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Stability of Bulk Materials at High Pressure Through Improved Quantum Monte Carlo Methods: Preliminary Study on Graphene

Standard methods for electronic structure calculations of material properties like Density Functional Theory (DFT) in Local Density Approximation (LDA) or Generalised Gradient Approximation (GGA), although very successful for most cases, are not reliable for some interesting compounds which display strong electron-electron correlations. A well-known example of materials that show this kind of strong correlations is provided by transition metal oxides (4). More recently, accurate simulations of simple carbon-based material like Graphene and Graphite have shown that non-local electron-electron correlations beyond LDA or GGA strongly effect mechanical response of those materials (1). Having in mind these findings, we have chosen Graphene as a test-bench for alternative approaches to compound stability calculations by stochastic (or Monte Carlo) methods like Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC) (2). This is the first step of a long-period project focus on the application of VMC and DMC to the computation of material stability at high pressure and high temperature.

By Monte Carlo methods is possible to deal with the many-body wave-function directly, through appropriate parametrisation. In particular, we employed the code TurboRVB[1] which makes use of a so-called Jastrow factor (3) to introduce part of the non-local electron-electron correlations neglected in LDA and GGA.

Here we report results for a frozen phonon calculation of the E_{2g} phonon at Γ in Graphene. Testing of the code and simulations have been done on the Barcelona Supercomputing Center facilities[2] and on the local cluster of the host institution of this project[3].

In practise, we minimised the total energy of the system by optimising the parameters of a trial many-body wave-function, through the state-of-the-art VMC implemented in the TurboRVB code. This process has been repeated for different cells — all multiples of an orthorhombic cell containing 4 Carbon atoms — and by displacing the atoms according to the E_{2g} mode sketched in Fig. 1.

By fitting the total energy (per atom) of the various geometry, we obtained the frequencies of the E_{2g} phononic mode. Results are shown in Fig. 2. A tentative extrapolation of the VMC frequencies by taking larger cells, to be compared to LDA frequencies for the same geometries[4], is shown in the small inset of that figure.

Although a certain degree of convergence can be seen, there are still large fluctuations due to the finite size effects. Unfortunately, the VMC method we used, yet very precise, is quite expensive, and calculations for larger geometries becomes rapidly unaffordable. For this reason, we are currently considering possible alternatives — for instance DMC — to get more converged results. A full account of methods and results of our investigations on mechanical properties of Graphene will be the object of a future publication.

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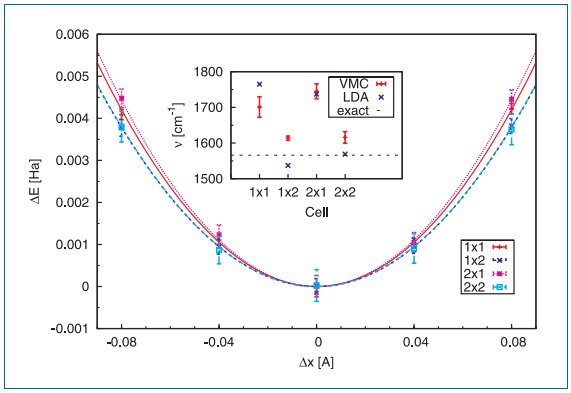

Fig. 1. – Sketch of the E_{2g} mode for Graphene. Arrows indicate the direction of the atomic displacements. Their magnitudes is not proportional to the actual displacement and they are only meant to help the visualisation of the lattice distortion.

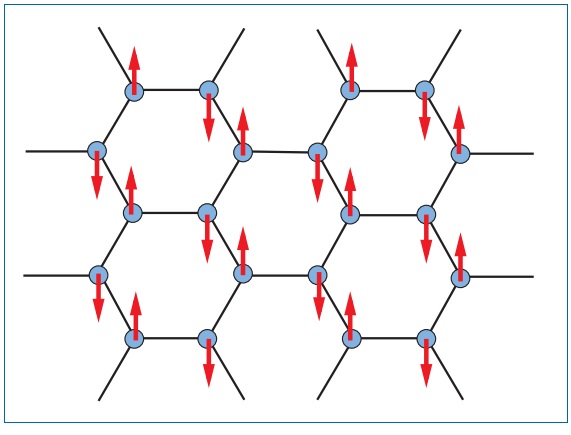

Fig. 2. – Results of VMC calculations. The increment of total energy (per atoms) due to lattice distortions are reported for several cells (see text). Parabola from a quadratic fitting of the data are also reported. In the small inset, VMC frequencies for different cells are compared to LDA calculation of the same geometries. The dotted line indicate the converged LDA value (1).

[1] see http://people.sissa.it/sorella/web/
[2] http://www.bsc.es
[3] http://nano-bio.ehu.es/
[4] for DFT calculations, we made use of the code PWSCF: see http://www.quantum-espresso.org/

References

(1) W.M.C. Foulkes, L. Mitas, R.J. Needs and G. Rajagopal, *Quantum Monte Carlo simulation of solids*, Rev. Mod. Phys., **73**, 33, (2001).
(2) M. Casula, C. Attaccalite and S. Sorella, *Correlated geminal wave functions for molecules: an efficient resonating valence bond approach*, J. Chem. Phys., **121**, 7110, (2004).
(3) W.E. Pickett, *Electronic structure of the high-temperature oxide superconductors*, Rev. Mod. Phys., **61**, 433, (1989).

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