10	4250.5	0.02	4250.5	0.00	4250.6	0.08	4250.6	0.07	4250.5	0.02	4248.7	1.8
4252.0	−1.05	4252.1	−0.98	4252.1	−0.95	4252.2	−0.92	4252.8	−0.25	4252.7	−0.40	4253.8	−1.1

Flynn & Mandelshtam (JCTC 2021): using **quasi-regular** Gaussian basis with N = 10 000 for the lowest 50 eigenenergies
(The improvement is about factor of 3 compared to the results of Manzhos & Carrington)

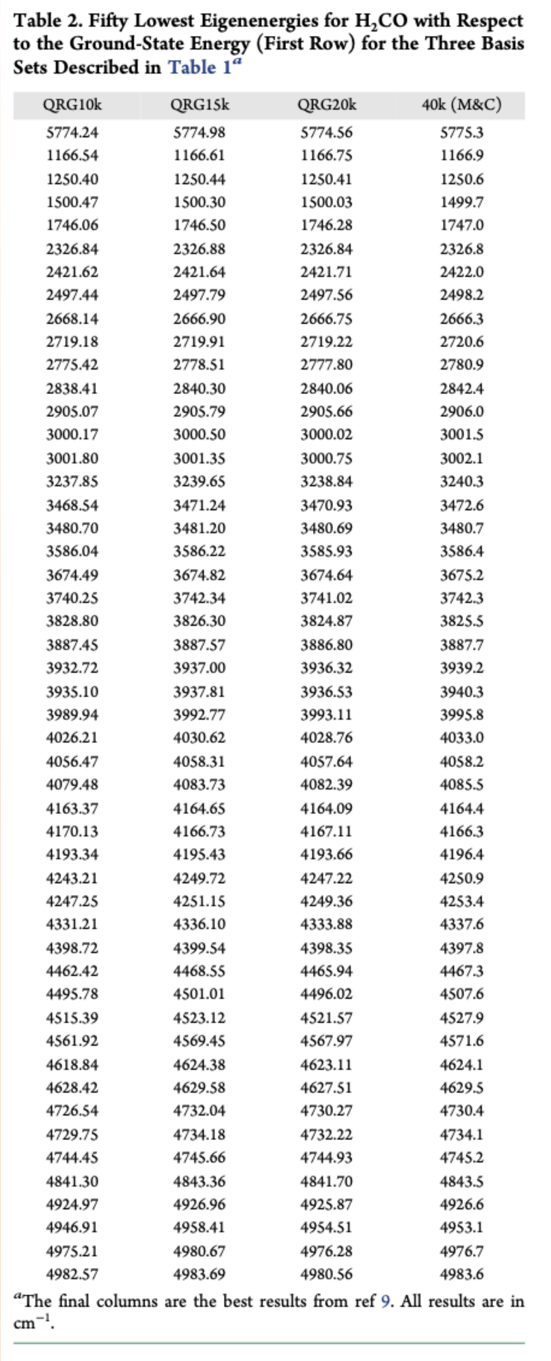


Table 2. Fifty Lowest Eigenenergies for H_2CO with Respect to the Ground-State Energy (First Row) for the Three Basis Sets Described in Table 1[a]

QRG10k	QRG15k	QRG20k	40k (M&C)
5774.24	5774.98	5774.56	5775.3
1166.54	1166.61	1166.75	1166.9
1250.40	1250.44	1250.41	1250.6
1500.47	1500.30	1500.03	1499.7
1746.06	1746.50	1746.28	1747.0
2326.84	2326.88	2326.84	2326.8
2421.62	2421.64	2421.71	2422.0
2497.44	2497.79	2497.56	2498.2
2668.14	2666.90	2666.75	2666.3
2719.18	2719.91	2719.22	2720.6
2775.42	2778.51	2777.80	2780.9
2838.41	2840.30	2840.06	2842.4
2905.07	2905.79	2905.66	2906.0
3000.17	3000.50	3000.02	3001.5
3001.80	3001.35	3000.75	3002.1
3237.85	3239.65	3238.84	3240.3
3468.54	3471.24	3470.93	3472.6
3480.70	3481.20	3480.69	3480.7
3586.04	3586.22	3585.93	3586.4
3674.49	3674.82	3674.64	3675.2
3740.25	3742.34	3741.02	3742.3
3828.80	3826.30	3824.87	3825.5
3887.45	3887.57	3886.80	3887.7
3932.72	3937.00	3936.32	3939.2
3935.10	3937.81	3936.53	3940.3
3989.94	3992.77	3993.11	3995.8
4026.21	4030.62	4028.76	4033.0
4056.47	4058.31	4057.64	4058.2
4079.48	4083.73	4082.39	4085.5
4163.37	4164.65	4164.09	4164.4
4170.13	4166.73	4167.11	4166.3
4193.34	4195.43	4193.66	4196.4
4243.21	4249.72	4247.22	4250.9
4247.25	4251.15	4249.36	4253.4
4331.21	4336.10	4333.88	4337.6
4398.72	4399.54	4398.35	4397.8
4462.42	4468.55	4465.94	4467.3
4495.78	4501.01	4496.02	4507.6
4515.39	4523.12	4521.57	4527.9
4561.92	4569.45	4567.97	4571.6
4618.84	4624.38	4623.11	4624.1
4628.42	4629.58	4627.51	4629.5
4726.54	4732.04	4730.27	4730.4
4729.75	4734.18	4732.22	4734.1
4744.45	4745.66	4744.93	4745.2
4841.30	4843.36	4841.70	4843.5
4924.97	4926.96	4925.87	4926.6
4946.91	4958.41	4954.51	4953.1
4975.21	4980.67	4976.28	4976.7
4982.57	4983.69	4980.56	4983.6

[a] The final columns are the best results from ref 9. All results are in cm^{-1}.

Thank you

Shane Flynn

Sandra Brown