

FIRST-PRINCIPLES CALCULATION OF MAGNETISM IN Fe ATOM ADSORPTION ON GRAPHENE

In order to understand the initial magnetic properties of graphene, we have performed density functional theory based calculations to investigate the effect of Fe atom adsorption on graphene and the graphene-Fe stacked structure. The surface structure is modeled as a graphene layer with a vacuum region, and Fe atoms placed on the surface. In the stacked structure, alternating layers of graphene and Fe are arranged. All calculations were performed with the generalized gradient approximation of Perdew-Burke-Ernzerhof for the exchange-correlation functional and the projector-augmented wave method. According to our calculations, with increasing surface Fe coverage, the graphene surface becomes activated, reaching a peak at a specific coverage. Furthermore, in comparison to the stacked structure, one structure was found to be activated and magnetic, indicating that it was activated by Fe adsorption on the surface. Our results show that Fe atoms influence adsorption on the graphene surface.

Keywords: Density functional theory; magnetic properties; coverage; metal adsorption; graphene surface

1. Introduction

Graphene has a hexagonal structure composed of carbon atoms and possesses a variety of properties [1], including a one-atom-thick structure, strength, and excellent electrical properties. These properties have been extensively studied by researchers, mainly in materials science. Much of the theoretical work on graphene surfaces has focused on its magnetism and stability. Theoretical studies on the adsorption of metals on graphene surfaces have been reported by Hu et al., comparing the effects of various metal adsorptions on graphene surfaces [2]. Hu et al. found that transition metals, including Fe and rare metals such as vanadium, exhibit magnetism when adsorbed on graphene surfaces. Fe adsorption on graphene surfaces has been studied using density functional theory (DFT) based first-principles simulations. However, the complex adsorption mechanism remains not fully understood at the microscopic level. The spacing and position of adsorbed atoms are crucial in metal adsorption on graphene. The purpose of this study is to provide insights into the adsorption of Fe atoms on graphene from a nano-level perspective.

Although graphene is inherently nonmagnetic, it exhibits magnetism and is expected to have applications in spintronics, a field where electron spins are manipulated. Recently, Guan et al. studied transition metal adsorption on graphene nanoribbons and found that they exhibit unusual electrical properties,

affecting spin polarization and magnetism [3]. This suggests that spintronics will play an important role in a wide range of precision electronic devices [4].

In this study, as a first step to clarify the nature of adsorption on graphene, we focused on Fe, which has shown strong magnetism in previous studies, and investigated the adsorption effect of Fe atoms on graphene and the graphene-Fe interaction structure using DFT computer simulations. The results showed that the Fe-Fe interatomic distance during adsorption and the number of graphene layers adjacent to Fe have a significant effect.

2. Computational approach

Our calculations using spin-polarized DFT [5] were performed with the Quantum Espresso software package [6]. The DFT calculations were performed with the projector-augmented wave (PAW) pseudopotentials. Exchange and correlation effects were described using the generalized gradient approximation (GGA) functional of Perdew-Burke-Ernzerhof (PBE) [7].

The Kohn-Sham orbitals were expanded in a plane-wave basis set with a kinetic energy cutoff of 90 Ry (900 Ry for the charge-density cutoff). A $6 \times 6 \times 1$ k-point sampling grid was employed, along with a convergence condition of 1×10^{-8} and a smearing width of 0.02 Ry. The results of these cutoff energies

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and k-point sampling details are shown in Fig. 1. The convergence of the energies is confirmed and is sufficiently accurate.

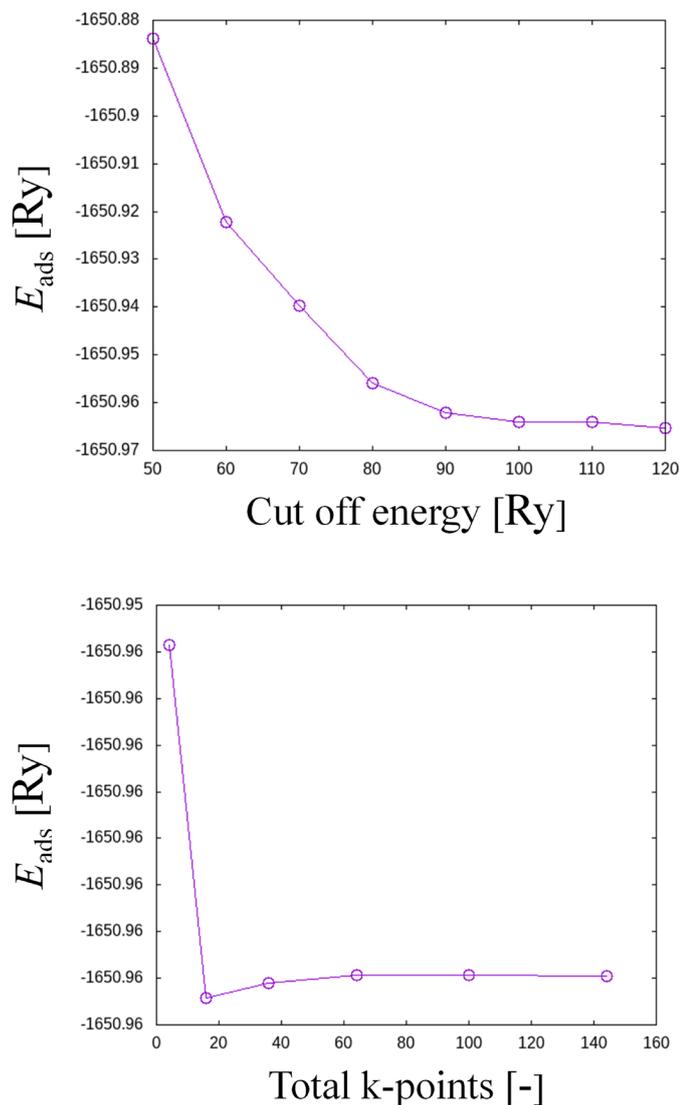


Fig. 1. Energy transition as a function of k-point and cutoff energy

The periodic boundary conditions were set so that the graphene was kept flat on the plane. To prevent the effect of the periodic boundary conditions on the Z axis, a vacuum layer of 10 Å was placed above and below the graphene, sufficiently large to prevent interactions between the neighboring Fe and graphene. Fe was adsorbed on the H sites (the centers of the hexagons).

3. Results and discussion

Confirmation of the potential of Fe atoms was calculated for a body-centered cubic (bcc) iron bulk crystal, and the lattice parameter $a = 2.860$ Å (2.867 Å [8]) is in good agreement with the experimental value. The bulk modulus is 163.7 GPa (165.0 GPa [9]), which is in excellent agreement with the experimental value.

Checking the carbon atomic potential was calculated using diamond and graphite structures. For the diamond structure,

the lattice constant is 3.57 Å (3.56 Å [10]), which is in good agreement with the experimental value. The bulk modulus is 421.5 GPa (420.0 GPa [11]), which agrees well with the experimental value. In the graphite calculations, the lattice constants are $a = 2.47$ Å (2.46 Å [12]) and $c = 6.91$ Å (6.71 Å [12]), which agree well with the experimental value. The calculated lattice constants were used as input parameters for the calculation.

Fig. 2 shows the unit lattice in the adsorption structure where one Fe atom is adsorbed on a single graphene layer and the ratio of Fe atom coverage (θ) is varied.

The adsorption energy for each structure was calculated as

$$|E_{ads}| = |E_{total} - E_{gra} - E_{Fe}| \quad (1)$$

where E_{ads} , E_{gra} , and E_{Fe} are the total energies of the whole structure, graphene, and isolated Fe atom, respectively. Therefore, a larger energy value indicates a more stable structure.

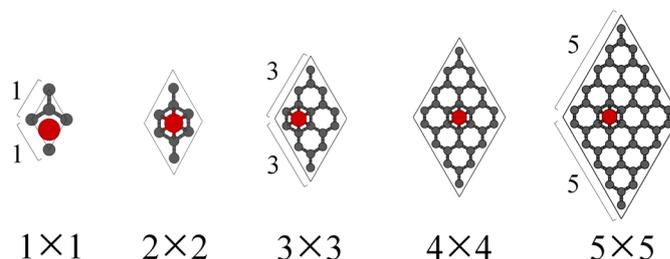


Fig. 2. Top views of the optimized structures of Fe adsorbed on the graphene surface: starting with the 1×1 unit cell, we created four different sizes of rhomboid graphene (2×2 to 5×5) based on this unit cell and adsorbed one Fe atom onto each

Fig. 3 illustrates the change in adsorption energy as a function of Fe atom coverage (θ), both with and without considering electron spin. Since the energy value decreases significantly when spin is not taken into account, it is likely that electron spin plays a significant role in the stability of the structure.

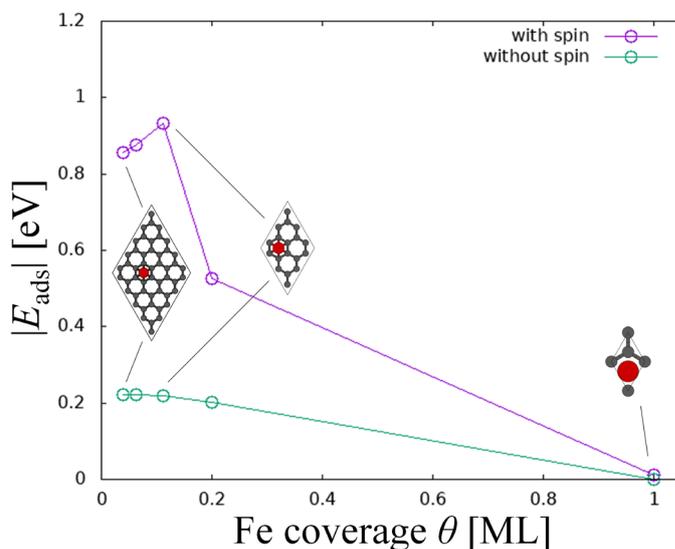


Fig. 3. Calculated adsorption energies ($|E_{ads}|$) with and without electron spin as a function of Fe atom coverage (θ)

The interatomic distance of a molecule with covalent bonds reaches a minimum at a certain distance, beyond which the energy increases and the molecule becomes unstable. [13]. This peak at a 3×3 coverage is also considered to be the distance at

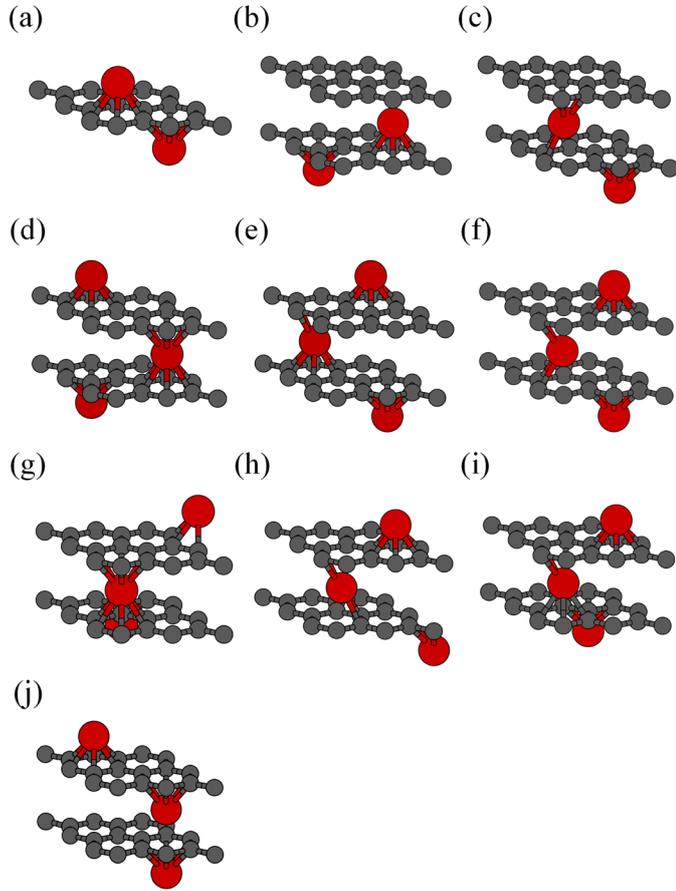


Fig. 4. Views of the optimized stacked structures with alternating layers of graphene and Fe: (a) consists of one graphene layer and two Fe, (b) and (c) consist of two graphene layers and two Fe, and (d)–(j) consist of two graphene layers and three Fe

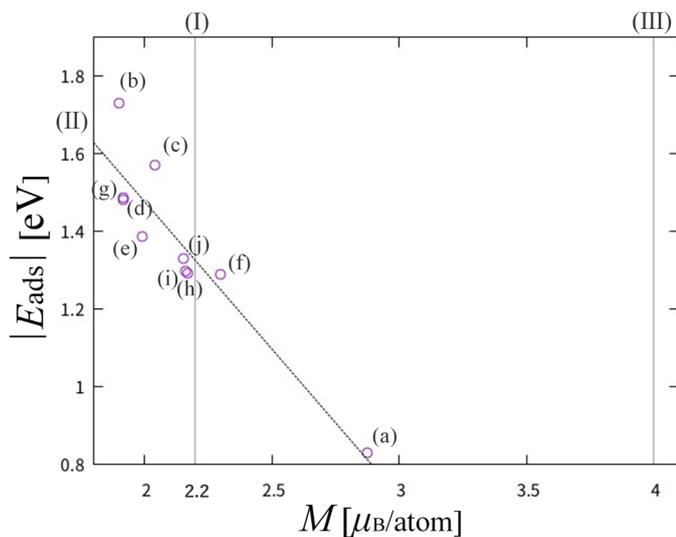


Fig. 5. Calculated adsorption energies ($|E_{ads}|$) as a function of magnetic moment (M): (I) magnetic moment of the Fe crystal (BCC), (II) approximation line in (a)–(j), and (III) magnetic moment of an isolated Fe atom

which Fe molecules remain stable on graphene. This finding represents an important step in understanding the underlying mechanism of the adsorption process on graphene.

Fig. 4 shows a structure of alternating layers of graphene and Fe based on 3×3 coverage. They are shown as an optimized geometry. Fig. 5 shows the relationship between the adsorption energy $|E_{ads}|$ and the magnetic moment M for structures (a)–(j).

As the magnetic moment decreases, the adsorption energy tends to increase. This result indicates that energy stability is lost when magnetic properties occur in the structure.

Fig. 6 presents the density of states (DOS) results for the system shown in (f). Fe2, which is adjacent to two layers of

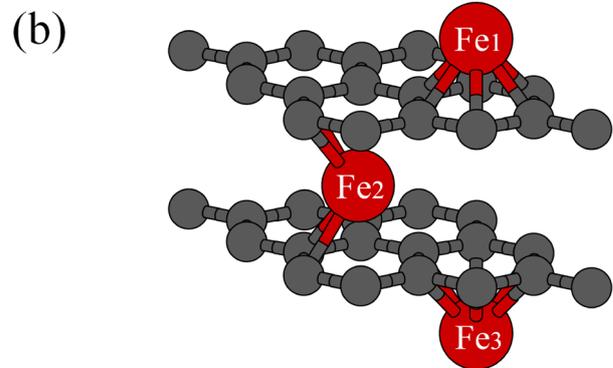
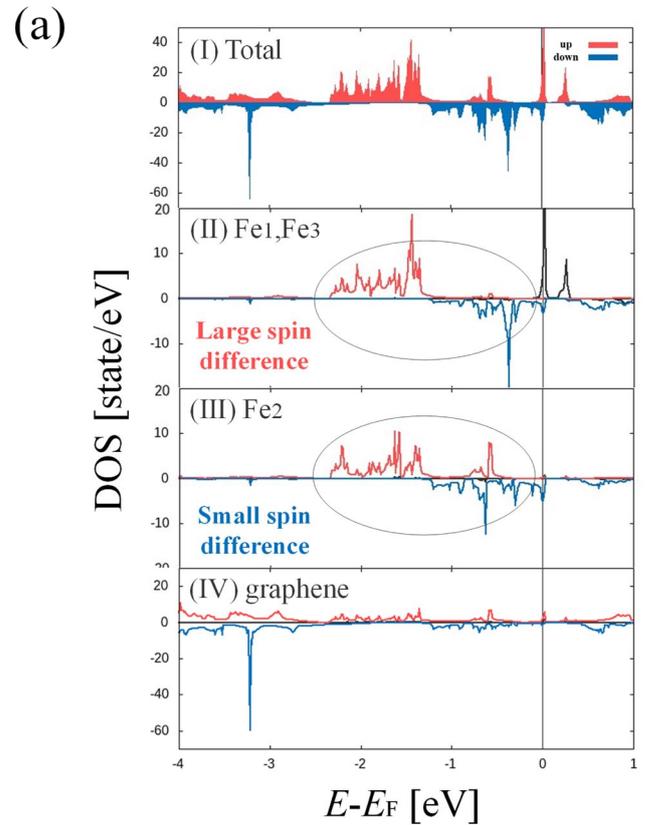


Fig. 6. Density of states analysis in a multilayered structure. (a) Plot of the density of states (DOS) for (f) relative to energy of the entire structure minus the Fermi energy ($E-E_F$): (I) Density of states for entire structure, (II) Density of states for isolated Fe1 and Fe3 atoms, (III) Density of states for the isolated Fe2 atom, (IV) Density of states for isolated graphene. (b) Structure with labels assigned to each of the three Fe atoms

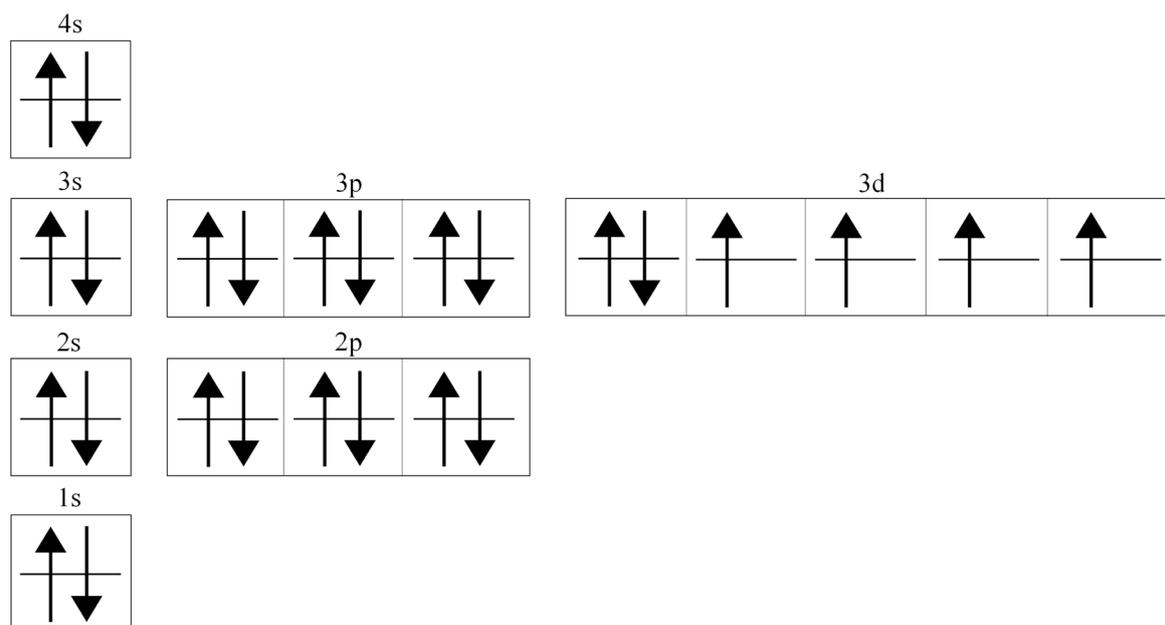


Fig. 7. Electron configuration of Fe in the different orbitals

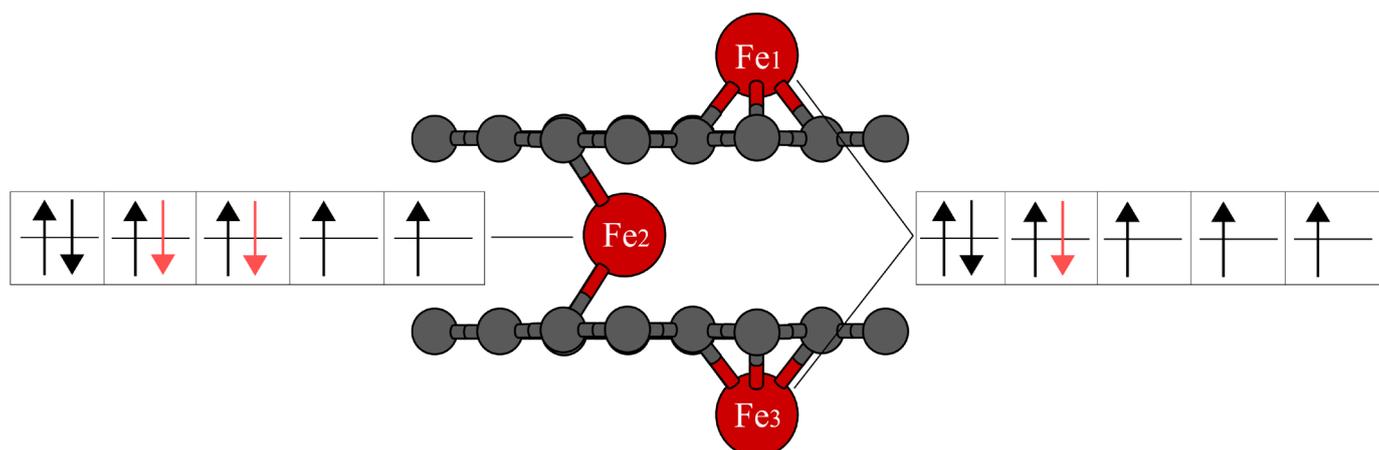


Fig. 8. Schematic illustrating electron sharing between the iron atoms and graphene in (f). Red arrows indicate the electrons from graphene that are shared with the Fe atoms

graphene, shows a small difference between the up-spin and down-spin states and contributes a small magnetic moment. In contrast, Fe1 and Fe3, which are adjacent to a single layer of graphene, exhibit a pronounced difference between the up-spin and down-spin states and significantly affect the graphene's electronic properties.

Fig. 7 shows the electron configuration of Fe. Fe has 6 electrons in the 3d shell. According to the Pauli exclusion principle, no two electrons can have the same set of quantum numbers. Therefore, if two electrons occupy the same orbital, they must have opposite spins. In this arrangement, the magnetic moments of paired electrons cancel out. However, the presence of unpaired electrons in the 3d orbitals gives rise to Fe's magnetism, making Fe one of the most magnetic metals, as unpaired electrons contribute to its overall magnetic moment.

Fig. 8 shows a schematic diagram of charge transfer between Fe and graphene. As more graphene layers come into

contact with Fe, electrons are transferred from graphene to Fe, leading to a decrease in the number of unpaired electrons in Fe. Consequently, as the number of graphene layers in contact with Fe increases, its magnetic properties decrease.

4. Conclusions

DFT calculations were used to study the influence of Fe coverage on the graphene surface and the stacked structure, consisting of alternating layers of graphene and Fe. In conclusion, as Fe coverage on the surface increases, the surface becomes more activated, with the strongest adsorption occurring at a 3×3 coverage. In the stacked adsorption system, density of states analysis suggests that electron transfer from Fe atoms adjacent to a single layer of graphene to the graphene layers is more likely.

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REFERENCES

- [1] Changgu Lee, Xiaoding Wei, Jeffrey W. Kysar, James Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* **321**, 385-388 (2008). DOI: <https://www.science.org/doi/full/10.1126/science.1157996>
- [2] Leibo Hu, Xianru Hu, Chenlei Du, Yunchuan Dai, Jianbo Deng, Density functional calculation of transition metal adatom adsorption on graphene. *Physica. B* **405**, 3337-3341 (2010). DOI: <https://iopscience.iop.org/article/10.1088/0953-8984/20/11/115209>
- [3] Zhaoyong Guan, Shuang Ni, Shuanglin Hu, *ACS Omega* **6**, 5900, 2020. DOI: <https://doi.org/10.1021/acsomega.9b04154>
- [4] Wei Han, Roland K. Kawasaki, Martin Gmitra, Jaroslav Fabian, Graphene spintronics. *Nat. Nanotechnol.* **9**, 794 (2014). DOI: <https://doi.org/10.1038/nnano.2014.214>
- [5] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter.* **21** 395502 (2009). DOI: <https://iopscience.iop.org/article/10.1088/0953-8984/21/39/395502>
- [6] W. Kohn, L. Sham, Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev. A* **140**, 1133-1138 (1965). DOI: <https://journals.aps.org/pr/abstract/10.1103/PhysRev.140.A1133>
- [7] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865-3868 (1996). DOI: <https://doi.org/10.1103/PhysRevLett.77.3865>
- [8] <http://webelements.com/>
- [9] W. Zhong, G. Overney, D. Tomanek, Structural properties of Fe crystals. *Phys. Rev. B* **47**, 95-99 (1993). DOI: <https://doi.org/10.1103/PhysRevB.47.95>
- [10] Helen M. J. Smith, The theory of the vibrations and the Raman spectrum of the diamond lattice. *Philos. T. R. Soc. A* **241**, 105-145 (1948). DOI: <https://doi.org/10.1098/rsta.1948.0010>
- [11] T. Kondo, H. Sawamoto, A. Yoneda, M. Kato, A. Matsumuro, T. Yagi, T. Kikegawa, The use of sintered diamond anvils in the MA8 type high-pressure apparatus. *Pure. Appl. Geophys* **141**, 601-611 (1993). DOI: <https://doi.org/10.1007/BF00998347>
- [12] Y. Ishizawa, Tanngennisou graphite no seisitu to sono ouyou (in Japanese) [Properties of monoatomic layer graphite and its applications] *Gypsum & Lime* **247**, 481-489(1993). DOI: <https://doi.org/10.11451/mukimate1953.1993.481>
- [13] <https://ch301.cm.utexas.edu/section2.php?target=atomic/bonding/covalent-bonding.html>