Topological insulator gap in graphene with heavy adatoms

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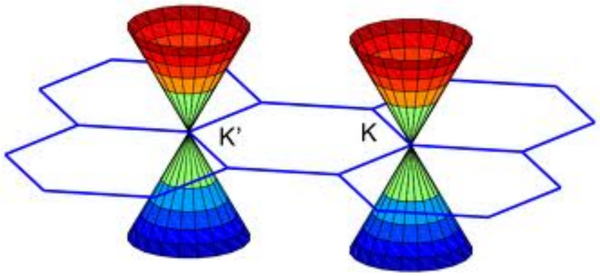
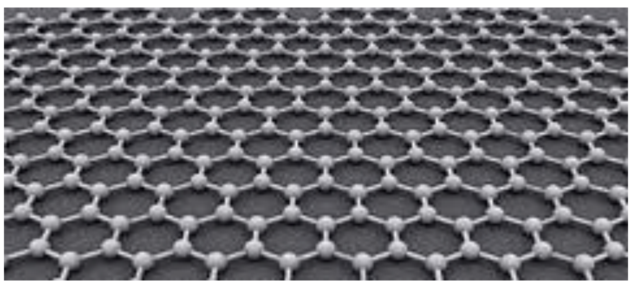
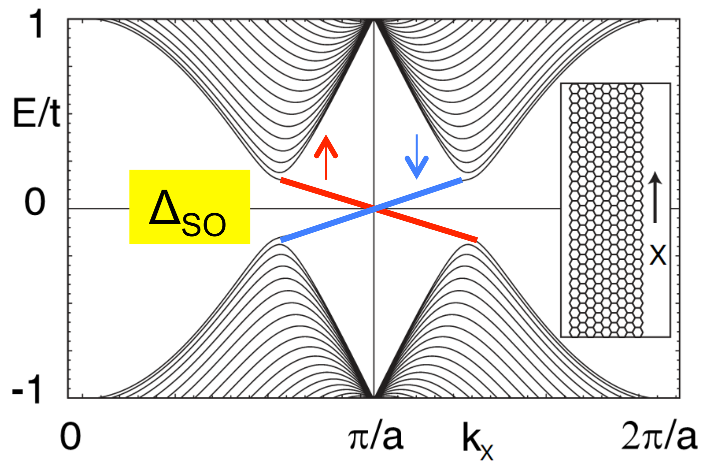
Background: 2D Topological Insulator State of graphene

Graphene was predicted to be TI

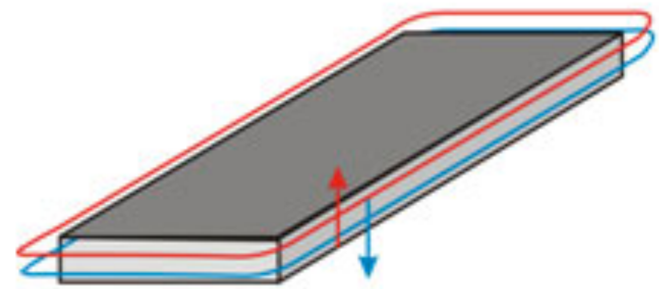
see C. L. Kane and E. J. Mele, PRL 95, 226801 (2005).







Bands of a graphene ribbon

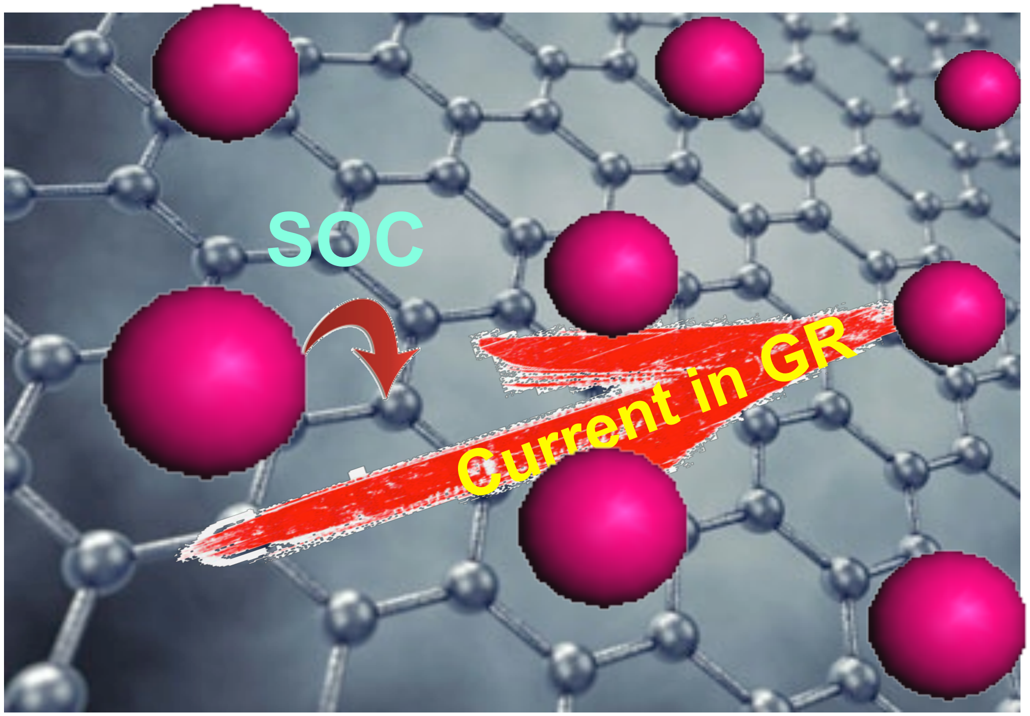


2D topological insulator

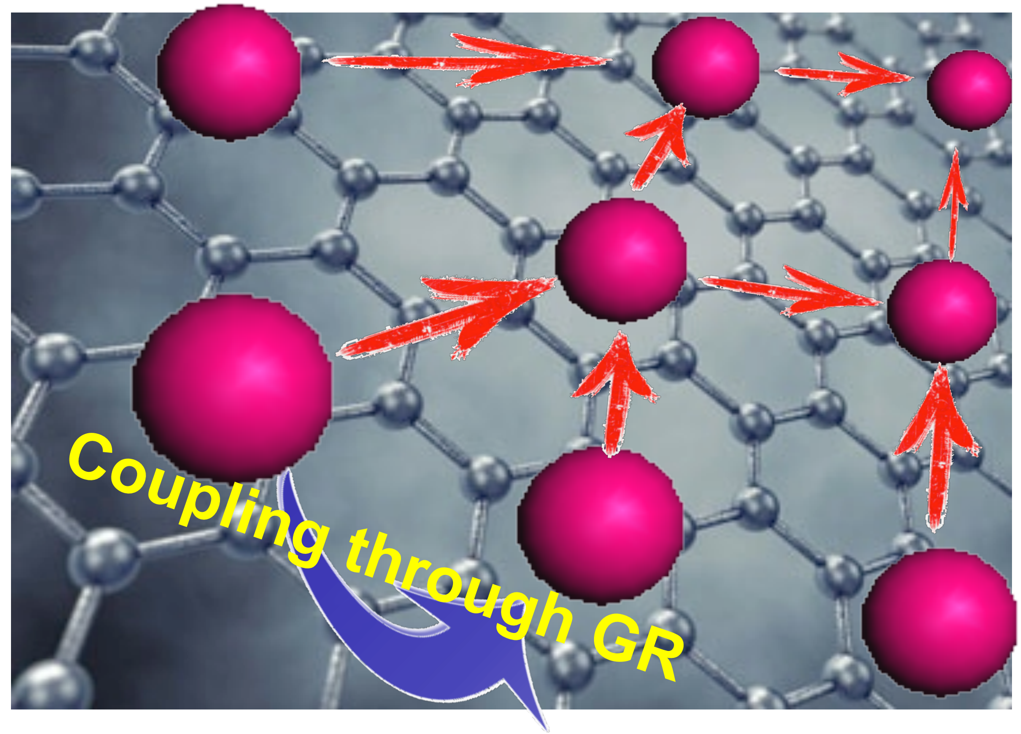
Main problem: the spin-orbit gap (Δ_{SO}) of graphene is very small (Δ_{SO}<0.1 meV ~ 1K), because of the exceedingly weak spin-orbit coupling (SOC) of carbon atoms.

The objective of this work: to enhance Δ_{SO} with adatoms for the realization of QSH at room temperature.

Two ways to produce TI states in graphene systems



Inject SOC of metal adatoms into graphene

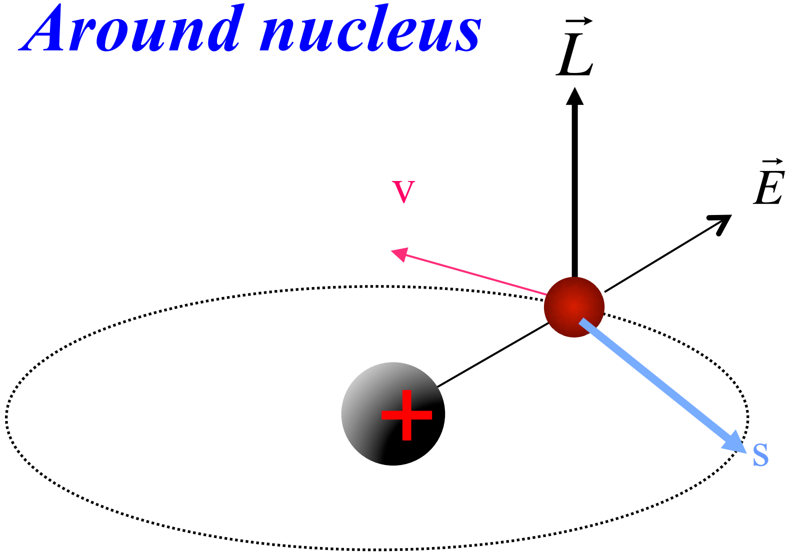


Transport in metal network that is mediated through graphene

- C. Weeks, J. Hu, J. Alicea, M. Franz and R.Q. Wu, "Engineering a robust quantum spin Hall state in graphene via adatom deposition", *Phys. Rev. X*, **1**, 021001 (2011).
- J. Hu, J. Alicea, R.Q. Wu, and M. Franz, "Giant topological insulator gap in graphene with 5d adatoms", *Phys. Rev. Lett.* **109**, 266801 (2012).

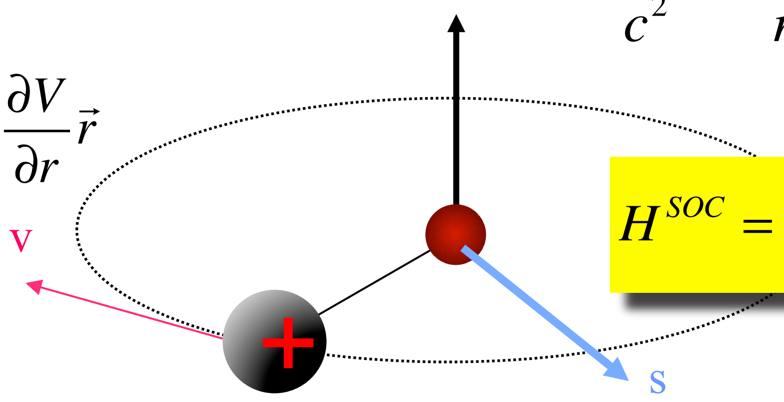
Why spin-orbit coupling: relativistic effect

Around nucleus



$$\vec{E} = -\frac{1}{r}\frac{\partial V}{\partial r}\vec{r}$$

$$\vec{B} = -\frac{\vec{v}\times\vec{E}}{c^2} = \frac{1}{mc^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{L}$$



$$H^{SOC} = \frac{\mu_B}{2mc^2 r}\frac{\partial V}{\partial r}\vec{\sigma}\bullet\vec{L}$$

Rest frame of the nucleus

Rest frame of the electron

From the Dirac equation

$$[c\vec{\alpha}\cdot\hat{p} + mc^2\beta + v(r)]\Psi = E\Psi$$

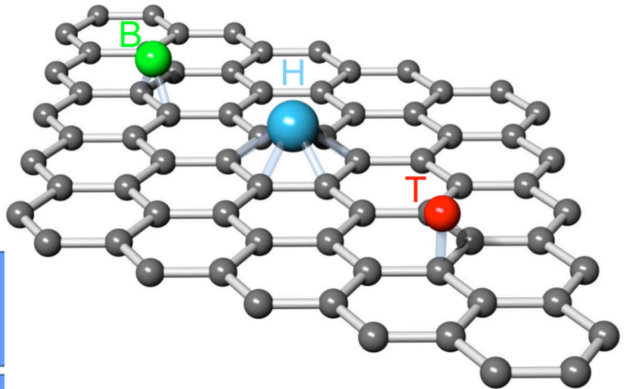
$$\Psi = \begin{pmatrix} g_\kappa \chi_{\kappa\mu} \\ if_\kappa \sigma_r \chi_{\kappa\mu} \end{pmatrix}$$

Spin-orbit coupling

$$\frac{-1}{2M}[g_l'' + \frac{2}{r}g_l' - (\frac{l(l+1)}{r^2} + v)g_l] - v'g_l' / 4M^2c^2 + \frac{v'[\sigma\cdot L]}{4M^2c^2 r}g_l = Eg_l$$

$$M \equiv m + (E - V)/2c^2$$

Basic requirements for adatoms



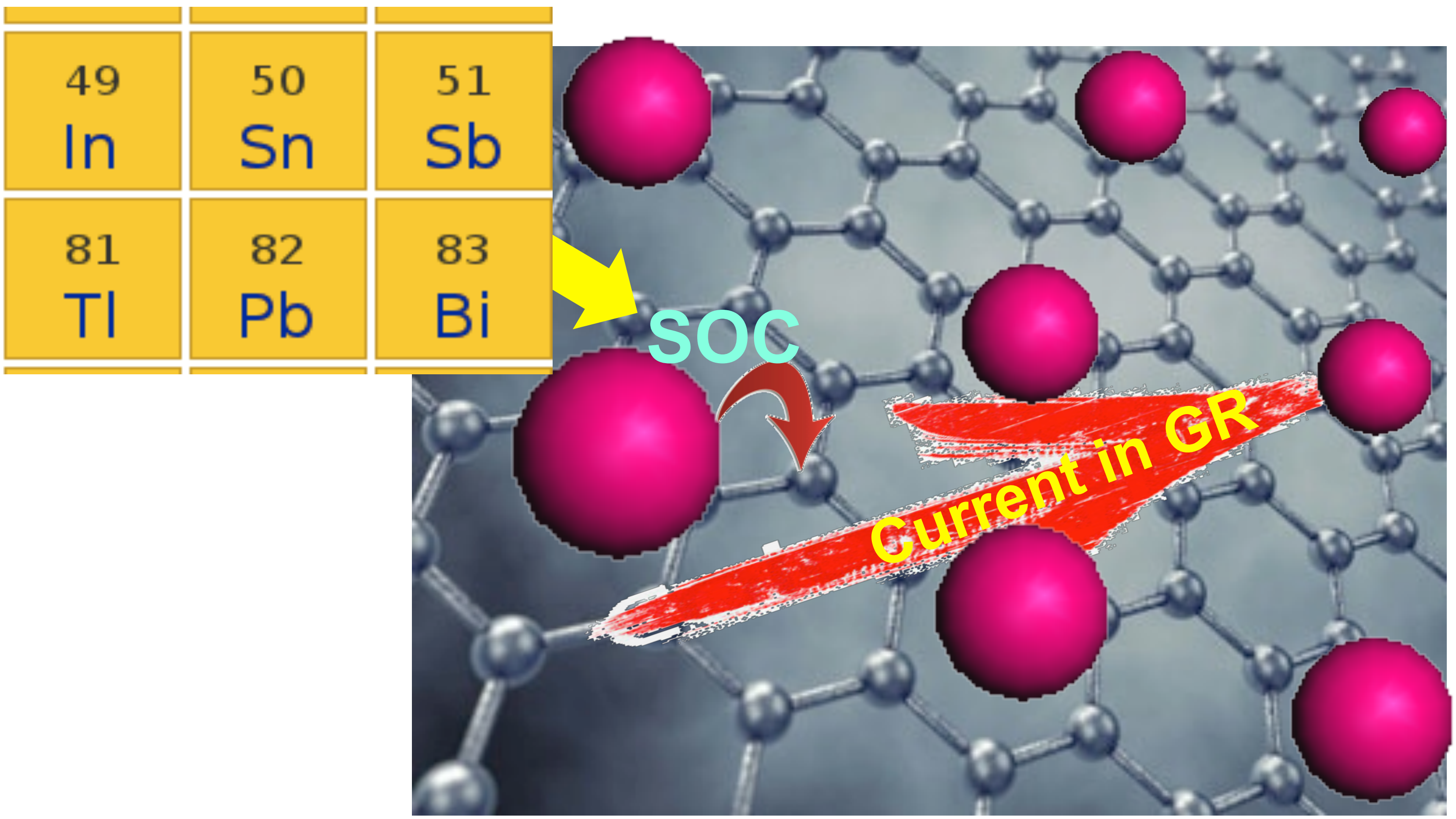
- **Carry large SOC (heavy elements)**
- **Preserve the time-reversal symmetry**
- **Take the hollow site**

1 H																		2 He
3 Li	4 Be													5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg													13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

1. Inject SOC into graphene with p-valent adatoms

p-valent metal adatoms

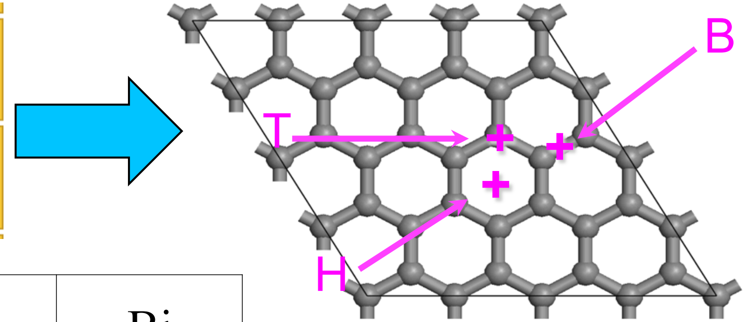
- Adatoms provide SOC
- Current in graphene



Results of heavy p-valent adatoms on graphene

Site preference

$$E_b = E_{Gr} + E_M - E_{Gr+M}$$



	In	Tl	Sn	Pb	Sb	Bi
H	0	0	278	210	0	316
T	91	83	10	17	175	26
B	84	80	0	0	117	0

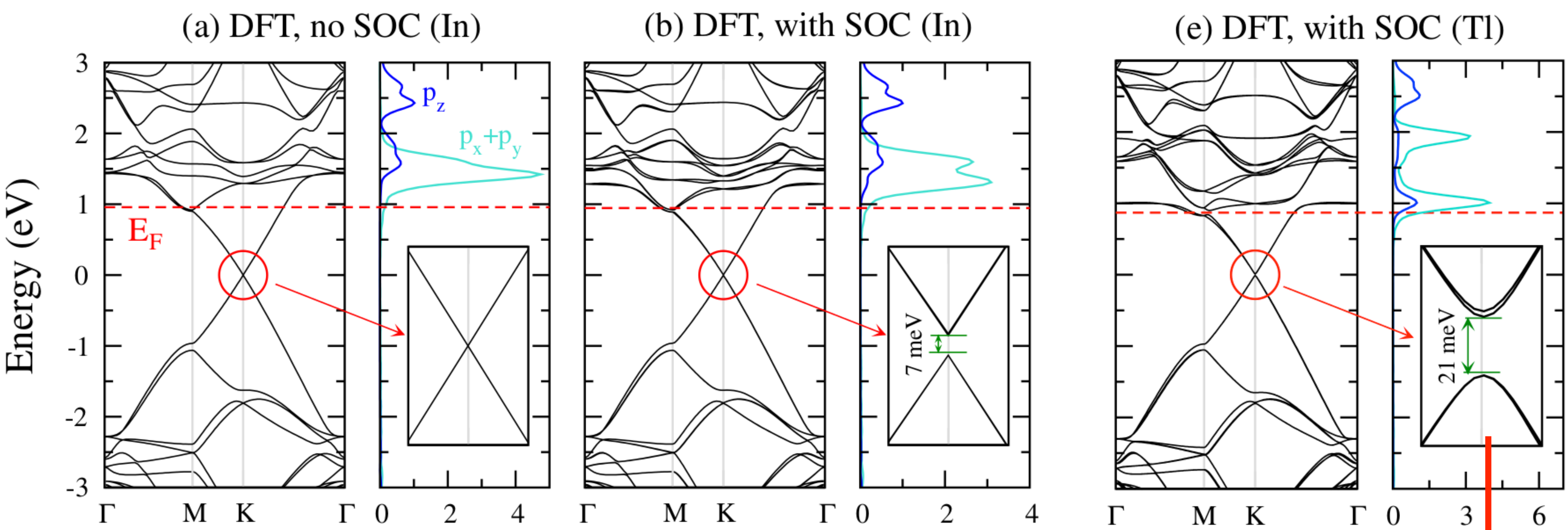
Time reversal

Sb/graphene is magnetic with a spin moment of 3.0 μ_B, so Sb should also be excluded

Detailed results for two "good" p-valent adatoms, In and Tl

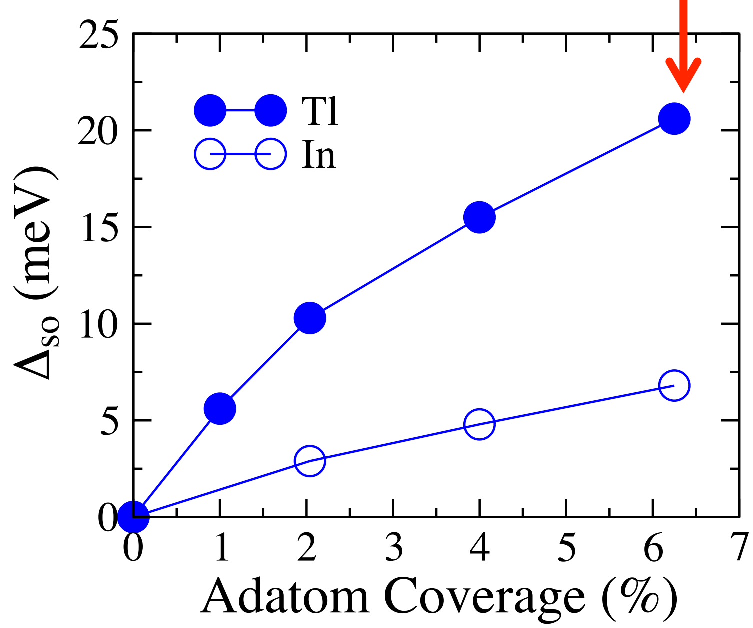
	E_b (eV) GGA	Height(Å) GGA	d_{C-M} (Å) GGA	Height(Å) LDA	d_{C-M} (Å) LDA
In	**1.029**	2.44	2.83	2.35	2.74
Tl	**1.027**	2.52	2.90	2.46	2.84

The In- and Tl-induced SOC gap for the Dirac state



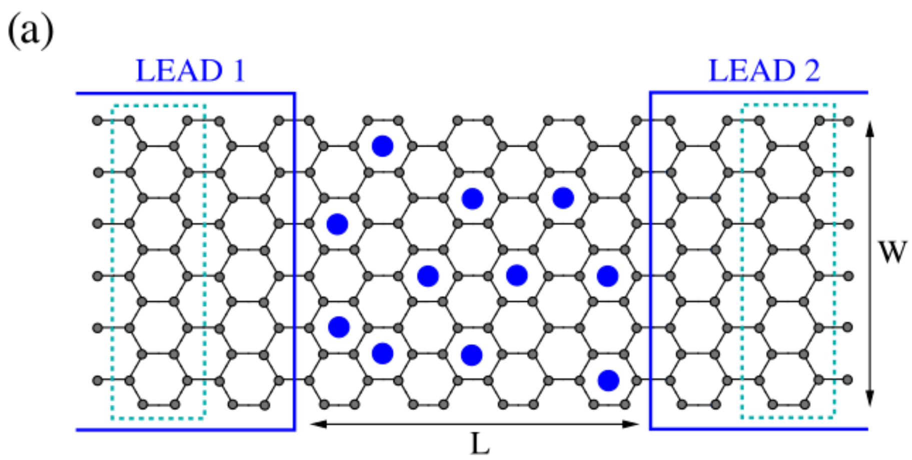
The coverage dependence of Δ_{SO} for In/Gr

Supercell	4×4	5×5	7×7
Coverage (%)	6.25	4	2.04
Δ_{SO} (meV)	7	5	3

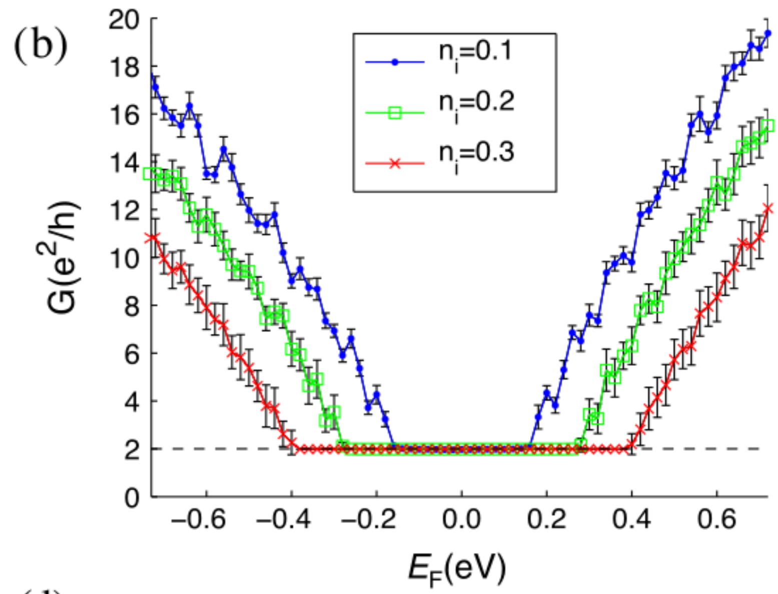


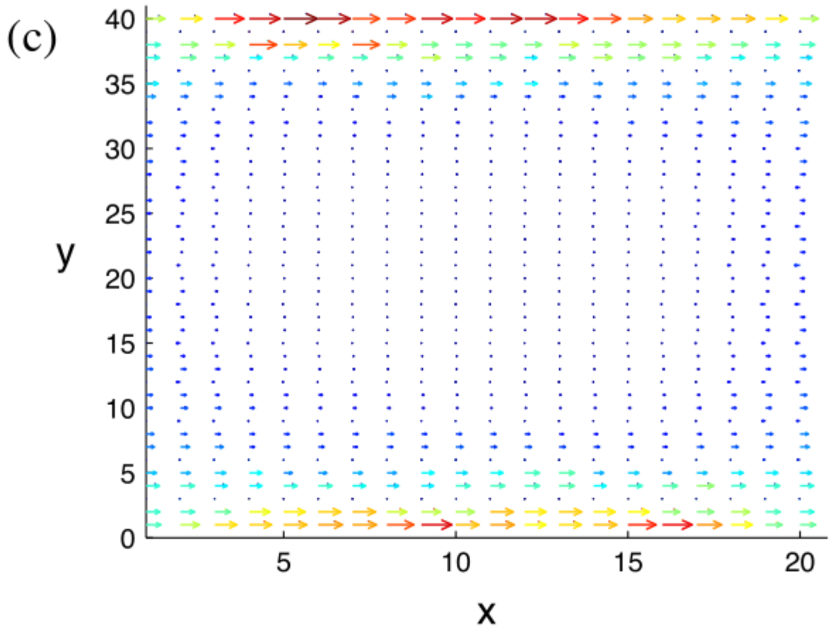
Δ_{SO} of Tl/graphene is still substantial (6.5 meV) even when the coverage decreases to about 1%.

Transport simulation of Tl/graphene with the TB approach

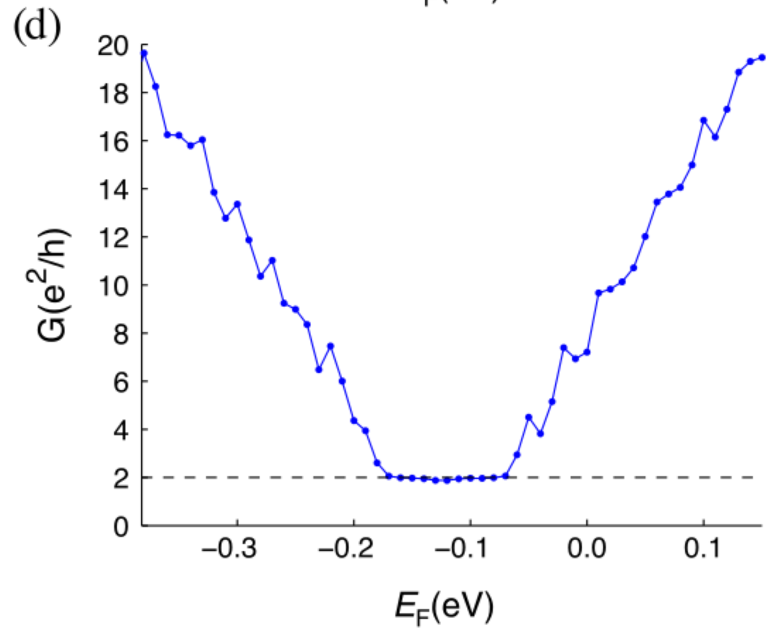


Two-terminal model for conductance





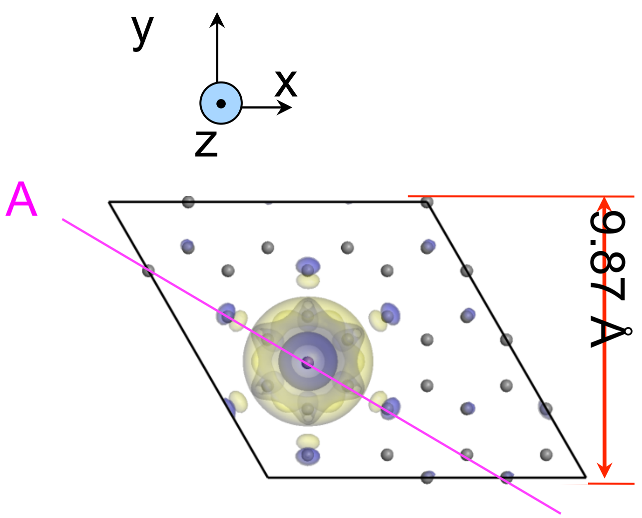
Current distribution across a sample



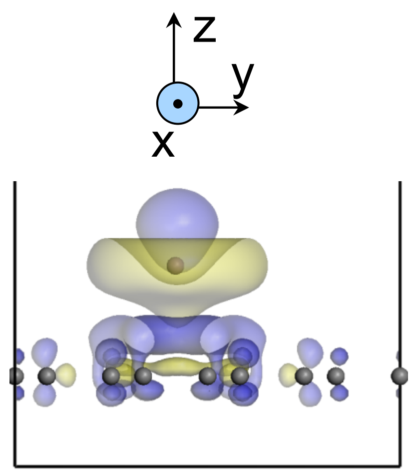
G of Tl/Gr with realistic parameters from DFT

Charge transfer from Tl to graphene: (4×4) supercell

$$\Delta\rho = \rho(Gr+Tl) - \rho(Gr) - \rho(Tl)$$

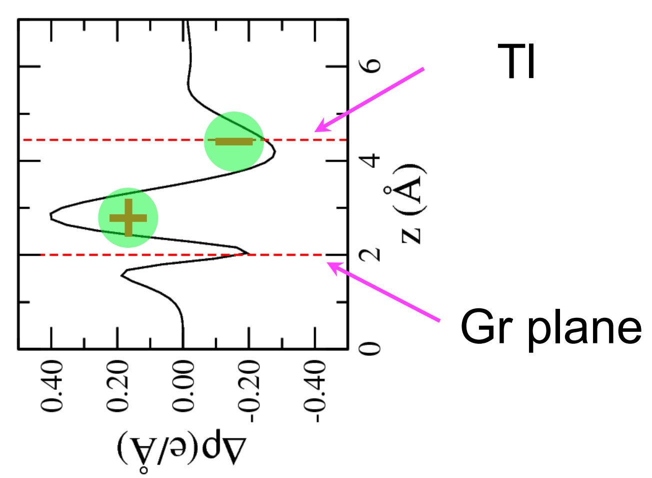


Top view

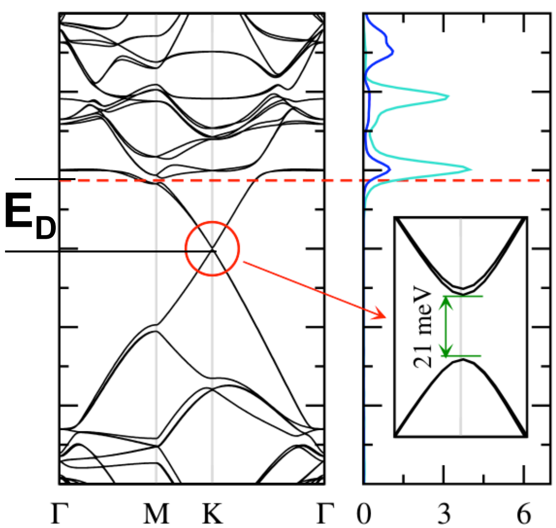


Side view

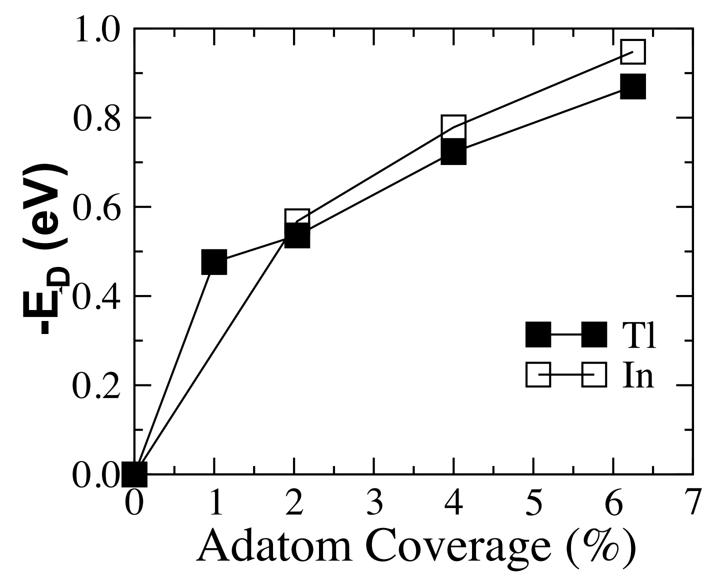
Planar average of Δρ



The Bader charge analysis indicates that each Tl adatom transfer 0.76 electron to graphene.



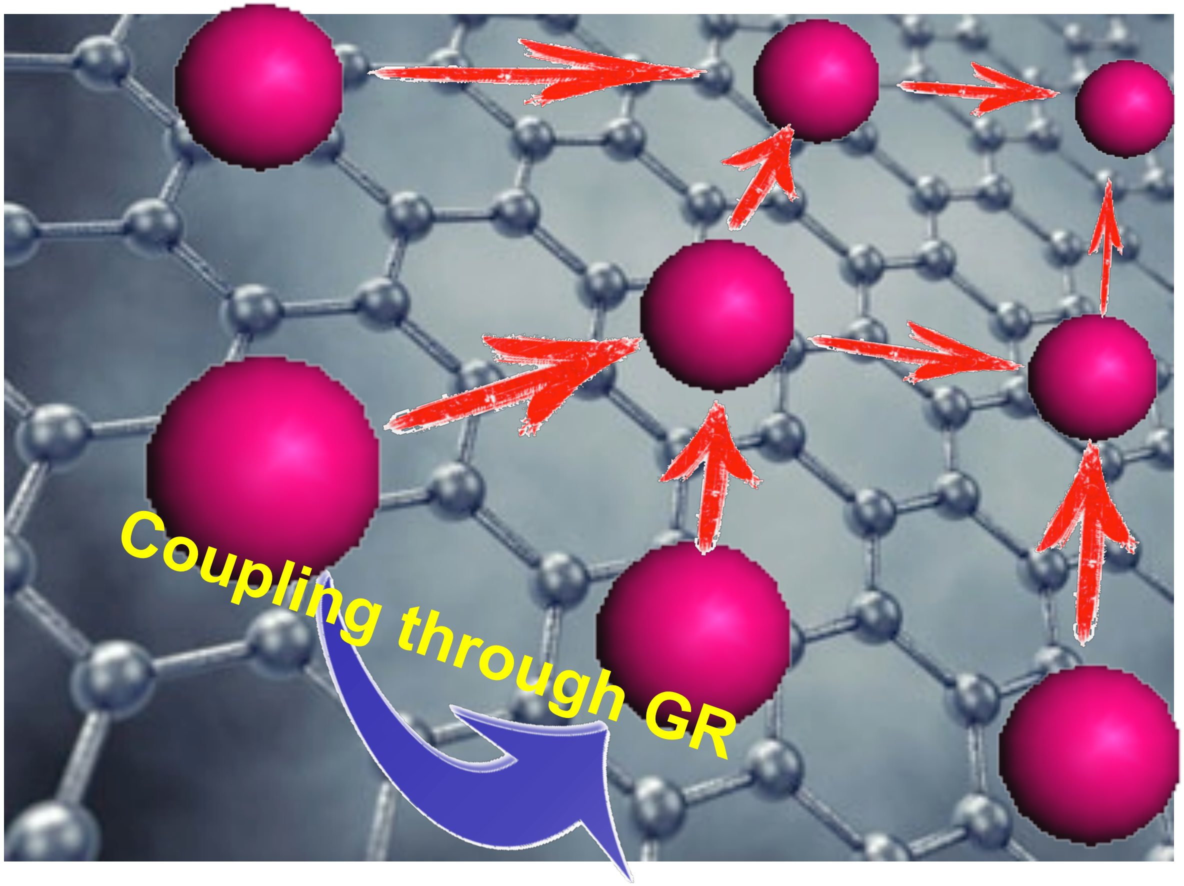
This causes the Dirac point to shift down by more than 0.5 eV. It might be an important technical issue for the realization fo QSH in Tl(In)/ Graphene.



2. Transport through 5d adlayer on graphene

5d transition metal adatoms

- Graphene mediates interaction between adatoms
- Current in adatom network
- Large SOC in the conducting channel



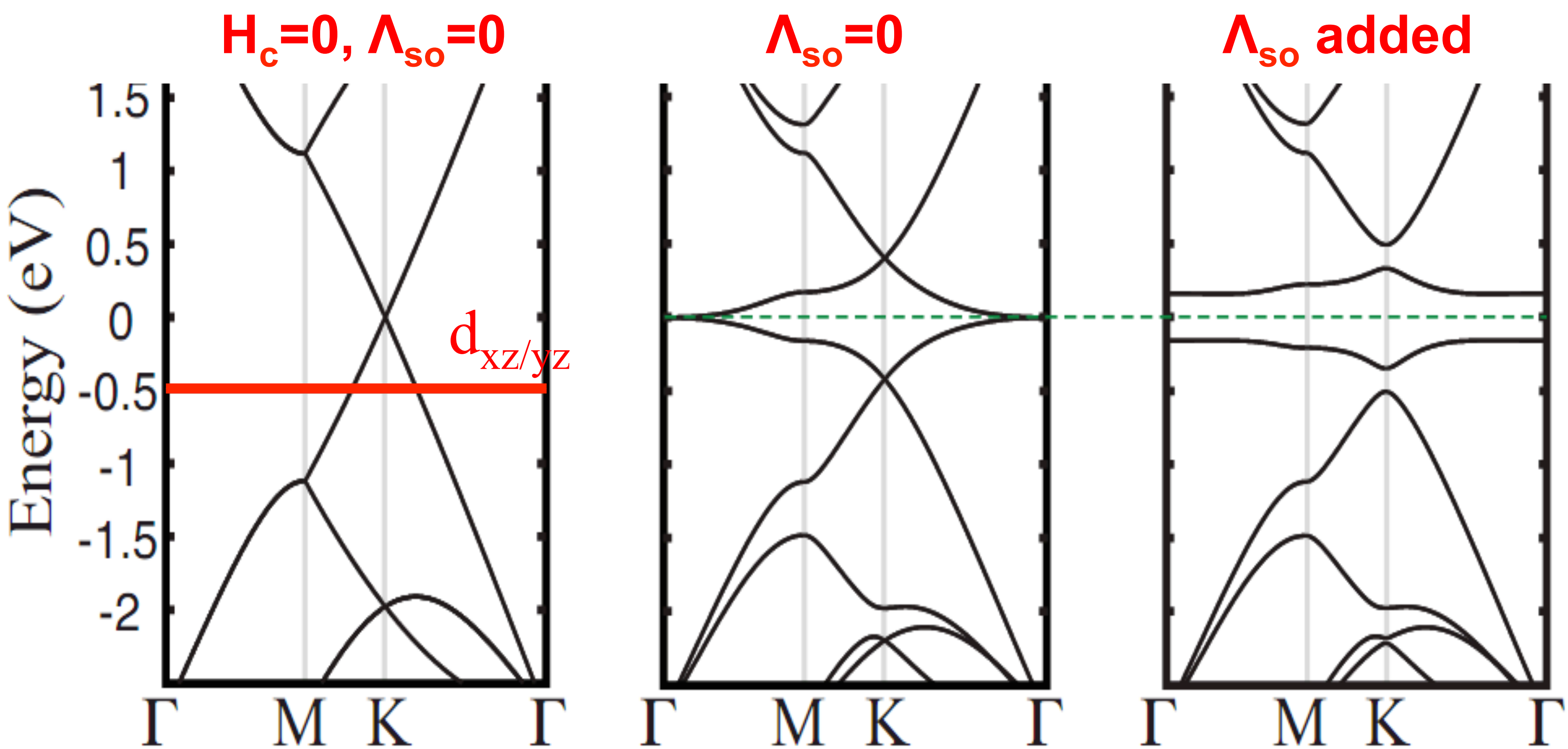
Evolvement of band structure of 5d/graphene: TB analysis

$$H = H_g + H_a + H_c$$

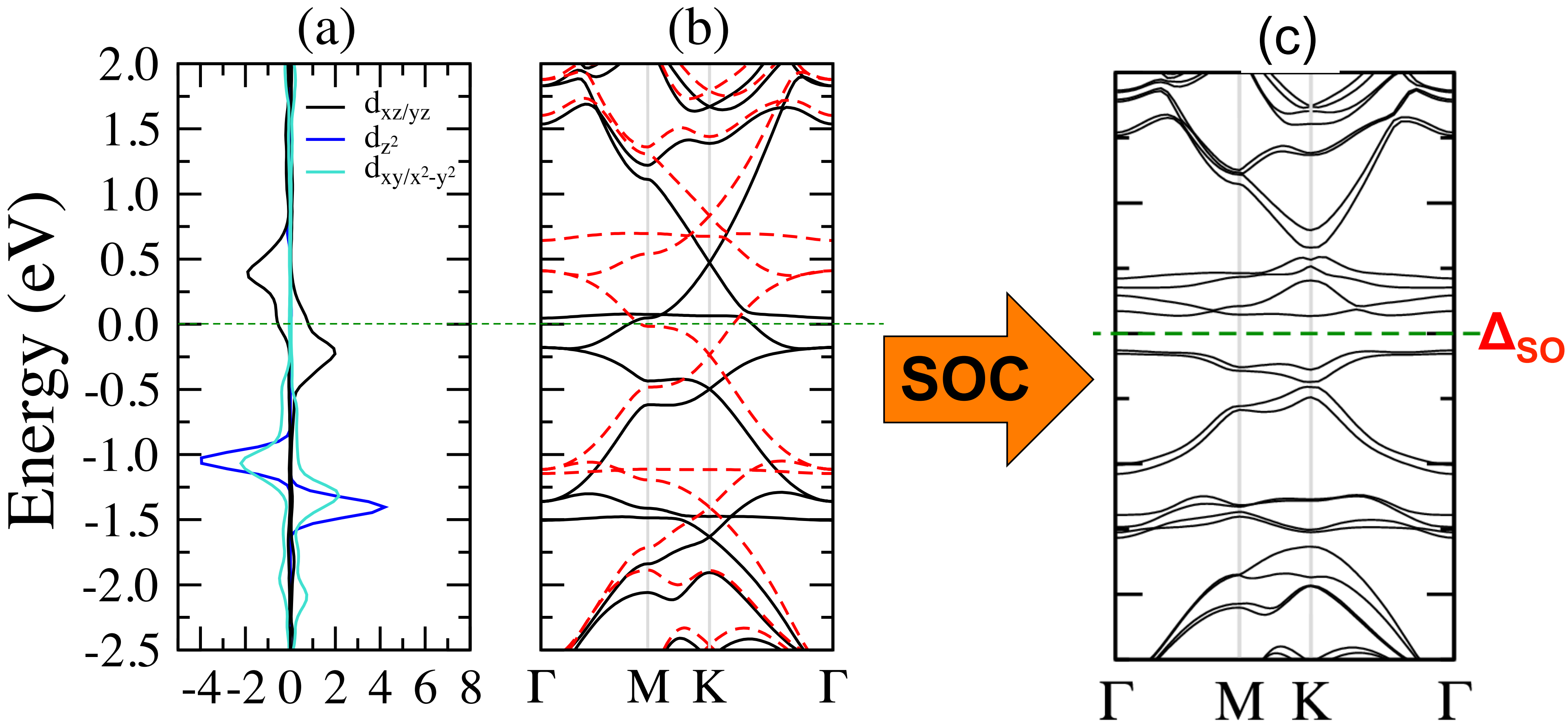
$$H_g = -t \sum_{\alpha=\uparrow,\downarrow} \sum_{\langle \mathbf{r}\mathbf{r}' \rangle} (c^\dagger_{\mathbf{r}\alpha} c_{\mathbf{r}'\alpha} + H.c.)$$

$$H_a = \sum_{\mathbf{R}} \left[\sum_{\alpha=\uparrow,\downarrow} \sum_{m=\pm 1} \epsilon f^\dagger_{m\mathbf{R}\alpha} f_{m\mathbf{R}\alpha} + \sum_{\alpha,\beta=\uparrow,\downarrow} \Lambda_{so} (f^\dagger_{1\mathbf{R}\alpha} s^z_{\alpha\beta} f_{1\mathbf{R}\beta} - f^\dagger_{-1\mathbf{R}\alpha} s^z_{\alpha\beta} f_{-1\mathbf{R}\beta}) \right]$$

$$H_c = -t_c \sum_{\mathbf{R}} \sum_{\alpha=\uparrow,\downarrow} \sum_{m=\pm 1} (i C^\dagger_{m\mathbf{R}\alpha} f_{m\mathbf{R}\alpha} + H.c.)$$



DFT band structures of Os/Graphene before and after SOC being invoked



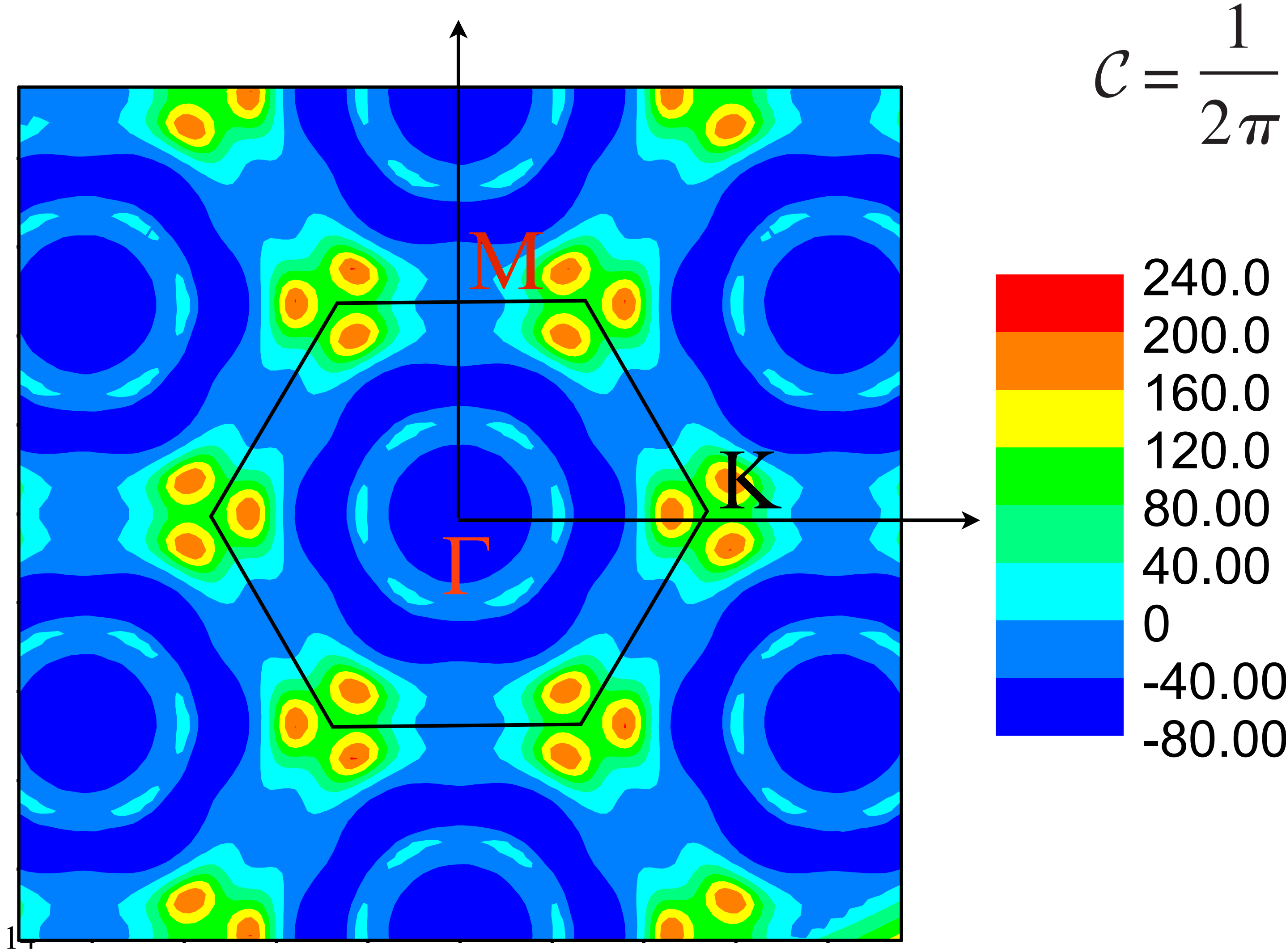
The band gap originates from SOC and have the topological insulator feature

Berry curvature distribution of Os/graphene

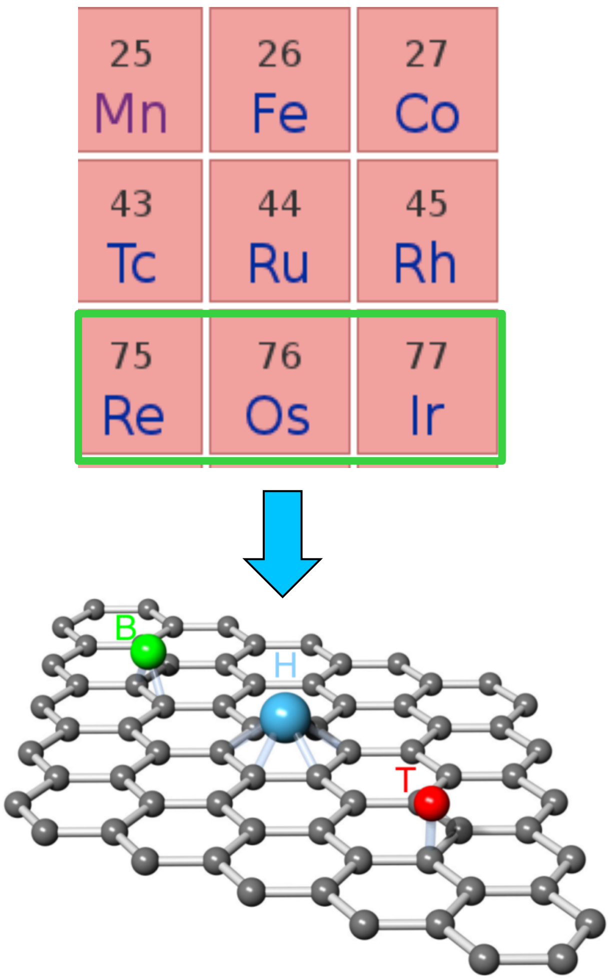
$$\Omega_n(\boldsymbol{k}) = -\sum_{n'\neq n} \frac{2\,\mathrm{Im}\langle\psi_{n\boldsymbol{k}}|v_x|\psi_{n'\boldsymbol{k}}\rangle\langle\psi_{n'\boldsymbol{k}}|v_y|\psi_{n\boldsymbol{k}}\rangle}{(\omega_{n'}-\omega_n)^2}$$

$$\Omega(\vec{k}) = \sum_{n\in occ}\Omega_n(\vec{k})$$

$$\mathcal{C} = \frac{1}{2\pi}\sum_n \int_{\mathrm{BZ}} d^2k\,\Omega_n$$



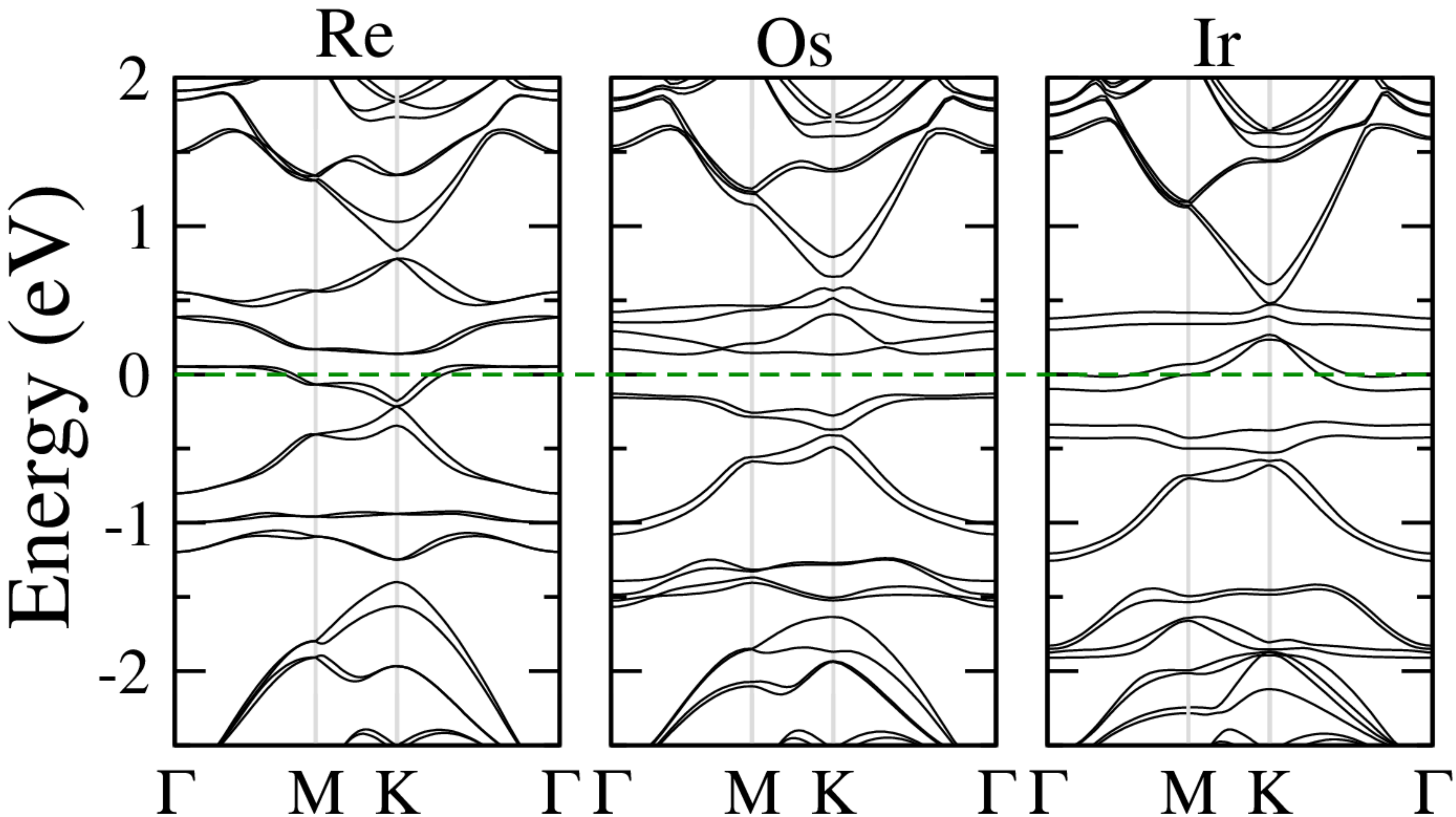
5d transition metal elements with large SOC: Re, Os and Ir



		H	T	B
Re	E_b (eV)	1.90	0.89	0.89
	M_S (μ_B)	0.35	4.93	3.32
	h (Å)	1.64	2.09	1.86
	$d_{C\text{-}Re}$ (Å)	2.17	2.09	2.09
Os	E_b (eV)	2.33	1.61	1.50
	M_S (μ_B)	0.46	1.89	1.15
	h (Å)	1.66	1.99	1.92
	$d_{C\text{-}Os}$ (Å)	2.19	1.99	2.06
Ir	E_b (eV)	2.17	1.94	2.12
	M_S (μ_B)	0.30	0.01	0.89
	h (Å)	1.71	1.96	1.89
	$d_{C\text{-}Ir}$ (Å)	2.23	1.96	2.03

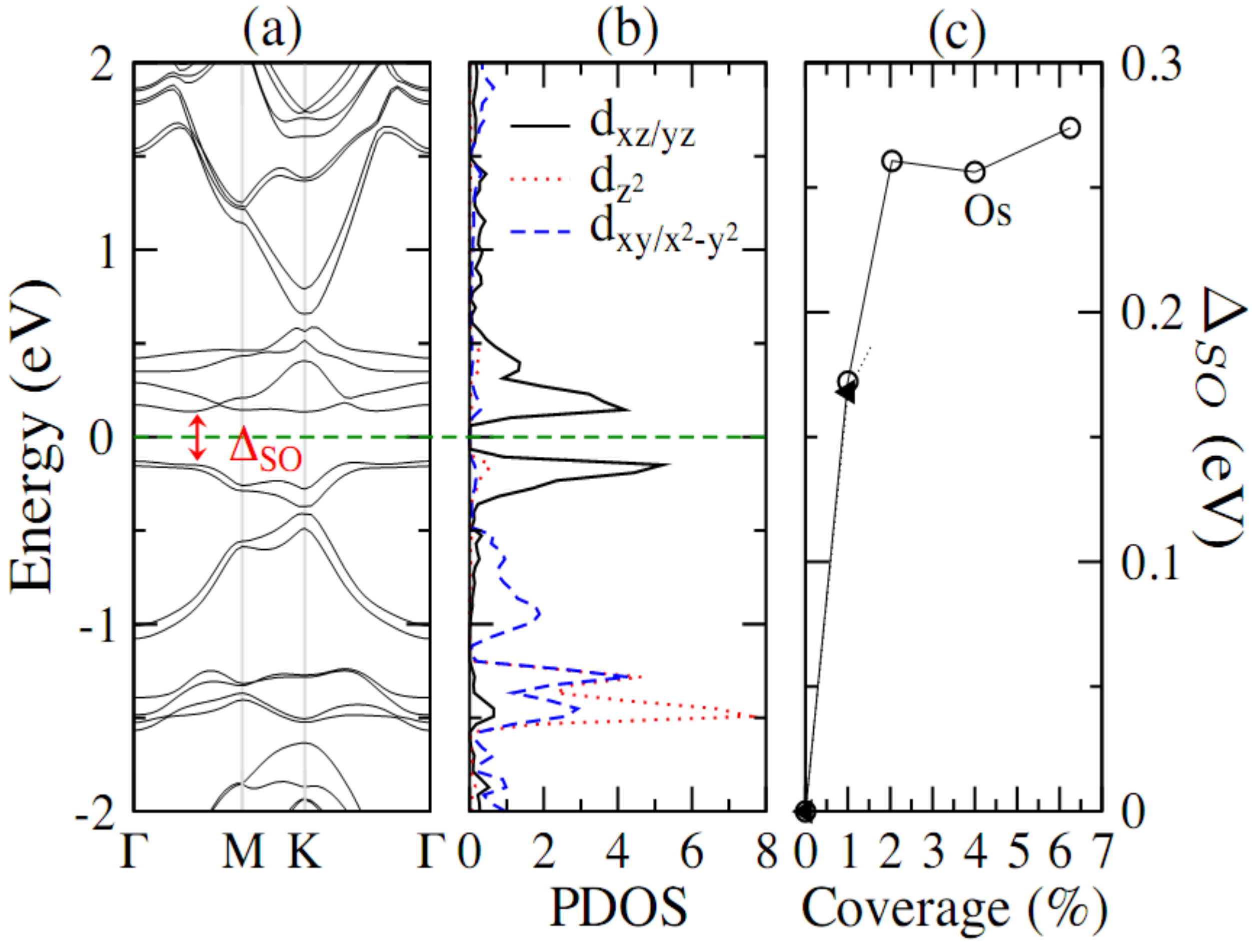
Re and Os are good candidates in terms of high segregation barriers away from the hollow site to other sites and small spin moments.

DFT Band structures of graphene with 5d adatoms



Os/graphene is the most interesting system due to both the huge Δ_{SO} and the TI nature.

More analysis of electronic structure of Os/graphene



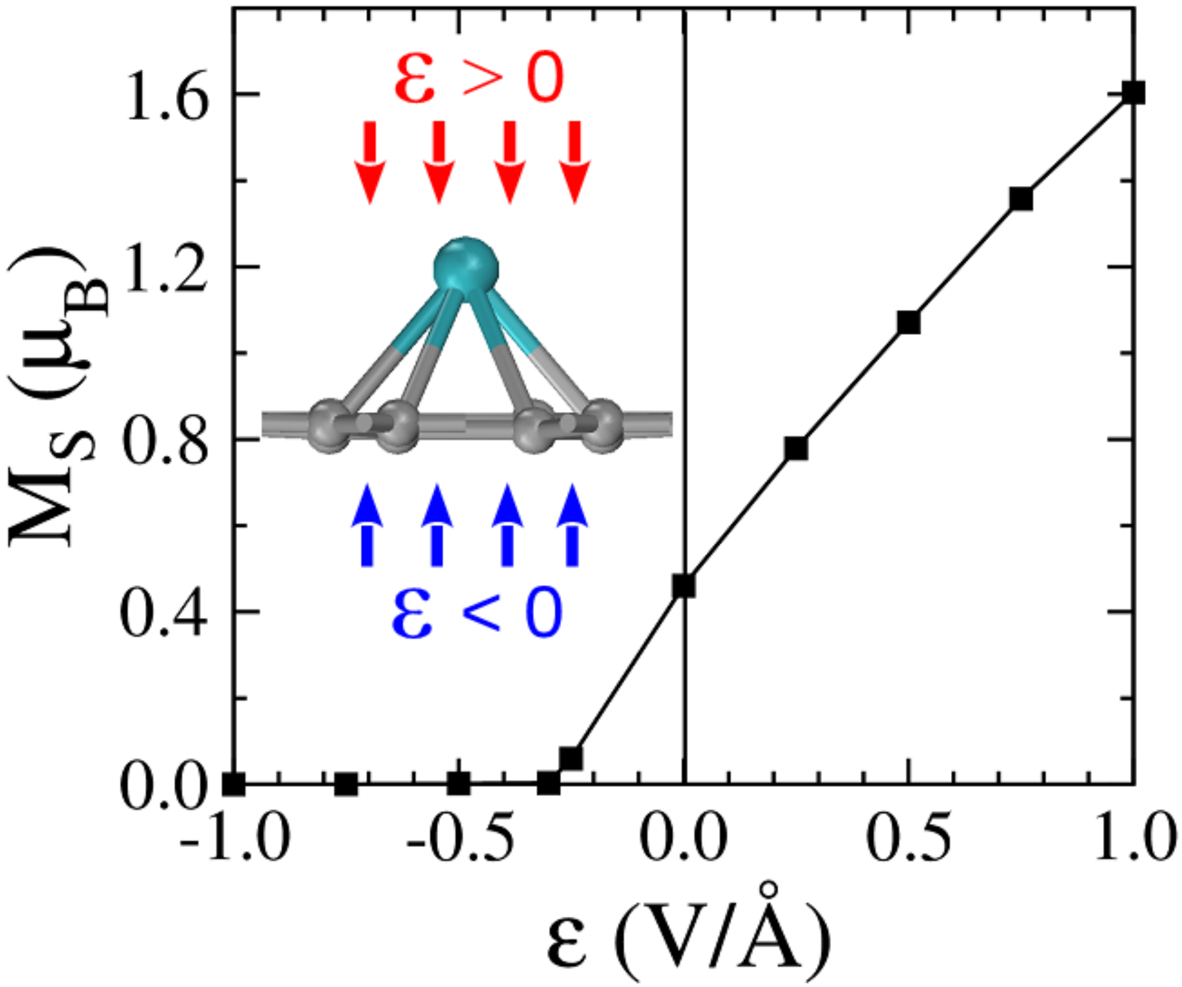
Gap is large in a broad range of coverage.

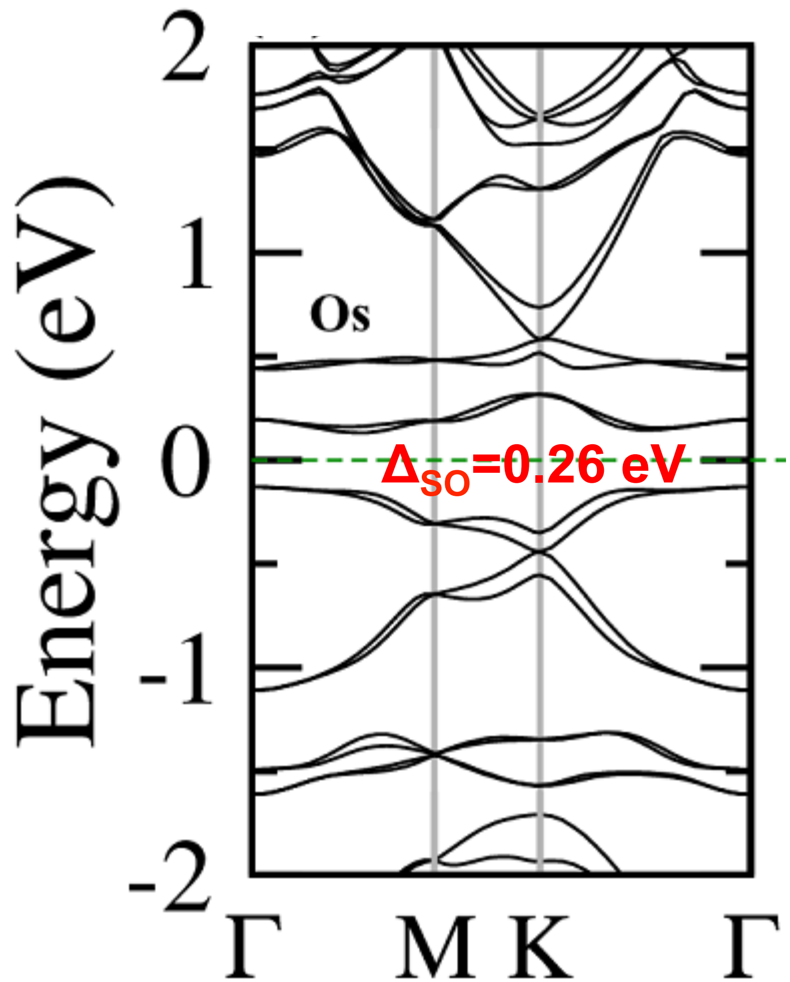
This striking feature is actually rather natural since the local atomic spin-orbit splitting for the Os d_{xz} and d_{yz} orbitals essentially sets Δ_{SO}.

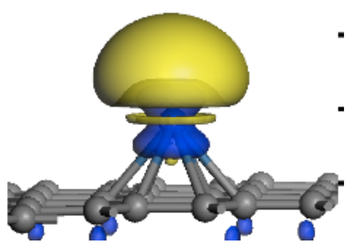
But Os/Gr is magnetic.

supercell	4×4	5×5	7×7	10×10
Coverage(%)	6.25	4	2.04	1
Δ_{SO} (eV)	**0.27**	**0.26**	**0.26**	**0.17**

Electric field to diminish magnetic moment of Os/graphene



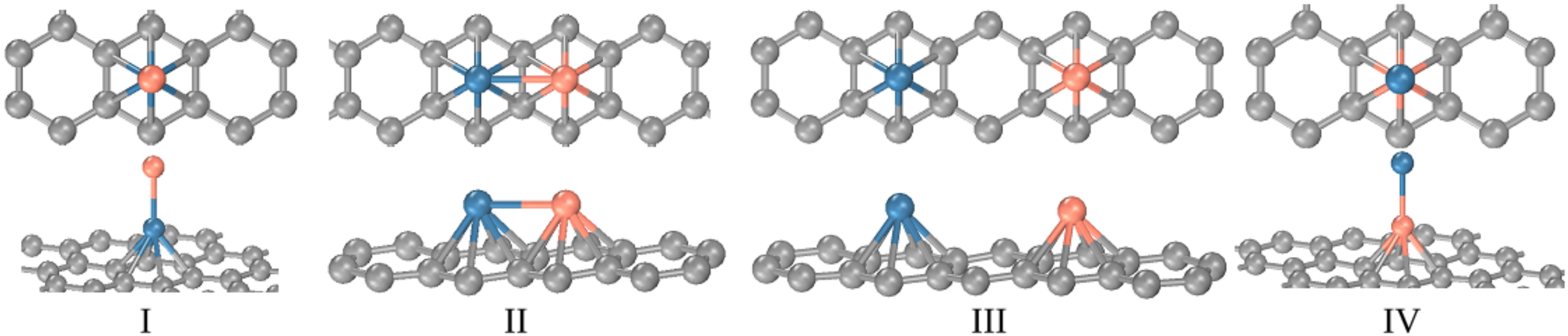


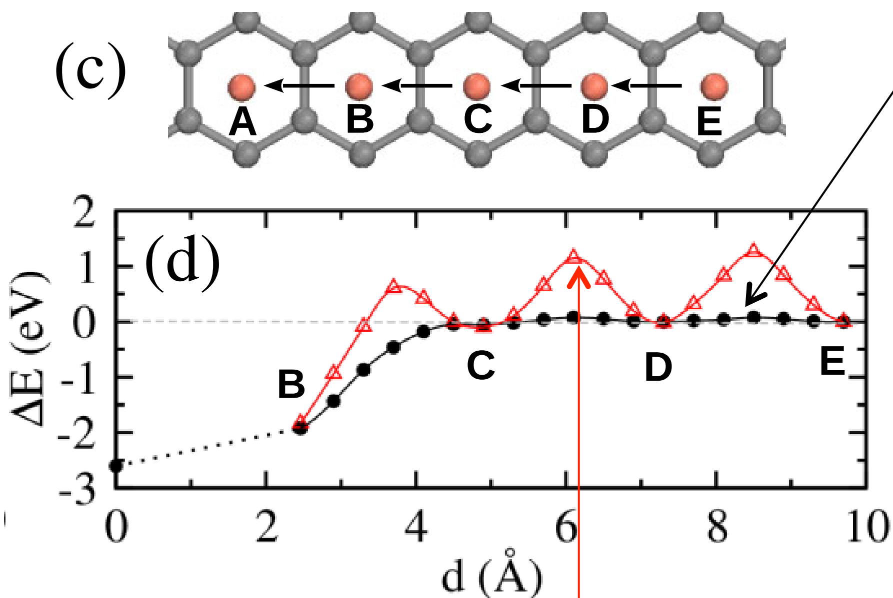


Negative electric field extracts electron charge on Os to graphene.

Using co-adsorption to modify properties of Os/graphene

Co-adsorbates: weak interaction with graphene but strong interaction with Os to extract electron charge from Os. The magnetic moment of Os is quenched.

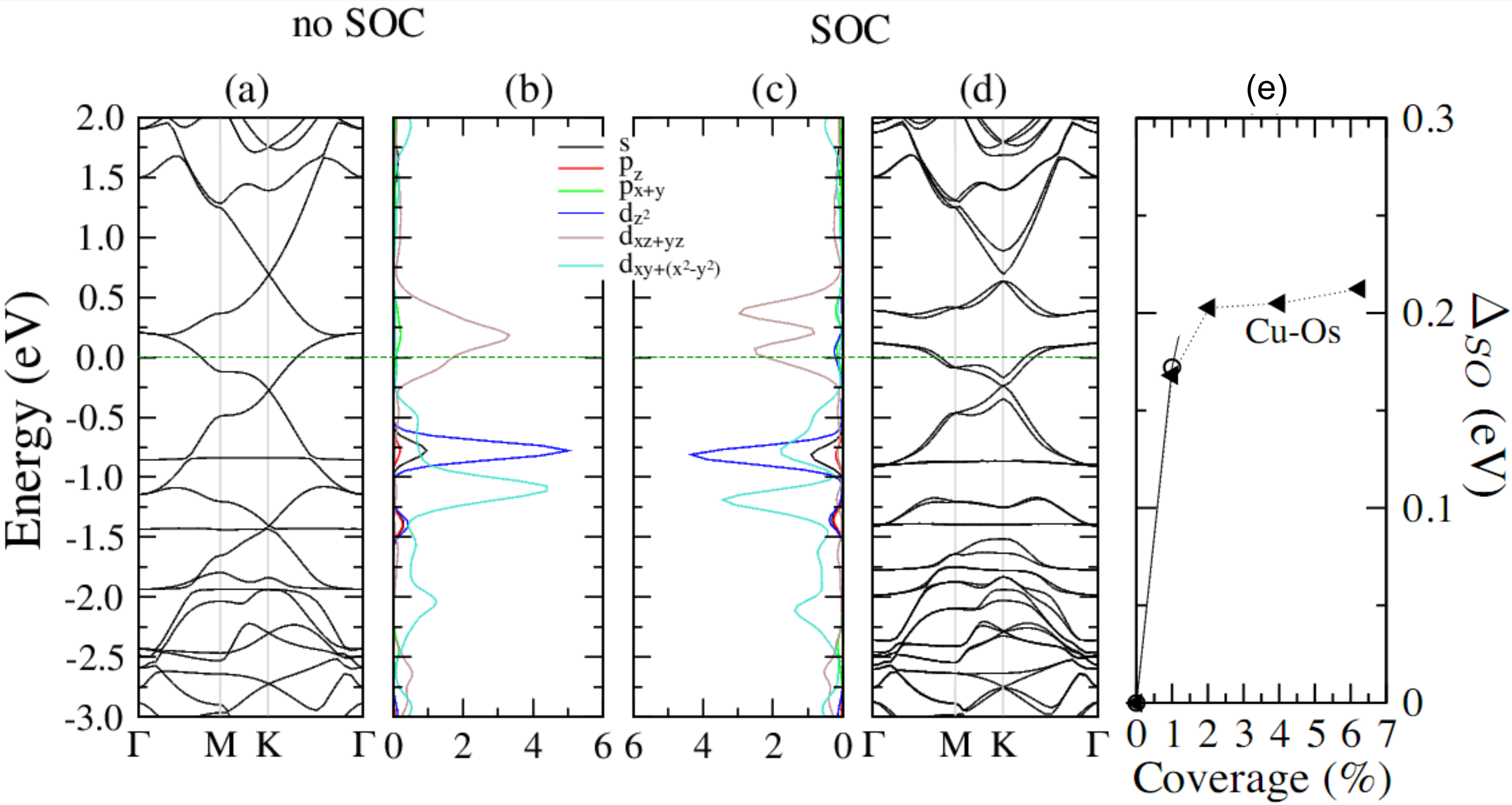




The small diffusion barrier and large energy gain evident for the Cu atom indicates that Cu–Os dimers should readily form.

Calculated energies for a CuOs dimer moving toward another CuOs dimer show that there is an high barrier, 1.3 eV. So the clustering of metals dimers are essentially blocked at room temperature.

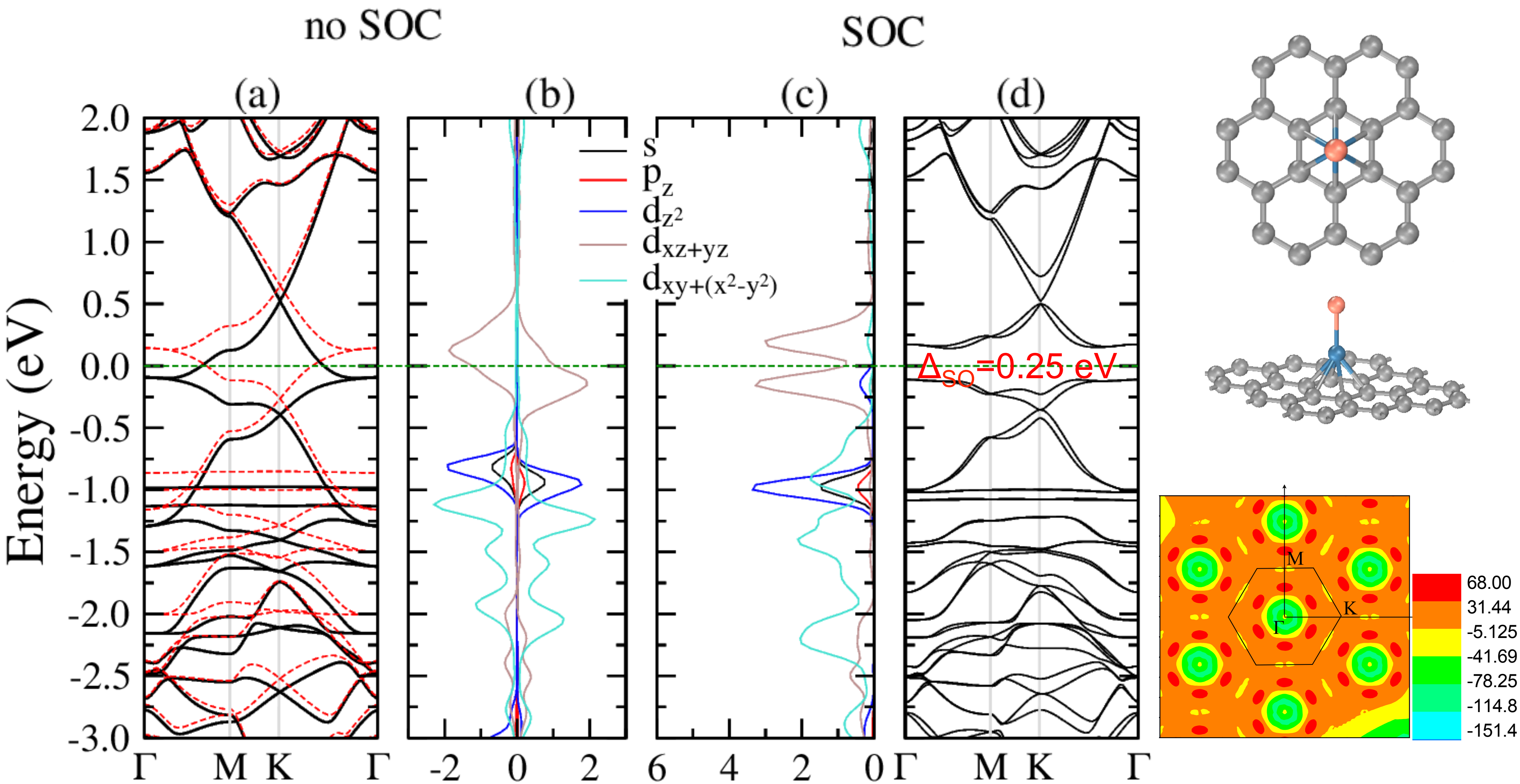
Electronic properties of (Cu-Os)/graphene



The (Cu-Os)/graphene is nonmagnetic and topological insulator gap is still giant (Δ_{SO}=0.21 eV at coverage of 6.25%).

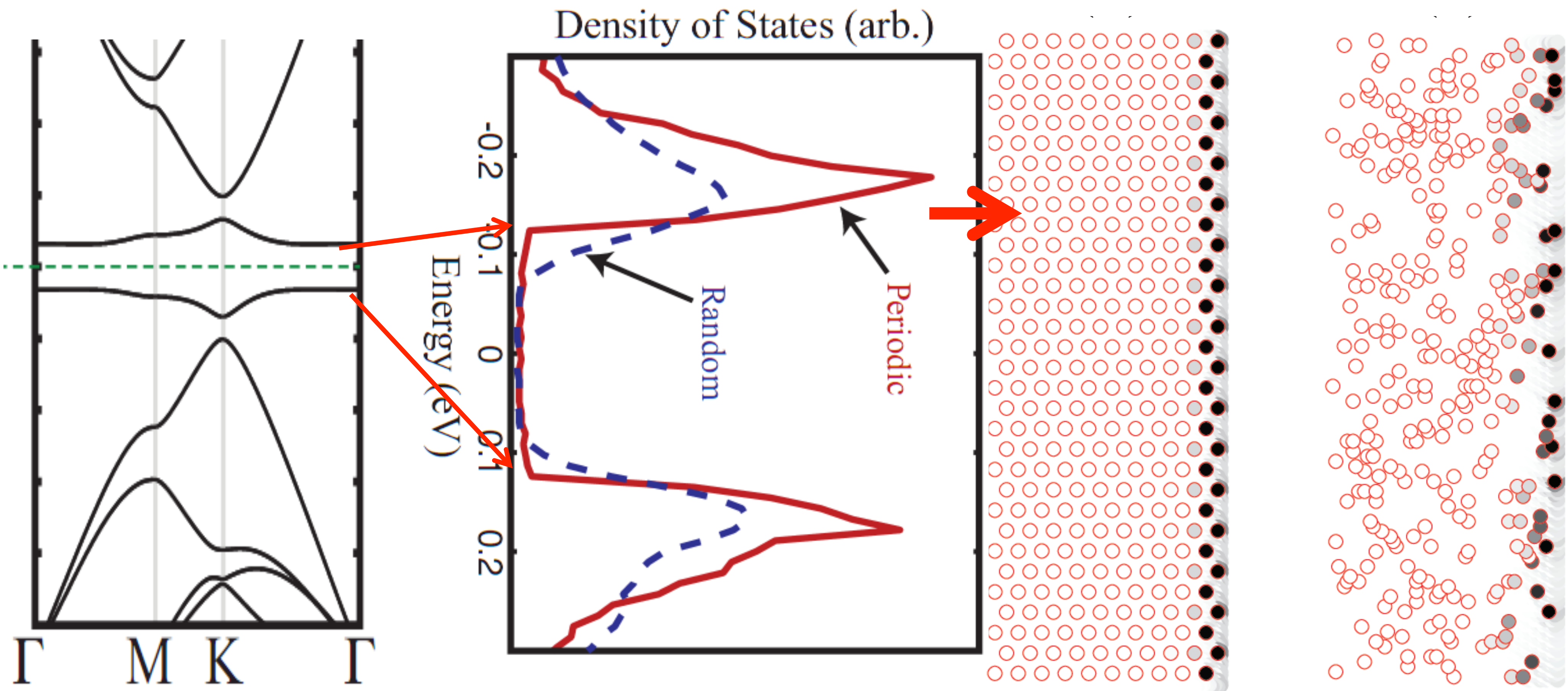
The drawback is that the Fermi level is about 0.1 eV bellow the valence band maximum, which implies that holes are introduced in graphene by Cu-Os dimers. This shortcoming may be eliminated by replacing Os by Ir.

Electronic properties of (Cu-Ir)/graphene



With SOC, (Cu-Ir)/graphene is a nonmagnetic “semiconductor” with Δ_{SO}=0.25 eV. Another significant advantage is that Fermi level resides in the gap.

The edge state and effect of randomness: TB results



TB calculations for a graphene strip with armchair edges clearly show the edge state within the bulk gap. These edge states remarkably survive even for randomly distributed adatoms.

Conclusions

- Large SOC-gap can be produced in graphene using adatoms.
- p-valent adatoms may easily form clusters, so low temperature is essential for deposition and measurement.
- 5d adatoms produce large and robust SOC-gap.
- The magnetic moment of 5d atoms can be tuned by using either electric field or co-adsorption of Cu.

- Cu-Ir/graphene is an ideal system for the realization of 2D QSH.

Collaborators

Jun Hu, UC Irvine
Jason Alicea, CalTech
Marcel Franz, UBC