Phononics 2011: First International Conference on Phononic Crystals, Metamaterials and Optomechanics

Santa Fe, New Mexico, USA, May 29-June 2, 2010

PHONONICS-2011-XXXXX

SAND2011-3009C

Divide and Conquer Quantum Mechanical Methods for Phononic Applications

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Abstract: Density functional theory is a highly efficient computational framework that describes structural properties of materials such as phonon frequencies and densities of states. Applications of DFT demonstrate the theory's reliability for calculating bond lengths and phonon frequencies. One of the greatest challenges to applying DFT to general problems is the increasing computational cost required when treating larger systems. Ideally, the cost would increase linearly with the number of atoms involved, but current workhorse implementations typically increase greater than quadratically. The divide and conquer scheme that was first proposed many years ago has seen a recent resurgence in the study of energetic materials and provides a route towards linear scaling calculations of atomic forces and phonon frequencies. In this talk, we suggest how the divide and conquer scheme may be well suited to determine phononic response in materials with super-molecular scale features. We illustrate this with some examples using a computational tool newly developed at Sandia. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of the Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Phonons are manifestations of the collective vibrations of a group of nuclei held together through quantum mechanical bonds resulting from the interplay of mutually interacting electrons in allowed quantum states screening the inter-nuclear repulsions. Density functional theory provides a practical method to compute the energies and related observables of a system based in principle on only the governing equations of quantum mechanics. For bulk systems, DFT calculations are routinely used to compute the phononic band structure with reliable accuracy [1]. But the cost of DFT calculations typically scales as the cube of the number of electrons involved. For modestly large systems (beyond 1000s of atoms), full DFT calculations become impractical. Typically, phononic structures are much larger than what is possible to simulate in full DFT. Approximate solution schemes are required. Towards this end, we have developed a computer program that performs the divide and conquer algorithm [2] to obtain energies and forces on macro-molecules and clusters. The method is designed to scale linearly with the number of electrons allowing the treatment of systems magnitudes larger in size than full solve methods.

The divide and conquer algorithm in DFT and quantum chemistry reduces the computation cost of diagonalizing the Fock operator. For a system with N basis functions, this requires N^3 operations. However, the Fock matrix is sparse for many systems of interest in phononics such as single molecules and oxides, systems with an energy gap in the density of electronic states. For a sparse matrix, many of these operations are on negligibly small contributions. The divide and conquer scheme takes advantage of this sparsity by partitioning the problem into smaller sub-problems that can be diagonalized separately. If each of the sub-problems is much smaller than the total system size, the scheme effectively reduces the required computations to order N. In practice it is convenient to define buffer zones around each fragment that are included in the subsys-

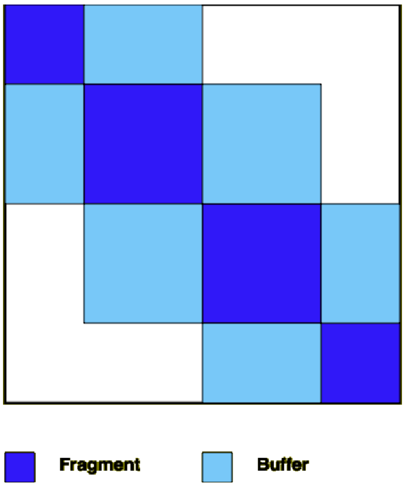

Figure 1: Graphical representation of the density matrix in a divide and conquer calculation in a local-atom centered basis. The problem is effectively only diagonalized within the blue region greatly reducing the computational cost of the method.

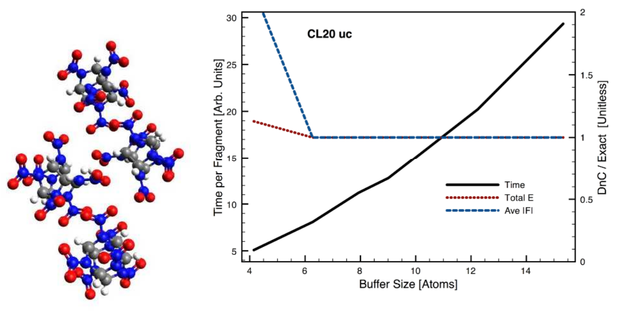

Figure 2: Unit cell of crystalline CL20 with 144 atoms and 156 bonds on the left and convergence tests with respect to the buffer size on the right.

tem calculations but do not contribute fully to the total energy.

Our implementation is for finite systems. For a given set of atom positions, the total energy is calculated using the divide and conquer method. Phonons can be related to the restoring forces experienced by each atom in a finite crystal. The restoring frequency of vibration for each atom can be calculated by perturbing the structure from equilibrium and using finite energy differences over displacements, assuming harmonic confinement. In a stable configuration of atoms, the force on each atom vanishes. The force can be calculated using differences in total energy at slightly different positions of the nuclei. $: F_{i,x} = \left(E(x_0+\Delta) - E(x_0)\right)/\Delta$. Small perturbations about the equilibrium configuration result in harmonic motion of the nuclei with a frequency that can also be determined from total energy calculations: $\omega^2_{ii,x} = \left(E(x_0+\Delta) + E(x_0-\Delta) - 2E(x_0)\right)/4\Delta$. Information about the vibrational frequencies can be used to determine the phononic spectrum once all modes are known.

In this presentation, we describe some tests on short chain polymers and units cells of energetic crystals. Accurate calculation of forces is related to accurate calculation of vibrational models. We show that divide and conquer methodology can provide accurate determinations of the forces for sufficiently large buffer regions. The accurate and fast calculation of forces is important in the description of reactions of energetic materials. In that context, the main driver for developing divide and conquer methods is the validation of yet lower cost reactive force field methods. Since phonons do not break bonds, the accurate description of phonon spectra within this formalism is an important validation step towards the goal of describing reacting detonating materials. The first version of our implementation uses a semi-empirical quantum chemistry method MINDO3, chosen here for its simplicity and speed. More accurate density functional methods will also be tested.

The tool can be applied to larger systems such as heterostructures in periodic systems, as considered by Ramprasad [3]. Another promising application for this tool is to probe the vibrational modes of large molecules allowing for the further tuning of single-molecule transistors for phonons extending the work in Ref. [4].

[1] “Phonons and related crystal properties from density –functional perturbation theory,” S. Baroni, S. de Gironcolli, and A. Dal Coso, Rev. Mod Phys. **73**, 515 (2001).

[2] "The divide-and-conquer density-functional approach: molecular internal rotation and density of states," C. Lee and W. Yang, J. Chem. Phys., **96**, 2408, (1992).

[3] “Scalability of phononic crystal hetrostructures,” R. Ramprasad and N .Shi, App. Phys. Lett. **87**, 111101 (2005).

[4] “Proposal for a single-molecule field-effect transistor for phonons,” M. G. Menezes, A. Saraiva-Souza, J. Del Nero, and R. B. Capaz, Phys. Rev. B **81**, 012302 (2010).