Fast Evaluation of Many-Body Perturbation Integrals (FEMPI)

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Computational Challenge in Quantum Chemistry

- Accurate computational prediction of key molecular properties requires *ab initio* all-electron theories.
  - *Ab initio* = from first principles of quantum mechanics,
  - Density Functional Theory not accurate enough.

- Series of tensor contractions and (dense) matrix manipulations - nonscalable!

- Better scaling achieved via enhancements of Monte-Carlo.

QUEST

improve integration efficiency and scalability via advanced UQ methods.

Second-order many-body perturbation (MP2) theory

MP2 is the lowest member of the systematic series of many-body perturbation approximations converging toward the exact solution of the Schrödinger equation. One of its energy components

$$E_1^{(2)} = 2 \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{vir.}} \frac{\langle ij|ab\rangle \langle ab|ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b},$$

where i and j label occupied molecular orbitals (MO's), $\varphi_i(\boldsymbol{r})$ and $\varphi_j(\boldsymbol{r})$, respectively, a and b virtual MO's, ϵ_p is the pth MO energy, and $\langle pq|rs\rangle$ is a two-electron integral in the MO basis defined by

$$\langle pq|rs\rangle = \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{\varphi_p^*(\boldsymbol{r}_1)\varphi_q^*(\boldsymbol{r}_2)\varphi_r(\boldsymbol{r}_1)\varphi_s(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|},$$

where $\varphi_p(\boldsymbol{r}) = \sum_\kappa C_p^\kappa \chi_\kappa(\boldsymbol{r})$.

MP2 integrals

- Storage/scalability challenge

Laplace transform reformulates the integral into a 13D integral that is tackled by MC.

$$E_1^{(2)} = -2 \iiiint d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 d\boldsymbol{r}_4 \int_0^\infty d\tau \times \frac{G^-(\boldsymbol{r}_1,\boldsymbol{r}_3,-\tau)G^-(\boldsymbol{r}_2,\boldsymbol{r}_4,-\tau)G^+(\boldsymbol{r}_3,\boldsymbol{r}_1,\tau)G^+(\boldsymbol{r}_4,\boldsymbol{r}_2,\tau)}{|\boldsymbol{r}_1-\boldsymbol{r}_2||\boldsymbol{r}_3-\boldsymbol{r}_4|},$$

with

$$G^+(\boldsymbol{r}_m,\boldsymbol{r}_n,\tau) = \sum_a^{\text{vir.}} \varphi_a^*(\boldsymbol{r}_m)\varphi_a(\boldsymbol{r}_n)\exp(-\epsilon_a\tau),$$

$$G^-(\boldsymbol{r}_m,\boldsymbol{r}_n,\tau) = \sum_i^{\text{occ.}} \varphi_i^*(\boldsymbol{r}_m)\varphi_i(\boldsymbol{r}_n)\exp(-\epsilon_i\tau).$$

MP2 integrals

- Storage/scalability challenge

Laplace transform reformulates the integral into a 13D integral that is tackled by MC. Can we improve on MC?

$$E_1^{(2)} = -2 \iiiint d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 d\boldsymbol{r}_4 \int_0^\infty d\tau \times \frac{G^-(\boldsymbol{r}_1,\boldsymbol{r}_3,-\tau)G^-(\boldsymbol{r}_2,\boldsymbol{r}_4,-\tau)G^+(\boldsymbol{r}_3,\boldsymbol{r}_1,\tau)G^+(\boldsymbol{r}_4,\boldsymbol{r}_2,\tau)}{|\boldsymbol{r}_1-\boldsymbol{r}_2||\boldsymbol{r}_3-\boldsymbol{r}_4|},$$

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$$G^-(\boldsymbol{r}_m,\boldsymbol{r}_n,\tau) = \sum_i^{\text{occ.}} \varphi_i^*(\boldsymbol{r}_m)\varphi_i(\boldsymbol{r}_n)\exp(-\epsilon_i\tau).$$

MP2 integrals: singularity challenge

It all boils down to

$$\int \frac{f(\boldsymbol{r})}{|\boldsymbol{r}|} d\boldsymbol{r} = \iiint \frac{f(x,y,z)}{\sqrt{x^2+y^2+z^2}} dxdydz$$

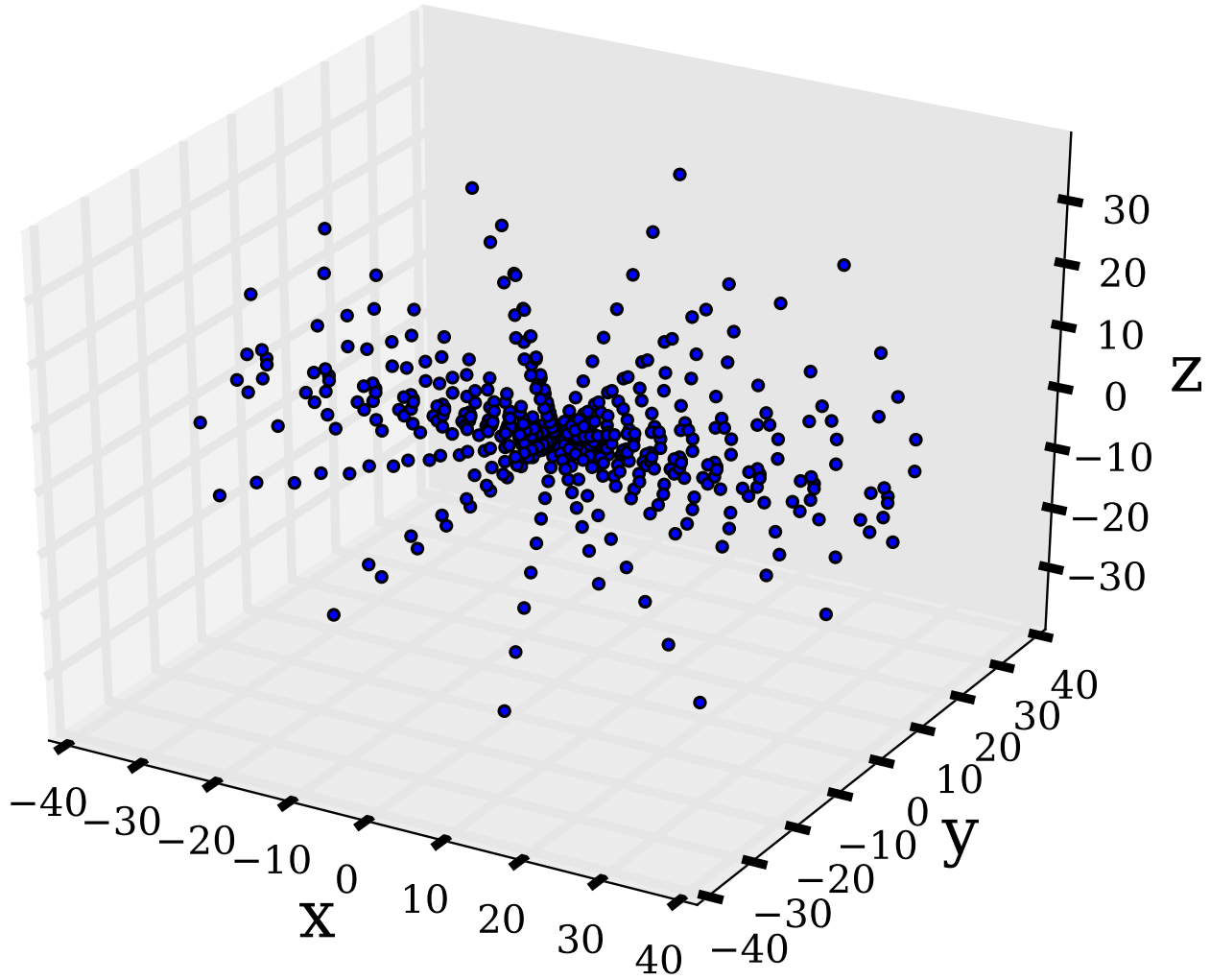
- Spherical transformation (SNL)
- Poisson equation (UIUC)
- Partial wave expansion (UIUC)

Spherical transformation

$$
\begin{aligned}
x &= r\cos\phi \\
y &= r\sin\phi\cos\theta \qquad\qquad J = r^2\sin\theta \\
z &= r\sin\phi\sin\theta
\end{aligned}
$$

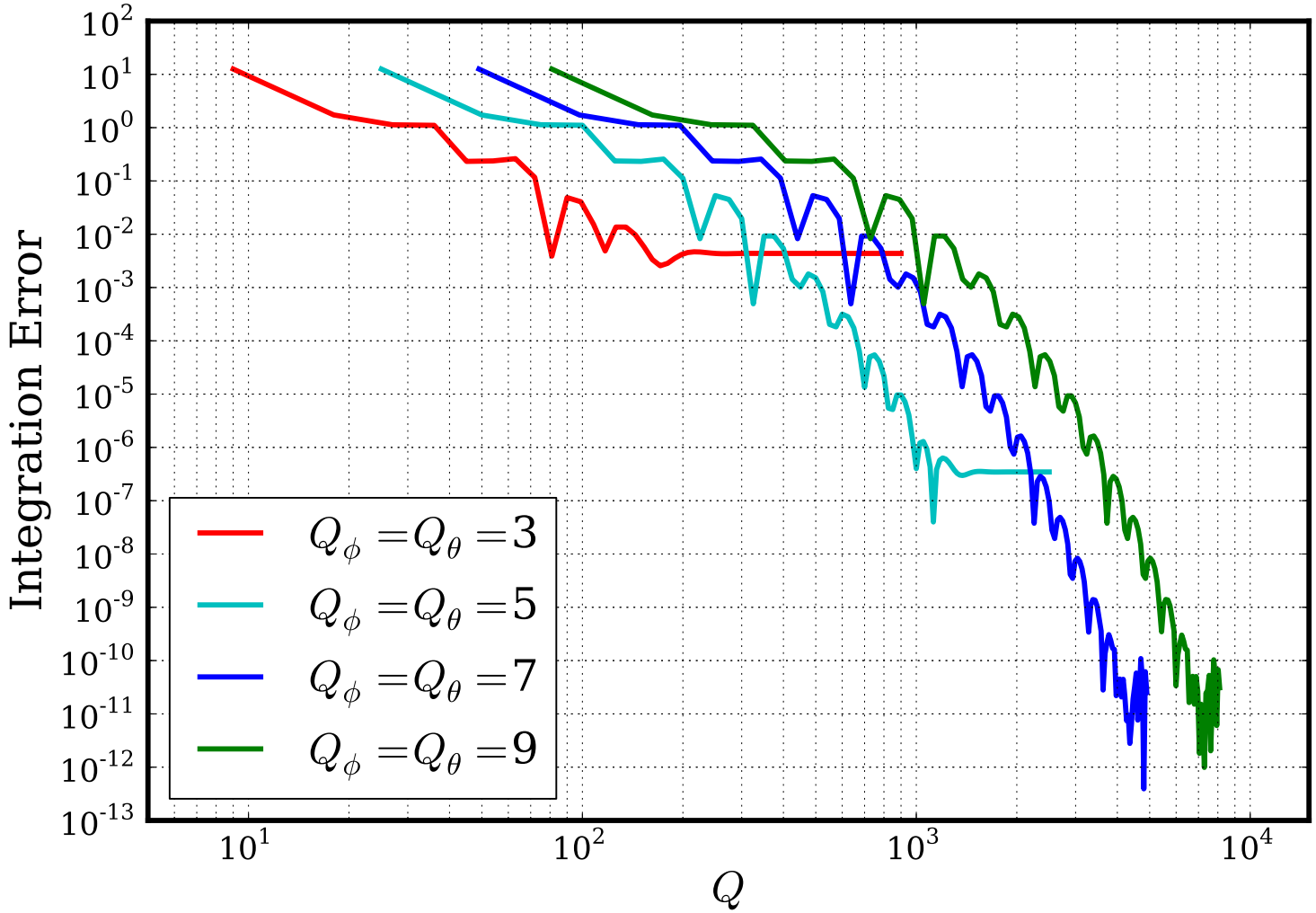
$$
\begin{aligned}
\int \frac{f(\boldsymbol{r})}{|\boldsymbol{r}|}d\boldsymbol{r} &= \iiint \frac{f(x,y,z)}{\sqrt{x^2+y^2+z^2}}dxdydz \\
&= \int_0^{+\infty} \mathrm{d}r \int_0^{2\pi} \mathrm{d}\theta \int_0^{\pi} \mathrm{d}\phi \, \frac{f(r\cos\phi, r\sin\phi\cos\theta, r\sin\phi\sin\theta)}{r} r^2\sin\phi = \\
&= \int_0^{+\infty} \mathrm{d}r \int_0^{2\pi} \mathrm{d}\theta \int_0^{\pi} \mathrm{d}\phi \, \underbrace{\tilde{f}(r,\phi,\theta)}_{\text{smooth}} = [\mathit{Laguerre} \times \mathit{Legendre} \times \mathit{Legendre}] \\
&\approx \sum_{i=1}^{Q_r}\sum_{j=1}^{Q_\theta}\sum_{k=1}^{Q_\phi} 2\pi^2 e^{r_i} w_i v_j v_k \tilde{f}\left(r_i, \pi(\theta_j+1), \pi(\phi_k+1)/2\right), \\
&= 2\pi^2 \sum_{q=1}^{Q} \underbrace{W_q}_{w_i v_j v_k} \underbrace{e^{\sqrt{x_q^2+y_q^2+z_q^2}}}_{e^{r_i}} \underbrace{\sqrt{y_q^2+z_q^2}}_{r_i \sin \pi(\phi_k+1)/2} f(x_q, y_q, z_q)
\end{aligned}
$$

Spherical grid



Convergence looks good if the function is simple

$$f(x,y,z) = e^{-(x^2+y^2+z^2)}$$



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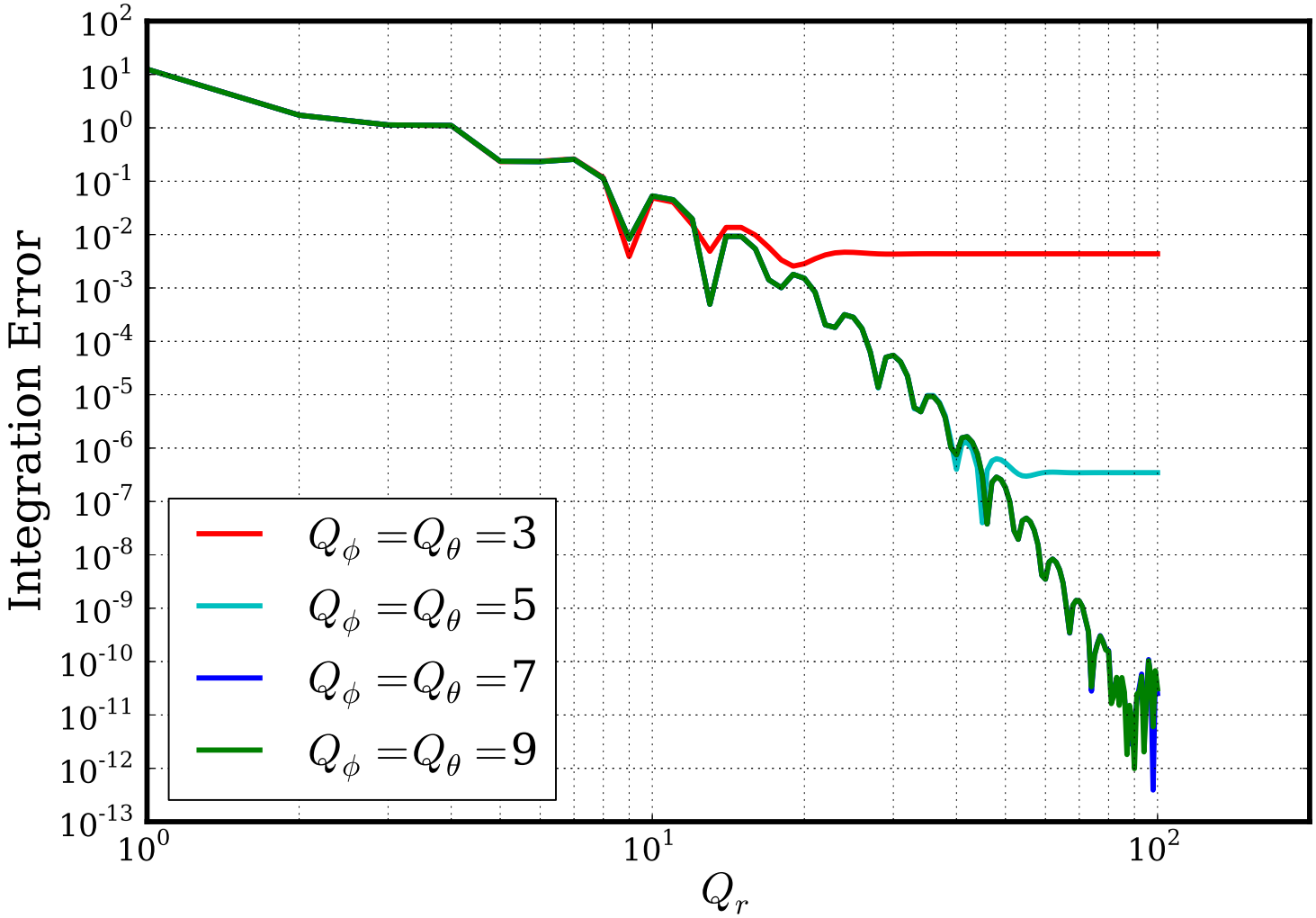
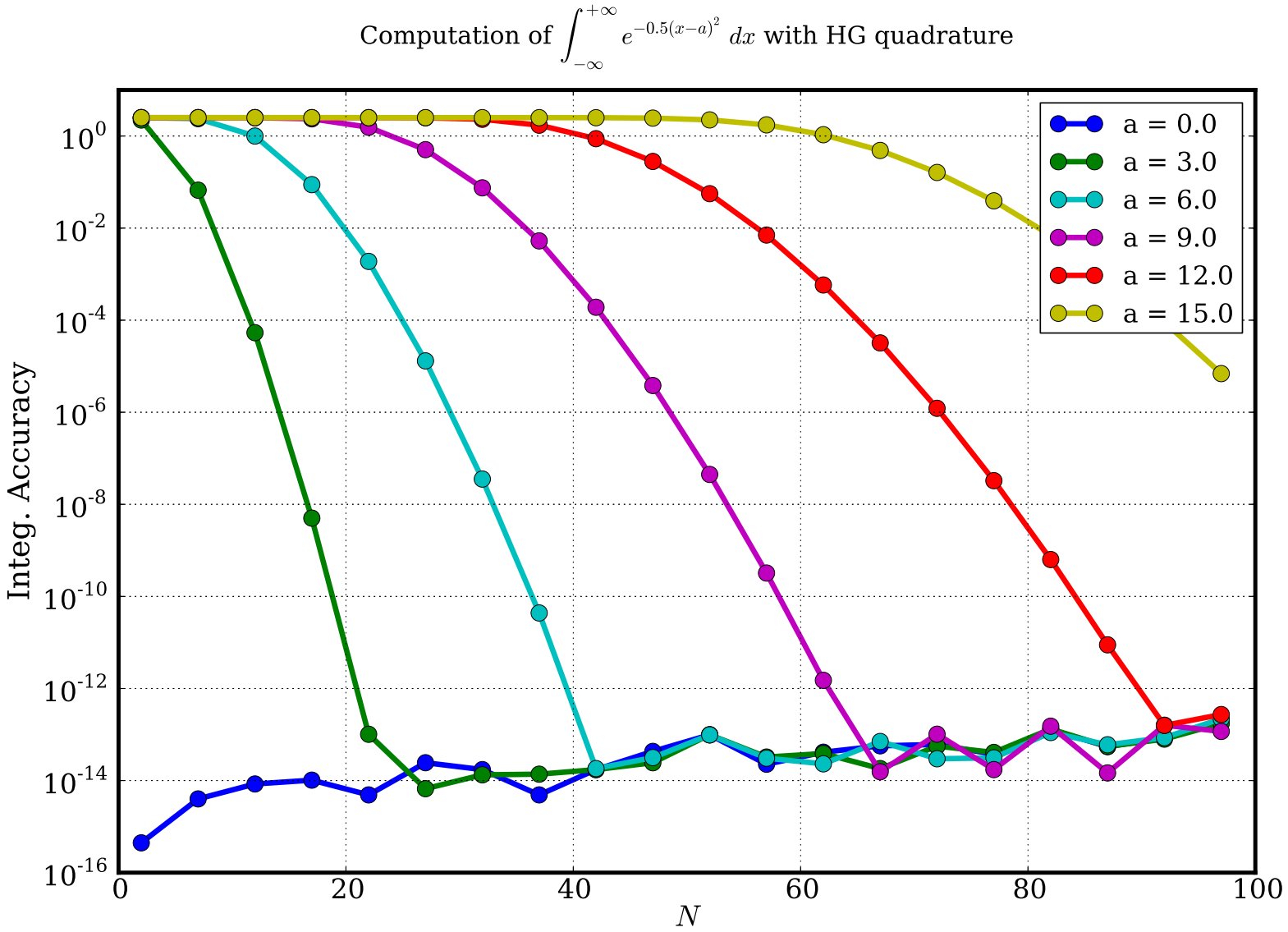


Gauss-Hermite quadrature needs to centered



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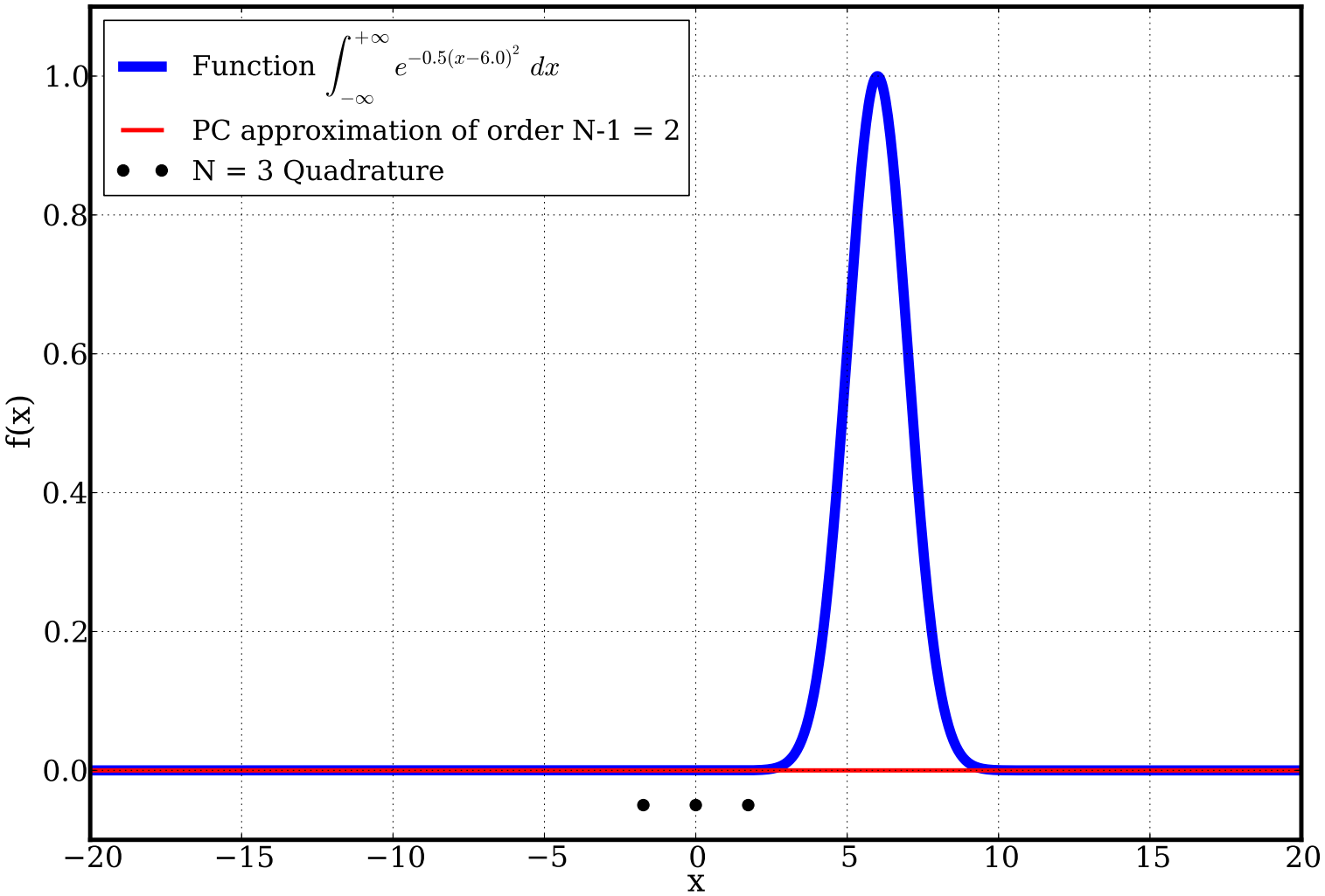

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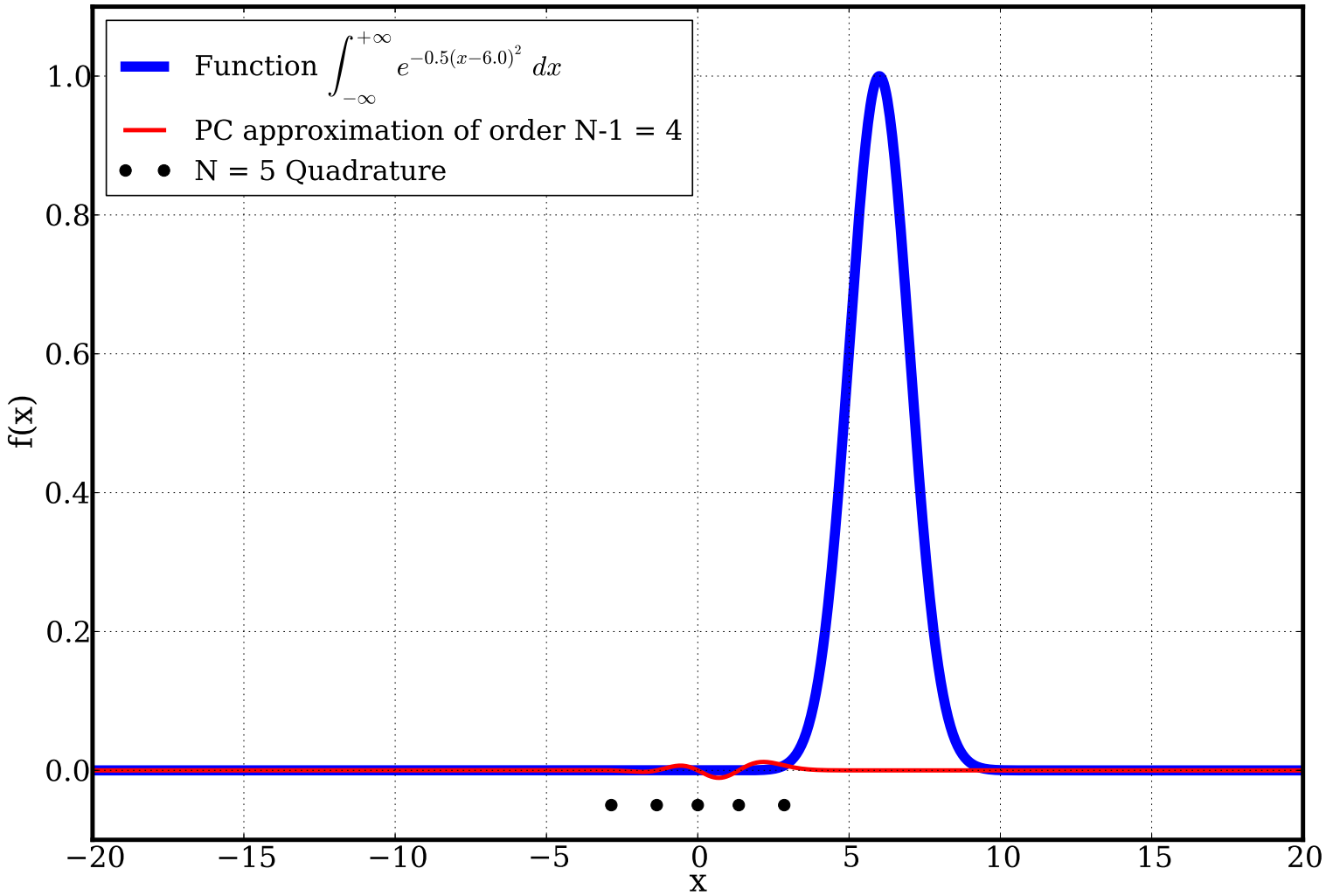

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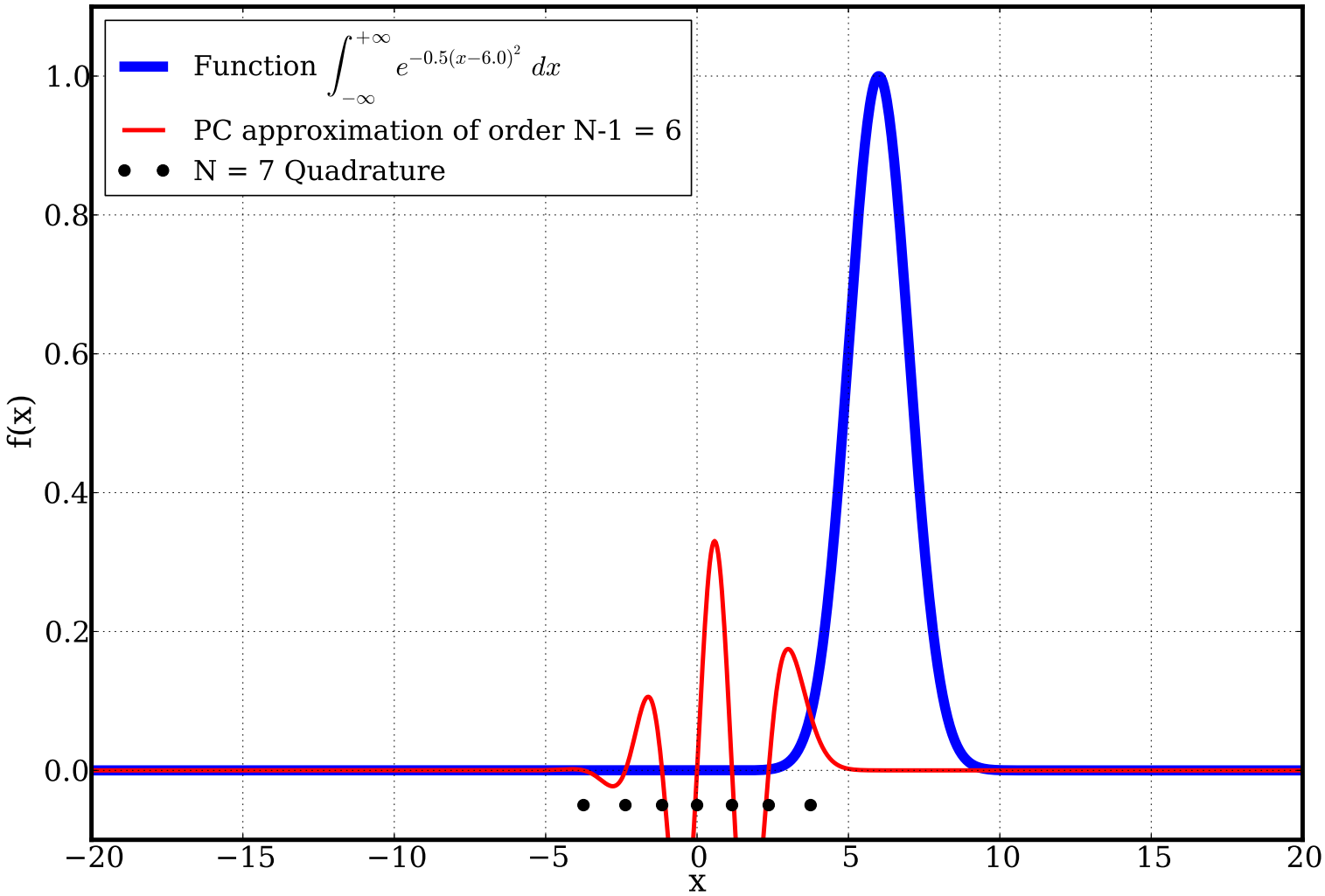

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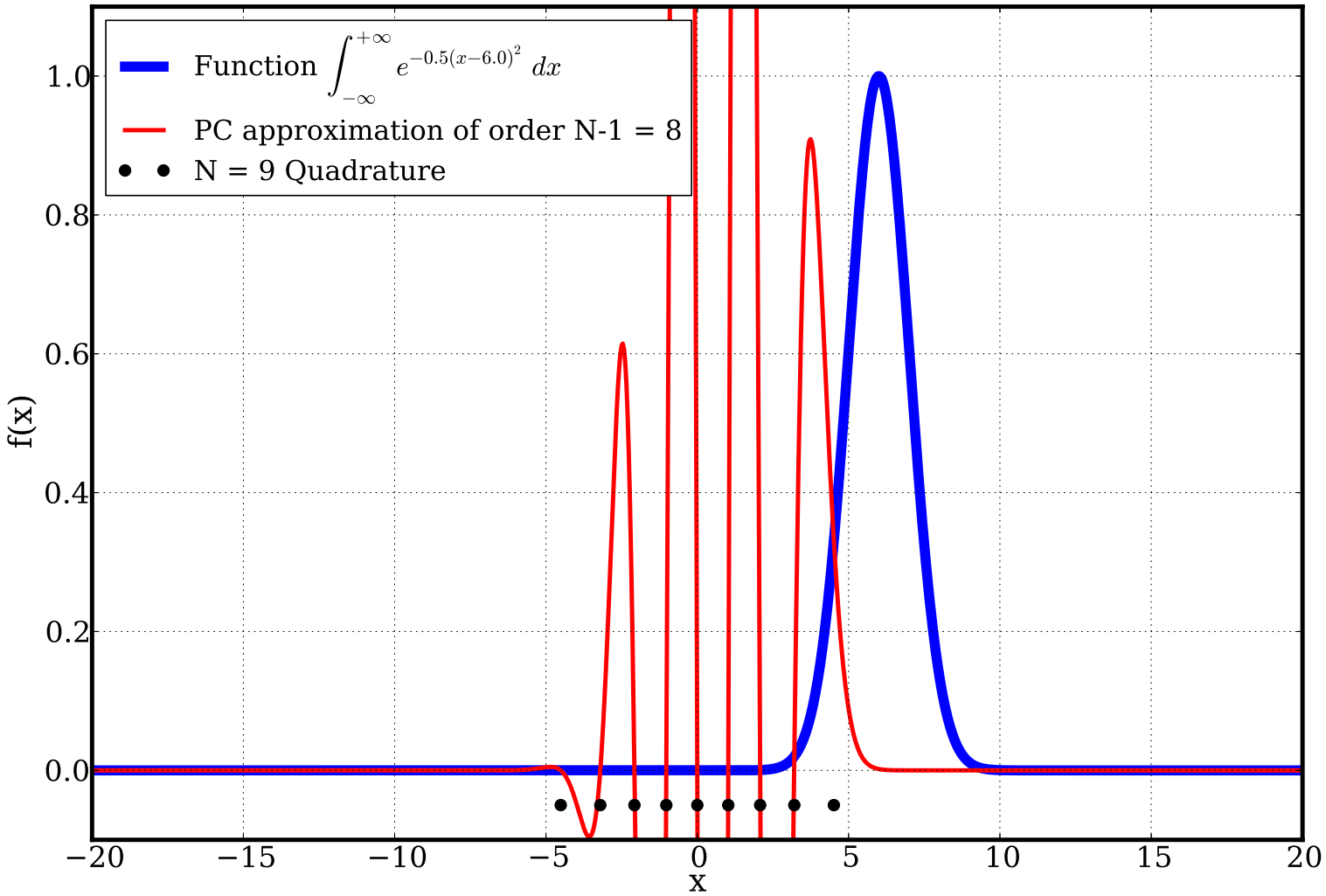

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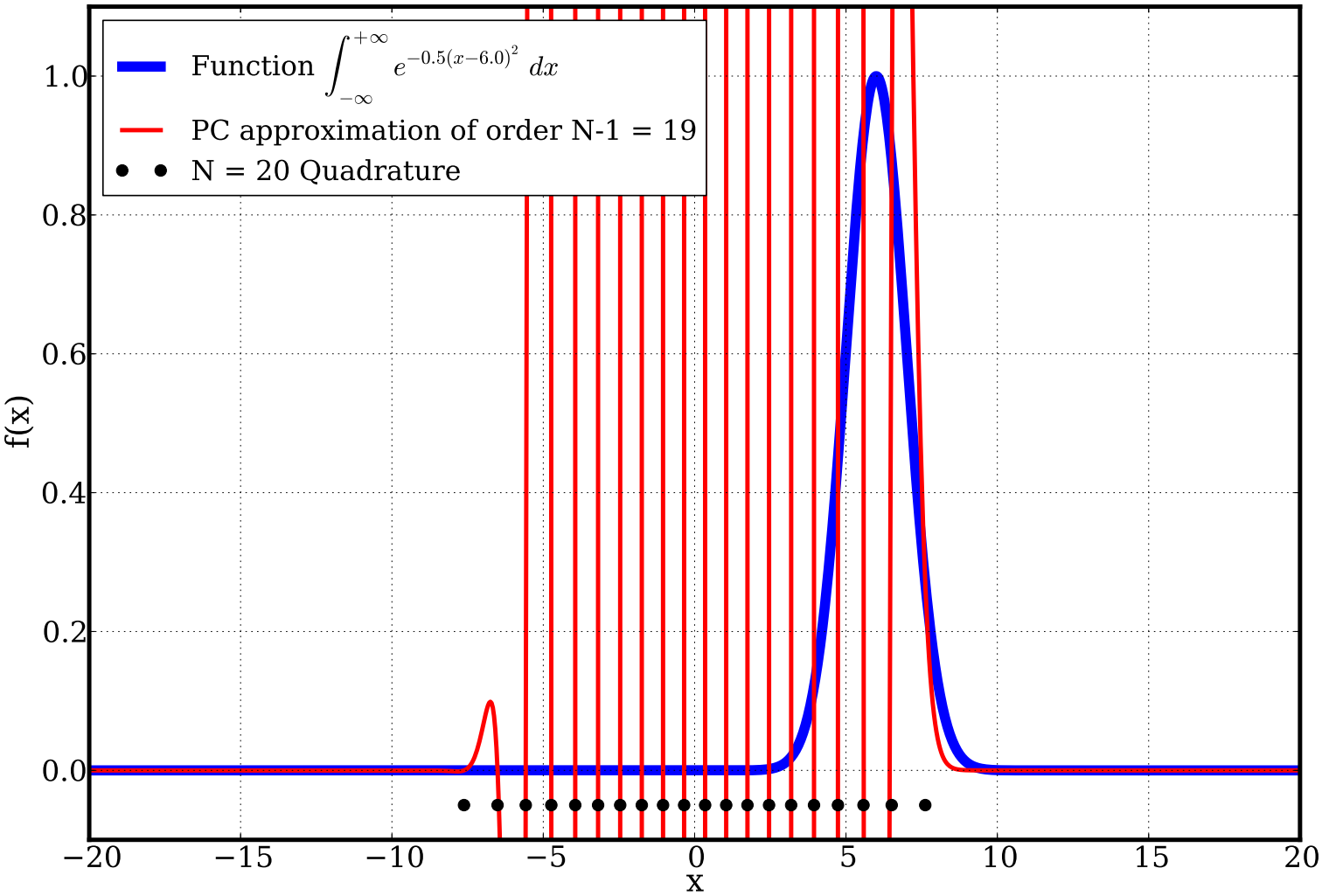

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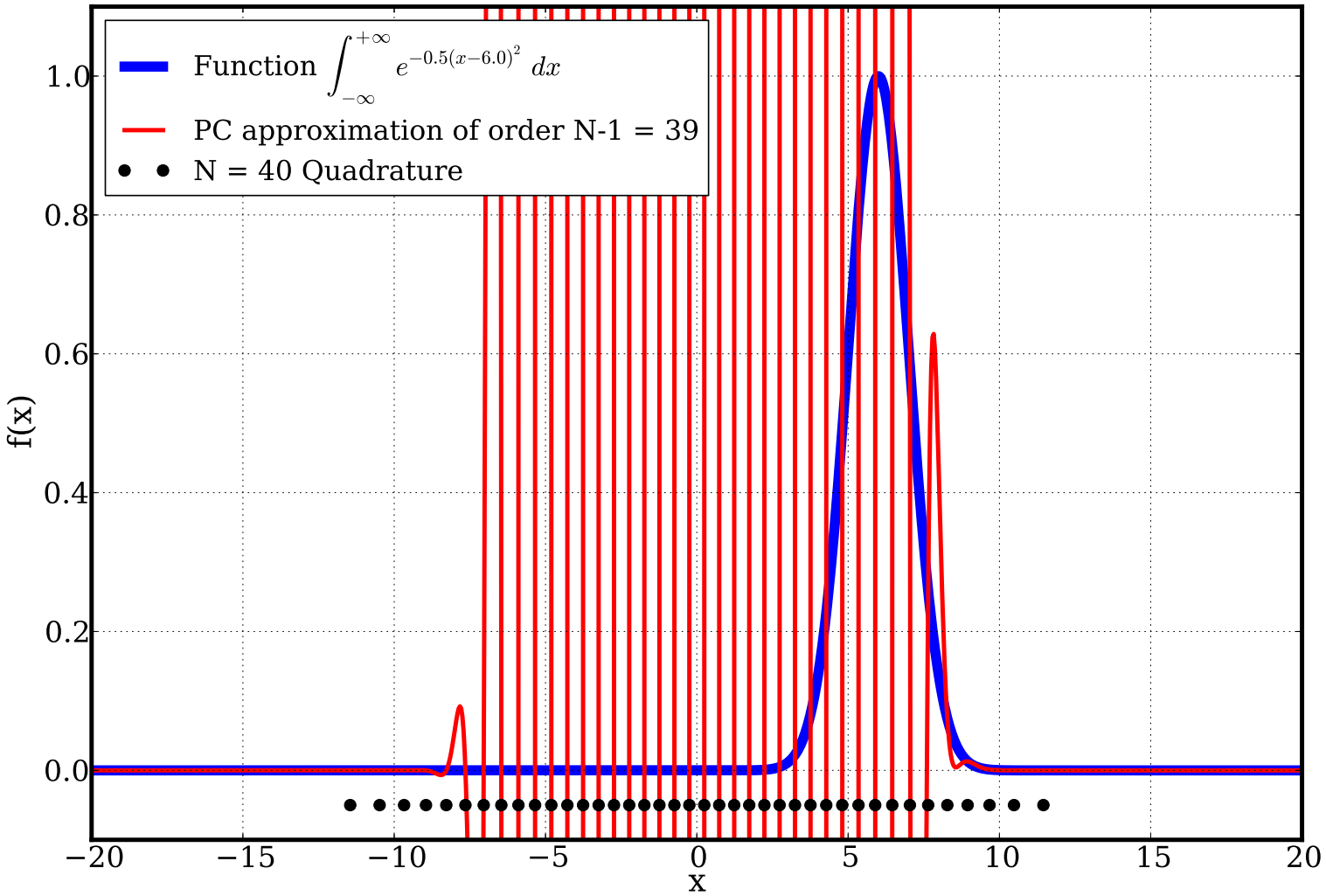

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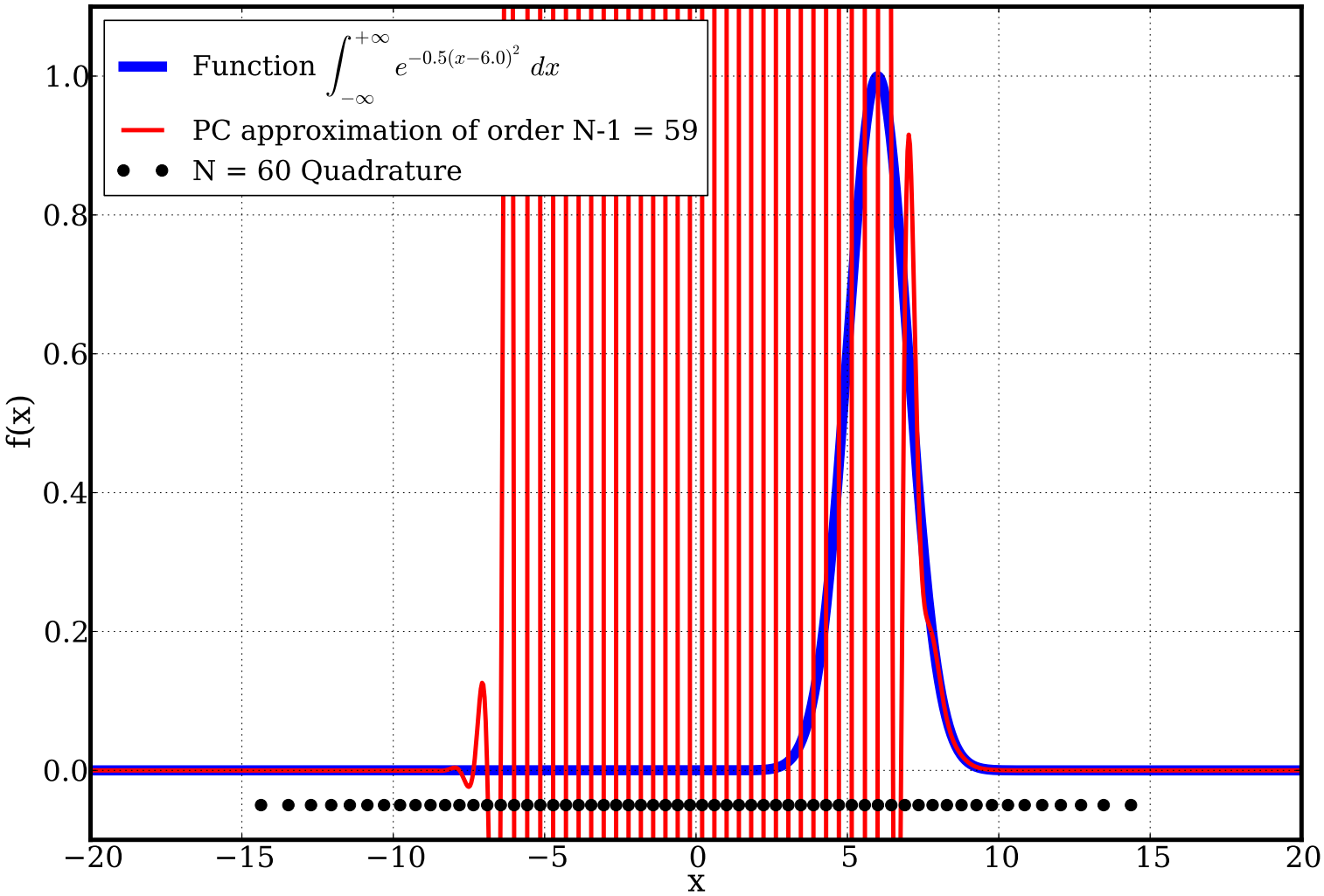

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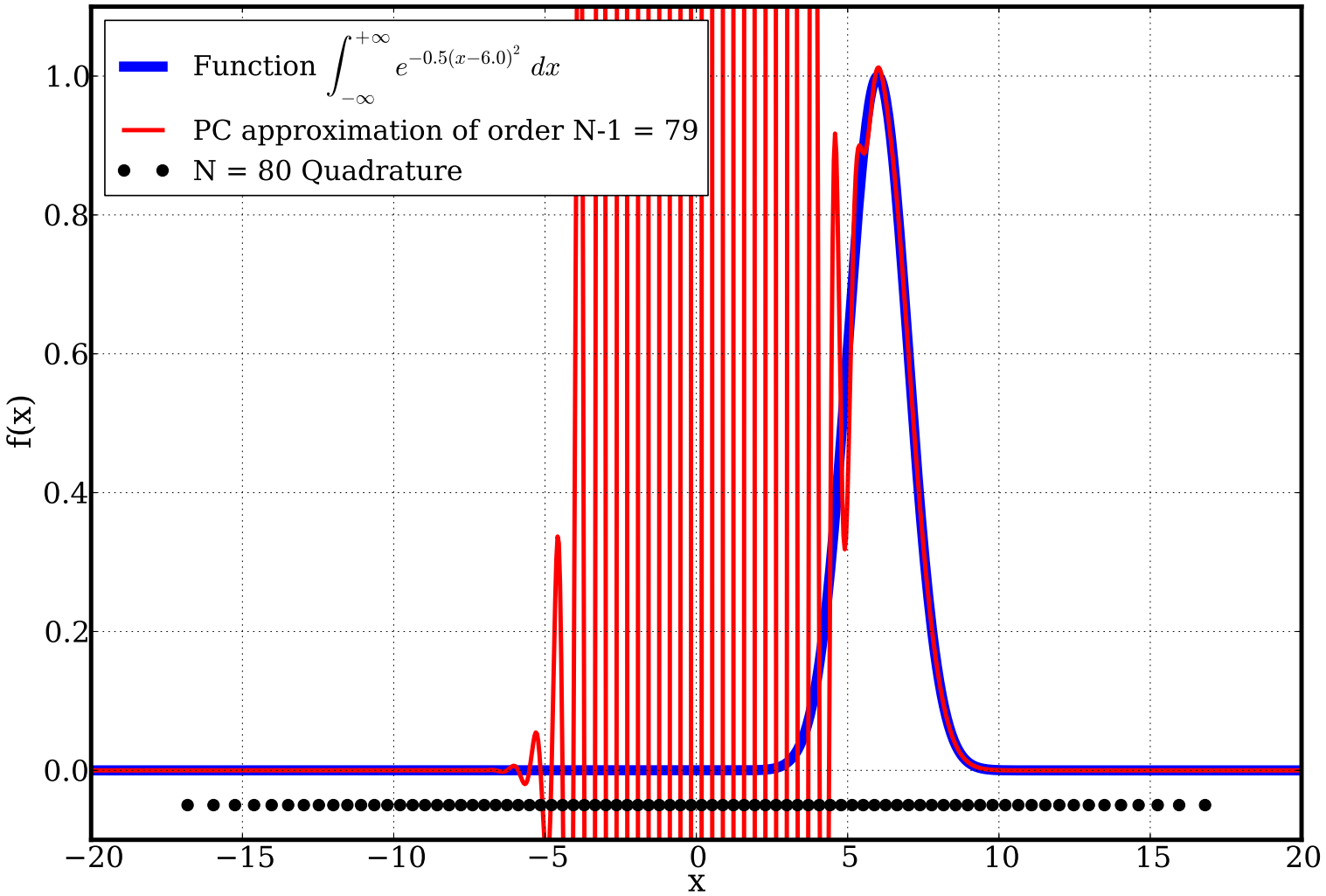

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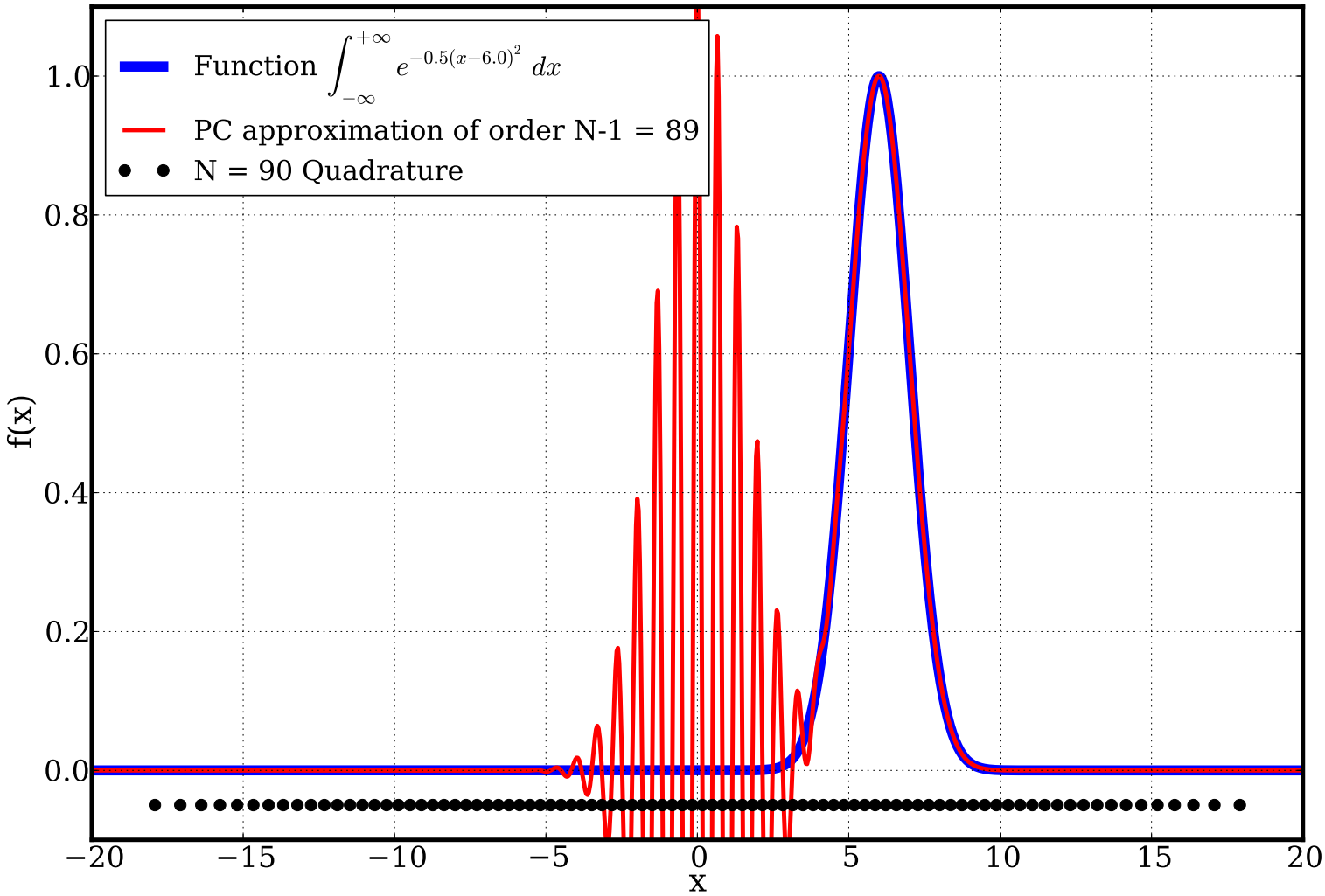

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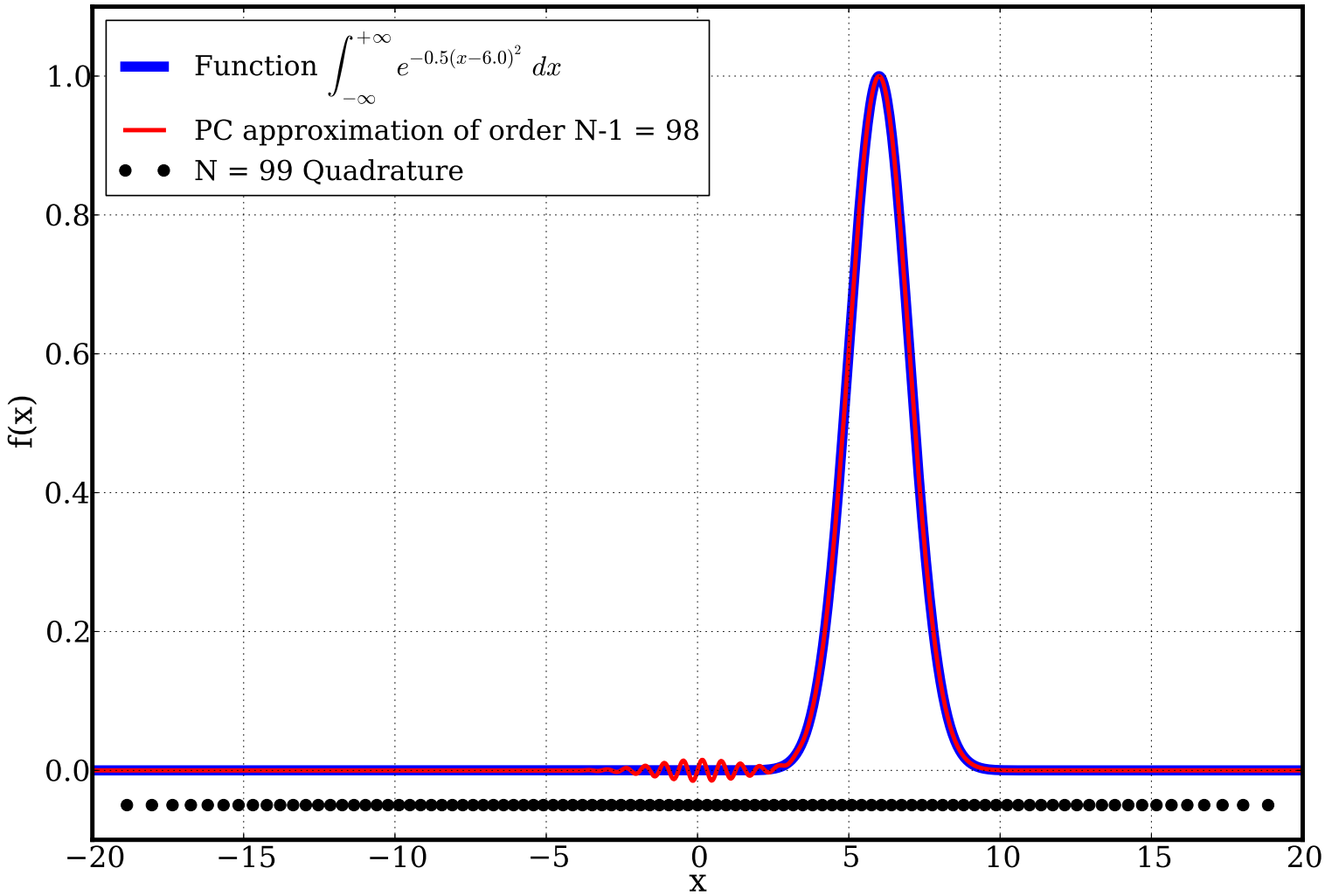
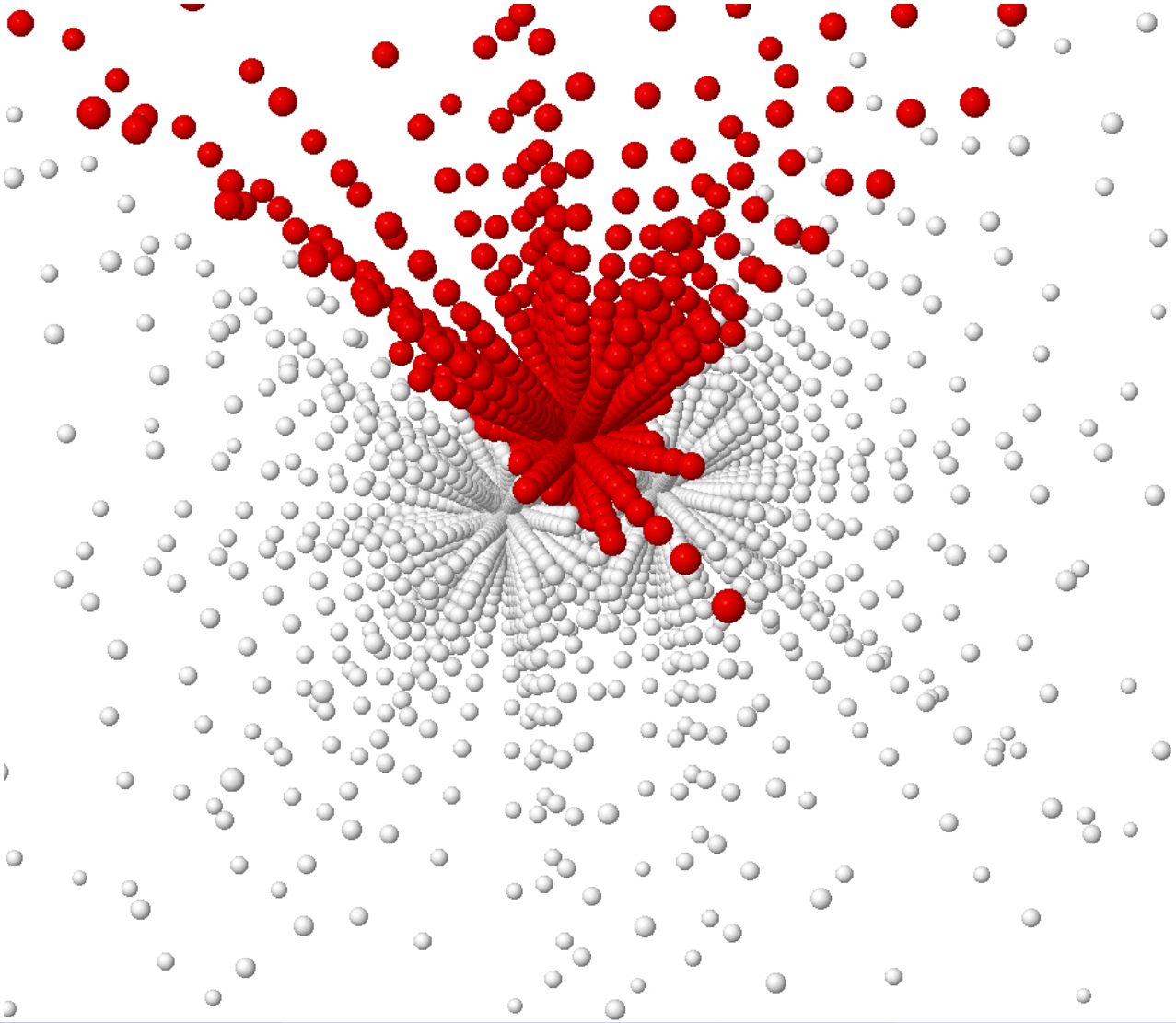


UIUC: a combination of Gauss-Chebyshev and spherical Lebedev rules for multi-center integral

white: hydrogen, red: oxygen



Stochastic many-body perturbation theory for anharmonic molecular vibrations

- Prediction of vibrational spectra of molecules
- Anharmonic approximations of potential energy surfaces
- First- and second-order corrections to energy
- First- and second-order corrections to frequencies per d.o.f.
- Integrals are non-singular, but can be high-order and multicenter
- Scalability of integrand evaluation still challenging

First order correction to energy

$$E_0^{(1)} = \int \Phi_0(\boldsymbol{x}) \Delta V(\boldsymbol{x}) \Phi_0(\boldsymbol{x}) d\boldsymbol{x}$$

where the fluctuation potential

$$\Delta V(\boldsymbol{x}) = V(\boldsymbol{x}) - V_{\text{ref}} - \frac{1}{2} \sum_{i=1}^{m} \omega_i^2 x_i^2$$

is the unharmonicity of the PE surface due to cubic and higher-order terms, and zero-point/wave function is

$$\Phi_0(\boldsymbol{x}) = \prod_{i=1}^{m} \eta_0(x_i)$$

First order correction to energy

$$E_0^{(1)} = \int \Phi_0(\boldsymbol{x}) \Delta V(\boldsymbol{x}) \Phi_0(\boldsymbol{x}) d\boldsymbol{x}$$

$$\Delta V(\boldsymbol{x}) = V(\boldsymbol{x}) - V_{\text{ref}} - \frac{1}{2} \sum_{i=1}^{m} \omega_i^2 x_i^2$$

$$\Phi_0(\boldsymbol{x}) = \prod_{i=1}^{m} \eta_0(x_i)$$

Definitions:

- m: vibrational degrees of freedom. For the water molecule, $m = 3$.
- $V(\boldsymbol{x})$: Potential energy (PE) containing up to n-the order force constants. As a default scenario, $n = 4$.
- V_{ref}: the minimum/reference PE, *i.e.* at the equilibrium geometry.
- $\eta_{n_i}(x_i)$: the harmonic-oscillator wave function with quantum number n_i along the i-th normal mode x_i.
- ω_i: the i-th mode frequency of a reference mean-field theory. Found by solving Dyson equation.

Second order correction to energy

$$E_0^{(2)} = \int_{\boldsymbol{x}} \int_{\boldsymbol{x}'} \Phi_0(\boldsymbol{x}) \Delta V(\boldsymbol{x}) G^{(2)}(\boldsymbol{x}, \boldsymbol{x}') \Delta V(\boldsymbol{x}') \Phi_0(\boldsymbol{x}') d\boldsymbol{x} d\boldsymbol{x}'$$

using real-space Green's function

$$G^{(2)}(\boldsymbol{x}, \boldsymbol{x}') = \sum_{N=1}^{N_{\max}} \frac{\Phi_N(\boldsymbol{x}) \Phi_N(\boldsymbol{x}')}{E_0^{(0)} - E_N^{(0)}},$$

where $N_{\max}$ is the number of states reachable by $\Delta V(\boldsymbol{x})$ from Φ_0. $N_{\max} = \mathcal{O}(m^n)$ scales badly, so Laplace transform is used:

$$\frac{1}{E_0^{(0)} - E_N^{(0)}} = -\frac{1}{\sum_{i=1}^m n_i \omega_i} = -\int_0^\infty \exp\left(-\sum_{i=1}^m n_i \omega_i \tau\right) d\tau$$

where n_i us the quantum number of the i-th mode in the N-th state.

Second order correction to energy, cont.

$$E_0^{(2)} = \int_{\boldsymbol{x}} \int_{\boldsymbol{x}'} \Phi_0(\boldsymbol{x}) \Delta V(\boldsymbol{x}) G^{(2)}(\boldsymbol{x}, \boldsymbol{x}') \Delta V(\boldsymbol{x}') \Phi_0(\boldsymbol{x}') d\boldsymbol{x} d\boldsymbol{x}'$$

Green's function is written in 'imaginary time':

$$G^{(2)}(\boldsymbol{x}, \boldsymbol{x}') = -\int_0^\infty g^{(2)}(\boldsymbol{x}, \boldsymbol{x}', \tau) d\tau,$$

where

$$g^{(2)}(\boldsymbol{x}, \boldsymbol{x}', \tau) = \prod_{i=1}^{m} \zeta_i(x_i, x_i', \tau) - \Phi_0(\boldsymbol{x}) \Phi_0(\boldsymbol{x}')$$

and

$$\zeta_i(x_i, x_i', \tau) = \sum_{n_i=0}^{n_{\max}} \eta_{n_i}(x_i) \eta_{n_i}(x_i') e^{-n_i \omega_i \tau}$$

Weight functions appear naturally

Both integrals $E_0^{(1)} = \int_{\boldsymbol{x}} \Phi_0(\boldsymbol{x}) \Delta V(\boldsymbol{x}) \Phi_0(\boldsymbol{x}) d\boldsymbol{x}$

$$E_0^{(2)} = \int_{\boldsymbol{x}} \int_{\boldsymbol{x}'} \Phi_0(\boldsymbol{x}) \Delta V(\boldsymbol{x}) G^{(2)}(\boldsymbol{x}, \boldsymbol{x}') \Delta V(\boldsymbol{x}') \Phi_0(\boldsymbol{x}') d\boldsymbol{x} d\boldsymbol{x}'$$

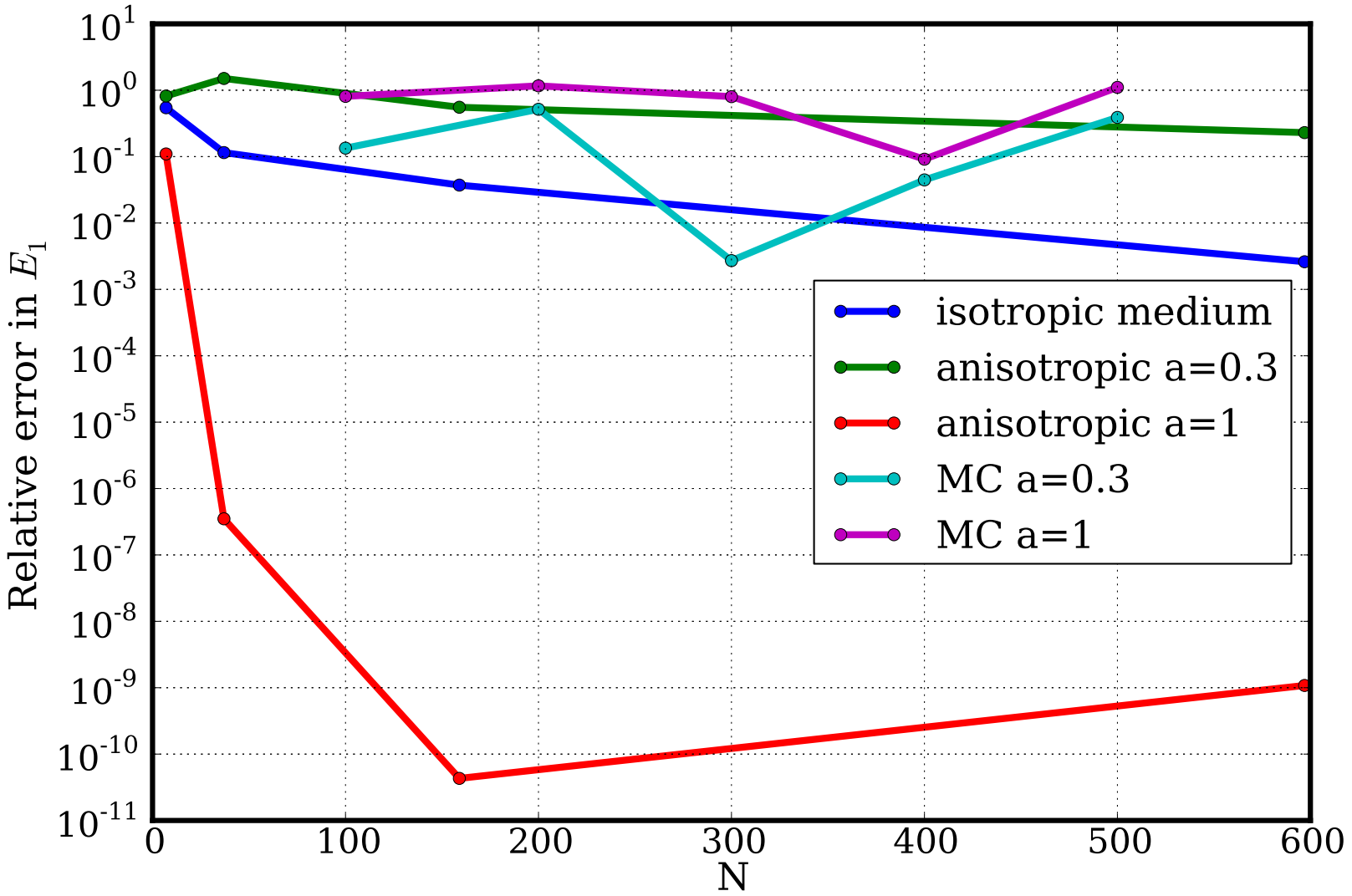
include harmonic wave functions $\eta_n(x_i) \propto e^{-\omega_i x_i^2} H_n(x_i)$ leading to weight functions employed in MC importance sampling

$$w_1(\boldsymbol{x}) = \prod_{i=1}^{m} \left(\frac{\alpha \omega_i}{\pi} \right)^{1/2} e^{-\alpha \omega_i x_i^2} \qquad \text{and} \qquad w_2(\boldsymbol{x}, \boldsymbol{x}') = w_1(\boldsymbol{x}) w_1(\boldsymbol{x}')$$

for the first-order and second-order corrections, respectively.

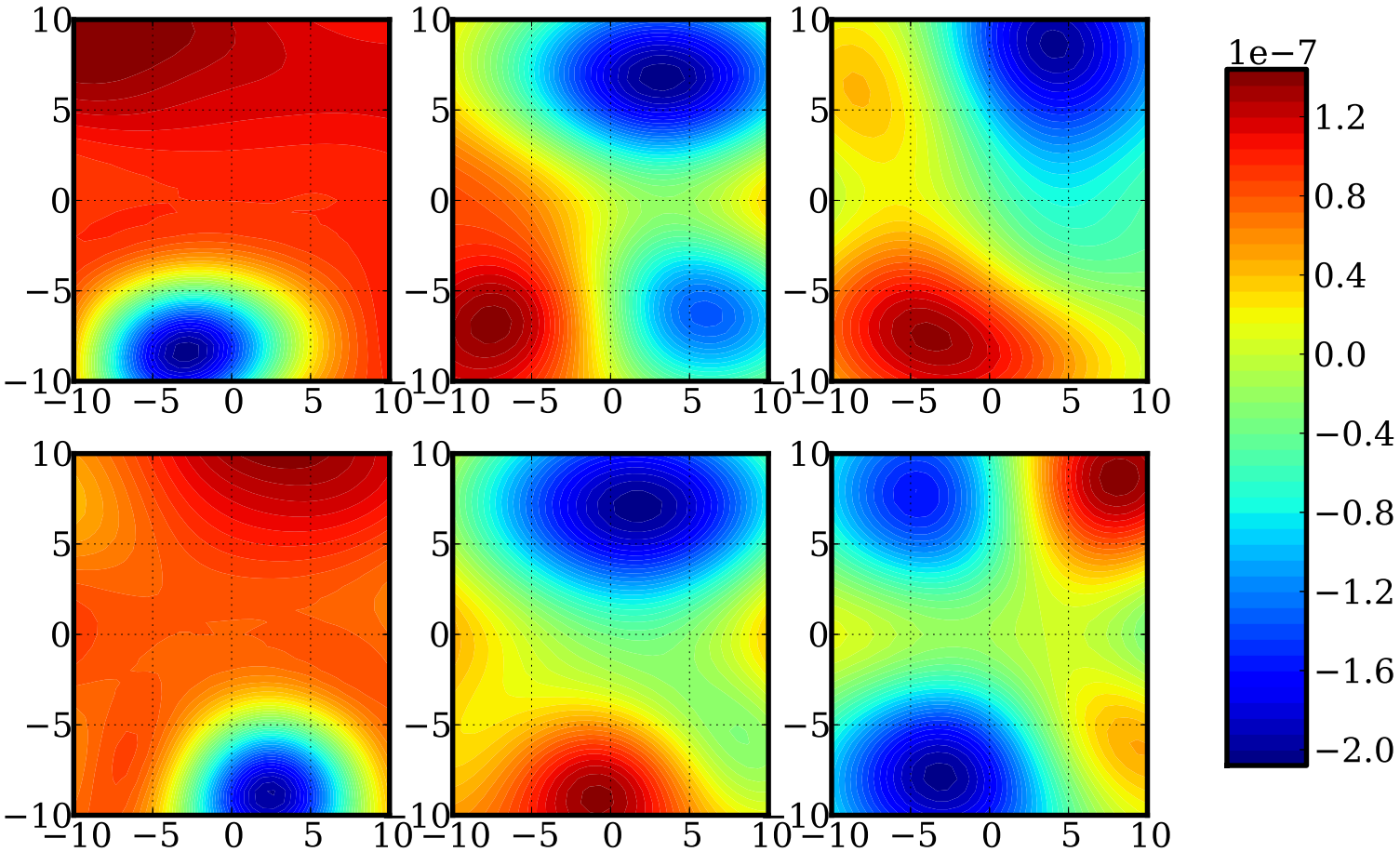
Just like MC importance sampling, it is crucial to pick a quadrature rule with appropriate shift and scaling.

First-order correction is easily handled by anisotropic quadrature with appropriate scaling



Second-order correction... not so easy

Random 2-d slices of the 6-d integrand.



The same 'multi-center' structure appears.
Similar to MP2, we take functional approximation approach.

MUQ for adaptive polynomial approximation

- We used MUQ (MIT UQ library) for adaptive polynomial construction for integrand approximation:

$$f(x) \approx p_{\boldsymbol{c}}(x) = \sum_{k \in \mathbb{I}} c_k \Psi_k(x),$$

  where the basis set $\mathbb{I}$ and the associated sampling locations $x^{(i)}$ are chosen adaptively.
- Only interested in the average, *i.e.* c_0 for Legendre-Uniform PC.
- Full results pending, but so far not successful.
- Not the type of adaptivity we need.
- ... Regression-based integration perhaps?

RBF regression of the integrand

- Typical formulation:

$$f(x) \approx f_{\boldsymbol{c}}^{RBF}(x) = \sum_{k=1}^{N} c_k \exp\left(-\frac{||x - x^{(k)}||^2}{w^2}\right)$$

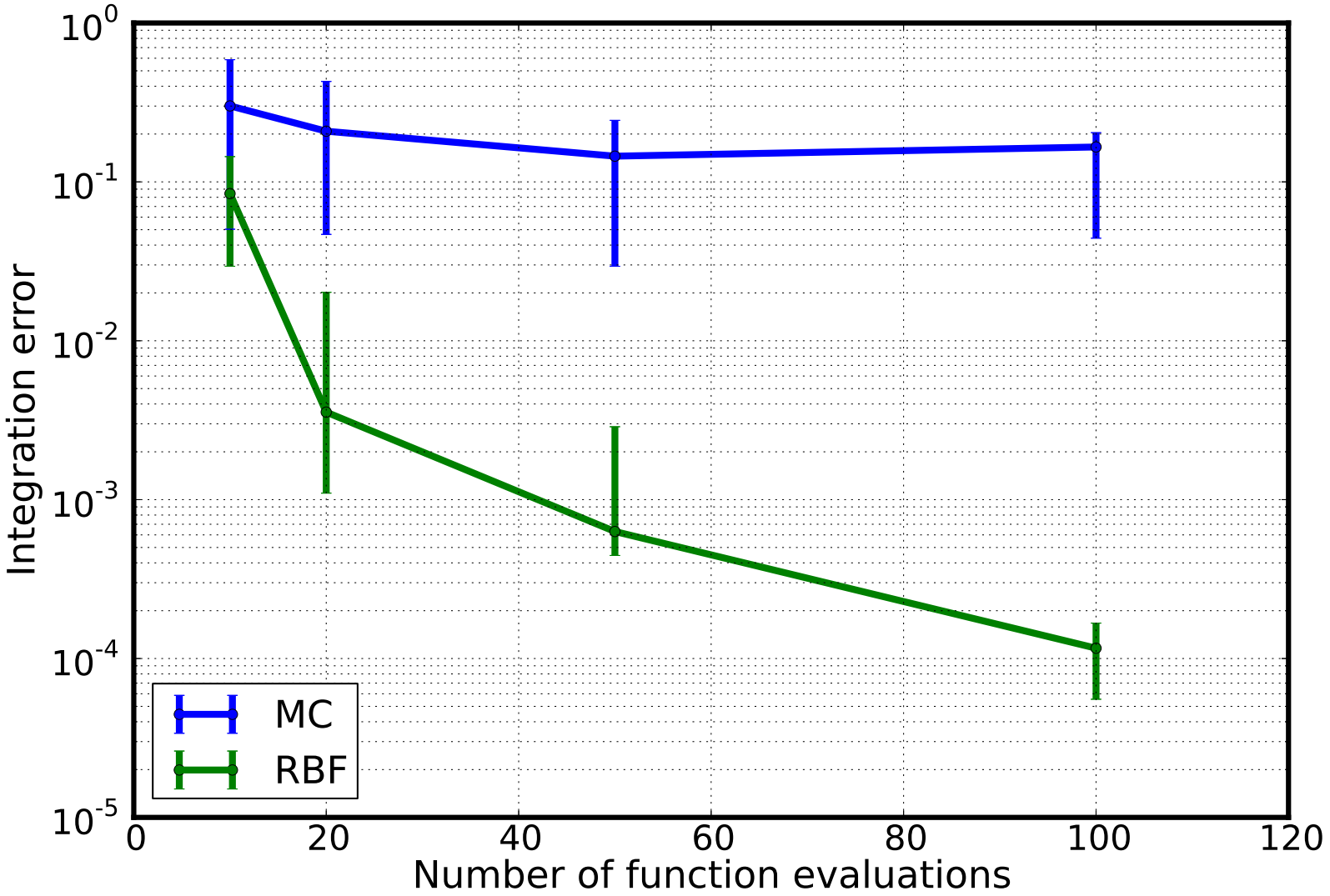
- Minimization problem:

$$\min_{\boldsymbol{c}} \left(||f(x) - f_{\boldsymbol{c}}^{RBF}(x)||^2 + \lambda ||\boldsymbol{c}||^2\right)$$

- λ found beforehand by minimizing Leave-One-Out (LOO) error.
- Integral of RBF expansion can be computed exactly

$$\int_{\mathbb{R}^d} f(x)dx \approx \int_{\mathbb{R}^d} f_{\boldsymbol{c}}^{RBF}(x)dx = (2\pi w^2)^{d/2} \sum_{k=1}^{N} c_k$$

RBF beats MC on the *same* set of samples



Low rank approximations are promising, too

- Based on separated representation

$$f(x) \approx \tilde{f}(x) = \sum_{i=1}^{r} \tilde{f}_i^1(x_1) \otimes \cdots \otimes \tilde{f}_i^d(x_d)$$

- Minimization problem:

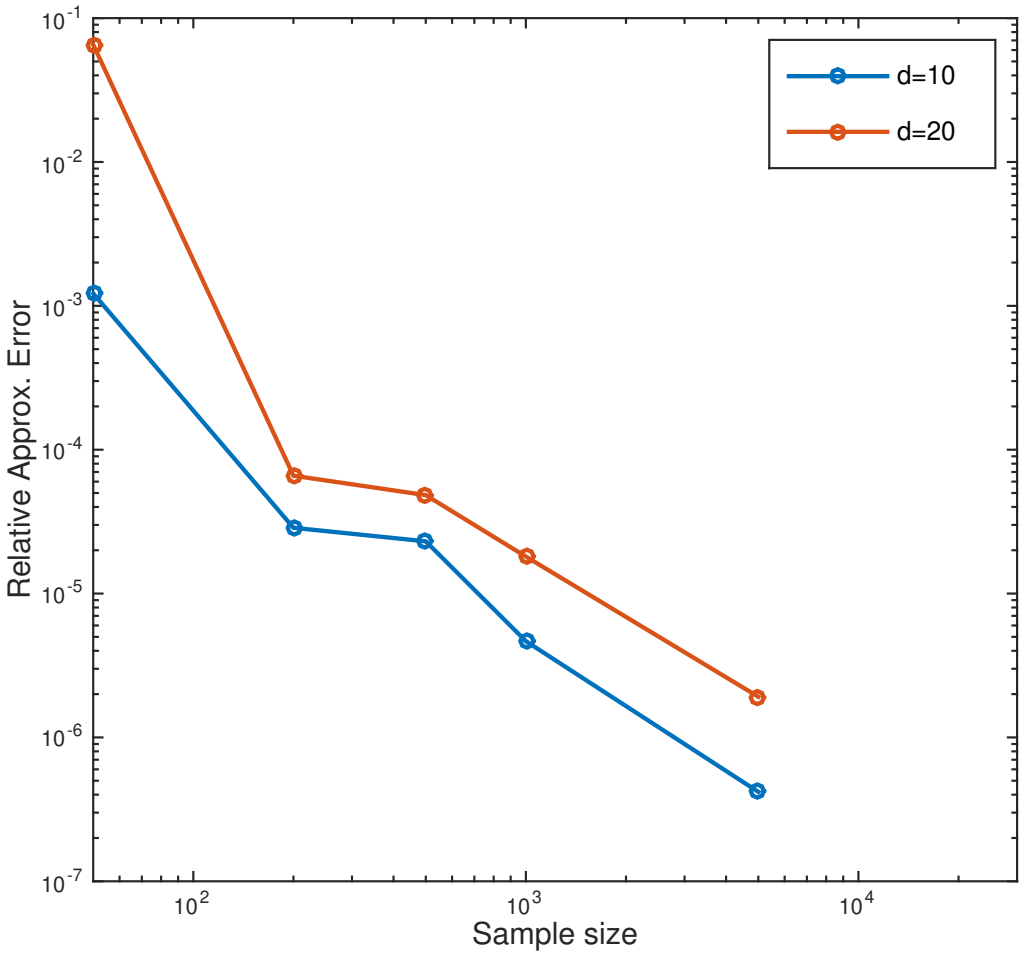
$$\min_{\tilde{f} \in \mathcal{M}} \|f(x) - \tilde{f}(x)\|^2 + \lambda \mathcal{R}(\tilde{f}(x))$$

  where $\mathcal{M}$ is a suitable tensor subset (Canonical, Tensor Train) and $\mathcal{R}$ is a regularization function
- Selection of optimal rank r and regularization coefficient λ using cross validation
- Integration:

$$\int_{\mathbb{R}^d} f(x)dx \approx \int_{\mathbb{R}^d} \sum_i \prod_k \tilde{f}_i^k(x_k)dx = \sum_i \prod_k \int_{\mathbb{R}} \tilde{f}_i^k(x_k)dx_k$$

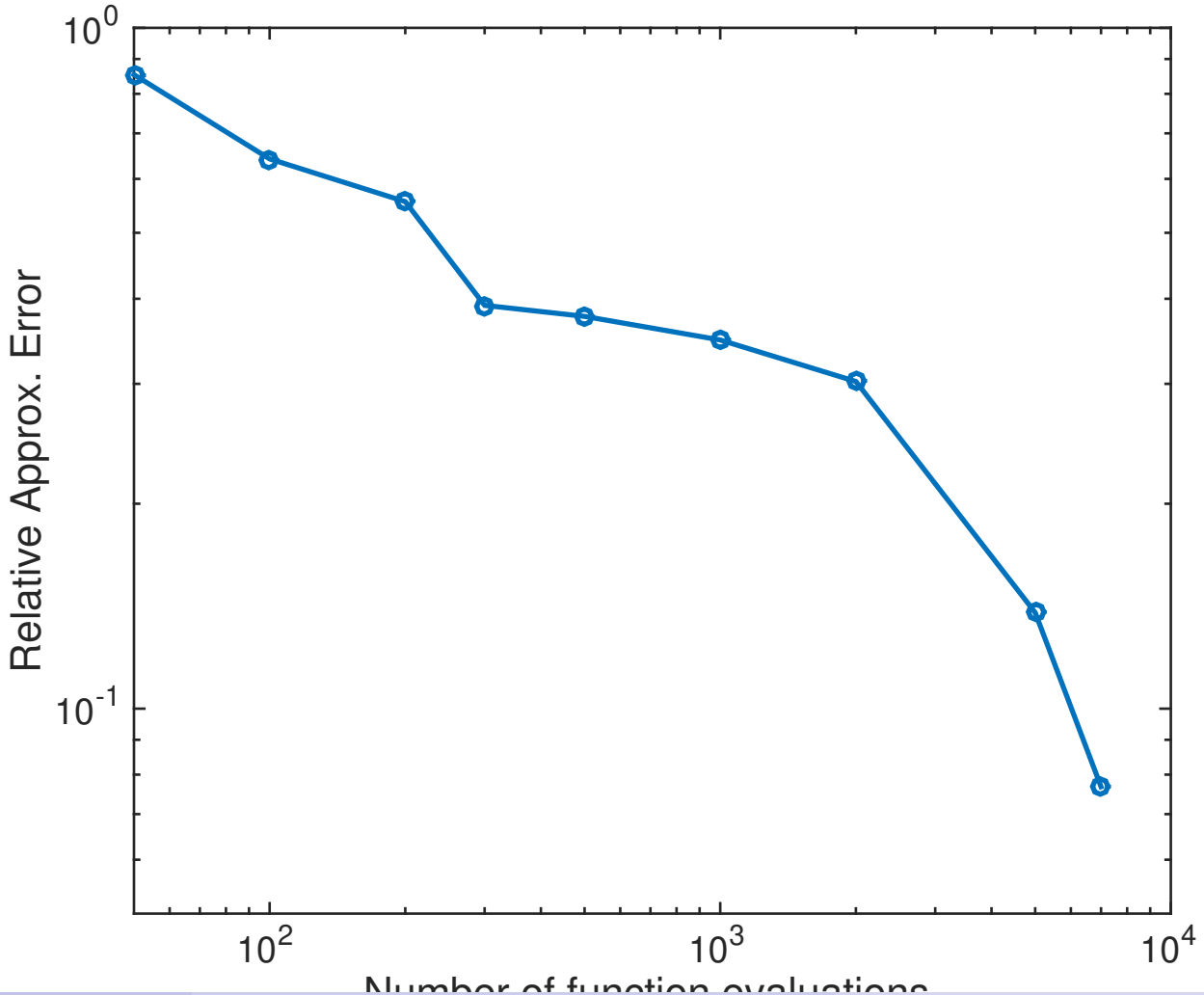
Low rank approximation: synthetic tests

- Genz Gaussian: $f(x) = \exp\left(-\sum_{i=1}^{d} c^2(x_i - w)^2\right),\ c = 0.1, w = 0.5$
- $\mathcal{M}$: Canonical rank-r, $\mathcal{R} : l_1$



Low rank approximation of $E_0^{(2)}$ integrand

- Canonical low rank approximation of $E_0^{(2)}$ integrand $(-5 \leq x_i \leq 5,\ 1 \leq i \leq 6)$



Summary

- Two main families of integrals tackled
  - MP2: second-order many-body perturbation theory
  - XVH2: perturbation theory for vibrational energy levels
- Singularity
  - Several ways to tackle it,
    Laplace method, spherical transformations...
- Scalability
  - More realistic than H_2O, *i.e.* $m \gg 3$: in future.
- Multi-center integrand
  - Quadrature challenging, even anisotropic or adaptive/MUQ
  - Approximation-based integration
- RBF regression, in progress.
- Low-rank approximation, in progress.

Literature

- S. Yoo Willow, K. Kim and S. Hirata, “Stochastic evaluation of second-order many-body perturbation energies”, *J Chem Phys*, 137, 204122, 2012.
- M. Hermes and S. Hirata, “Stochastic many-body perturbation theory for anharmonic molecular vibrations”, *J Chem Phys*, 141, 084105, 2014.

Thank You