Problem 1: Integrals in perturbation theory

- **Context**
  - Accurate computational prediction of key molecular properties requires ab-initio electron or vibrational theories
  - Ab initio is 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

- **Problem**
  - Prediction of vibrational energy levels of molecules involves first and second order corrections to zero point energy given by
    \[ E_{1}^{(1)} = \int \phi_{0}(x) \Delta V(x) \phi_{0}(x) \, dx \]
    \[ E_{1}^{(2)} = \int e^{-\frac{1}{2} |x|^{2}} \Delta V(x) H(x, x') e^{-\frac{1}{2} |x'|^{2}} \Delta V(x') \, dx \, dx' \]
  - Both integrands involve wave functions proportional to product of exponential and Hermite polynomials leading to weight functions employed in MC importance sampling
  - Very accurate \( E_{1}^{(1)} \) approximation \( E_{1}^{(2)} \) involves high order interactions and hence not easy to approximate

Low rank approximation of integrands

- Construct a separated approximation in a suitable (sparse) low rank tensor format
  \[ f(x) \approx \sum_{i=1}^{N} \prod_{k=1}^{m} f_{i}^{k}(\bar{x}_{k}) \quad \bar{x}_{k} \subset x = \{x_{1}, \ldots, x_{d}\}, \quad \bigcup_{k=1}^{m} \bar{x}_{k} = x \]
  \[ f_{i}^{k}(\bar{x}_{k}) = \sum_{j=1}^{n_{k}} c_{i,j}^{k} \psi_{i}^{k}(\bar{x}_{k}) = \langle \psi_{i}^{k}, \psi^{k} \rangle; \quad \| \psi^{k} \|_{1} \leq \lambda_{k} \]
- 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
  \[ \int_{\Omega_{k}} f(x) \, dx \approx \sum_{i=1}^{R} \prod_{k=1}^{m} f_{i}^{k}(\bar{x}_{k}) \, d\bar{x}_{k} \]
- Low dimensional integrals can be evaluated using suitable quadrature rules
  \[ \int_{\Omega_{k}} f_{i}^{k}(\bar{x}_{k}) \, d\bar{x}_{k} \approx \sum_{j=1}^{n_{k}} \omega_{j} f_{i}^{k}(\bar{x}_{j}^{k}) \]
  A high dimensional integral is estimated via several low dimensional integrals

Current and Future Work

- **Problem 2**
  - 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
    \[ E_{2}^{(1)} = \sum_{i=1}^{\text{occ.}} \sum_{j=1}^{\text{vir.}} \sum_{a,b} \epsilon_{ij} + \epsilon_{ab} - \epsilon_{ai} - \epsilon_{bj}, \]
    where
    \[ (pq|rs) = \int dr_{1} dr_{2} \varphi_{p}(r_{1}) \varphi_{q}(r_{2}) \varphi_{r}(r_{1}) \varphi_{s}(r_{2}) \frac{\varphi_{p}(r)}{r_{1} - r_{2}} \]  
  - Evaluating the above integral is challenged by singularities (inverse of distance) and by storage/scalability

- **Key Ideas**
  - Tackle singularities in integrands using exponential sums
    \[ \frac{1}{\sqrt{a^{2} + b^{2} + z^{2}}} \approx \sum_{k=1}^{N} \omega_{k} e^{-\alpha_{k} (a^{2} + b^{2} + z^{2})} \]
  - 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