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Low-Rank Approximation Based Quadrature for Fast Evaluation of Quantum Chemistry Integrals

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Context

- Accurate prediction of vibrational spectra of molecules using perturbation theory require
  - Anharmonic approximation of potential energy surface
  - First and second order corrections to energy
  - First and second order corrections to frequencies per d.o.f
- Energy and frequency corrections are formulated as non singular integrals which can be high order and multi-centered

QUEST

improve integration efficiency and scalability via advanced UQ methods.

First Order Corrections

$$I_1 = \int \Phi_0(\mathbf{x}) \Delta V(\mathbf{x}) \Phi_0(\mathbf{x}) \lambda_1(\mathbf{x}) d\mathbf{x}$$

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

- $V(\mathbf{x})$: Potential energy (PE) containing up to n-th order force constants. As a default scenario, $n = 4$.
- V_{ref}: the minimum/reference PE, *i.e.* at the equilibrium geometry.
- ω_i: the i-th mode frequency of a reference mean-field theory. Found by solving Dyson equation.

$$\Phi_0(\mathbf{x}) = \prod_{i=1}^{m} \eta_0(x_i); \quad \eta_{n_i}(x_i) = C(n_i, \omega_i) e^{\frac{-\omega_i x_i^2}{2}} h_{n_i}(\sqrt{\omega_i} x_i)$$

- m: vibrational degrees of freedom. For H_2O (water), $m = 3$ and H_2CO (formaldehyde), m=6.
- $\eta_{n_i}(x_i)$: the harmonic-oscillator wave function with quantum number n_i along the i-th normal mode x_i.
- h_{n_i}: Hermite polynomial of degree n_i

First Order Corrections (contd..)

$$I_1 = \int \Phi_0(\mathbf{x}) \Delta V(\mathbf{x}) \Phi_0(\mathbf{x}) \lambda_1(\mathbf{x}) d\mathbf{x}$$

I_1	$\lambda_1(\mathbf{x}) = \prod_{i=1}^{m} \lambda_1(x_i)$
Energy (E_1)	$\lambda_1^i(x_i) = 1, 1 \leq i \leq m$
Frequencies (Σ_1^i)	$\lambda_1^i(x_i) = \frac{2^{1/2}\eta_2(x_i)}{\eta_0(x_i)}, \lambda_1^{j \neq i} = 1$

Quadrature based Integration

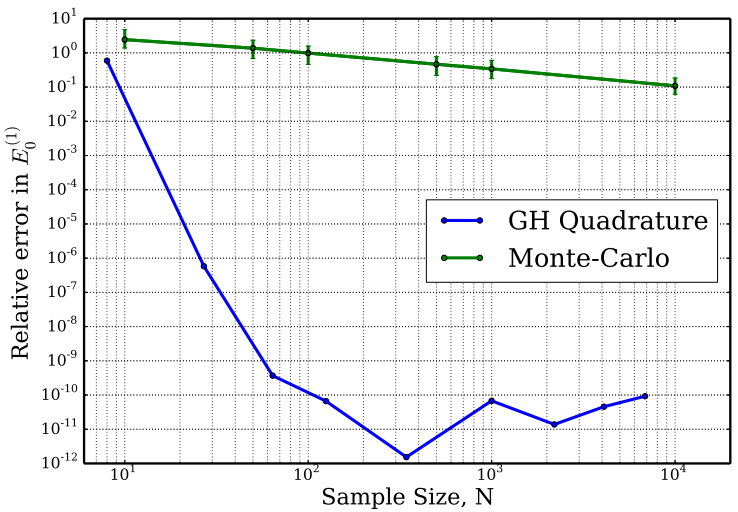
- First order correction integrands can be reformulated as Gaussian times polynomials

$$I_1 = \int_{\mathbf{x}} \prod_{i=1}^{m} e^{-\omega_i x_i^2} \lambda_1^i(x_i) \Delta V(\mathbf{x}) d\mathbf{x}$$

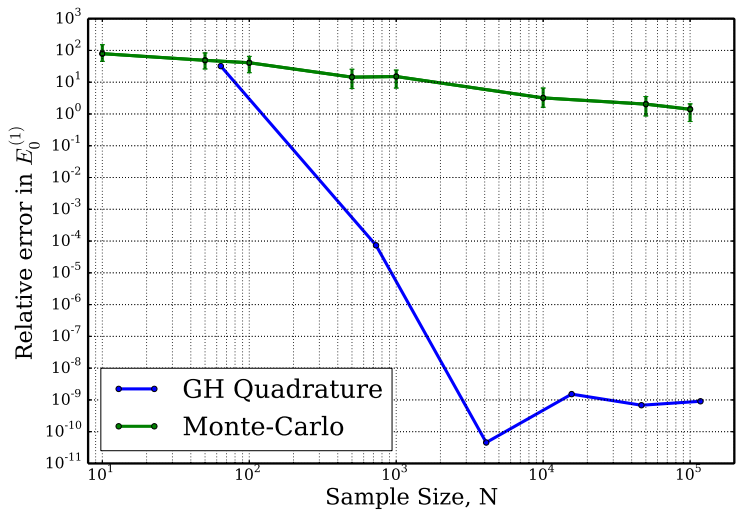
- Use of Gauss Hermite quadrature (with appropriate scaling)

E_1 Using Quadrature

H_2O $(m = 3)$



H_2CO $(m = 6)$



Quadrature based integration, in general, is not scalable

Second Order Corrections

$$I_2 = \int_{\mathbf{x}} \int_{\mathbf{x}'} \Phi_0(\mathbf{x}) \Delta V(\mathbf{x}) G_2(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}') \Phi_0(\mathbf{x}') \lambda_2(\mathbf{x}, \mathbf{x}) d\mathbf{x} d\mathbf{x}'$$

using real-space Green's function

$$G_2(\mathbf{x}, \mathbf{x}') = \sum_{N=1}^{N_{\max}} \frac{\Phi_N(\mathbf{x}) \Phi_N(\mathbf{x}')}{E_0^{(0)} - E_N^{(0)}},$$

$$\Phi_N(\mathbf{x}) = \prod_{i=1}^{m} \eta_{n_i}(x_i); \quad E_0^{(0)} - E_N^{(0)} = -\sum_{i=1}^{m} n_i \omega_i$$

Relation between N and n_i is given by the mapping

$$\mathcal{I} : (n_1, \ldots, n_m) \in \times_{i=1}^{m} \{1, \ldots, n_{max}\} \rightarrow N \in \{0, \ldots, n_{max}^m - 1 = N_{max}\}$$

$$G_2(\mathbf{x}, \mathbf{x}') = \frac{1}{-\sum_{i=\mathbf{1}}^{m} n_i \omega_i} \prod_{i=1}^{m} e^i(x_i, x_i') H^i(x_i, x_i')$$

$$e^i(x_i, x_i') = e^{-\omega_i (x_i^{\mathbf{2}} + x_i'^{\mathbf{2}})}; \quad H^i(x_i, x_i') = \sum_{n_i}^{n_{max}} C^2(n_i, \omega_i) h_{n_i}(\sqrt{\omega_i} x_i) h_{n_i}(\sqrt{\omega_i} x_i')$$

Second Order Corrections (contd...)

$$I_2 = \int_{\mathbf{x}} \int_{\mathbf{x}'} \Phi_0(\mathbf{x}) \Delta V(\mathbf{x}) G_2(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}') \Phi_0(\mathbf{x}') \lambda_2(\mathbf{x}, \mathbf{x}') d\mathbf{x} d\mathbf{x}'$$

I_2	$\lambda_2(\mathbf{x}, \mathbf{x}') = \prod_{i=1}^{m} \lambda_2^i(x_i, x_i')$
Energy (E_2)	$\lambda_2^i(x_i, x_i') = 1$
Frequencies (Σ_{2p}^i)	$\lambda_2^i(x_i, x_i') = \frac{(n_i+2)^{\mathbf{1/2}}(n_i+1)^{\mathbf{1/2}}\eta_{n_i+\mathbf{2}}(x_i')}{\eta_{n_i}(x_i')}, \lambda_2^{j\neq i} = 1$
Frequencies (Σ_{2b}^i)	$\lambda_2^i(x_i, x_i') = \frac{(n_i+1)\eta_{n_i+\mathbf{1}}(x_i)\eta_{n_i+\mathbf{1}}(x_i')}{\eta_{n_i}(x_i')}, \lambda_2^{j\neq i} = 1$

Second order correction integrands can also be formulated as Gaussian times polynomials

$$E_2 = \int_{\mathbf{x}} \int_{\mathbf{x}'} e(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}) H(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}') \lambda_2(\mathbf{x}, \mathbf{x}') d\mathbf{x} d\mathbf{x}'$$

$$H(\mathbf{x}, \mathbf{x}') = \frac{\prod_{i=1}^{m} H(x_i, x_i')}{-\sum_{i=1}^{m} n_i \omega_i}$$

Separated Integration

Integration Problem

$$I(u) = \int_{\Omega} u(\mathbf{x})\rho(\mathbf{x})d\mathbf{x}$$

- $u(\mathbf{x}) = u(x_1, \ldots, x_m)$
- $\rho(\mathbf{x}) = \rho(x_1) \cdots \rho(x_m)$

Low rank approximation of $u(\mathbf{x})$

$$u(\mathbf{x}) \approx v(x_1, \ldots, x_m) = \sum_{\mu=1}^{r} v_{\mu}^{1}(x_1) \cdots v_{\mu}^{m}(x_m)$$

Separated Integration

$$I(u) \approx I(v) = \sum_{\mu=1}^{r} \left(\int_{\Omega_1} v_{\mu}^{1}(x_1)\rho(x_1)dx_1 \cdots \int_{\Omega_m} v_{\mu}^{m}(x_d)\rho(x_m)dx_m \right)$$

Application: Second Order Energy Correction in Quantum Chemistry

$$I_2 = \int_{\mathbf{x}} \int_{\mathbf{x}'} e(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}) H(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}') \lambda_2(\mathbf{x}, \mathbf{x}') d\mathbf{x} d\mathbf{x}',$$

where

$$e(\mathbf{x}, \mathbf{x}') = \prod_{i=1}^{m} e^{(i)}(x_i, x_i'); \; e^{(i)}(x_i, x_i') = e^{-\omega_i (x_i^{\mathbf{2}} + x_i'^{\mathbf{2}})},$$

$$\Delta V(\mathbf{x}) \approx \sum_{\mu_{\mathbf{1}}=1}^{r_{\mathbf{1}}} \prod_{i=1}^{m} \Delta V_{\mu_{\mathbf{1}}}^{(i)}(x_i),$$

$$H(\mathbf{x}, \mathbf{x}') \approx \sum_{\mu_{\mathbf{2}}=1}^{r_{\mathbf{2}}} \prod_{i=1}^{m} H_{\mu_{\mathbf{2}}}^{(i)}(x_i, x_i'),$$

$$\lambda_2(\mathbf{x}, \mathbf{x}') = \prod_{i=1}^{m} \lambda_2^i(x_i, x_i')$$

$$I_2 \approx \sum_{\mu_{\mathbf{1}}}^{r_{\mathbf{1}}} \sum_{\mu_{\mathbf{2}}}^{r_{\mathbf{2}}} \sum_{\mu_{\mathbf{3}}}^{r_{\mathbf{1}}} \prod_{i=1}^{d} \int_{x_i} \int_{x_i'} e^i(x_i, x_i') \Delta V_{\mu_{\mathbf{1}}}^i(x_i) H_{\mu_{\mathbf{2}}}^i(x_i, x_i') \Delta V_{\mu_{\mathbf{3}}}^i(x_i') \lambda_2^i(x_i, x_i') dx dx'.$$

Tensor Approximation of $\Delta V(\mathbf{x})$

Tensor Representation

$$\mathcal{S}^{(i)} = \left\{ v^{(i)}(x_i) = \sum_{k=1}^{n_{max}} v_k \phi_k^{(i)}(x_i);\ v_k \in \mathbb{R} \right\}.$$

If $\phi_k^{(i)} = x_i^k$, then $\Delta V(\mathbf{x}) \in \mathcal{S} = \mathcal{S}^{(1)} \otimes \cdots \otimes \mathcal{S}^{(m)}$. $\forall v \in \mathcal{S}$ can be identified as

$$v = \sum_{k_1=1}^{n_{max}} \cdots \sum_{k_m=1}^{n_{max}} v_{k_1 \ldots k_d} \phi_{k_1}(x_1) \cdots \phi_{k_m}(x_m).$$

Canonical Subset

$$\mathcal{R}_r = \left\{ v = \sum_{\mu=1}^{r} \prod_{i=1}^{m} v_\mu^{(i)}(x_i);\ v_\mu^{(i)}(x_i) = \langle \mathbf{v}_\mu^{(i)}, \boldsymbol{\phi}^{(i)}(x_i) \rangle \in \mathcal{S}^{(i)} \right\}.$$

Given fixed ϕ's, we just need coefficients i.e. $v = F_{\mathcal{R}_r}(\mathbf{v}^1, \ldots, \mathbf{v}^m)$, $\mathbf{v}^i \in \mathbb{R}^{n_{max} \times m}$

Alternating Least Squares Approximation

Least squares problem

$$\min_{\mathbf{v^1},\ldots,\mathbf{v}^m} \|u - F_{\mathcal{R}_r}(\mathbf{v}^1,\ldots,\mathbf{v}^m)\|_Q^2 \quad \text{with} \quad \|u-v\|_Q^2 = \sum_{q=1}^{Q} |u(x_q) - v(x_q)|^2$$

where x_q is q^{th} sample, $q = 1,\ldots,Q$.

Alternating least squares (ALS)

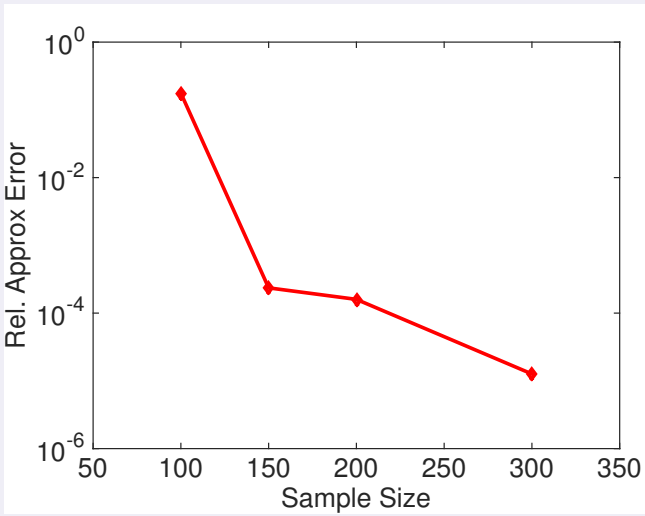
- For $r \in \{1,\ldots,R\}$
  - For $1 \leq k \leq m$ and for fixed $\mathbf{v}^j, j \neq k$

$$\min_{\mathbf{v}^k} \|u - F_{\mathcal{R}_r}(\mathbf{v}^1,\ldots,\mathbf{v}^k,\ldots,\mathbf{v}^m)\|_Q^2$$

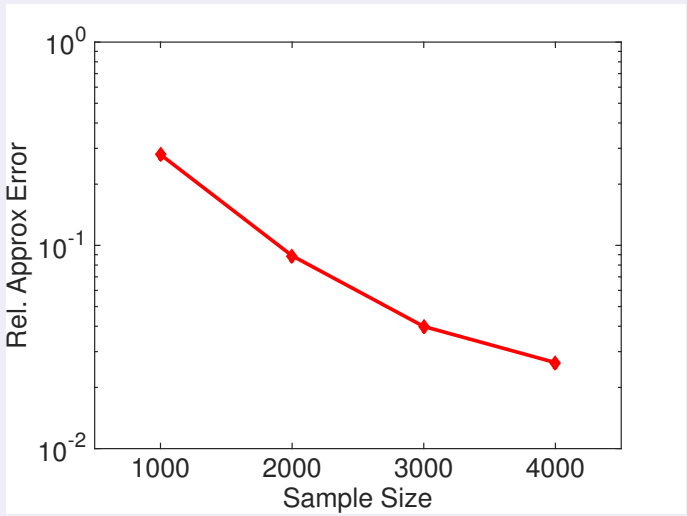
- Select optimal rank using cross validation

Results: Approximation of ΔV

H_2O $(m = 3)$



H_2CO $(m = 6)$



Tensor Approximation of $H(\mathbf{x}, \mathbf{x}')$

$$I_2 = \int_{\mathbf{x}} \int_{\mathbf{x}'} e(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}) H(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}') \lambda_2(\mathbf{x}, \mathbf{x}') d\mathbf{x} d\mathbf{x}',$$

where

$$H(\mathbf{x}, \mathbf{x}') = \frac{\prod_{i=1}^{m} H(x_i, x_i')}{-\sum_{i=1}^{m} n_i \omega_i}$$

Tensor representation of $H(\mathbf{x}, \mathbf{x}')$

$$\mathcal{S}_{\delta}^{(ii')} = \left\{ v^{(i)}(x_i, x_i') = \sum_{k=1}^{n_{max}} v_k \phi_k^{(ii')}(x_i, x_i');\ v_k \in \mathbb{R} \right\}$$

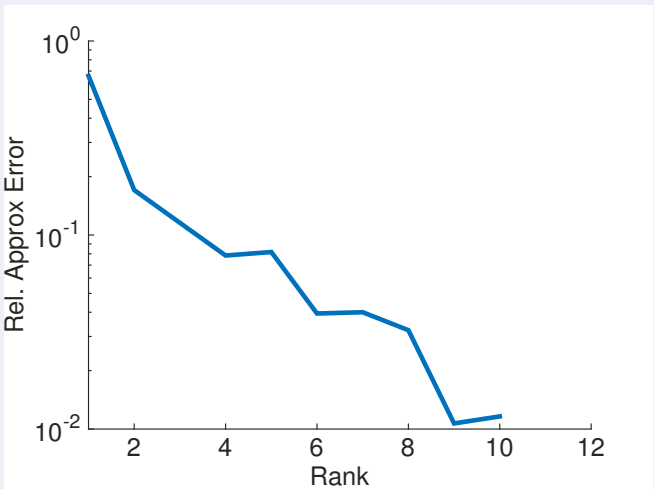
When $\phi_k^{(ii')}(x_i, x_i') = h_k(\sqrt{\omega_i} x_i) h_k(\sqrt{\omega_i} x_i')$, then $H(\mathbf{x}, \mathbf{x}') \in \mathcal{S}_{\delta} = \otimes_{i=1}^{m} \mathcal{S}^{(ii')}$ and can be identified with a coefficient tensor

$$\mathcal{H}(n_1, \ldots, n_m) = \frac{-\prod_{i=1}^{m} C^2(n_i, \omega_i)}{\sum_{i=1}^{m} n_i \omega_i}.$$

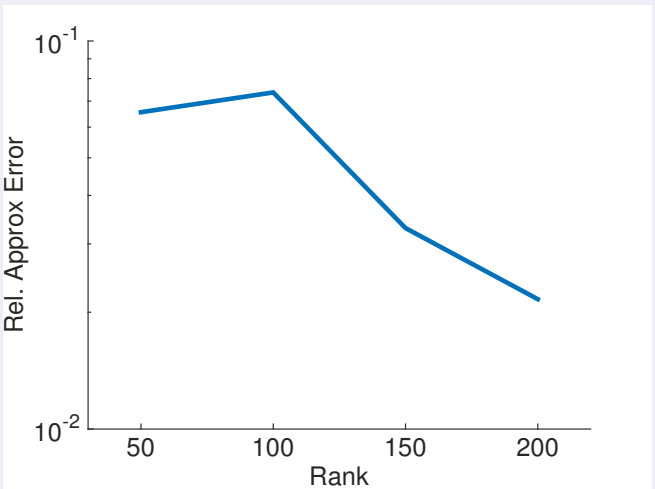
$\mathcal{H}$ can be approximated in $\mathcal{R}_r$

Second order Energy Corrections

H_2O

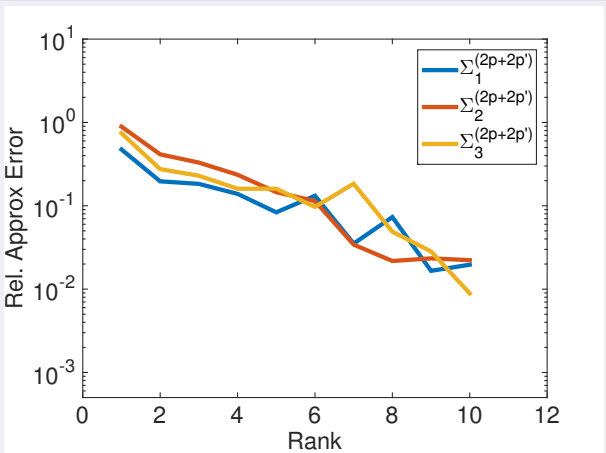


H_2CO

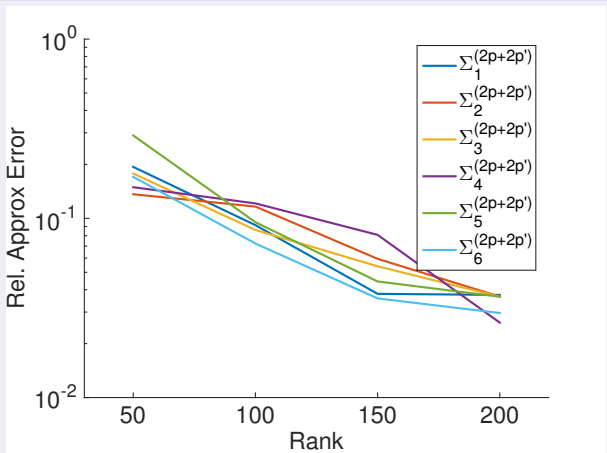


Second order Frequency (Σ_{2p}) Corrections

H_2O

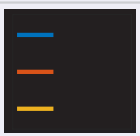


H_2CO

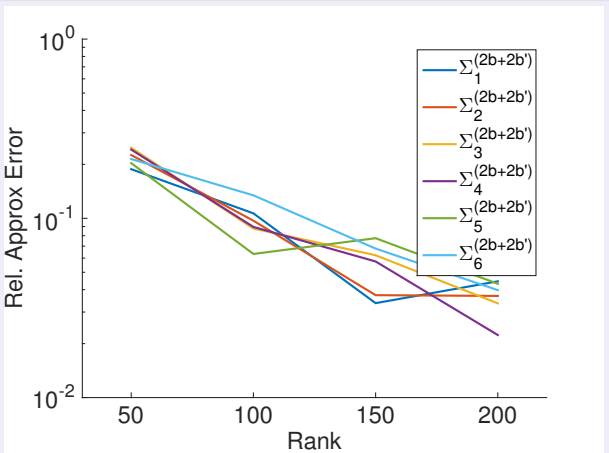


Second order Frequency (Σ_{2b}) Corrections Contd..

H_2O



H_2CO



Results

Method	Tensor	MC	Ref
E_1	51.6	51.3 $\pm$1.1	51.6
E_2	-120.5	-119.1$\pm$0.7	-120.6
ν_1	1566.9	1566.3 $\pm$2.1	1566.9
ν_2	3645.2	3646.9 $\pm$4.5	3645.1
ν_3	3767.4	3768.5 $\pm$3.2	3767.4
$\#\Delta V$	150	67500	-

Table: H_2O

Method	Tensor	Ref
E_1	-1.045	-1.006
E_2	-77.68	-77.72
ν_1	1166.18	1166.44
ν_2	1243.05	1242.97
ν_3	1506.41	1506.25
ν_4	1723.26	1723.34
ν_5	2810.64	2810.73
ν_6	2870.81	2870.77
$\#\Delta V$	4000	-

Table: H_2CO

Frequency corrections $\nu_i,\ i = 1, \ldots, m$ are obtained by solving non recursive inverse Dyson equation from $\Sigma_1^i, \Sigma_{2p}^i$ and Σ_{2b}^i

Summary and Perspectives

Conclusion

- Tensor approximations provides a good framework to handle high dimensional Quantum Chemistry integrals
- Approximation of PES can be formulated as a sampling based tensor approximation problem thus leading to low dimensional integrals using separated representation
- Significant cost savings as compared to Monte Carlo and its variants

Perspectives

- Use of other tensor formats (TT, HT) for PES approximation
- Better exploitation of structure of PES using gradient based information for dealing with even larger molecules

Literature

References

- M. Hermes and S. Hirata, “Second order many-body perturbation expansions of vibrational Dyson self-energies", *J Chem Phys*, 139, 034111, 2014.
- M. Hermes and S. Hirata, “Stochastic many-body perturbation theory for anharmonic molecular vibrations", *J Chem Phys*, 141, 084105, 2014.

Papers in preparation

- P. Rai, K. Sargsyan, H. Najm, M. Hermes, S.Hirata, “Sampling based approximation of Potential Energy Surfaces (PES) for fast evaluation of high dimensional quantum chemistry Integrals"
- P. Rai, K. Sargsyan, H. Najm, M. Hermes, S.Hirata, “A tensor approximation framework for evaluation of high dimensional integrals in anharmonic molecular vibrations"

Thank You