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

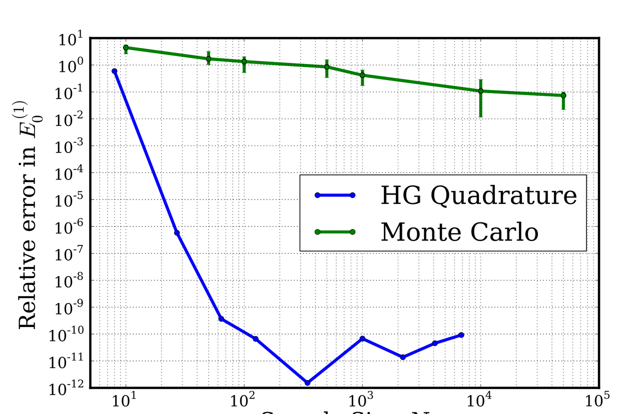
Problem 1: Integrals in perturbation theory for anharmonic molecular vibrations

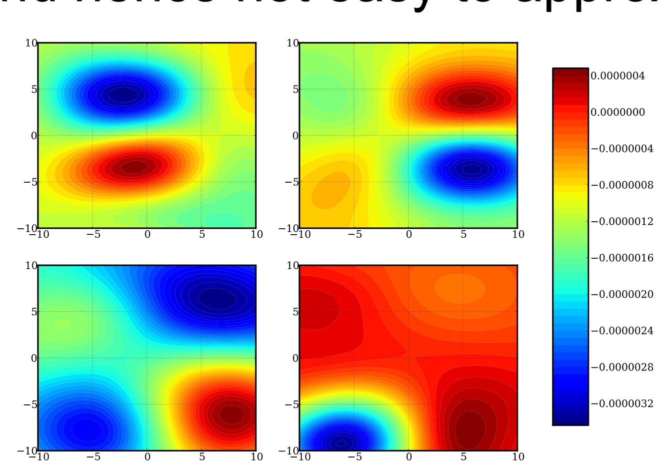
- Prediction of vibrational energy levels of molecules involves first and second order corrections to zero point energy given by

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

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

- 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 using scaled quadrature
- $E_0^{(2)}$ 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

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

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

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

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

- 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

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

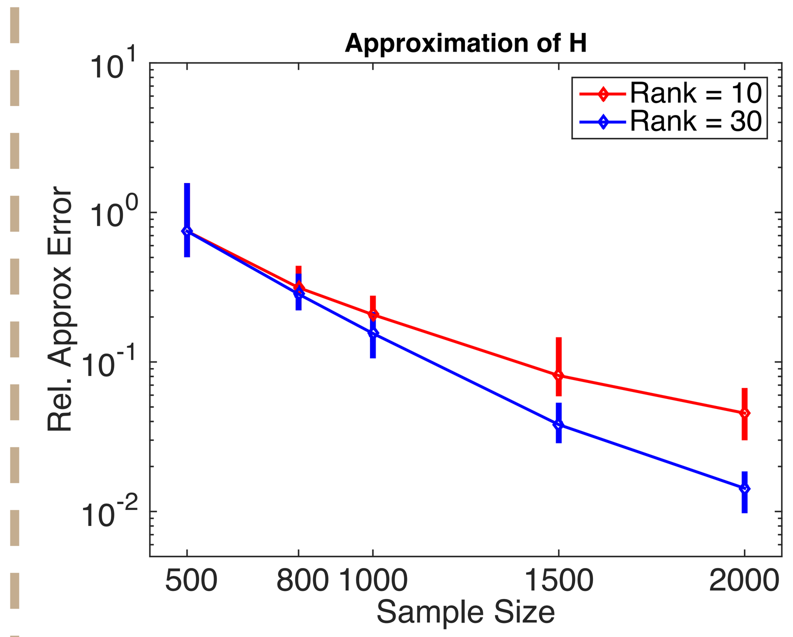
- Low dimensional integrals can be evaluated using suitable quadrature rules

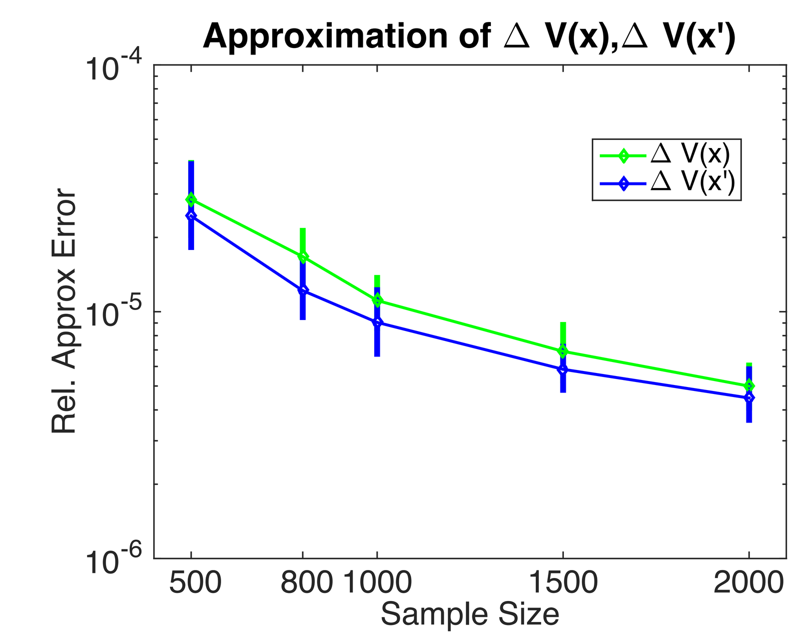
$$\int_{\Omega_{\tilde{\boldsymbol{x}}_k}} f_i^k(\tilde{\boldsymbol{x}}_k)d\tilde{\boldsymbol{x}}_k \approx \sum_{j=1}^{n}\omega_j f_i^k(\tilde{\boldsymbol{x}}_k^j)$$

A high dimensional integral is estimated via several low dimensional integrals

Illustrations

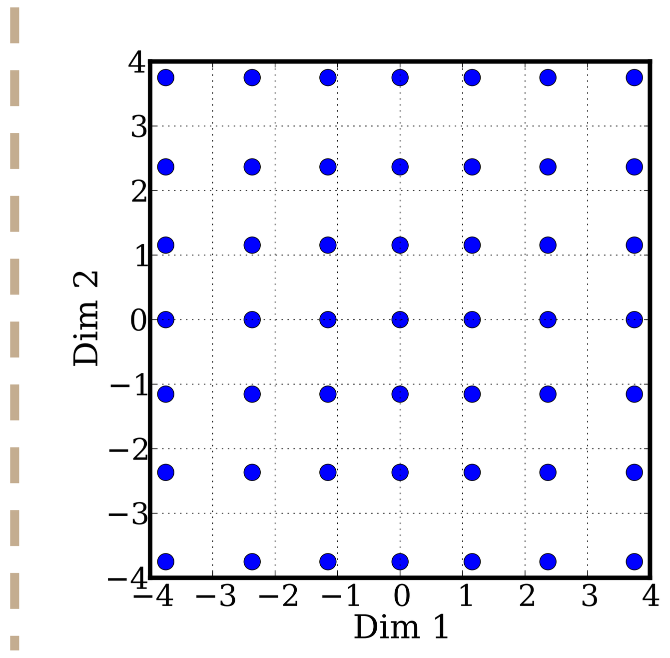
Function	$H(\boldsymbol{x},\boldsymbol{x}')$	$\Delta V(\boldsymbol{x}),\Delta V(\boldsymbol{x}')$
Grouping $\tilde{\boldsymbol{x}}_k$	$\{x_k,x_k'\}$	$\{x_k\},\{x_k'\}$
Basis $\psi^k(\tilde{\boldsymbol{x}}_k)$	Hermite	Monomial

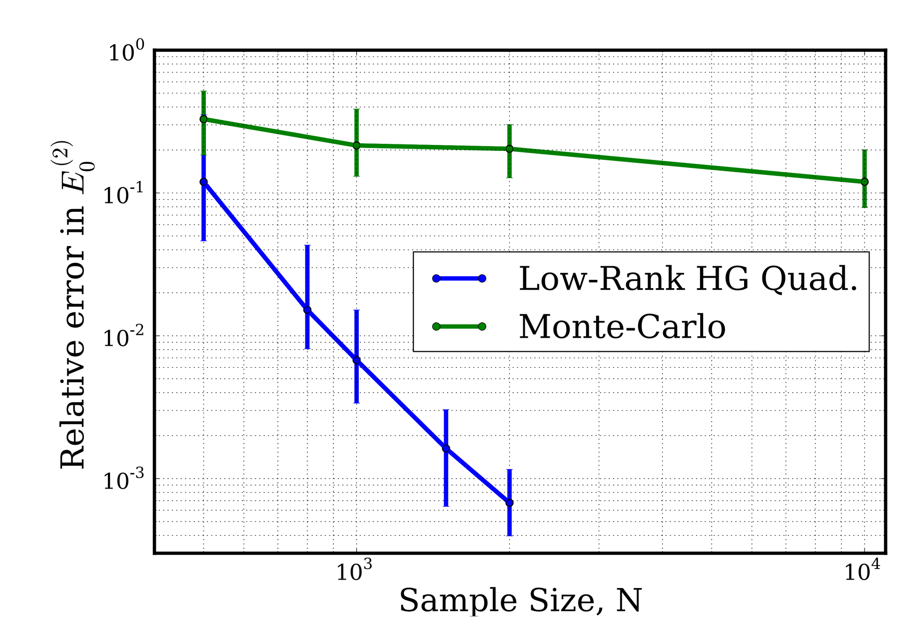




$$I_{qrs}^k = \underbrace{\int_{\Omega_{x_k}\times\Omega_{x_k'}} e^{-\sqrt{\omega_k}(x_k^2+x_k'^2)}\Delta V_q^k(x_k)H_r^k(x_k,x_k')\Delta V_s^k(x_k')dx_kdx_k'}_{\text{Evaluated using Gauss Hermite quadrature rule}}$$

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

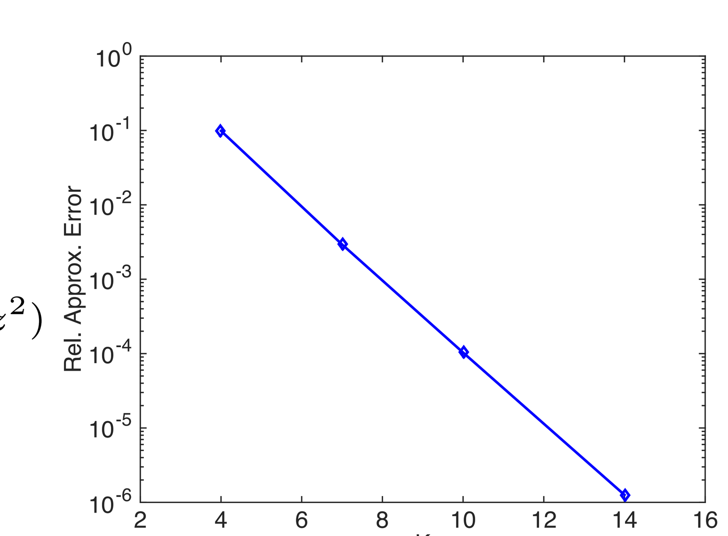




Current and Future Work

- 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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