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Structural and dynamical properties of graphite by incorporating dispersion correction: An ab-initio study

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ABSTRACT

An accurate dispersion corrected study of structural and vibrational properties of graphite using the dispersion corrected density functional theory (DFT–D) is carried out. The dispersion corrected Tkatchenko and Scheffler (TS) scheme has been implemented with generalized gradient approximation (GGA) for the exchange and correlation functional in the formalism of Perdew, Burke and Ernzerhof (PBE) in order to include the long range interactions. The structural and vibrational properties of the graphite system are improved after adding the Van der Waals interactions. The calculated low frequency dispersion corrected modes of vibration have an excellent comparison with available experimental inelastic X-ray scattering and coherent inelastic neutron scattering results.

1. Introduction

A considerable research has been performed to study the structural and vibrational properties of graphite. Yoshimori and Kitano [1] performed the first study of lattice vibration of graphite. Nicklow et al. [2] investigated normal modes of vibration of graphite lattices for high quality pyrolytic graphite by using coherent inelastic neutron scattering. Kresse et al. [3] performed vibrational study of graphite using the supercell approach and local density approximation and results were compared with neutron inelastic data for low energy modes. Piscanec et al. [4] used ab initio DFPT–GGA method in order to study the dispersion curve for graphite system. Lazzeri et al. [5] introduced Green's function approaches based on the screened electron-electron interaction. However, these interactions would be neglected in GGA and LDA approaches. Most of the theoretical calculations discussed about the underestimate or overestimate the properties of graphite. Therefore these studies have a major lack that they did not consider into account the long range interactions. In this study, these interactions are included to study the structural and vibrational properties of graphite.

2. Computational methodology

The total energy expression can be written as

$$E_{DFT-D} = E_{KS-DFT} + E_{disp}$$

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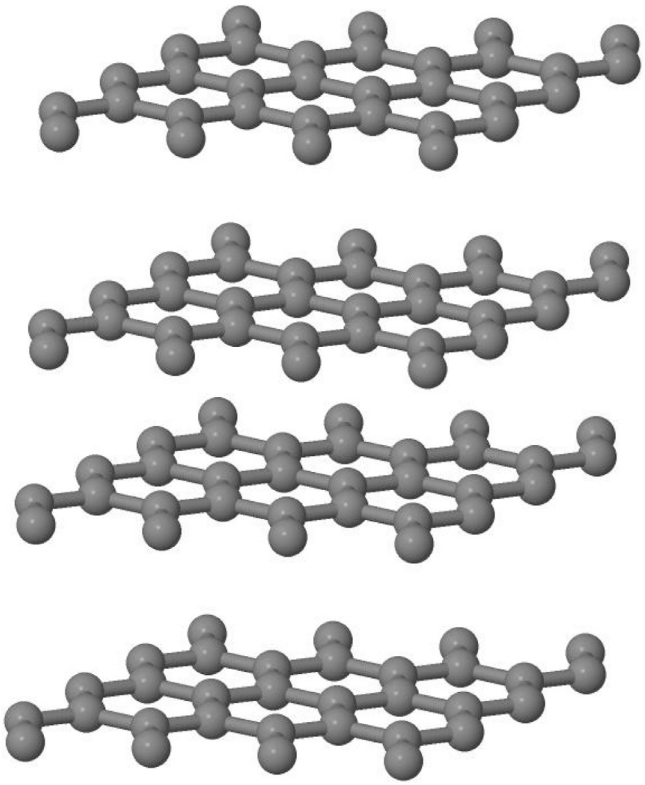

Fig. 1. The geometrically optimized supercell $(4\times4\times2)$ for graphite system.

Where E_{KS-DFT} the usual self-consistent Kohn–Sham energy [6] as is obtained from the chosen density functional and E_{disp} is an empirical dispersion correction given by

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}\left(R_{ij}\right)$$

Here, N_{at} is the number of atoms in the system, C_6^{ij} denotes the dispersion coefficient for the atom pair ij, s_6 is the global scaling factor that only depends on density functional used, and R_{ij} is an inter-atomic distance. In order to avoid near singularities for small R, a damping function f_{dmp} must be used, which is given by

$$f_{dmp}\left(R_{ij}\right) = \frac{1}{1+e^{-d\left(\frac{R_{ij}}{s_r R}-1\right)}}$$

Where R is the sum of the atomic VdW radii, d is a parameter which controls the damping function steepness and s_r is called the scaling factor [7]. The TS scheme [8] is parameter free non empirical method. The TS scheme is given by replacing the s_6 by a constant factor ½. In this scheme, the scaling factor s_r is functional dependent. The default values for s_r and d are 0.94 and 20 for TS scheme in CASTEP code. These values are sufficient for geometry optimization in graphite. However, values of s_r and d should be adjusted for vibrational properties of graphite system.

In the present study, Tkatchenko and Scheffler (TS) dispersion correction scheme along with the generalized gradient approximation for the exchange and correlation functional in the formalism of Perdew, Burke and Ernzerhoff (PBE) [9] has adopted to improve the structural and vibrational properties of graphite material. Ultra-soft pseudopotential [10] generated using on the fly scheme [11] in CASTEP [12] was used to study various properties of graphite. Cut off energy of plane wave basis was chosen to be 500 eV in order to converge the total energy within the value of 1 meV/atom. Brillouin zone was sampled at $16\times16\times8$ mesh having 25 k-points. Fast Fourier Transform (FFT) grid having a value of 2.0 was selected. For dynamical calculations, a grid $8\times8\times4$ was picked to generate the frequencies from the dynamical matrix. Finite displacement method [13] was used to perform the phonon calculations. A Supercell with $4\times4\times2$ size was selected to calculate the dispersion curve of graphite.