Supplemental material to "Spin relaxation mechanism in graphene: resonant scattering by magnetic impurities."

Denis Kochan, Martin Gmitra, and Jaroslav Fabian

Institute for Theoretical Physics, University of Regensburg,
93040 Regensburg, Germany

Details to first-principles calculations.

Density functional theory [1] has been used to calculate the electronic structure of hydrogenated graphene in the supercell approach. We used the generalized gradient approximation for the exchange-correlation functional [2]. The atomic positions in the supercell calculations have been relaxed using the quasi-newton algorithm based on the trust radius procedure implemented within the plane wave pseudopotential code Quantum ESPRESSO [3]. For the atomic species we have used ultra-soft pseudopotentials [4, 5] with PBE exchange-correlation functional [2] with kinetic energies cut-offs of 30 Ry for the wave function and 300 Ry for the density. The vacuum of 15 Å to separate the hydrogenated graphene planes has been used. We found that the covalent C-H bond length d_H is close to 1.13 Å. Next-nearest distance a between the three closest carbon atoms to the hydrogenated carbon, a tetrahedral edge length, is 2.516 Å. The hydrogen bonding distorts the graphene plane by pulling the hydrogenated carbon atom out of plane by about 0.36 Å.

The relaxed structure was then used in the full-potential spin-polarized self-consistent calculations using the linearized augmented plane wave (FLAPW) method as implemented in the FLEUR code [6] in the film mode. We used the cut-off parameter for the plane wave-expansion $k_{max} = 4.7$ bohr^{-1} and 64 k-points in the irreducible wedge of the Brillouin zone. The muffin-tin radii for carbon of 1.32 bohr and for hydrogen 0.81 bohr were used.

Spin-polarized band structure of hydrogenated graphene.

The electronic structure of a relaxed 5×5 supercell with a single H atom on top of a C atom (denoted below as C_H) has been calculated using the FLEUR code [6]. Figure 1(a-f) shows the results. The valence and conduction bands are separated at K point due to covalent bonding of carbon p_z and hydrogen s orbitals by about 1 eV. In between lies the mid-gap band formed mainly by p_z orbitals of C atoms closest to H. The ground state is ferrimagnetic, for details see Fig. 1(c-e). The magnetic moment is significant in a close neighborhood of C_H only, oscillating as a function of position. The largest moment, of 0.054 μ_B, is on the nearest neighbors to C_H. Hence

the spin splitting of the mid-gap states is maximal and gradually decreases for the bands away from the Fermi level, whose character is less influenced by the H. Employing criterion for the formation of magnetic moment [7], we conclude that hydrogen adatom on graphene creates a stable magnetic moments formation. In supercell calculations, however, these magnetic moments are periodically repeated, which can lead to an artificial coupling due to long-range interactions [7, 8]. Defect induced magnetism on graphene and its underlying magnetic texture are in focus of intensive discussion [9–14]. We note that particular magnetic ordering for the present study is not inevitable.

To parameterize the first-principles data, we have extended the hopping Hamiltonian studied in Refs. [15–17]. The scheme is in Fig. 1(g). The orbital effects due to H are captured by on-site energy ε_h and hopping T. To this we add local Zeeman couplings J_h, J_1 and J_2, on the sites of large magnetic moments, inspired by Fig. 1(f). The impurity Hamiltonian H'_{eff}, which is added to graphene's $H_0 = -t \sum_{\langle m,n \rangle} c_m^\dagger c_n$ ($t = 2.6$ eV) is

$$H'_{eff} = \sum_\sigma h_\sigma^\dagger (\varepsilon_h - J_h \sigma) h_\sigma + T(h_\sigma^\dagger c_{C_H,\sigma} + c_{C_H,\sigma}^\dagger h_\sigma)$$
$$- J_1 \sum_{m_1,\sigma} \sigma\, c_{m_1,\sigma}^\dagger c_{m_1,\sigma} - J_2 \sum_{m_2,\sigma} \sigma\, c_{m_2,\sigma}^\dagger c_{m_2,\sigma} \,.$$

$$\tag{1}$$

Here $h_\sigma^\dagger$ (h_σ) and $c_\sigma^\dagger$ (c_σ) are fermionic creation (annihilation) operators acting on the hydrogen and graphene carbon sites, respectively. Subscript $\sigma = \{\uparrow, \downarrow\} = \{+1, -1\}$ stands for the spin component along the z-direction (quantization axis). Subscripts m_1 and m_2 label the three first-nearest and the six second-nearest neighbors of C_H.

Orbital parameters $\varepsilon_h = 0.16$ eV and $T = 7.5$ eV were fitted already in Ref. [17]. Least-square fitting the model Hamiltonian H'_{eff}, Eq. (1), to our supercell spin-polarized first-principles data, gives $J_h = -0.82$ eV, $J_1 = 0.69$ eV, and $J_2 = -0.18$ eV. We fitted the valence, mid-gap, and conduction bands at 100 equidistant points along $\Gamma - K - M - \Gamma$ lines in Brillouin zone. The fits, shown in Fig. 1(a) and detailed in Fig. 1(c-e), are remarkably good especially around K. We find that J_h alone controls the exchange splitting of the valence and conduction bands in a large region around K point.