

# Low Rank Approximation-based Quadrature for Fast Evaluation of Multi-Particle Integrals

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## Quantum Chemistry Integrals

### Context

- Accurate computational prediction of key molecular properties requires ab-initio electron or vibrational theories
  - Ab initio = from first principles of quantum mechanics
  - Density functional theory or the harmonic approximation is not accurate enough
- Series of tensor contractions and dense matrix manipulations: non-scalable!
- Current state of the art : Monte-Carlo (MC) and its enhancements

**QUEST: Improve integration efficiency and scalability via advanced UQ methods**

### Problem 1: Integrals in perturbation theory for anharmonic molecular vibrations

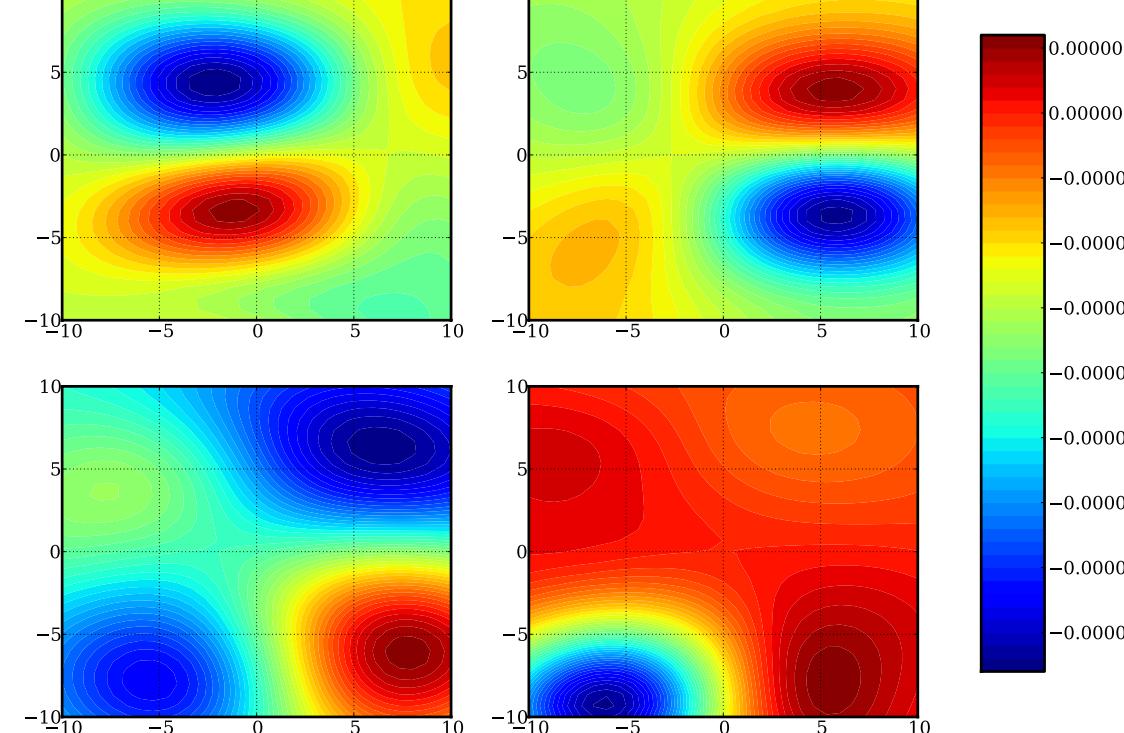
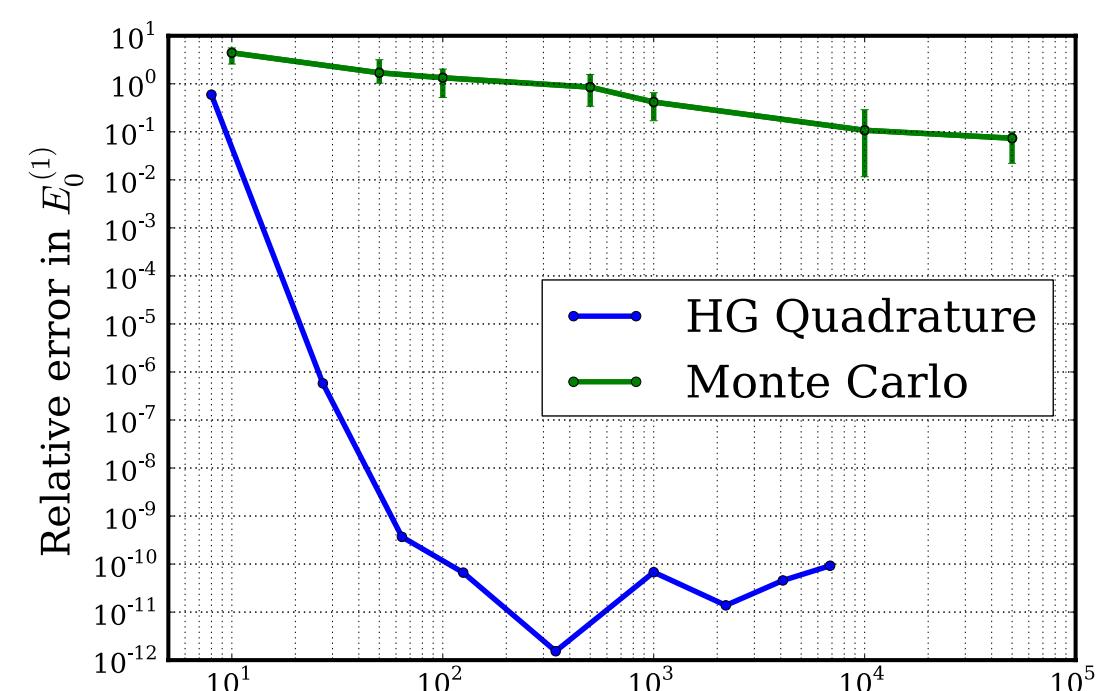
- Prediction of vibrational energy levels of molecules involves first and second order corrections to zero point energy given by

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

$$E_0^{(2)} = \int \int e^{-\|\omega^T \mathbf{x}\|^2} \Delta V(\mathbf{x}) H(\mathbf{x}, \mathbf{x}') e^{-\|\omega^T \mathbf{x}'\|^2} \Delta V(\mathbf{x}') d\mathbf{x} d\mathbf{x}'$$

- Both integrands involve wave functions proportional to product of exponential and Hermite polynomials leading to weight functions employed in MC importance sampling

- Very accurate  $E_0^{(1)}$  approximation  $E_0^{(2)}$  involves high order interactions and hence not easy to approximate



### Problem 2: Integrals in second-order many-body perturbation (MP2) theory

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

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

where

$$\langle pq|rs\rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\varphi_p^*(\mathbf{r}_1) \varphi_q^*(\mathbf{r}_2) \varphi_r(\mathbf{r}_1) \varphi_s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad \varphi_p(\mathbf{r}) = \sum_{\kappa} C_p^{\kappa} \chi_{\kappa}(\mathbf{r})$$

- Evaluating the above integral is challenged by singularities (inverse of distance) and by storage/scalability

## Key Ideas

### Low rank approximation of integrands

- Construct a separated approximation in a suitable (sparse) low rank tensor format

$$f(\mathbf{x}) \approx \sum_{i=1}^R \prod_{k=1}^m f_i^k(\tilde{\mathbf{x}}_k), \quad \tilde{\mathbf{x}}_k \subset \mathbf{x} = \{x_1, \dots, x_d\}, \quad \bigcup_{k=1}^m \tilde{\mathbf{x}}_k = \mathbf{x}$$

$$f_i^k(\tilde{\mathbf{x}}_k) = \sum_{j=1}^{n_k} v_{i,j}^k \psi_j^k(\tilde{\mathbf{x}}_k) = \langle \mathbf{v}_i^k, \boldsymbol{\psi}^k \rangle; \quad \|\mathbf{v}_i^k\|_1 \leq \lambda_k$$

- The approximation can be constructed from samples of the function using Alternating Least-Squares algorithm
- Selection of suitable groupings of input parameters can be based on physics or a priori model information

### Low dimensional quadrature

- Evaluate integral of the function as sum of products of low dimensional integrals

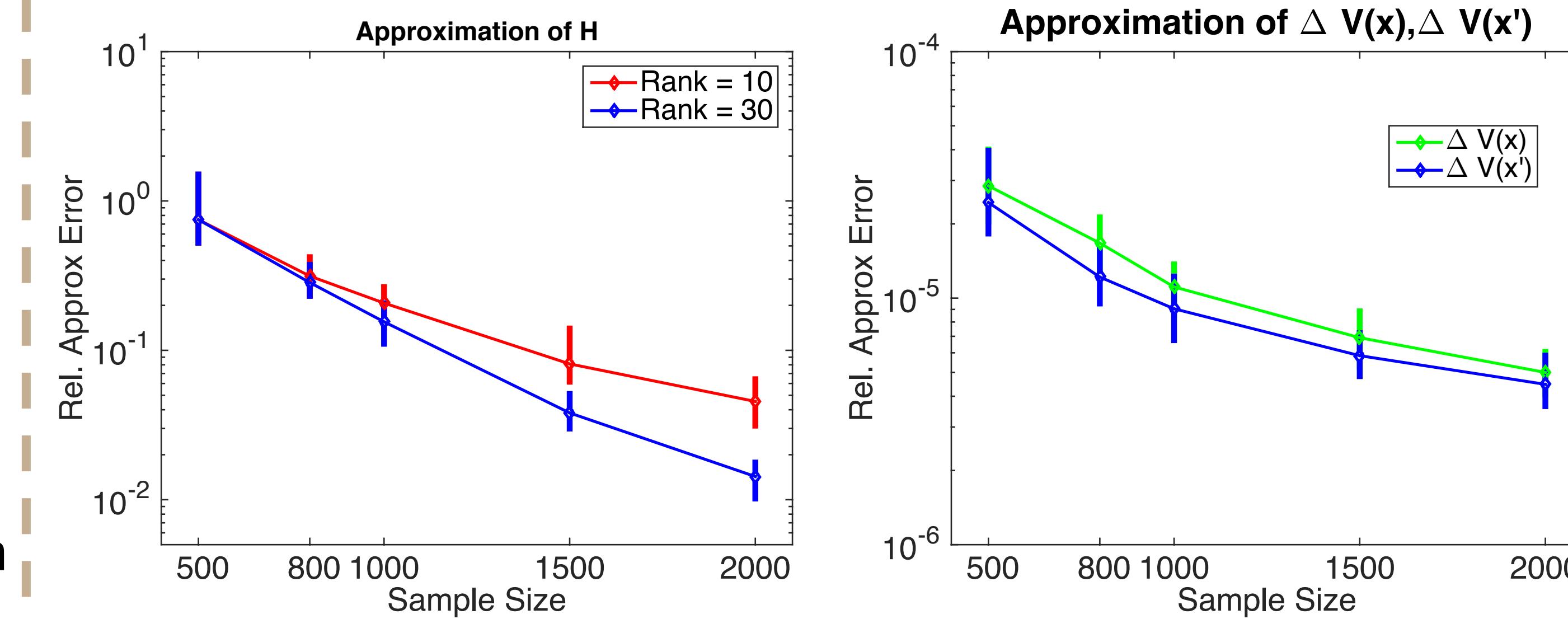
$$\int_{\Omega_{\mathbf{x}}} f(\mathbf{x}) d\mathbf{x} \approx \sum_{i=1}^R \prod_{k=1}^m \int_{\Omega_{\tilde{\mathbf{x}}_k}} f_i^k(\tilde{\mathbf{x}}_k) d\tilde{\mathbf{x}}_k$$

- Low dimensional integrals can be evaluated using suitable quadrature rules

$$\int_{\Omega_{\tilde{\mathbf{x}}_k}} f_i^k(\tilde{\mathbf{x}}_k) d\tilde{\mathbf{x}}_k \approx \sum_{j=1}^n \omega_j f_i^k(\tilde{\mathbf{x}}_k^j)$$

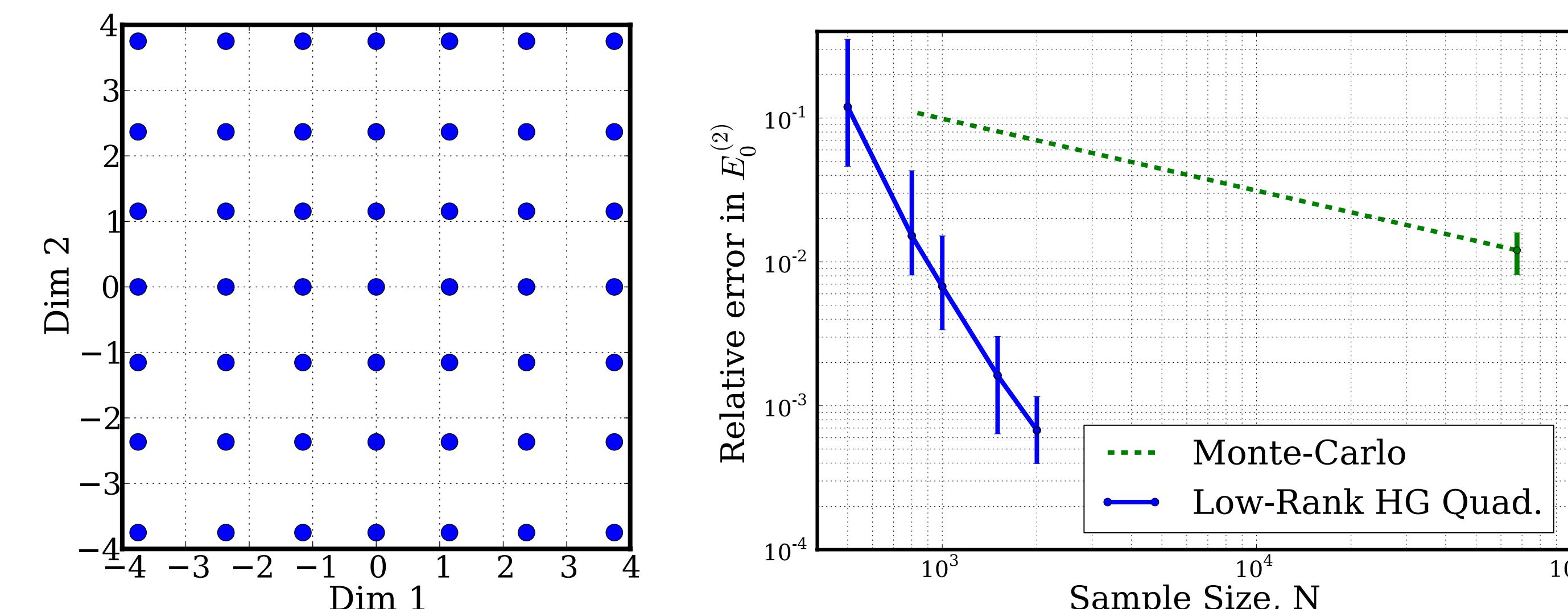
A high dimensional integral is estimated via several low dimensional integrals

Function	$H(\mathbf{x}, \mathbf{x}')$	$\Delta V(\mathbf{x}), \Delta V(\mathbf{x}')$
Grouping $\tilde{\mathbf{x}}_k$ Basis $\psi^k(\tilde{\mathbf{x}}_k)$	$\{x_k, x'_k\}$ Hermite	$\{x_k\}, \{x'_k\}$ Monomial



$$I_{qrs}^k = \underbrace{\int_{\Omega_{x_k} \times \Omega_{x'_k}} e^{-\sqrt{\omega_k}(x_k^2 + x'^2)} \Delta V_q^k(x_k) H_r^k(x_k, x'_k) \Delta V_s^k(x'_k) dx_k dx'_k}_{\text{Evaluated using Gauss Hermite quadrature rule}}$$

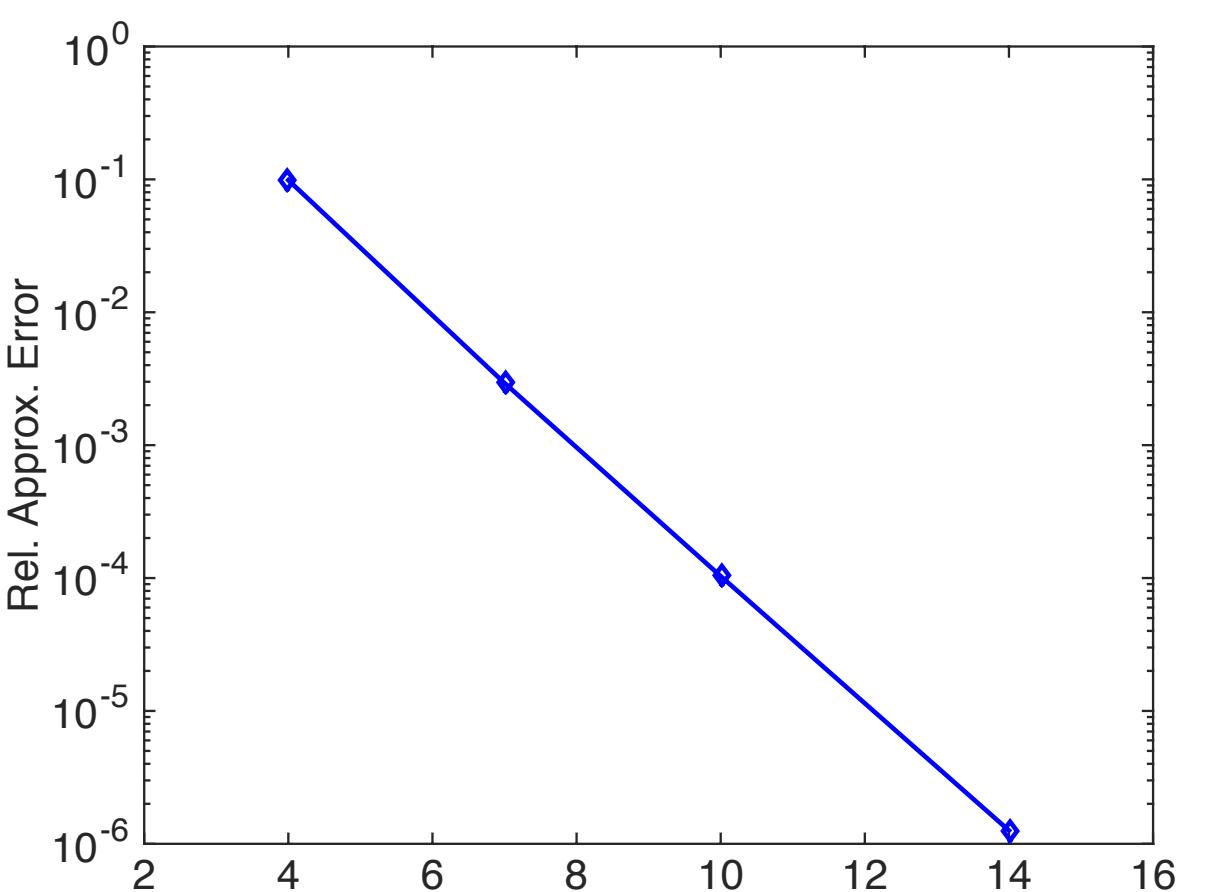
$$E_0^{(2)} \approx \sum_{q=1}^Q \sum_{r=1}^R \sum_{s=1}^S \prod_{k=1}^m I_{qrs}^k$$



## Current and Future Work

- Tackle singularities in integrands using exponential sums

$$\frac{1}{\sqrt{x^2 + y^2 + z^2}} \approx \sum_{k=1}^K \omega_k e^{-\alpha_k(x^2 + y^2 + z^2)}$$



- Automatic detection of sparsity pattern and variable regrouping in low rank tensor subsets
- Scaling to larger systems, possibly polymers/solids
- Demonstration of low rank quadrature based approach for MP2 integrals

## References

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