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Divide and Conquer Quantum Mechanical Methods for Phononic Applications

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Phonons from First Principles

- Vibrational frequencies calculated for individual atoms
- Complicated super cell and molecular geometries
- Model Hamiltonians for phonons once frequencies are calculated

Frequencies ~ Thz

Distances ~ nm

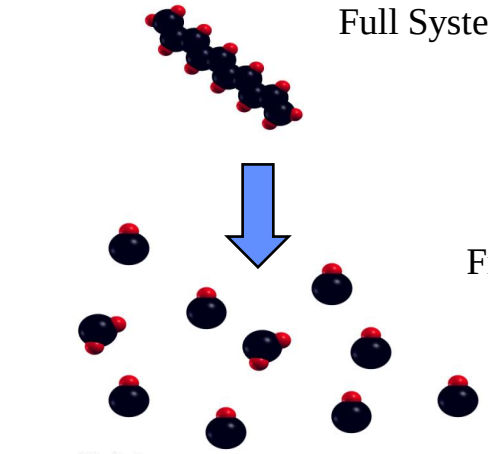
Sound speeds ~ km/sec

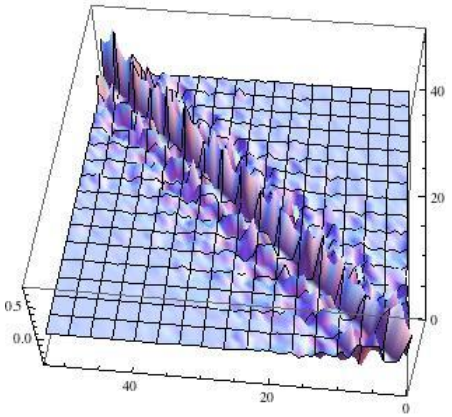
Why Quantum Mechanical Simulations?

- Quantum-inspired dynamic simulations of large systems 1000s-10000s of atoms
- Currently quantum simulations of such large sizes are limited
- Benchmark ReaxFF force field and tight-binding simulations
- Increasing the time and spatial scales of quantum informed calculations
- Test systems: Benzene, polyacetylene, CL20 clusters

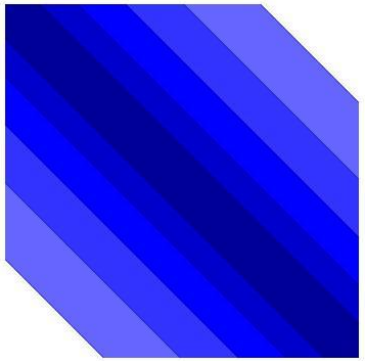
Divide and Conquer

- **Decompose many atomic system into fragments**
- **Assign buffer regions to each fragment**
- **Solve problem in each fragment**
- **Use the fragment results to obtain a global result for example for total energy**
- **Scaling as $N_{fragments} << N_{atoms}$**





Support Regions
of the Density Matrix



Graphical Representation
of the Density Matrix

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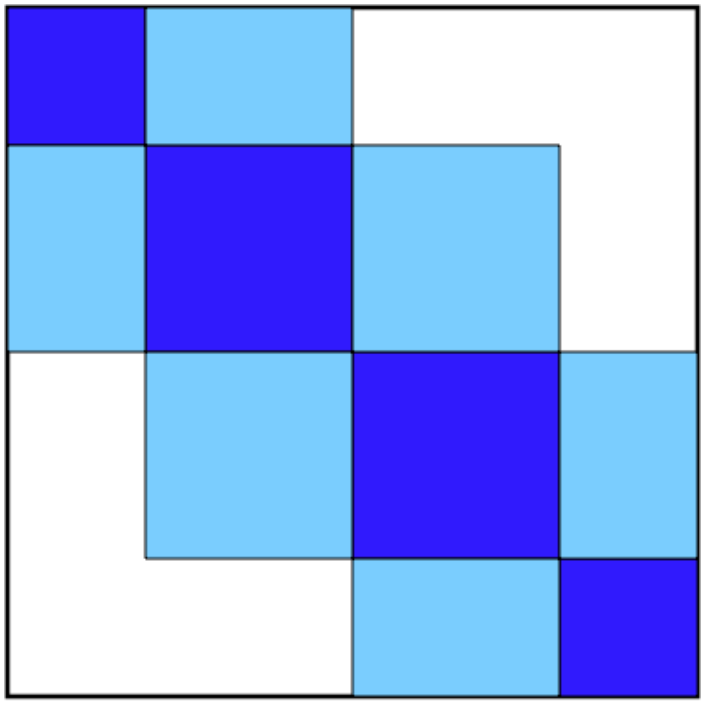
Partitioning the Density Matrix

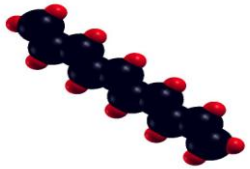


Fragment Buffer

DM(exact)=( )

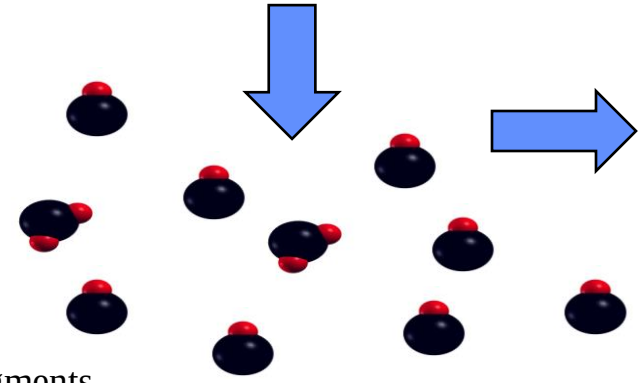
DM(Frag.)=( )

DM(Frag.+Buff.)=( )



Full System

Subsystem = Fragment + Buffer



Fragments

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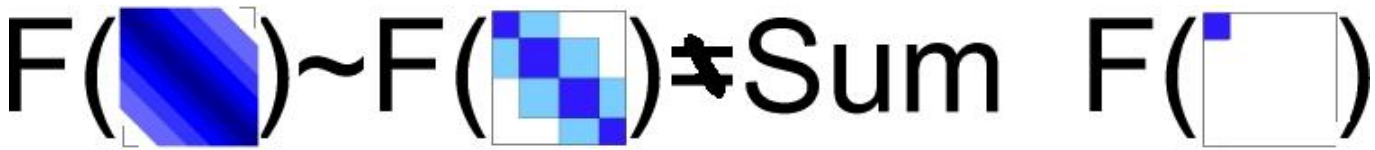
Large Matrices come into Play

$$E = Tr(DF) \approx \sum_{i=\{fragments\}} Tr(D_i F_i)$$

$$F = func(D) \overset{?}{\approx} \sum_{i=\{fragments\}} func(D_i)$$



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Forces and Vibrations

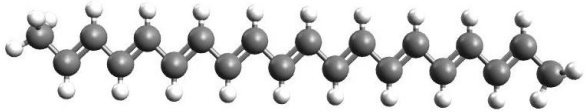
$$F_{i,x} = \left(E(x_0 + \mathrm{D}) - E(x_0) \right) / \mathrm{D}$$

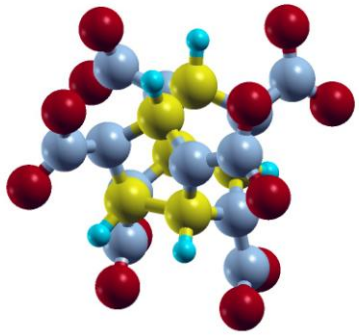
$$w^2_{ii,x} = \left(E(x_0 + \mathrm{D}) + E(x_0 - \mathrm{D}) - 2E(x_0) \right) / 4\mathrm{D}$$

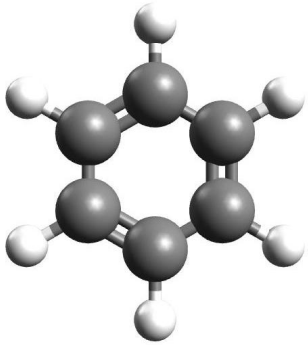
- **Total energies can be calculated in various quantum mechanical formalisms using divide and conquer techniques: DFT, semi-empirical, Hartree-Fock**

Testing on Small Systems

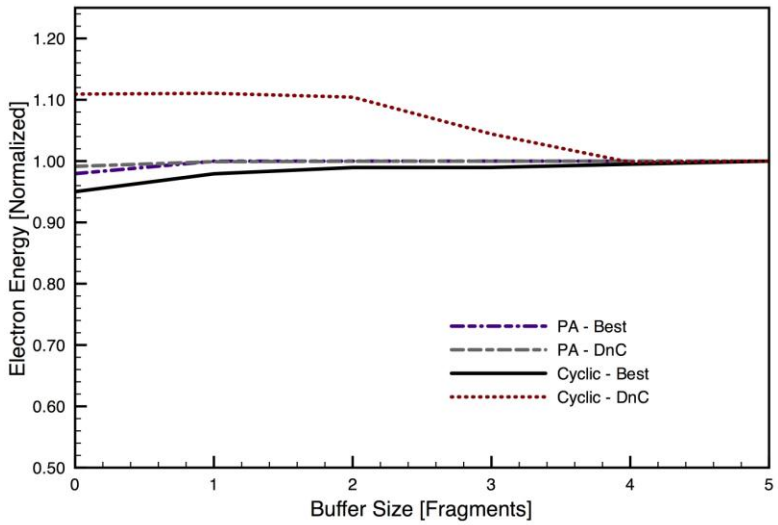
- Small systems can be calculated exactly and in the divide and conquer formalism
- Validation of method
- MINDO3 – semi-empirical

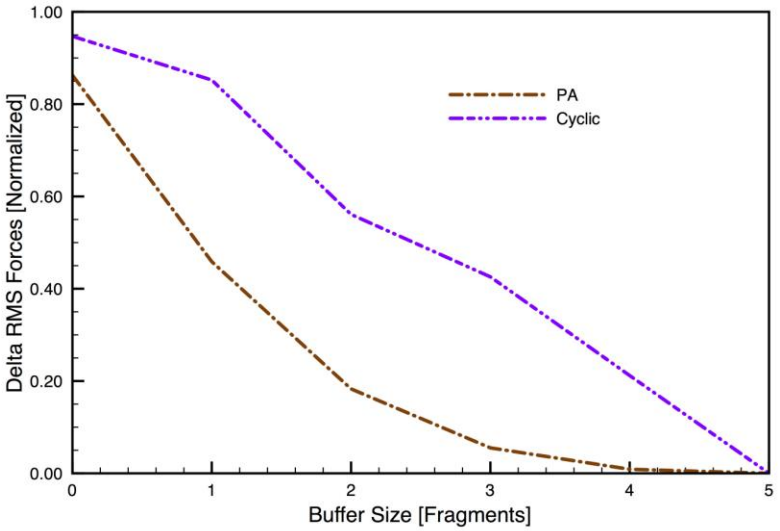






Energy Convergence

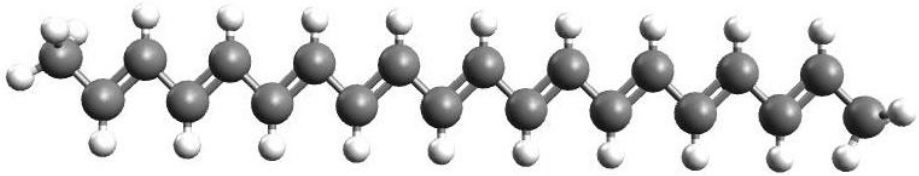


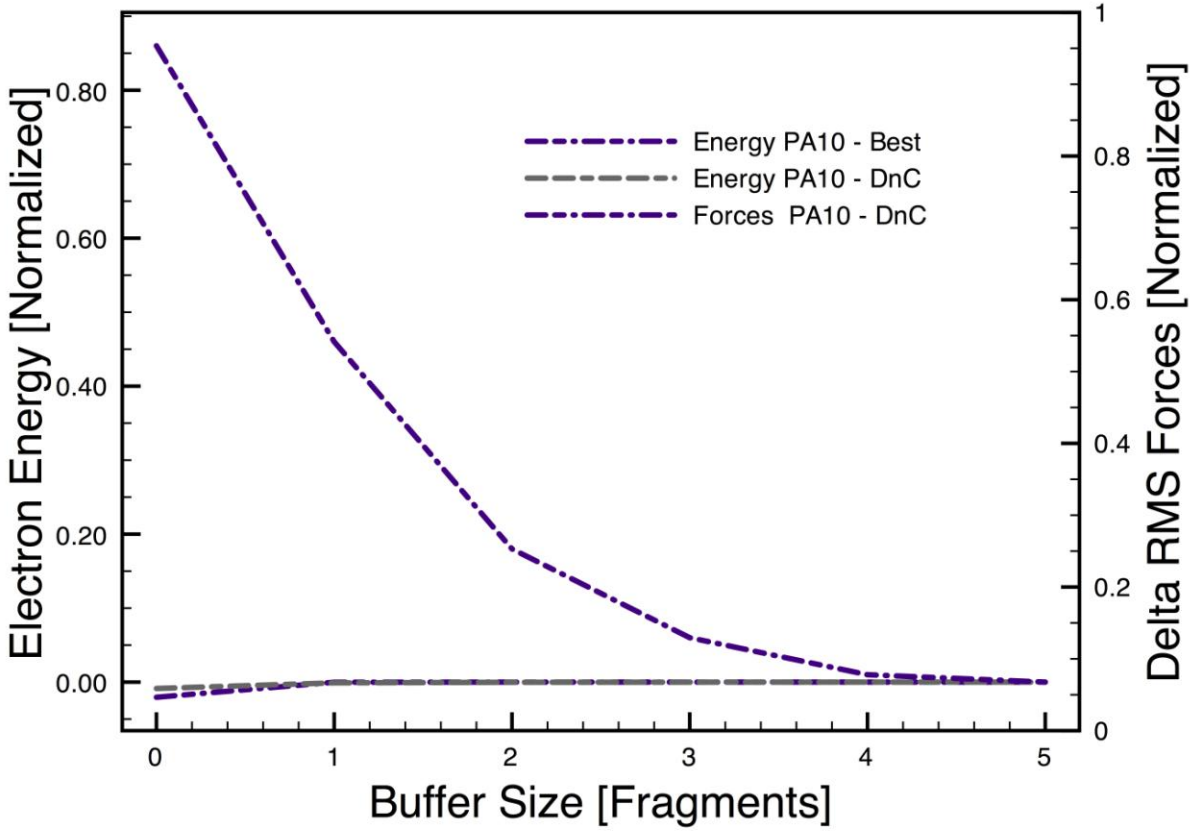


Faster for linear Poly-Acetylene than for the cyclic 10-Alkane due to Coulomb contributions from opposite sides of loop

Best indicates the result using matrix elements from the exact solution.

PA10





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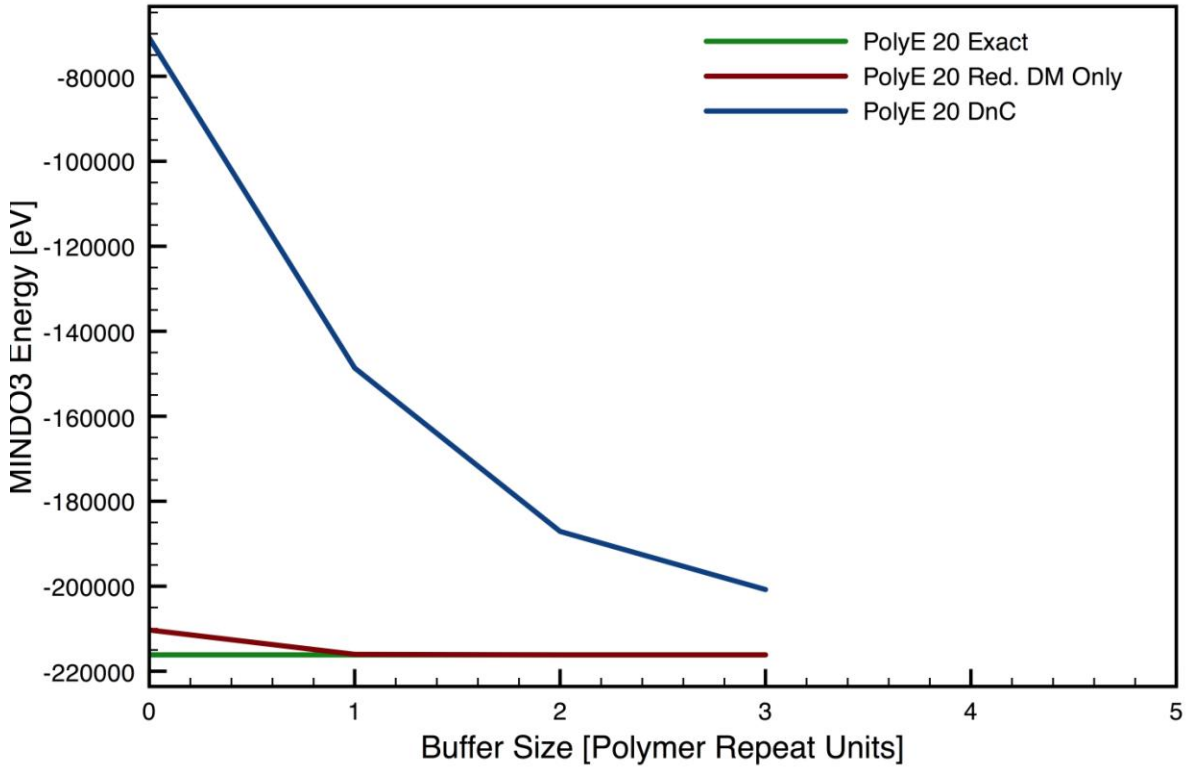
PA20



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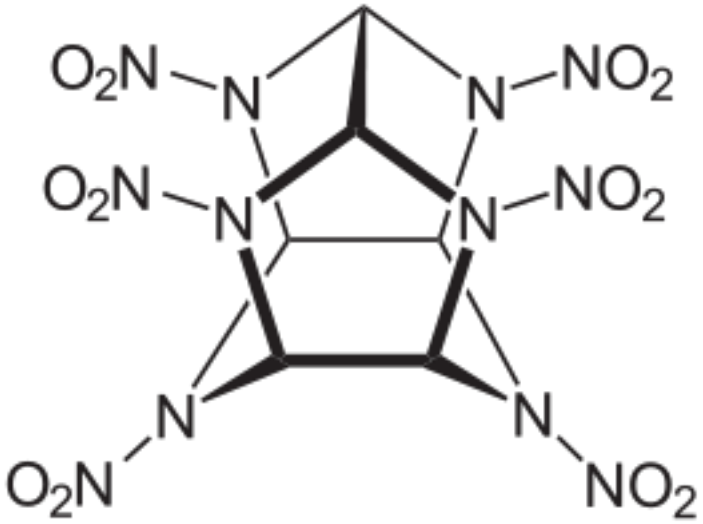
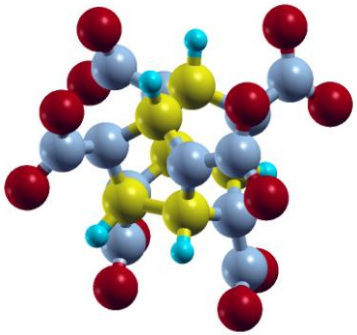
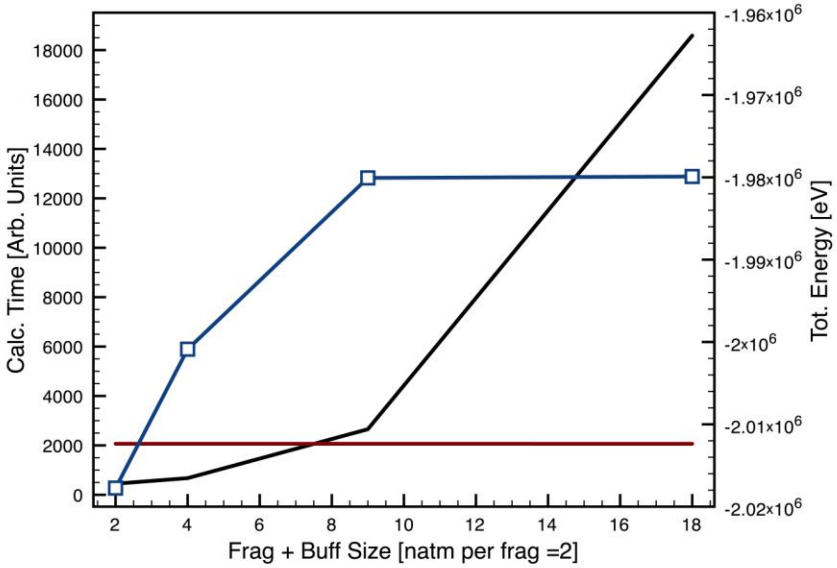
CL20 Molecule







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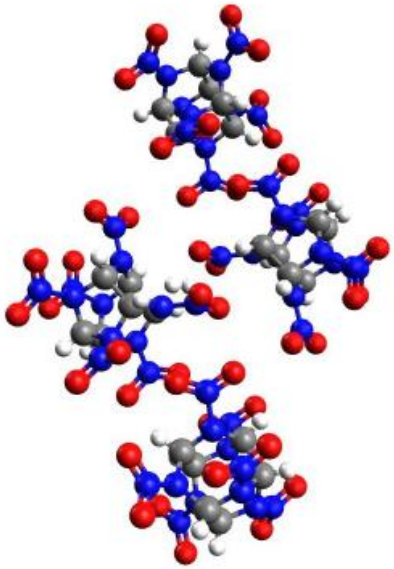
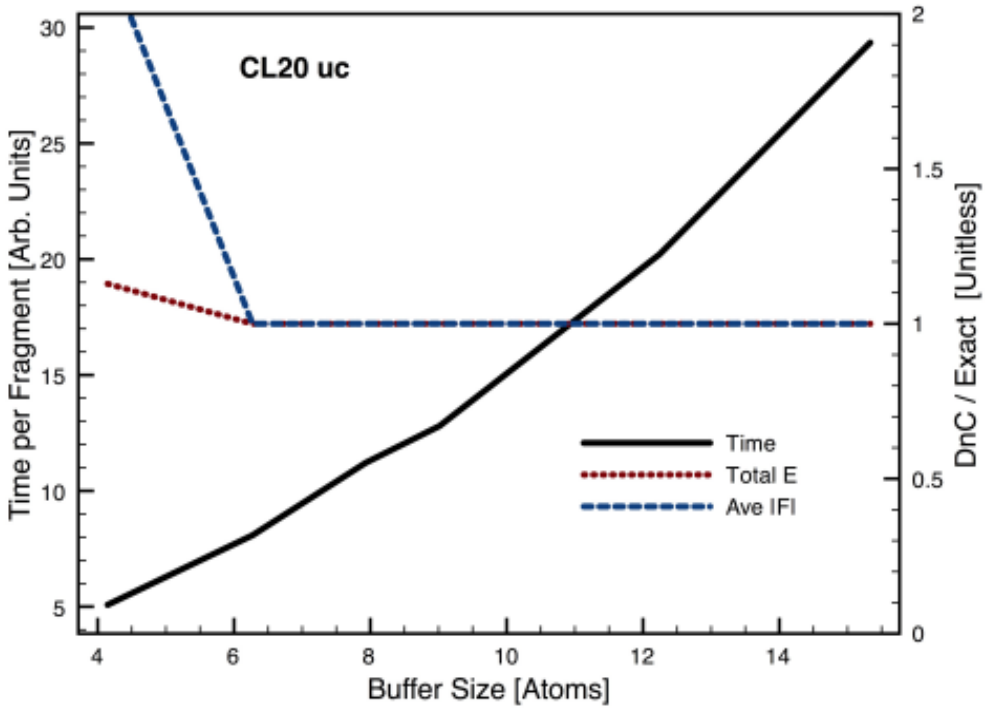
CL20 Cluster





Unit cell of crystalline CL20 with 144 atoms and 156 bonds and convergence tests with respect to the buffer size.

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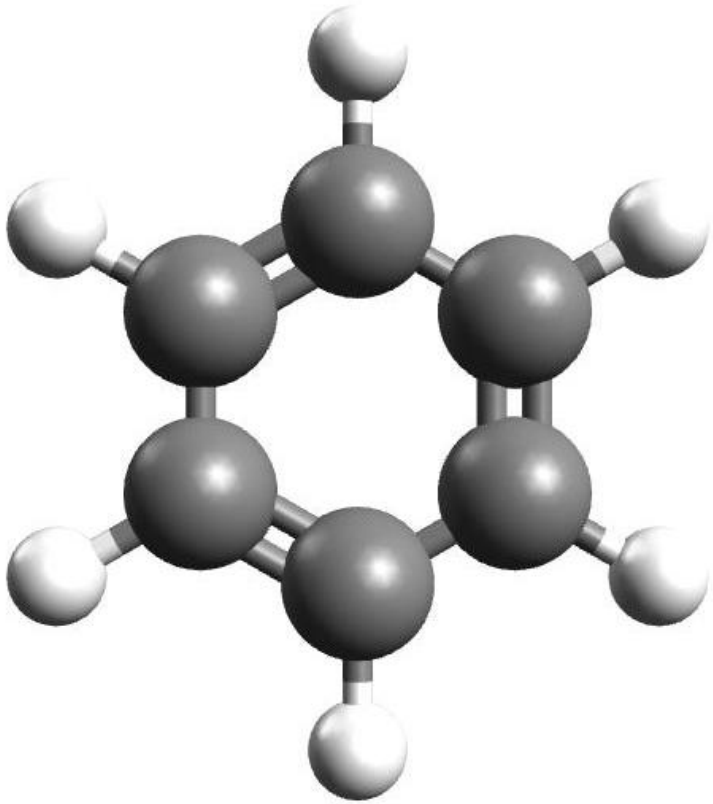
Benzene – Frequencies Expensive in Current Implementation



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Ways to Get the Most Out of DnC

- Typical 1% agreement between full calculation and DnC in total energy seems to require 3x buffer-sizes.
- Need to add classical long-range Coulomb effects into F based on information about the subsystems to reduce the need for large buffer sizes
- Possible additional improvements possible through modification of chemical potnetials of the subsystems

Work Underway

- Improve convergence for total system and fragments
- Overcome size limits in Pyquante by calling other quantum solvers
- Implement unrestricted DFT formalism
- Parallelize quantum fragment calculations
- Add inter-fragment long range forces

Conclusions

- Divide and conquer offers a powerful new tool to calculate vibrational frequencies as input for phonon band-structure calculations
- Various nanostructures are accessible
- First principles method