Spin-orbit coupling in hydrogenated graphene

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First-principles calculations of the spin-orbit coupling in graphene with hydrogen adatoms in dense and dilute limits are presented. The chemisorbed hydrogen induces a giant local enhancement of spin-orbit coupling due to $sp^3$ hybridization which depends strongly on the local lattice distortion. Guided by the reduced symmetry and the local structure of the induced dipole moments we use group theory to propose realistic minimal Hamiltonians that reproduce the relevant spin-orbit effects for both single-side semihydrogenated graphene (graphone) and for a single hydrogen adatom in a large supercell. The principal linear spin-orbit band splittings are driven by the breaking of the local pseudospin inversion symmetry and the emergence of spin flips on the same sublattice.

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Spin-orbit coupling is central for a variety of spintronics phenomena \cite{1 2} such as spin relaxation, spin transport, or topological quantum spin Hall effects. Itinerant electrons in graphene have weak spin-orbit coupling as they are formed from $p_z$ orbitals. The Dirac cones are separated by what is called intrinsic spin-orbit coupling of $2\lambda_I = 24 \mu \text{eV}$ due to $p_z-d$ mixing \cite{3 4}. This small value is desirable for long spin lifetimes, but experiments suggest \cite{7 10} that spin relaxation is governed by much stronger spin-orbit, or perhaps magnetic \cite{11}, interactions than the intrinsic one. Potential culprits are light adatoms \cite{12 14} which are typically not important for momentum scattering but may be essential for spin-flip scattering. On the other hand, large spin-orbit coupling, when controlled, is desirable for engineering robust quantum topological phases in graphene covered with heavy adatoms \cite{15 17}.

Hydrogen is an ideal light adatom to study induced spin effects in graphene. Not only can it produce local magnetic moments \cite{18 21}, as recently experimentally demonstrated \cite{22}, but it should also enhance graphene’s spin-orbit coupling (SOC), as proposed in Ref. \cite{12}. Unlike for heavy adatoms whose cores can directly contribute to SOC, the enhancement of SOC from hydrogen is solely due to $sp^3$ hybridization facilitated by local structural deformation. The SOC effects can thus directly probe $sp^3$ phenomena in graphene.

The presence of both magnetic moment and large spin-orbit coupling makes the spin physics exciting, but also challenging to explain the spin relaxation experiments. To disentangle the two contributions, as well as to see what new phenomena they can lead to, it is important to consider them separately. Here we present a quantitative and qualitative study of SOC induced by hydrogen on graphene in two limits. One is the dense limit, represented here by single-side semihydrogenated graphene (also called graphone) \cite{23}. This structure is relatively simple and allows for a quantitative analysis of the $sp^3$ hybridization effects on various spin-orbit parameters. Our results indeed show a giant enhancement of SOC, strongly dependent on the buckling deformations of this structure. We introduce a single-band and tight-binding Hamiltonians to describe the main SOC effects. In particular, we show how pseudospin inversion asymmetry (PIA) introduces new terms (we call them PIA SOC), which couple the opposite spins on the same sublattice, in addition to Bychkov-Rashba nearest neighbor hoppings.

We also quantify the local spin-orbit structure and propose a minimal realistic SOC Hamiltonian in the dilute limit, represented by large supercells (starting with $5 \times 5$), intensively studied for orbital effects \cite{24 27}. Based on first-principles calculations we demonstrate a giant local—and we identify the local impurity region from the dipole moments distribution—enhancement of SOC due to $sp^3$ hybridization and formulate a minimal realistic SOC hopping model. We believe that this is a benchmark model to study spin relaxation, spin transport, but also weak (anti)localization \cite{11 25} phenomena in which spin-flip and spin-orbit scattering play an important role.

**Dense limit:** single-side semihydrogenated graphene (SHG). The effects of $sp^3$ hybridization on SOC are studied using single-side semihydrogenated graphene [inset in Fig. 1(a)] with different degrees of out-of-plane lattice distortion $\Delta$ of the hydrogenated carbon site which is on sublattice A. The C-H bond length $d_H$ is 1.13 Å, and we take the lattice constant to be the relaxed distance $a \approx 2.516$ Å between the nearest neighbors around the adatom site in the supercell calculations below; in graphene the lattice constant is 2.46 Å. (The relaxed SHG structure of lattice constant 2.535 Å would have $\Delta/a = 9.7\%$ and the $sp^3$ tetrahedron 20.41\%.) In examples we choose $\Delta/a = 14\%$ which corresponds to relaxed large supercell structures.

To study SOC effects we restrict the computational basis to be spin unpolarized. The calculated electronic structure and the projected local density of states for SHG are shown in Fig. 1(top) for $\Delta/a = 14\%$. Compared to graphene, in which $\pi$ and $\pi^*$ bands without SOC touch...
at K \cite{29}, the C-H bonding pulls them apart: the π band, which at K comes mainly from sublattice A, is shifted to about 5 eV below the Fermi level (the GW approximation predicts a greater shift by about 2 eV \cite{19}). The π∗ band, which comes from sublattice B, lies at the Fermi level. This band, which we consider for our SOC analysis, is narrow since the nearest-neighbor hopping is inhibited for \(p_z\) electrons on B. The inset in Fig. 1(a) shows the π∗ probability density at K that has the \(p_z\) character on sublattice B.

Hamiltonian can be expressed via the spin Pauli matrices \(\sigma\). The small group of K (Γ) is \(C_3\) (\(C_{3v}\)). Up to terms linear in momentum, which is here measured from K and Γ, the SOC Hamiltonians compatible with those symmetries are

\[
\mathcal{H}_{\text{eff}}^K = \lambda^K_{\text{BR}}(k_x \hat{s}_y - k_y \hat{s}_x) + \tau \lambda I \hat{s}_z, \quad (1)
\]

\[
\mathcal{H}_{\text{eff}}^\Gamma = \lambda^\Gamma_{\text{BR}}(k_y \hat{s}_x - k_x \hat{s}_y). \quad (2)
\]

Here \(\tau = 1\) \((-1)\) stands for K (Γ), \(\lambda_1\) is the adatom-modified intrinsic spin-orbit coupling and \(\lambda_{\text{BR}}\) is the adatom-induced (Bychkov-Rashba-like as in semiconductor physics \cite{30}) spin-orbit coupling. We will see that the latter comes from the space and pseudospin inversion asymmetry. Contrary to graphene, the BR SOC at K depends on the momentum magnitude. Higher-order terms in \(\mathcal{H}_{\text{eff}}^K\) and \(\mathcal{H}_{\text{eff}}^\Gamma\) are presented in \cite{31}.

Figure 1 (bottom) shows the extracted SOC parameters as functions of \(\Delta/a\). The intrinsic SOC \(\lambda_1\) is obtained from the splitting of the band at K, see inset in Fig. 1(c). Parameter \(\lambda^K_{\text{BR}}\) is extracted by fitting the linear dependence of the ratio of the spin expectation values, \(\langle \hat{s}_x \rangle/\langle \hat{s}_y \rangle\) \(k_z=0 = \lambda^K_{\text{BR}} k_y / \lambda_1 + O(k_y^2)\), close to K. The trigonally warped spin texture around K is shown in the inset of Fig. 1(d) and can be described by higher-order terms in \(\mathcal{H}_{\text{eff}}^K\). Finally, \(\lambda^\Gamma_{\text{BR}}\) is obtained by fitting the spin splitting at Γ, see inset in Fig. 1(e). SOC is significantly enhanced in comparison to graphene. Directly comparable is the intrinsic SOC parameter whose value in graphene is \(2\lambda_1 = 24\) μeV \cite{4}.

The above single-band model can be obtained from a tight-binding (TB) Hamiltonian using the carbon \(p_z\) and hydrogen \(s\) orbital basis. The Hamiltonian contains orbital and SOC parts, \(\mathcal{H} = \mathcal{H}_{\text{orb}} + \mathcal{H}_{\text{so}}\). We denote by \(c^\dagger_{i\sigma} = (a^\dagger_{i\sigma}, b^\dagger_{i\sigma})\) and \(c_{i\sigma} = (a_{i\sigma}, b_{i\sigma})\) the creation and annihilation operators for the \(p_z\) orbitals on the sublattices (A, B), with spin \(\sigma\) and lattice site \(i\). Similarly, we define \(h^\dagger_{i\sigma}\) and \(\hat{h}_{i\sigma}\) for the hydrogen \(s\) orbitals on adatom sites \(m\). For the orbital part \(\mathcal{H}_{\text{orb}}\) we take the TB model Hamiltonian introduced in Refs. \cite{26} and \cite{32} which assumes the nearest neighbor carbon-carbon (C-C) hopping \(t = 2.6\) eV, direct carbon-hydrogen (C-H) hopping \(T\), and the adatom on-site energy \(\varepsilon_h\):

\[
\mathcal{H}_{\text{orb}} = \varepsilon_h \sum_m h^\dagger_{i\sigma} h_{i\sigma} + T \sum_{(m,i)} h^\dagger_{m\sigma} c_{i\sigma} - t \sum_{(i,j)} c^\dagger_{i\sigma} c_{j\sigma}. \quad (3)
\]

The angle brackets denote the nearest neighbors. Fitting the TB model to the first-principles band structure for \(\Delta/a = 14\%\) (distortion in the single-adatom limit, see below) we obtain \(\varepsilon_h = 3\) eV and \(T = 6.5\) eV. The values are reliable in the vicinity of K point where \(p_z\) carbon orbitals dominate the projected local DOS.

We now extract the SOC parameters for the states at K and Γ for the π∗ band which is at the Fermi level. Since this band is nondegenerate, the effective spin-orbit

FIG. 1. (Color online) Top: Calculated electronic band structure of single-side semihydrogenated graphene. (a) Sublattice resolved band structure for the distortion \(\Delta/a = 14\%\). The filled (red) circles correspond to sublattice A whereas the open (blue) to sublattice B. The circles radii correspond to the carbon atom charge densities. The inset shows the structure and the probability density of the flat band at the K point. (b) Orbital resolved local density of states. Bottom: Extracted spin-orbit coupling parameters for the π∗ band at K and Γ as functions of \(\Delta/a\): (c) Intrinsic spin-orbit coupling splitting \(2\lambda_1\) at K. The inset shows the band splitting. (d) Adatoms-induced SOC splitting \(\lambda^\Gamma_{\text{BR}}\) at K. The inset shows the spin texture around K for the lower spin-orbit split band. The in-plane components are shown by the arrows while the z component by the color map. (e) Adatoms-induced SOC splitting \(\lambda^\Gamma_{\text{BR}}\) at Γ. The inset shows the band splitting around Γ with the identified Bychkov-Rashba energy \(E_{\text{BR}} = 0.87\) μeV for \(\Delta/a = 14\%\).
only—to the one corresponding to SHG. First, the C-H covalent bonds break the space inversion symmetry and the point group reduce to $C_{6v}$. This structure inversion asymmetry induces the Bychkov-Rashba-like term $\Lambda_{BR}$. Second, the hydrogenated carbons on sublattice A cannot be interchanged with the non-hydrogenated carbons on sublattice B. This breaks the pseudospin inversion symmetry and $C_{6v}$ is reduced to $C_{3v}$. The effect of the latter reduction is twofold: (i) The intrinsic SOC depends on the sublattice: $\Lambda_{A}$ and $\Lambda_{B}$; (ii) New SOC terms emerge due to the pseudospin inversion asymmetry, $\Lambda_{PIA}$ and $\Lambda_{PIB}$, discussed below.

As the hydrogen $s$ orbitals do not directly contribute to SOC, we can express the SOC TB Hamiltonian in the $p_{z}$ basis. In the next-nearest-neighbor limit this Hamiltonian has five real parameters and reads,

$$
\mathcal{H}_{so} = \frac{2i}{3} \sum_{\langle ij \rangle} c_{i\sigma}^\dagger c_{j\sigma}^\star \left[ \Lambda_{BR} (\hat{s} \times \mathbf{d}_{ij}) \right]_{\sigma\sigma},
$$

$$
+ \frac{i}{3} \sum_{\langle ij \rangle} c_{i\sigma}^\dagger c_{j\sigma}^\star \left[ \frac{\Lambda_{C}^c}{\sqrt{3}} \nu_{ij} \hat{s}_{z} + 2\Lambda_{PIA} \left( \hat{s} \times d_{ij} \right) \right]_{\sigma\sigma}.
$$

(4)

The double angle bracket stands for the next nearest neighbors and label $c$ denotes sublattice A or B. Factors $\nu_{ij} = 1 (-1)$ for clockwise (counterclockwise) hopping path $j$ to $i$. The nearest-neighbor $d_{ij}$ and next-nearest-neighbor $d_{ij}$ unit vectors point from $j$ to $i$ (in a flat lattice). The first term in Eq. (4) is the standard Bychkov-Rashba hopping as for graphene. The second term describes the sublattice resolved intrinsic SOC which couples same spins, and the PIA term which couples opposite spins on the same sublattice. Hamiltonian $\mathcal{H}_{so}$ in Eq. (4) applies to any hexagonal lattice system with $C_{3v}$ point group symmetry, such as BN, or silicene in a transverse electric field.

The single-band limit described by Eq. (4) can be obtained from the TB Hamiltonian $\mathcal{H} = \mathcal{H}_{orb} + \mathcal{H}_{so}$ by downfolding to sublattice B. This gives,

$$
\lambda_{BR}^{K} \simeq -a\Lambda_{PIA}^{B} - \sqrt{3}a\Lambda_{BR}^{K} \frac{t \varepsilon_{h}}{T^{2}},
$$

$$
\lambda_{I} \simeq -\Lambda_{I}^{B} - 2\Lambda_{BR}^{K} \frac{\varepsilon_{h}}{T^{2}}.
$$

(5)

(6)

Both PIA and BR SOC hopping terms contribute to the effective band SOC parameters. This is the likely reason for the extracted nonmonotonic dependence of $\lambda_{I}$ and the decrease of $\lambda_{BR}^{K}$ as a function of $\Delta/a$ shown in Fig. 1 (bottom). The TB model cannot be reliably used at $\Gamma$ as there other bands (orbitals) mix in, see Fig. 1(a) and Ref. [31].

We also present an effective SOC Hamiltonian close to K. After transforming $\mathcal{H}_{so}$ to the ordered Bloch basis $[\psi_{A1}(k), \psi_{A2}(k), \psi_{BR}(k), \psi_{B1}(k)]$ and linearizing near K(K') we obtain,

$$
\mathcal{H}_{so}^{K} = \Lambda_{BR}(\tau \hat{\sigma}_{x} \hat{s}_{y} - \hat{\sigma}_{y} \hat{s}_{x}) + \frac{1}{2} [\Lambda_{I}^{A+B} \hat{\sigma}_{x} + \Lambda_{I}^{A-B} \hat{\sigma}_{y}] \tau \hat{s}_{z}
$$

$$
+ \frac{1}{2} [\Lambda_{PIA}^{A+B} \hat{\sigma}_{x} + \Lambda_{PIA}^{A-B} \hat{\sigma}_{y}] a(k_{x} \hat{s}_{y} - k_{y} \hat{s}_{x}).
$$

(7)

Here ($\hat{\sigma}_{0}, \hat{\sigma}$) and ($\hat{s}_{0}, \hat{s}$) stand for the unit and Pauli matrices in the pseudospin and spin spaces, respectively. The momentum is measured form $K(K')$ and parameters $\Lambda^{A+B} = \Lambda^{A} \pm \Lambda^{B}$. If $z$-inversion symmetry is restored, $\Lambda_{BR}^{A+B}$, $\Lambda_{PIA}^{A+B}$, and $\Lambda_{I}^{A-B}$ vanish and one obtains the silicene limit [33].

**Hydrogen on a supercell: single-adatom limit.** The single-adatom limit is represented by a $5 \times 5$ supercell with a single hydrogen (2% coverage). We use a fully relaxed structure with $\Delta \approx 0.36$ Å (14% distortion) and the next nearest neighbor distance $a = 2.516$ Å of the carbon atoms around the hydrogenated site $C_{H}$.

Figure 2(a) shows the calculated spin-unpolarized electronic band structure of our $5 \times 5$ supercell. The low energy spectrum contains three characteristic bands: the valence and conduction bands, and the mid-gap impurity-like band. These three bands can be nicely fitted by two parameters $T = 7.5$ eV, and $\varepsilon_{h} = 0.16$ eV entering the Hamiltonian $\mathcal{H}_{orb}$, Eq. (3), as seen in Fig. 2(a). Our values differ from Refs. [30] and [32] the comparison is discussed in [31]. Larger supercells are also well described by these parameters, confirming that the $5 \times 5$ one already describes the dilute limit, see [31]. The TB model with $s$ and $p_{z}$ orbitals is also supported by the projected $p_{z}$ local density of states per carbon atoms around the hydrogenated carbon as compared to the total density of states, see Fig. 2(b).

The calculated spin-orbit splittings are shown in Fig. 2(c). To explain them we propose a minimal realistic SOC model which is locally $C_{3v}$ invariant in the impurity region with the C-H bond as the threefold axis of symmetry. We deduce the impurity region from the induced dipole moments, shown in Fig. 3(a). The main effects are confined up to the second nearest neighbors of the hydrogenated site $C_{H}$ (in sublattice A), defining our impurity region. We use $A_{i}^L(a)$ for the creation (annihilation) operators on $C_{H}$ and $B_{m,\sigma}^L(a)$ on the three nearest neighbors. Otherwise the terminology follows the SHG case. The SOC Hamiltonian compatible with the
The spin texture is governed mainly by PIA SOC. Those parameters have been determined from the spin expectation values around the K point, shown in Fig. 2(f). Tight-binding model least-square fits are performed within the shaded regions around K. (f) Spin expectation values around K for the spin-orbit split valence and conduction states are normalized to the corresponding number of atoms in the set. Conduction (c), impurity (d), and valence (e) band splittings along high-symmetry lines; symbols as in (a). Tight-binding model least-square fits are performed containing (this is denoted by the primed summation symbol) C_H. The second term describes the adatom induced intrinsic spin-orbit coupling coupling \( \Lambda_I \), which couples the same spins on the same sublattice. The third term, with Bychkov-Rashba hopping parameter \( \Lambda_{BR} \), describes the induced nearest neighbor spin flips. Finally, the fourth term, with PIA parameter \( \Lambda_{PIA} \), comes from the pseudospin inversion asymmetry. This term couples opposite spins of the next nearest neighbors. We remark that C_H symmetry allows more spin-orbit hopping terms in our impurity region. We considered them all but found only the three \( \Lambda \)'s in Eq. (8) relevant to explain our ab-initio results, see the scheme in Fig. 3(b).

Figures 2(c,d,e) show spin-orbit coupling induced band splittings along high symmetry lines. The multiband least-square fit around K point gives the following values for the SOC parameters: \( \Lambda_I = -0.21 \text{ meV} \), which is about 17 times larger than that of graphene \( \lambda_I \); \( \Lambda_{BR} = 0.33 \text{ meV} \), more than 60 times the value in graphene where \( \lambda_{BR} = 5 \mu\text{eV} \) in a representative transverse electric field of 1 V/nm [3]; \( \Lambda_{PIA} = -0.77 \text{ meV} \), which has no counterpart in flat graphene. The signs of the above parameters have been determined from the spin expectation values around the K point, shown in Fig. 2(f). The spin texture is governed mainly by PIA SOC. Those parameters also fit larger supercells [31] and we propose them, together with Hamiltonian Eq. (8), to describe the

$\mathcal{H}_{so} = \frac{i}{3} \sum_{\langle i,j \rangle} c^\dagger_{i\sigma} c_{j\sigma'} \left[ \frac{\lambda_I}{\sqrt{3}} \nu_{ij} \hat{s}_z \right]_{\sigma\sigma'}$
single adatom limit important for investigating spin-flip
and spin-orbit scattering in graphene.

In conclusion, we investigated spin-orbit coupling in-
duced by hydrogen, representing light adatoms, on
graphene in dense and dilute limits. We introduced real-
istic model spin-orbit Hamiltonians and provided quan-
titative values for their parameters that can be used to
study spin relaxation, spin transport, and mesoscopic
transport in graphene with adatoms or in similar two-
dimensional structures of the same symmetry.

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Spin-orbit coupling in hydrogenated graphene

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Computational method

The electronic structure calculations are based on density functional theory [1]. Generalized gradient approximation [2] has been applied to the exchange-correlation potential and used in the full-potential linearized augmented plane wave (FLAPW) method as implemented in the FLEUR code [3]. The self-consistent calculations with spin-orbit coupling (SOC) in the film mode for semihydrogenated graphene were carried out with cut-off parameter $k_{\text{max}}$ of 6.7 bohr$^{-1}$ and 144 k-points in the irreducible wedge of the Brillouin zone. For the supercell calculations we used $k_{\text{max}} = 4.7$ 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 taken.

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 [4]. For carbon and hydrogen we have used ultra-soft pseudopotentials [5, 6] with PBE exchange-correlation functional [2] with kinetic energies cut-offs of 30 Ry for the wave function and 300 Ry for the density. We used vacuum of 15 Å to separate the hydrogenated graphene planes. In Table I we list the relevant structural distances around the adatom site for different supercell sizes $n$. Covalent C-H bond length $d_{\text{H}}$ 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 bond distorts the graphene plane by pulling the hydrogenated carbon atom out of plane. Parameter $\Delta$ corresponds to the vertical shift of the hydrogenated carbon atom with respect to its three nearest-neighbors. The ratio $\Delta/a$ is about 14% in all studied supercells. We note that for an ideal tetrahedron (methane) the ratio $\Delta/a = 20.41\%$.

The binding energy, $E_{\text{bind}} = E_G - E_{\text{CH}} - E_{\text{H}}^H$, of the hydrogen on graphene, calculated as the difference between ground state energy $E_G$ of the hydrogenated graphene and ground state energies of graphene without hydrogen $E_{\text{CH}}$ and isolated hydrogen atom $E_{\text{H}}^H$, is about $-2.9$ eV.

The fine structure of relaxed atomic positions, especially the local distortion in terms of the vertical shift $\Delta$ of the hydrogenated carbon atom, see Fig. 1, significantly affects the impurity band width and consequently the value of the on-site impurity energy parameter $\epsilon_{\text{bind}}$.

Supplemental Material
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The fine structure of relaxed atomic positions, especially the local distortion in terms of the vertical shift $\Delta$ of the hydrogenated carbon atom, see Fig. 1, significantly affects the impurity band width and consequently the value of the on-site impurity energy parameter $\epsilon_{\text{bind}}$.

| $n \times n$ | $d_{\text{H}}$ [Å] | $a$ [Å] | $\Delta$ [Å] | $\Delta/a$ | $E_{\text{bind}}$ [eV] |
|-------------|--------------------|---------|--------------|------------|---------------------|
| 4 \times 4  | 1.1286             | 2.314   | 0.359        | 13.264\%  | -2.84              |
| 5 \times 5  | 1.1279             | 2.516   | 0.363        | 14.415\%  | -2.88              |
| 6 \times 6  | 1.1283             | 2.516   | 0.362        | 14.399\%  | -2.87              |
| 7 \times 7  | 1.1277             | 2.517   | 0.360        | 14.297\%  | -2.92              |
| 8 \times 8  | 1.1281             | 2.516   | 0.361        | 14.362\%  | -2.94              |
| 9 \times 9  | 1.1274             | 2.517   | 0.353        | 14.012\%  | -2.86              |
| 10 \times 10 | 1.1283             | 2.516   | 0.360        | 14.303\%  | -2.91              |

Table I. Structural parameters for supercell calculations obtained using Quantum Espresso code. Covalent bond carbon-hydrogen length $d_{\text{CH}}$, distance between the carbon atoms around the hydrogenated carbon $a$, vertical distance between hydrogenated carbon and its nearest neighbors $\Delta$, and binding energy $E_{\text{bind}}$ are listed.

Performing least-square fits to the $ab$-initio data around K we found $T = 7.5$ eV and $\epsilon_{\text{H}} = 0.16$ eV. Solid lines in Fig. 3(a) in the paper show the model fit to the 5 \times 5 supercell $ab$-initio data. In Fig. 2 we demonstrate the robustness of the model parameters by comparing with $ab$-initio data of larger supercells. The larger is the supercell the more narrower are the pseudogaps and the more flat is the impurity band. In the limit of an infinite supercell the band structure should contain the hydrogen energy level and the graphene band structure with the Dirac cone. We note that previous studies [7, 8] present different values for the C-H hopping $T$ and the on-site $\epsilon_{\text{H}}$. 

FIG. 1. Local distortion due to chemisorbed hydrogen on graphene gives the covalent bond of length $d_{\text{H}}$ between hydrogen and hydrogenated carbon, increased distance between the next-nearest neighbors around the hydrogenated site $a$, and pulling the hydrogenated carbon out of plane by $\Delta$ with respect to the three nearest neighbors of the hydrogenated site.
energy $\varepsilon_h$; the comparison is shown in Fig. 2.

To calculate the dipole moment of an atom $A$ at atomic center $\vec{r}_A$, we used $
abla_A(\vec{r}_A) = \int_{R_A} \theta(\vec{r}) (\vec{r} - \vec{r}_A) d^3r$, where $R_A$ is the atom muffin-tin radius, and $\theta(\vec{r})$ is the valence electronic charge. The integral is performed using a weighted sum for an arbitrary polynomial accuracy [9]. For this purpose we have implemented the new module r3dgl into FLEUR.

In Fig. 3 we show the dipole moment magnitude as a function of the in-plane distance from the adatom for a $5 \times 5$ supercell. There are significant dipole moments on the nearest-neighbor carbon atoms around the hydrogenated carbon. The dipole moments diminish at a distance of about 4 Å. In the inset to Fig. 3 we plot the in-plane components of the dipole moment directions (unit vectors). This figure quantifies the dipole-moments distribution picture in Fig. 2 of the paper.

**Single band spin-orbit Hamiltonian: symmetry approach**

Here we focus on the single-band spin-orbit effective Hamiltonian valid near $K(K')$ point. The guiding principle for constructing such a Hamiltonian is the invariance principle with respect to the small group of $K(K')$.

The group symmetry for both the single top positioned impurity and the single-side semi-hydrogenated graphene (SHG) is $C_{3v}$. The threefold axis (rotations $R_0 = \text{Id}$ and $R_{\pm 2\pi/3}$ about the z-axis) for the single impurity graphene is the carbon-hydrogen bond and three reflection planes ($\sigma_x$ and $\sigma_y \cdot R_{\pm 2\pi/3}$) are defined by the threefold axis and the lines connecting the hydrogenated carbon with its three nearest neighbors. The arrangement is slightly different in SHG, which has the threefold axis in the center of the primitive hexagonal cell, and the reflection planes are defined by the threefold axis and the lines connecting the opposite vertices of the hexagon, see Fig. 4.

The Brillouin zone remains hexagonal. The rotational subgroup $C_3 \subset C_{3v}$ leaves $K$ and $K'$ invariant. The min-
imal rotationally invariant $2 \times 2$ Hamiltonian reads

$$H_{\text{eff}}^{K} = \left[ a + b k_x k_z + c \left( k_x^2 + k_z^2 \right) + \cdots \right] \hat{s}_+ + \left[ \tilde{a} k_x + \tilde{b} k_z^2 + \tilde{c} k_x k_z^2 + \cdots \right] \hat{s}_+ + \text{H.c.} \right) \quad (1)$$

Here $k_x$ and $k_z$ are momenta measured from $K$ or $K'$, $k_{\pm} = k_x \pm i k_y$, and $\hat{s}_\pm = \frac{1}{2} (\hat{s}_x \pm i \hat{s}_y)$ are the spin raising and lowering operators; $a, b, c, \ldots$ are real and $\tilde{a}, \tilde{b}, \tilde{c}, \ldots$ complex parameters. Applying the time-reversal operator $\mathcal{T}$ to $H_{\text{eff}}^{K}$ we get an effective Hamiltonian $H_{\text{eff}}^{K'}$ valid near $K'$, but $K'$ can be mapped back to $K$ using a vertical reflection $\sigma_v \in C_{3v}$, i.e., apart from the rotations also the operator $\sigma_v \circ \mathcal{T}$ belongs to (the spinor extension of) the small group of $K(K')$. The small group invariance constraint,

$$(\sigma_v \circ \mathcal{T}) H_{\text{eff}}^{K} = H_{\text{eff}}^{K} (\sigma_v \circ \mathcal{T}), \quad (2)$$

restricts $\tilde{a}, \tilde{b}, \tilde{c}, \ldots$ to be purely imaginary, i.e., $\tilde{a} = i \alpha, \tilde{b} = i \beta, \tilde{c} = i \gamma, \ldots$. The expansion in momentum can be increased to an arbitrary order and can be rewritten in the form

$$H_{\text{eff}}^{K} = \mathbf{n}(k_x, k_y, \tau) \cdot \mathbf{\hat{s}}, \quad (3)$$

where the valley index $\tau = 1 (-1)$ for $K (K')$ points. The spin-orbit field $\mathbf{n}(k_x, k_y, \tau)$ up to the third order reads

$$n_x = \alpha k_y - \tau \beta (2k_x k_y) + \gamma (k_x^2 k_y + k_y^3),$$
$$n_y = -\alpha k_x + \tau \beta (k_x^2 - k_y^2) - \gamma (k_x^3 + k_x k_y^2),$$
$$n_z = \tau \alpha + \tau \beta (k_y^2 + k_x^2) + c (2k_y^3 + 6k_x k_y k_z^2). \quad (4)$$

From the effective Hamiltonian $H_{\text{eff}}^{K'}$ one can deduce basic properties of the underlying spin-orbit field texture in the vicinity of $K(K')$ point. For example, close to $K(K')$ the spin-orbit field is circulating, being of the semiconductor Bychkov-Rashba-type but with the valley dependent spin $z$-component,

$$H_{\text{eff}}^{K'} \approx \alpha (k_y \hat{s}_x - k_x \hat{s}_y) + \tau \hat{s}_z. \quad (5)$$

The above formula is used in the paper ($\alpha = \lambda^{BR}_{K} a = \lambda_{K}$) with SOC parameters extracted from the spin-orbit field around the $K$ point, see Fig. 1 in paper. Away from $K(K')$ nonlinear terms begin to play role, Eqs. (4), and the spin texture becomes trigonally warped, see Fig. 5.

Similarly, other high symmetry points in the Brillouin zone can be investigated. For example, in the vicinity of $\Gamma$ the SOC Hamiltonian reads

$$H_{\text{eff}}^{\Gamma} \approx \lambda^{\text{BR}}_{\Gamma} (k_y \hat{s}_x - k_x \hat{s}_y). \quad (6)$$

As discussed in the paper, the single band model can be microscopically justified by a tight-binding model with the basis of $p_z$ carbon and $s$ hydrogen orbitals. In Fig. 6 we show the spatial distribution of the probability density for a SHG at $K$ and $\Gamma$ points for the $\pi^*$ band close to the Fermi level. From the spatial distribution one recognizes the dominant $p_z$ character of the states which supports our tight-binding model built on the $p_z$ basis.

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