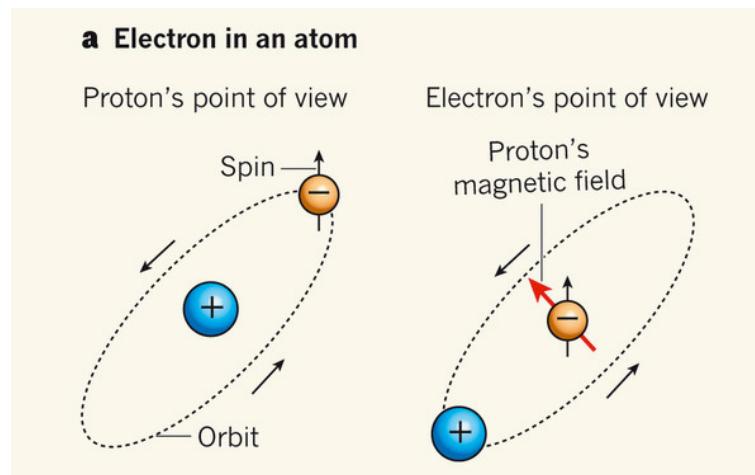


# Spin-orbit coupling: a relativistic effect



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Donostia-San Sebastián, Spain, 22-26 Aug 2016

## Outline

### Spin-orbit coupling in an atom

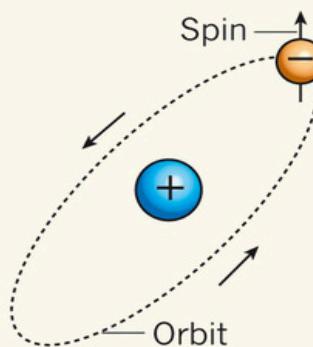
- Atom SOC
- Contraction of s and p shells

### Spin-orbit coupling in solids

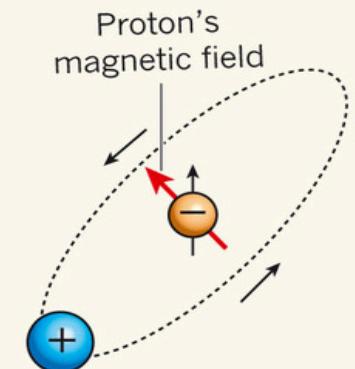
- Atomic SOC, such as HgTe
- Rashba effect
- Dresselhaus effect
- SOC in graphene

### a Electron in an atom

Proton's point of view

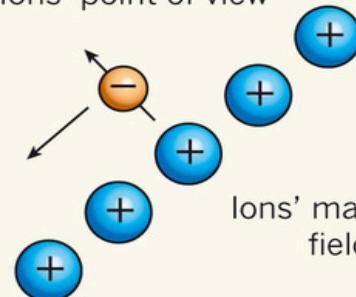


Electron's point of view



### b Free electron

Ions' point of view



Electron's point of view

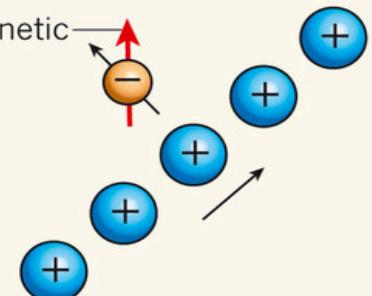


Figure credit: M. Chapman & C. Sá de Melo,  
Nature 471, 41–42 (2011)

# A hydrogen-like atom

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \quad (\text{Z is the atomic number})$$

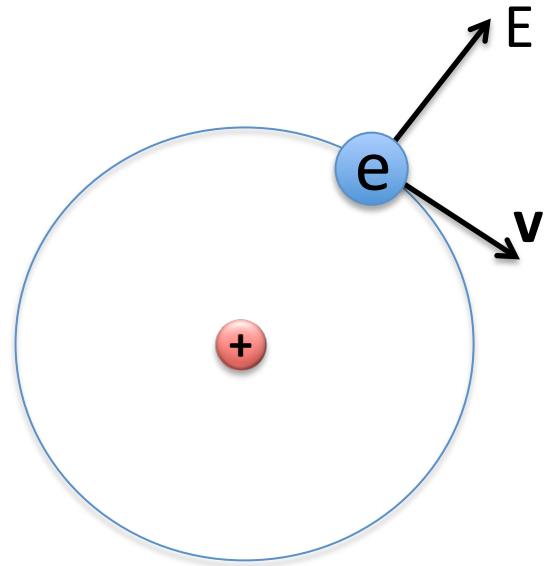
$$E_n = -\frac{\mu c^2 Z^2 \alpha^2}{2n^2}$$

$$r_1 \simeq \left( \frac{4\pi\epsilon_0}{e^2} \right) \frac{\hbar^2}{Zm_e}, \quad \sim Z^{-1}$$

$$v_1 = \frac{Ze^2}{4\pi\epsilon_0\hbar} \sim Z$$

$$mv^2 = \frac{Ze^2}{4\pi\epsilon_0 r_n} \sim Z^2$$

$$E = \nabla V(r) = \frac{1}{4\pi} \frac{Ze^2}{r^2} \hat{r} \quad \sim Z^3$$



# A hydrogen-like atom

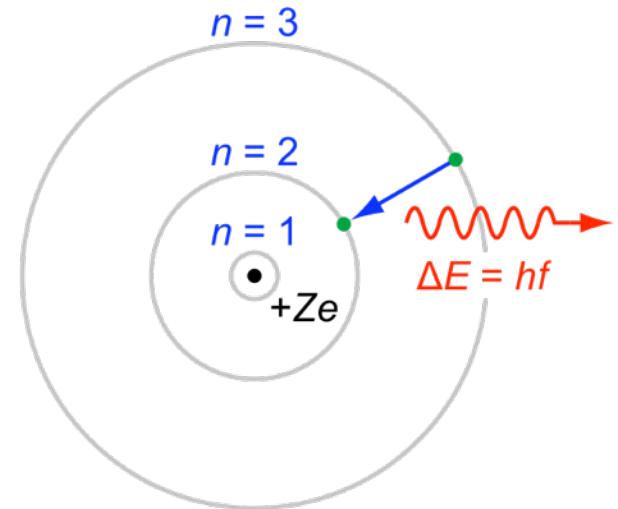
$$E_n = -\frac{\mu c^2 Z^2 \alpha^2}{2n^2} \sim -13.6 (Z^2/n^2) \text{ eV}$$

$$r_1 \simeq \left( \frac{4\pi\epsilon_0}{e^2} \right) \frac{\hbar^2}{Zm_e}, \sim a_0 = 0.529 Z^{-1} \text{ \AA}$$

$$v_1 = \frac{Ze^2}{4\pi\epsilon_0\hbar} \sim (Z/137) c$$

$$\gamma \stackrel{\text{def}}{=} \frac{1}{\sqrt{1 - v^2/c^2}}$$

Lorentz factor      Relativistic effect



$$m = \gamma m_0 = m_0 / \sqrt{1 - (v/c)^2}.$$
$$a_0 = \hbar^2 / me^2.$$

# A hydrogen-like atom

## Lorentz transformation

$$\mathbf{E}_{\parallel}' = \mathbf{E}_{\parallel}$$

$$\mathbf{B}_{\parallel}' = \mathbf{B}_{\parallel}$$

$$\mathbf{E}_{\perp}' = \gamma(\mathbf{E}_{\perp} + \mathbf{v} \times \mathbf{B})$$

$$\mathbf{B}_{\perp}' = \gamma \left( \mathbf{B}_{\perp} - \frac{1}{c^2} \mathbf{v} \times \mathbf{E} \right)$$

$$\mathbf{B} = \frac{1}{c^2} \mathbf{E} \times \mathbf{v}_e \sim Z^4$$

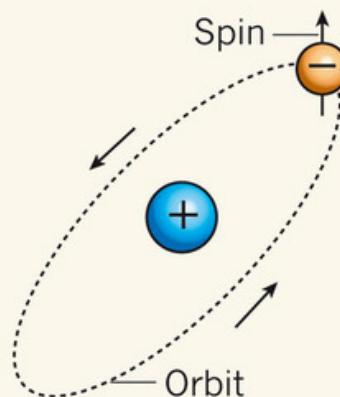
As  $\mathbf{l} = \mathbf{r} \times \mathbf{p}$ , and hence  $\mathbf{r} \times \mathbf{v} = \frac{1}{m_e} \mathbf{l}$ , we get the Hamiltonian

$$h_{SO} = -\mu_e \cdot \mathbf{B} = \frac{1}{m_e r c^2} \phi' \mu \cdot \mathbf{l} = \frac{e}{m_e^2 r c^2} \phi' \mathbf{s} \cdot \mathbf{l},$$

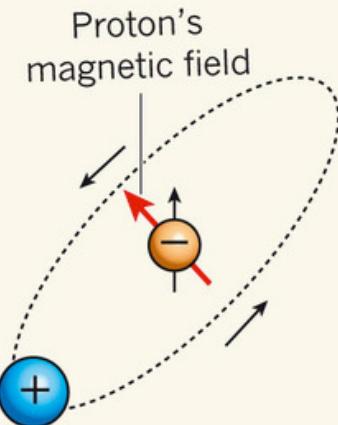
$\frac{1}{2}$   
Thomas factor

## a Electron in an atom

Proton's point of view



Electron's point of view



# Relativistic effects

## Relativity:

Switch the coordinate frame

Moving E →

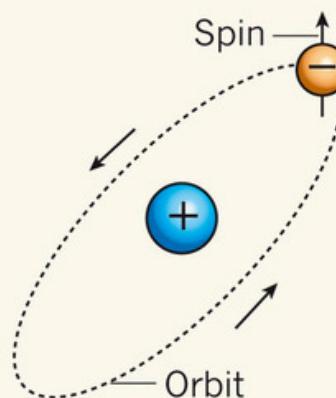
$$\mathbf{B} = \frac{1}{c^2} \mathbf{E} \times \mathbf{v}$$

## Quantum spin:

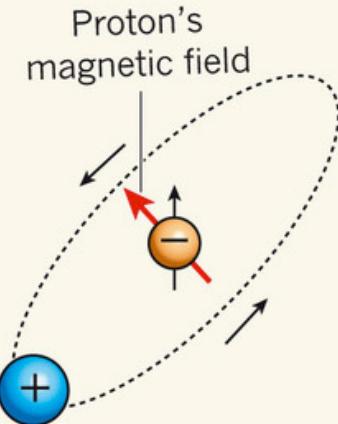
Electron has a spin  $s \rightarrow \mathbf{h} = -\mu_s \cdot \mathbf{B}$

## a Electron in an atom

Proton's point of view



Electron's point of view



## The Relativistic Hamiltonian

$$\left[ \frac{1}{2m_e} \left( \vec{p} - \frac{e}{c} \vec{A} \right)^2 - \frac{e\hbar}{2m_e c} \sigma \cdot \vec{\nabla} \times \vec{A} - \frac{\vec{p}^4}{8m_e^3 c^3} + \frac{e\hbar^2}{8m_e^2 c^2} \vec{\nabla} \cdot \vec{\nabla} \phi - \frac{e\hbar}{4m_e^2 c^2} \sigma \cdot \vec{\nabla} \phi \times \vec{p} \right] \psi = (E^{nr} - e\phi) \psi.$$

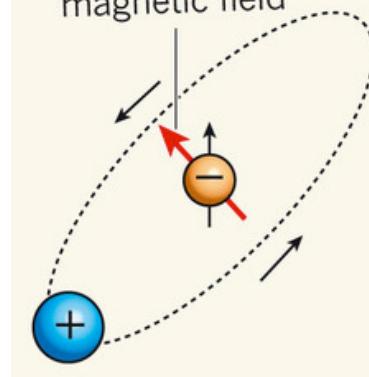
# The Fully Relativistic Hamiltonian

**Tab. 1.1** Summary of relativistic and spin-dependent interaction terms.

Perturbation	Description	Magnitude
$\frac{1}{2m_e} \left( \vec{p} - \frac{e}{c} \vec{A} \right)^2$	The nonrelativistic motion, $p^2/2m_e$ , and the interaction terms $\frac{e}{2m_ec} \vec{A} \cdot \vec{\nabla} + \frac{e^2}{2m_e c^2} \vec{A} \cdot \vec{A}$ . The latter terms are responsible for absorption and emission; they can be written as $-e \vec{r} \cdot \vec{E}$ (see Section 4.1.1).	$\gtrsim 10^5 \text{ cm}^{-1}$
$\frac{e\hbar}{2m_ec} \vec{\sigma} \cdot \vec{\nabla} \times \vec{A}$	The spin-1/2 ( $\vec{s} = \vec{\sigma}/2$ ) interaction with a magnetic field ( $\vec{B} \equiv \vec{\nabla} \times \vec{A}$ ). This term gives the correct g-factor, $g = 2$ , and magnetic moment of the electron, $\mu = \frac{e\hbar}{2m_ec} g \vec{s}$ .	$\approx 1 \text{ cm}^{-1}$
$\frac{\vec{p}^4}{8m_e^3 c^3}$	Relativistic mass correction term.	$\approx 0.1 \text{ cm}^{-1}$
$\frac{e\hbar^2}{8m_e^2 c^2} \vec{\nabla} \cdot \vec{\nabla} \phi$	The “Darwin” term responsible for s-state shifts. It represents the relativistic nonlocalizability of the electron and is related to both the negative-energy sea and its rapid motion.	$< 0.1 \text{ cm}^{-1}$
$\frac{e\hbar}{4m_e^2 c^2} \vec{\sigma} \cdot \vec{\nabla} \phi \times \vec{p}$	Spin-orbit interaction. As shown in Problem 1.4, this term can be written as $\frac{e\hbar^2}{2m_e^2 c^2} \frac{1}{r} \frac{d\phi}{dr} (\vec{l} \cdot \vec{s})$ , where $\vec{l}$ is the orbital angular momentum. In contrast to the previous term, this does not affect s states.	$10-10^3 \text{ cm}^{-1}$

Electron's point of view

Proton's magnetic field



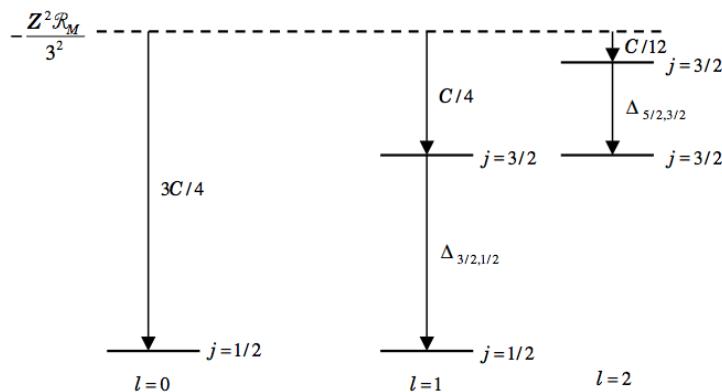
# Experimental consequence: fine structure

Total angular momentum,

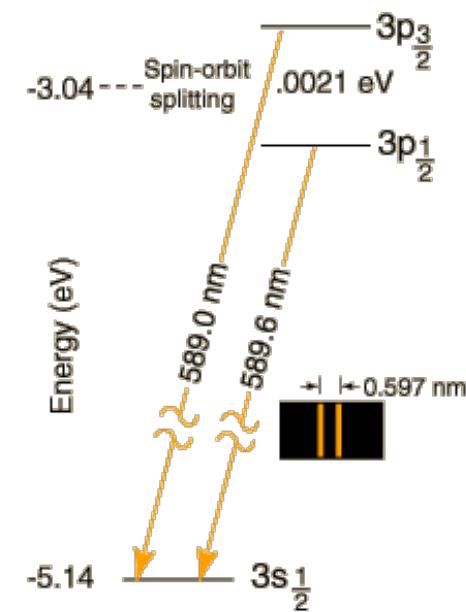
$$\vec{j} = \vec{l} + \vec{s},$$

with eigenvalues (of  $\vec{j}^2$ )  $j(j+1)$ .  
values that  $\vec{j}$  can assume are

$$j = \begin{cases} l \pm \frac{1}{2}, & l \neq 0, \\ \frac{1}{2}, & l = 0. \end{cases} \quad \Delta E_{nlj} = \Delta E_R + \Delta E_{so} = \alpha^2 \mathcal{R}_M \left( \frac{3}{4n} - \frac{1}{j + \frac{1}{2}} \right) \frac{Z^4}{n^3}.$$



**Fig. 1.7** Fine structure of hydrogen-like ions in wavenumbers for  $n = 3$  where  $C = \alpha^2 Z^4 \mathcal{R}_M / n^3$  and  $\Delta_{j+1,j} = \Delta E_{nlj+1} - \Delta E_{nlj} = C/l(l+1)$ . The levels are all shifted below  $-Z^2 \mathcal{R}_M / n^2$ , the nonrelativistic energy.



$$\mu_s g B = (5.79 \times 10^{-5} \text{ eV/T}) 2B = 0.0021 \text{ eV}$$

$$B = 18 \text{ Tesla}$$

$$\text{A huge field}$$

# Experimental consequence: *sp* contraction

$$\langle v_r \rangle_{1s} = Z$$

$$\gamma \stackrel{\text{def}}{=} \frac{1}{\sqrt{1 - v^2/c^2}} = 123 \%$$

$v$ , is = 80 for Hg

$c$ , is = 137.035999679

$$\Delta E_{nlj} = \Delta E_R + \Delta E_{so} = \alpha^2 \mathcal{R}_M \left( \frac{3}{4n} - \frac{1}{j + \frac{1}{2}} \right) \frac{Z^4}{n^3}.$$

- Contraction of s and p shells, decrease in  $E_n$
- Expansion of d and f shells, increase in  $E_n$

## Example 1: Hg

- Why Hg is in a liquid metal at room temperature?

The  $6s^2$  orbital is contracted so much that they only weakly contribute to any bonding, which is weak vdW type.

- The Hg-s state is lower in energy than Te-p states in HgTe (discuss later), giving rise to the topological insulator state.

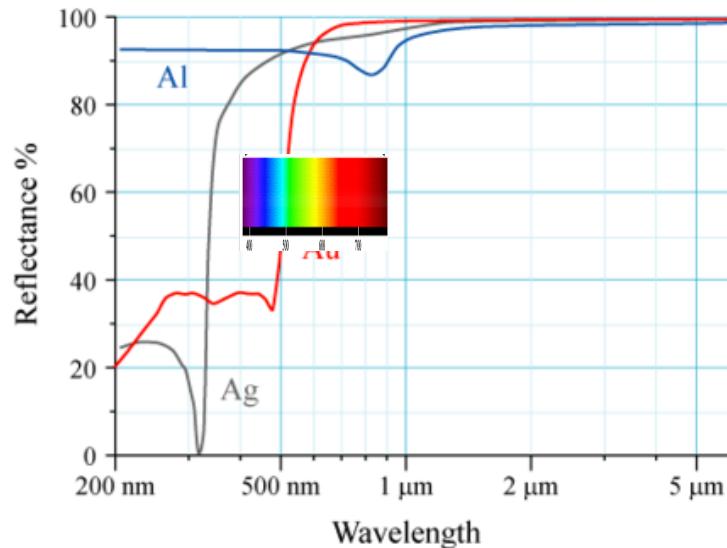
$$a_{rel} = \frac{\hbar^2}{me^2} = a_0/\gamma = a_0 81\%$$

Periodic Table of the Elements																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
1	H	Hydrogen 1.01	2	Be	Beryllium 9.01	3	Li	Lithium 6.94	4	Be	Beryllium 9.01	5	B	Boron 10.81	6	C	Carbon 12.01	7	N	Nitrogen 14.01	8	O	Oxygen 16.00	9	F	Fluorine 19.00	10	Ne	Helium 4.00	18	He	Helium 4.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
11	Na	Sodium 22.99	12	Mg	Magnesium 24.31	13	Al	Aluminum 26.98	14	Si	Silicon 28.09	15	P	Phosphorus 30.97	16	S	Sulfur 32.06	17	Cl	Chlorine 35.45	18	Ar	Argon 39.95	19	K	Potassium 39.10	20	Ca	Calcium 40.08	21	Sc	Scandium 44.96	22	Ti	Titanium 47.88	23	V	Vanadium 50.94	24	Cr	Chromium 51.99	25	Mn	Manganese 54.94	26	Fe	Iron 55.93	27	Co	Cobalt 58.93	28	Ni	Nickel 58.69	29	Cu	Copper 63.55	30	Zn	Zinc 65.39	31	Ga	Gallium 69.73	32	Ge	Germanium 72.61	33	As	Arsenic 74.92	34	Se	Selenium 78.09	35	Br	Bromine 79.90	36	Kr	Krypton 84.80	37	Rb	Rubidium 84.49	38	Sr	Samarium 87.62	39	Y	Yttrium 88.91	40	Zr	Zirconium 91.22	41	Nb	Niobium 92.91	42	Mo	Molybdenum 95.94	43	Tc	Techneium 98.91	44	Ru	Ruthenium 101.07	45	Rh	Rhenium 102.91	46	Pd	Palladium 106.42	47	Ag	Argentum 107.87	48	Cd	Cadmium 112.41	49	In	Inertium 114.82	50	Sn	Stannum 118.71	51	Sb	Sbismuth 121.76	52	Te	Tellurium 127.6	53	I	Iodine 126.90	54	Xe	Xenon 131.29	55	Cs	Cesium 132.91	56	Ba	Boron 137.33	57	La	Lanthanides 138.91	58	Hf	Hafnium 178.49	59	Ta	Tantalum 180.95	60	W	Tungsten 183.85	61	Re	Rhenium 190.22	62	Os	Osmium 190.22	63	Ir	Iridium 192.27	64	Pt	Platinum 195.08	65	Au	Gold 196.97	66	Hg	Mercury 200.59	67	Tl	Thallium 204.38	68	Pb	Bismuth 209.02	69	Bi	Bismuth 209.02	70	Po	Poliomeric 209.02	71	At	Atatomatic 209.02	72	Rn	Radon 222.02	73	Fr	Francium 223.02	74	Ra	Radium 226.03	75	Hf	Hafnium 261	76	Ta	Tantalum 262	77	W	Tungsten 266	78	Re	Rhenium 266	79	Os	Osmium 269	80	Ir	Iridium 269	81	Pt	Platinum 269	82	Au	Gold 272	83	Hg	Mercury 272	84	Tl	Thallium 272	85	Pb	Bismuth 289	86	Bi	Bismuth 289	87	Po	Poliomeric 289	88	At	Atatomatic 289	89	Rn	Radon 298	90	Fr	Francium 298	91	Ra	Radium 298	92	Hf	Hafnium 298	93	Ta	Tantalum 298	94	W	Tungsten 298	95	Re	Rhenium 298	96	Os	Osmium 298	97	Ir	Iridium 298	98	Pt	Platinum 298	99	Au	Gold 298	100	Hg	Mercury 298	101	Tl	Thallium 298	102	Pb	Bismuth 298	103	Bi	Bismuth 298	104	Po	Poliomeric 298	105	At	Atatomatic 298	106	Rn	Radon 298	107	Fr	Francium 298	108	Ra	Radium 298	109	Hf	Hafnium 298	110	Ta	Tantalum 298	111	W	Tungsten 298	112	Re	Rhenium 298	113	Os	Osmium 298	114	Ir	Iridium 298	115	Pt	Platinum 298	116	Au	Gold 298	117	Hg	Mercury 298	118	Tl	Thallium 298	119	Pb	Bismuth 298	120	Bi	Bismuth 298	121	Po	Poliomeric 298	122	At	Atatomatic 298	123	Rn	Radon 298	124	Fr	Francium 298	125	Ra	Radium 298	126	Hf	Hafnium 298	127	Ta	Tantalum 298	128	W	Tungsten 298	129	Re	Rhenium 298	130	Os	Osmium 298	131	Ir	Iridium 298	132	Pt	Platinum 298	133	Au	Gold 298	134	Hg	Mercury 298	135	Tl	Thallium 298	136	Pb	Bismuth 298	137	Bi	Bismuth 298	138	Po	Poliomeric 298	139	At	Atatomatic 298	140	Rn	Radon 298	141	Fr	Francium 298	142	Ra	Radium 298	143	Hf	Hafnium 298	144	Ta	Tantalum 298	145	W	Tungsten 298	146	Re	Rhenium 298	147	Os	Osmium 298	148	Ir	Iridium 298	149	Pt	Platinum 298	150	Au	Gold 298	151	Hg	Mercury 298	152	Tl	Thallium 298	153	Pb	Bismuth 298	154	Bi	Bismuth 298	155	Po	Poliomeric 298	156	At	Atatomatic 298	157	Rn	Radon 298	158	Fr	Francium 298	159	Ra	Radium 298	160	Hf	Hafnium 298	161	Ta	Tantalum 298	162	W	Tungsten 298	163	Re	Rhenium 298	164	Os	Osmium 298	165	Ir	Iridium 298	166	Pt	Platinum 298	167	Au	Gold 298	168	Hg	Mercury 298	169	Tl	Thallium 298	170	Pb	Bismuth 298	171	Bi	Bismuth 298	172	Po	Poliomeric 298	173	At	Atatomatic 298	174	Rn	Radon 298	175	Fr	Francium 298	176	Ra	Radium 298	177	Hf	Hafnium 298	178	Ta	Tantalum 298	179	W	Tungsten 298	180	Re	Rhenium 298	181	Os	Osmium 298	182	Ir	Iridium 298	183	Pt	Platinum 298	184	Au	Gold 298	185	Hg	Mercury 298	186	Tl	Thallium 298	187	Pb	Bismuth 298	188	Bi	Bismuth 298	189	Po	Poliomeric 298	190	At	Atatomatic 298	191	Rn	Radon 298	192	Fr	Francium 298	193	Ra	Radium 298	194	Hf	Hafnium 298	195	Ta	Tantalum 298	196	W	Tungsten 298	197	Re	Rhenium 298	198	Os	Osmium 298	199	Ir	Iridium 298	200	Pt	Platinum 298	201	Au	Gold 298	202	Hg	Mercury 298	203	Tl	Thallium 298	204	Pb	Bismuth 298	205	Bi	Bismuth 298	206	Po	Poliomeric 298	207	At	Atatomatic 298	208	Rn	Radon 298	209	Fr	Francium 298	210	Ra	Radium 298	211	Hf	Hafnium 298	212	Ta	Tantalum 298	213	W	Tungsten 298	214	Re	Rhenium 298	215	Os	Osmium 298	216	Ir	Iridium 298	217	Pt	Platinum 298	218	Au	Gold 298	219	Hg	Mercury 298	220	Tl	Thallium 298	221	Pb	Bismuth 298	222	Bi	Bismuth 298	223	Po	Poliomeric 298	224	At	Atatomatic 298	225	Rn	Radon 298	226	Fr	Francium 298	227	Ra	Radium 298	228	Hf	Hafnium 298	229	Ta	Tantalum 298	230	W	Tungsten 298	231	Re	Rhenium 298	232	Os	Osmium 298	233	Ir	Iridium 298	234	Pt	Platinum 298	235	Au	Gold 298	236	Hg	Mercury 298	237	Tl	Thallium 298	238	Pb	Bismuth 298	239	Bi	Bismuth 298	240	Po	Poliomeric 298	241	At	Atatomatic 298	242	Rn	Radon 298	243	Fr	Francium 298	244	Ra	Radium 298	245	Hf	Hafnium 298	246	Ta	Tantalum 298	247	W	Tungsten 298	248	Re	Rhenium 298	249	Os	Osmium 298	250	Ir	Iridium 298	251	Pt	Platinum 298	252	Au	Gold 298	253	Hg	Mercury 298	254	Tl	Thallium 298	255	Pb	Bismuth 298	256	Bi	Bismuth 298	257	Po	Poliomeric 298	258	At	Atatomatic 298	259	Rn	Radon 298	260	Fr	Francium 298	261	Ra	Radium 298	262	Hf	Hafnium 298	263	Ta	Tantalum 298	264	W	Tungsten 298	265	Re	Rhenium 298	266	Os	Osmium 298	267	Ir	Iridium 298	268	Pt	Platinum 298	269	Au	Gold 298	270	Hg	Mercury 298	271	Tl	Thallium 298	272	Pb	Bismuth 298	273	Bi	Bismuth 298	274	Po	Poliomeric 298	275	At	Atatomatic 298	276	Rn	Radon 298	277	Fr	Francium 298	278	Ra	Radium 298	279	Hf	Hafnium 298	280	Ta	Tantalum 298	281	W	Tungsten 298	282	Re	Rhenium 298	283	Os	Osmium 298	284	Ir	Iridium 298	285	Pt	Platinum 298	286	Au	Gold 298	287	Hg	Mercury 298	288	Tl	Thallium 298	289	Pb	Bismuth 298	290	Bi	Bismuth 298	291	Po	Poliomeric 298	292	At	Atatomatic 298	293	Rn	Radon 298	294	Fr	Francium 298	295	Ra	Radium 298	296	Hf	Hafnium 298	297	Ta	Tantalum 298	298	W	Tungsten 298	299	Re	Rhenium 298	300	Os	Osmium 298	301	Ir	Iridium 298	302	Pt	Platinum 298	303	Au	Gold 298	304	Hg	Mercury 298	305	Tl	Thallium 298	306	Pb	Bismuth 298	307	Bi	Bismuth 298	308	Po	Poliomeric 298	309	At	Atatomatic 298	310	Rn	Radon 298	311	Fr	Francium 298	312	Ra	Radium 298	313	Hf	Hafnium 298	314	Ta	Tantalum 298	315	W	Tungsten 298	316	Re	Rhenium 298	317	Os	Osmium 298	318	Ir	Iridium 298	319	Pt	Platinum 298	320	Au	Gold 298	321	Hg	Mercury 298	322	Tl	Thallium 298	323	Pb	Bismuth 298	324	Bi	Bismuth 298	325	Po	Poliomeric 298	326	At	Atatomatic 298	327	Rn	Radon 298	328	Fr	Francium 298	329	Ra	Radium 298	330	Hf	Hafnium 298	331	Ta	Tantalum 298	332	W	Tungsten 298	333	Re	Rhenium 298	334	Os	Osmium 298	335	Ir	Iridium 298	336	Pt	Platinum 298	337	Au	Gold 298	338	Hg	Mercury 298	339	Tl	Thallium 298	340	Pb	Bismuth 298	341	Bi	Bismuth 298	342	Po	Poliomeric 298	343	At	Atatomatic 298	344	Rn	Radon 298	345	Fr	Francium 298	346	Ra	Radium 298	347	Hf	Hafnium 298	348	Ta	Tantalum 298	349	W	Tungsten 298	350	Re	Rhenium 298	351	Os	Osmium 298	352	Ir	Iridium 298	353	Pt	Platinum 298	354	Au	Gold 298	355	Hg	Mercury 298	356	Tl	Thallium 298	357	Pb	Bismuth 298	358	Bi	Bismuth 298	359	Po	Poliomeric 298	360	At	Atatomatic 298	361	Rn	Radon 298	362	Fr	Francium 298	363	Ra	Radium 298	364	Hf	Hafnium 298	365	Ta	Tantalum 298	366	W	Tungsten 298	367	Re	Rhenium 298	368	Os	Osmium 298	369	Ir	Iridium 298	370	Pt	Platinum 298	371	Au	Gold 298	372	Hg	Mercury 298	373	Tl	Thallium 298	374	Pb	Bismuth 298	375	Bi	Bismuth 298	376	Po	Poliomeric 298	377	At	Atatomatic 298	378	Rn	Radon 298	379	Fr	Francium 298	380	Ra	Radium 298	381	Hf	Hafnium 298	382	Ta	Tantalum 298	383	W	Tungsten 298	384	Re	Rhenium 298	385	Os	Osmium 298	386	Ir	Iridium 298	387	Pt	Platinum 298	388	Au	Gold 298	389	Hg	Mercury 298	390	Tl	Thallium 298	391	Pb	Bismuth 298	392	Bi	Bismuth 298	393	Po	Poliomeric 298	394	At	Atatomatic 298	395	Rn	Radon 298	396	Fr	Francium 298	397	Ra	Radium 298	398	Hf	Hafnium 298	399	Ta	Tantalum 298	400	W	Tungsten 298	401	Re	Rhenium 298	402	Os	Osmium 298	403	Ir	Iridium 298	404	Pt	Platinum 298	405	Au	Gold 298	406	Hg	Mercury 298	407	Tl	Thallium 298	408	Pb	Bismuth 298	409	Bi	Bismuth 298	410	Po	Poliomeric 298	411	At	Atatomatic 298	412	Rn	Radon 298	413	Fr	Francium 298	414	Ra	Radium 298	415	Hf	Hafnium 298	416	Ta	Tantalum 298	417	W	Tungsten 298	418	Re	Rhenium 298	419	Os	Osmium 298	420	Ir	Iridium 

# Experimental consequence: *sp* contraction

Example 2: Au

- Why does Au have the golden color? (Known Al and Ag are white)



Periodic Table of the Elements

A standard periodic table of elements is shown, highlighting the transition metals (groups 3-12) in yellow. A red box highlights the element Gold (Au) located in the bottom right corner of the table.

1 H Hydrogen 1.01	2 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01
5 B Boron 10.81	6 C Carbon 12.01
7 N Nitrogen 14.01	8 O Oxygen 16.00
9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31
13 Al Aluminum 26.98	14 Si Silicon 28.09
15 P Phosphorus 30.97	16 S Sulfur 32.06
17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08
21 Sc Scandium 44.96	22 Ti Titanium 47.88
23 V Vanadium 51.99	24 Cr Chromium 54.94
25 Mn Manganese 54.94	26 Fe Iron 55.93
27 Co Cobalt 58.93	28 Ni Nickel 58.69
29 Cu Copper 63.55	30 Zn Zinc 65.39
31 Ga Gallium 69.73	32 Ge Germanium 72.61
33 As Arsenic 74.92	34 Se Selenium 78.09
35 Br Bromine 79.90	36 Kr Krypton 84.80
37 Rb Rubidium 84.49	38 Sr Strontium 87.62
39 Y Yttrium 88.91	40 Zr Zirconium 91.22
41 Nb Niobium 92.91	42 Mo Molybdenum 95.94
43 Tc Technetium 98.91	44 Ru Ruthenium 101.07
45 Rh Rhodium 102.91	46 Pd Palladium 106.42
47 Ag Silver 107.87	48 Cd Cadmium 112.41
49 In Indium 114.82	50 Sn Tin 118.71
51 Sb Antimony 121.76	52 Te Tellurium 127.6
53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33
57 La Lanthanides	57-71
58 Hf Helium 138.49	58-72
59 Ta Tantalum 145.95	59-73
60 W Tungsten 183.85	60-74
61 Re Ruthenium 190.22	61-75
62 Os Osmium 191.08	62-76
63 Ir Iridium 191.07	63-77
64 Pt Platinum 195.08	64-78
65 Au Gold 196.97	65-79
66 Hg Mercury 200.59	66-80
67 Tl Thallium 204.38	67-81
68 Pb Lead 207.20	68-82
69 Bi Bismuth 208.98	69-83
70 Po Polonium 208.98	70-84
71 At Astatine 209.02	71-85
72 Rn Radon 222.02	72-86
73 Fr Francium 223.02	73-87
74 Ra Radium 226.03	74-88
75 Ac Actinides	75-103
76 Hf Hafnium 261.01	76-104
77 Ta Tantalum 262.01	77-105
78 W Tungsten 263.05	78-106
79 Re Ruthenium 263.85	79-107
80 Os Osmium 263.85	80-108
81 Ir Iridium 264.22	81-109
82 Pt Platinum 269.08	82-110
83 Bi Bismuth 269.88	83-111
84 Po Polonium 269.88	84-112
85 At Astatine 269.98	85-113
86 Rn Radon 272.02	86-114
87 Fr Francium 273.02	87-115
88 Ra Radium 276.03	88-116
89 Ac Actinides	89-117
90 Hf Hafnium 281.01	90-118
91 Ta Tantalum 282.01	91-119
92 W Tungsten 283.05	92-120
93 Re Ruthenium 283.85	93-121
94 Os Osmium 283.85	94-122
95 Ir Iridium 284.22	95-123
96 Pt Platinum 289.08	96-124
97 Bi Bismuth 289.88	97-125
98 Po Polonium 289.88	98-126
99 At Astatine 289.98	99-127
100 Rn Radon 292.02	100-128
101 Fr Francium 293.02	101-129
102 Ra Radium 296.03	102-130
103 Ac Actinides	103-131

Small gap between filled 5d (expansion)  
and empty 6s (contraction)

Au:  $5d^{10} 6s^1$

More examples:

atomic ground-state changes, such as Mo  $4d^5 5s^1$  but W  $5d^4 6s^2$

CsAu is a relativistic semiconductor, and CsAu(NR) would be a metal ( $\text{Au}^{-1}$ )

# Two types of SOC in solids

## Symmetry-independent:

exists in all types of crystals

stem from SOC in atomic orbitals, similar to that in atoms.

## Symmetry-dependent:

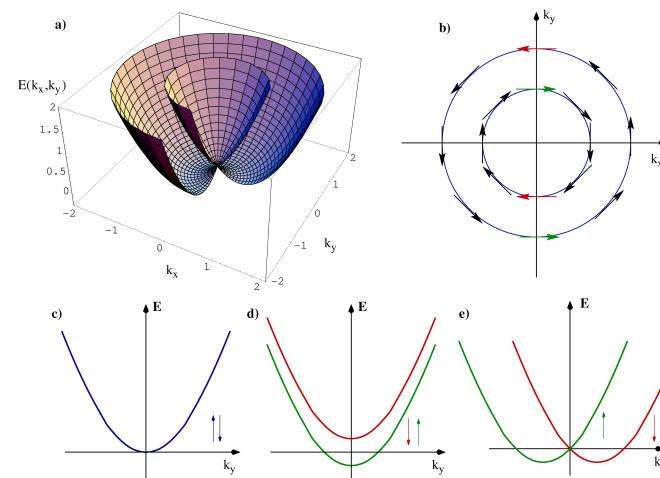
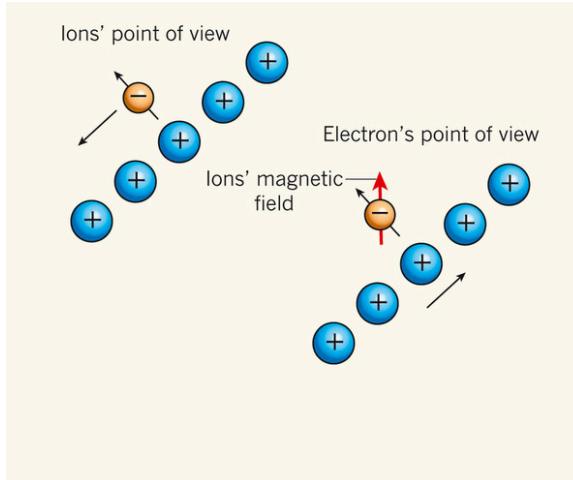
exists only in crystals without inversion symmetry

(a) Bychkov-Rashba (surface): usually referred to Surface-Induced-Assymmetry (SIA)

(b) Dresselhaus interaction (bulk): Bulk-Induced-Assymmetry (BIA)

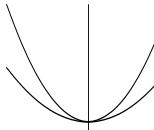
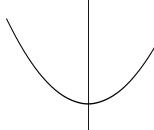
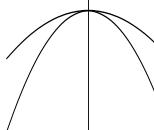
exists only in crystals with/without inversion symmetry

(c) General SOC: Local-Space-Assymmetry (LSA), surface and bulk



# Symmetry-independent SOC

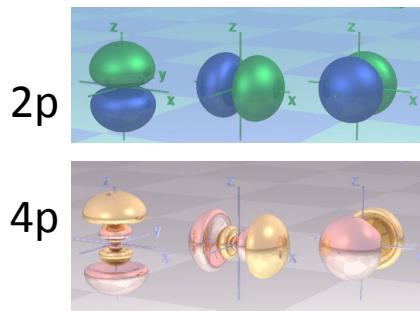
**Table 3.1.** Symmetry classification of the bands in the extended Kane model

Single group		Double group	
$O_h/T_d$		Full rotation group $\mathcal{R}$	$O_h/T_d$
	$\Gamma_5^-$	$l = 1 \quad (\mathcal{D}_1^-)$ p antibonding	$j = 3/2 \quad (\mathcal{D}_{3/2}^-) \rightarrow \Gamma_8^-$ $j = 1/2 \quad (\mathcal{D}_{1/2}^-) \rightarrow \Gamma_7^-$
	$\Gamma_1^-$	$l = 0 \quad (\mathcal{D}_0^-)$ s antibonding	$j = 1/2 \quad (\mathcal{D}_{1/2}^-) \rightarrow \Gamma_6^-$
	$\Gamma_5^+$	$l = 1 \quad (\mathcal{D}_1^+)$ p bonding	$j = 3/2 \quad (\mathcal{D}_{3/2}^+) \rightarrow \Gamma_8^+$ $j = 1/2 \quad (\mathcal{D}_{1/2}^+) \rightarrow \Gamma_7^+$

Zinc blend semiconductors  
 Si, Ge, GaAs, CdTe, HgTe

Winkler book 2003'

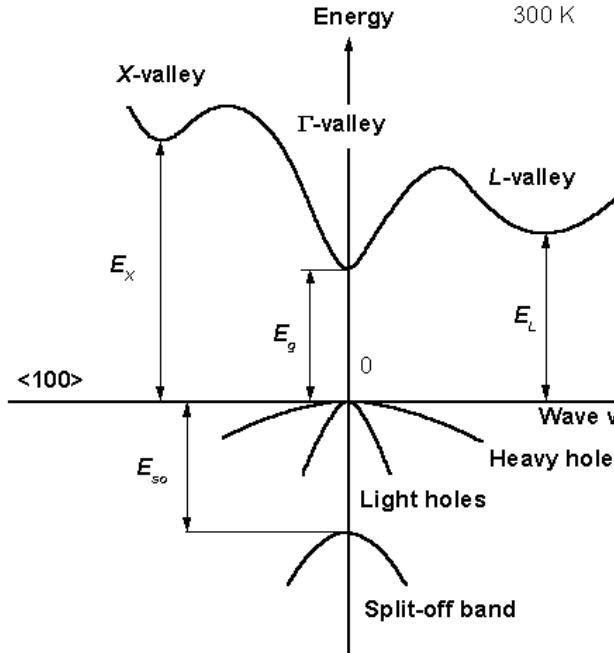
# Symmetry-independent SOC



$\Delta \sim Z^2$  (outer p shell)

$$\left(\frac{Z_{Ge}}{Z_{Si}}\right)^2 = \left(\frac{(Z_{Ga} + Z_{As})/2}{Z_{Si}}\right)^2 = \left(\frac{32}{14}\right)^2 = 5.2$$

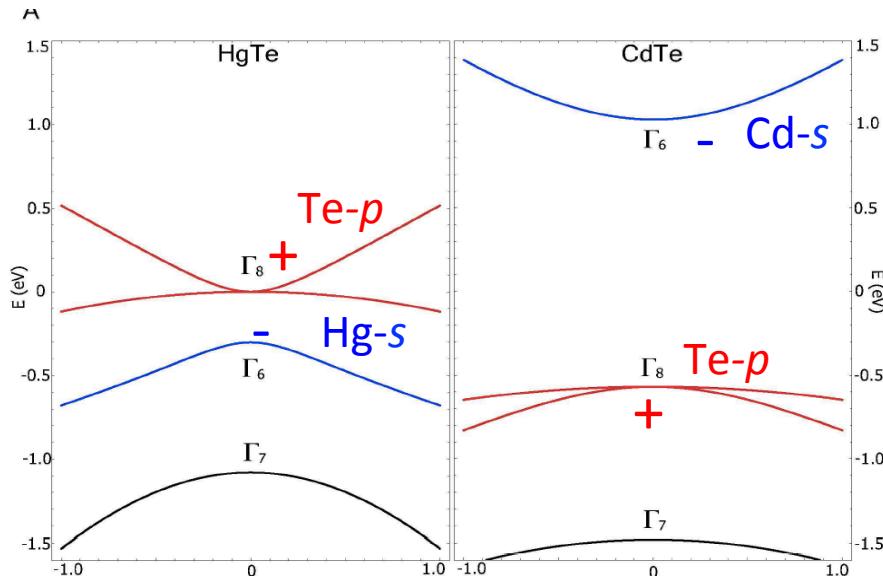
$$\frac{\Delta_{Ge}}{\Delta_{Si}} = 6.6 \quad \frac{\Delta_{GaAs}}{\Delta_{Si}} = 7.7$$



SOC splits bands.

Compound	$\Delta_0^{\text{exp}}$ (eV)
C	0.006
Si	0.044
Ge	0.29
$\alpha$ -Sn	
AlN	
AlP	
AlAs	
AlSb	0.75
GaN	0.011
GaP	0.127
GaAs	0.34
GaSb	0.80
InN	
InP	0.11
InAs	0.38
InSb	0.82
ZnO	-0.005
ZnS	0.07
ZnSe	0.43
ZnTe	0.93
CdS	0.066
CdSe	
CdTe	0.92
HgS	
HgSe	
HgTe	1.08

# Symmetry-independent SOC



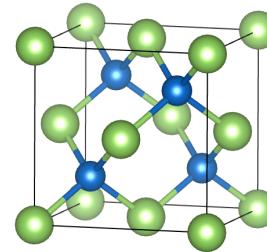
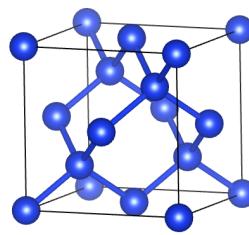
Due to the strong Hg-6s contraction, the Hg-6s band is lower than Te-5p bands.

The relativistic terms induce a band inversion.

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} + eV}_{\text{non-relativistic}} + \underbrace{\frac{\hat{p}^4}{8m^2c^2}}_{\text{K.E. correction}} + \underbrace{\frac{\hbar^2}{8m^2c^2}\nabla^2V}_{\text{Darwin term}} + \underbrace{\frac{\hbar}{4m^2c^2}\vec{\sigma} \cdot (\vec{\nabla}V \times \hat{\mathbf{p}})}_{\text{SOI}}$$

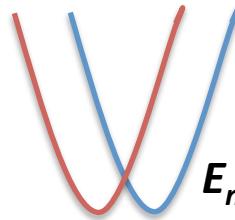
# Symmetry and band splitting

Time reversal symmetry:  $s \rightarrow -s, I \rightarrow -I, s.I \rightarrow s.I, k \rightarrow -k, E_n(s, k) = E_n(-s, -k)$   
Inversion symmetry:  $s \rightarrow s, I \rightarrow I, s.I \rightarrow s.I, k \rightarrow -k, E_n(s, k) = E_n(s, -k)$



$$E_n(s, k) = E_n(-s, k)$$

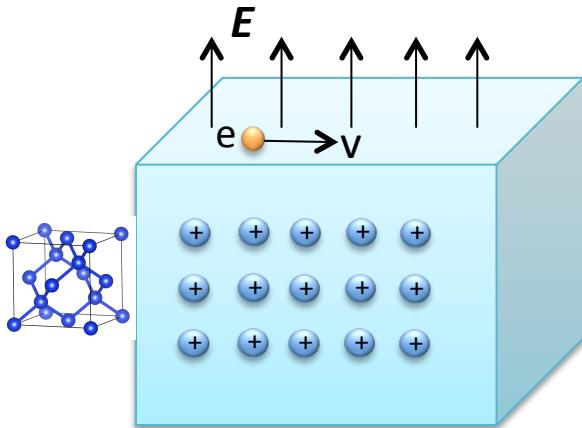
TRS + Inversion symmetry



$$E_n(s, k) \neq E_n(-s, k)$$

TRS + Inversion breaking

# Rashba SOC



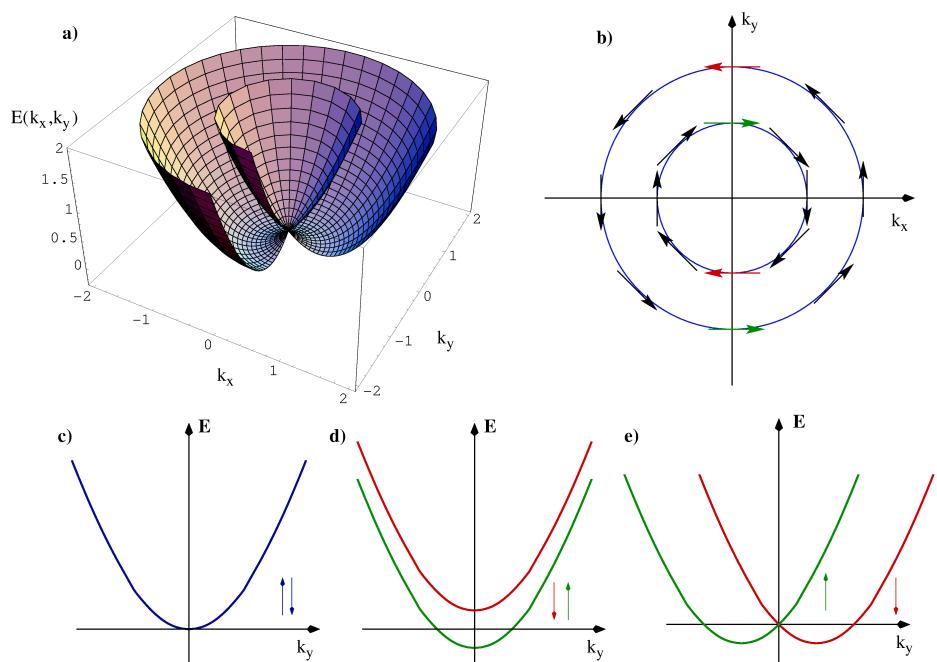
$$H_E = -E_0 z,$$

$$\mathbf{B} = \frac{1}{c^2} \mathbf{E} \times \mathbf{v}.$$

$$H_{SO} = \frac{g\mu_B}{2c^2} (\mathbf{v} \times \mathbf{E}) \cdot \boldsymbol{\sigma},$$

$$H_R = \alpha (\boldsymbol{\sigma} \times \mathbf{p}) \cdot \hat{z},$$

$$\alpha = \frac{g\mu_B E_0}{2mc^2} \quad \alpha \sim E_0 Z^2$$

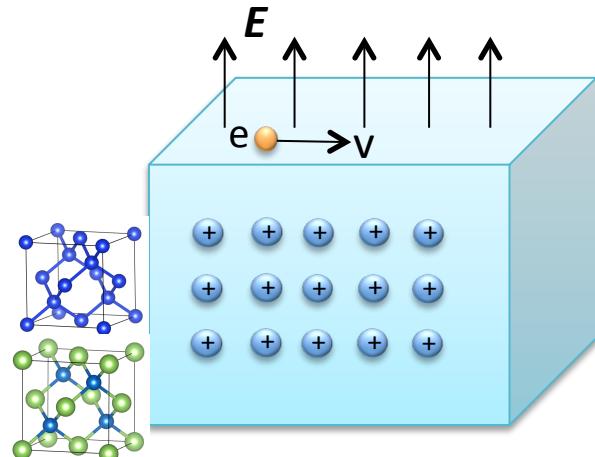


$$\hat{H}_R = \frac{k^2}{2m} + \alpha \hat{\mathbf{n}} \cdot (\vec{\sigma} \times \mathbf{k}) = \frac{k^2}{2m} + \alpha (\sigma^x k_y - \sigma^y k_x)$$

$t \rightarrow -t : \mathbf{k} \rightarrow -\mathbf{k}, \boldsymbol{\sigma} \rightarrow -\boldsymbol{\sigma}$

$$H_R = \begin{pmatrix} k^2 / 2m & \alpha(k_y + ik_x) \\ \alpha(k_y - ik_x) & k^2 / 2m \end{pmatrix} \Rightarrow \varepsilon_{\pm} = \frac{k^2}{2m} \pm \alpha k$$

# Rashba SOC



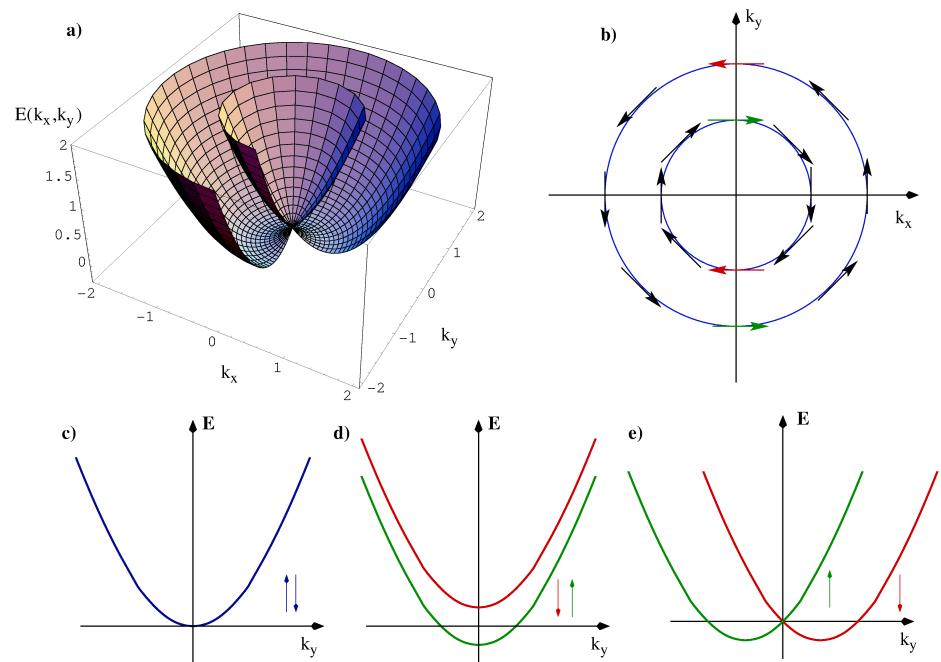
$$H_E = -E_0 z,$$

$$\mathbf{B} = \frac{1}{c^2} \mathbf{E} \times \mathbf{v}.$$

$$H_{SO} = \frac{g\mu_B}{2c^2} (\mathbf{v} \times \mathbf{E}) \cdot \boldsymbol{\sigma},$$

$$H_R = \alpha (\boldsymbol{\sigma} \times \mathbf{p}) \cdot \hat{z},$$

$$\alpha = \frac{g\mu_B E_0}{2mc^2} \quad \alpha \sim E_0 Z^2$$



$$\varepsilon_{\pm} = \frac{k^2}{2m} \pm \alpha k$$

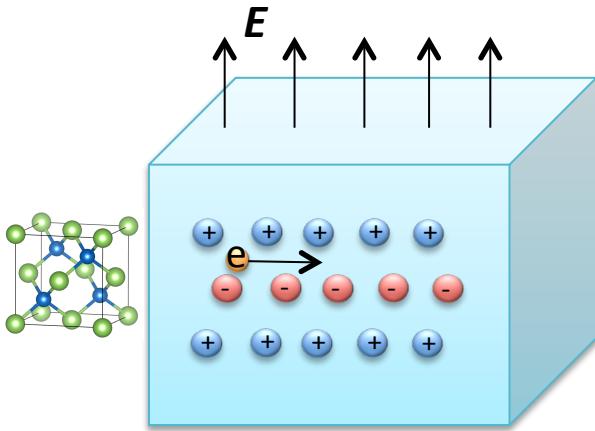
$$\psi_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \mp e^{i\phi_k} \end{pmatrix}$$

$$S_{z,\pm} = \frac{1}{2} \bar{\psi}_{\pm} \boldsymbol{\sigma}^z \psi_{\pm} = 0$$

$$S_{x,\pm} = \frac{1}{2} \bar{\psi}_{\pm} \boldsymbol{\sigma}^x \psi_{\pm} = \pm \frac{1}{2} \sin \phi_k; \quad S_{y,\pm} = \frac{1}{2} \bar{\psi}_{\pm} \boldsymbol{\sigma}^y \psi_{\pm} = \mp \frac{1}{2} \cos \phi_k$$

$$\mathbf{k} \cdot \mathbf{S}_{\pm} = 0$$

# Dresselhaus SOC



zincblende ( $A_{\text{III}}B_{\text{V}}$ ) lattice

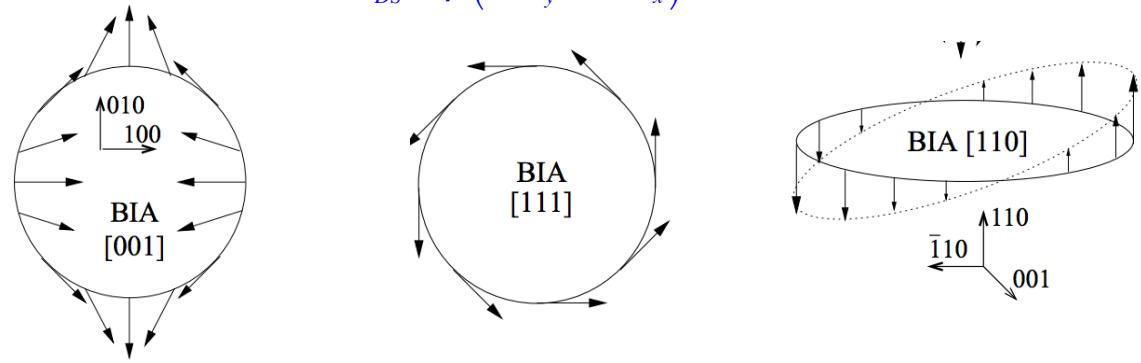
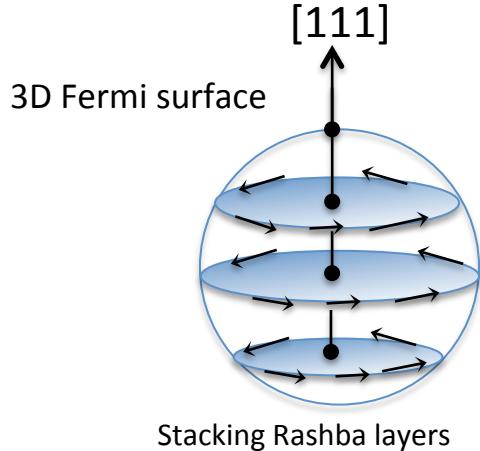
$$H_D = D \vec{\Omega}(\mathbf{k}) \cdot \vec{\sigma}$$

$$\vec{\Omega} = (k_x(k_y^2 - k_z^2), k_y(k_z^2 - k_x^2), k_z(k_x^2 - k_y^2))$$

(001) surface (interface) of a  $A_{\text{III}}B_{\text{V}}$  semiconductor

$$\langle \vec{\Omega} \rangle = \left( \underbrace{k_x k_y^2}_{\text{cubic} \rightarrow 0} - k_x \langle k_z^2 \rangle, k_y \langle k_z^2 \rangle - \underbrace{k_y k_x^2}_{\text{cubic} \rightarrow 0}, 0 \right) = \langle k_z \rangle^2 (-k_x, k_y, 0)$$

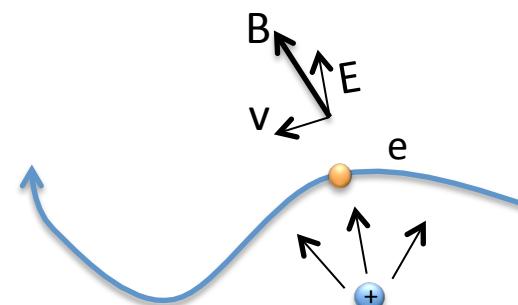
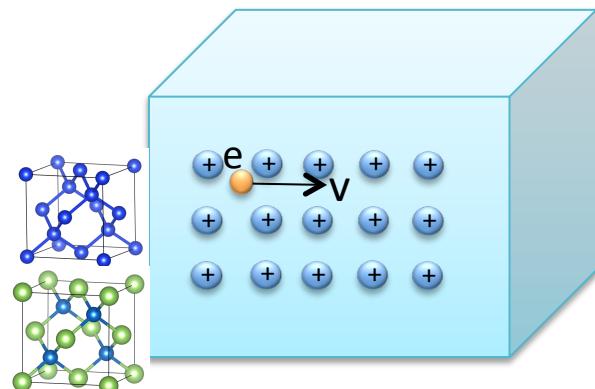
$$H_{DS} = \beta (\sigma^y k_y - \sigma^x k_x)$$



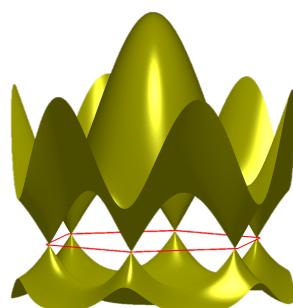
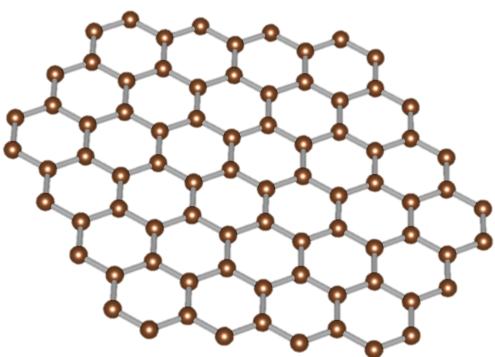
in general: Rashba+Dresselhaus

$$H = \frac{k^2}{2m} + \alpha (\sigma^x k_y - \sigma^y k_x) + \beta (\sigma^y k_y - \sigma^x k_x) = \frac{k^2}{2m} + \sigma^x (\alpha k_y - \beta k_x) + \sigma^y (\alpha k_x + \beta k_y)$$

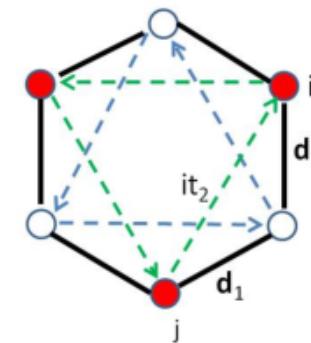
# Non Rashba-Dresselhaus SOC



$$\mathbf{B} = \frac{1}{c^2} \mathbf{E} \times \mathbf{v}.$$



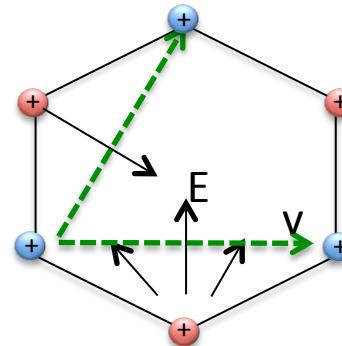
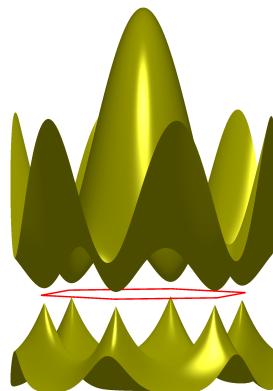
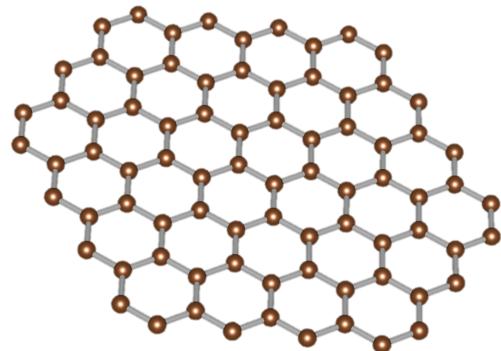
$$\mathcal{H} = \sum_{\langle ij \rangle \alpha} t c_{i\alpha}^\dagger c_{j\alpha}$$



# SOC in the graphene model

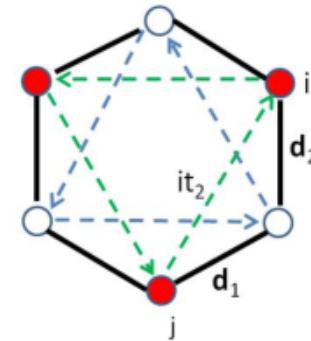
Refs:

- C. L. Kane and E. J. Mele,  
Phys. Rev. Lett. **95**, 226801 (2005).  
F. D. M. Haldane,  
Phys. Rev. Lett. **61**, 2015 (1988).



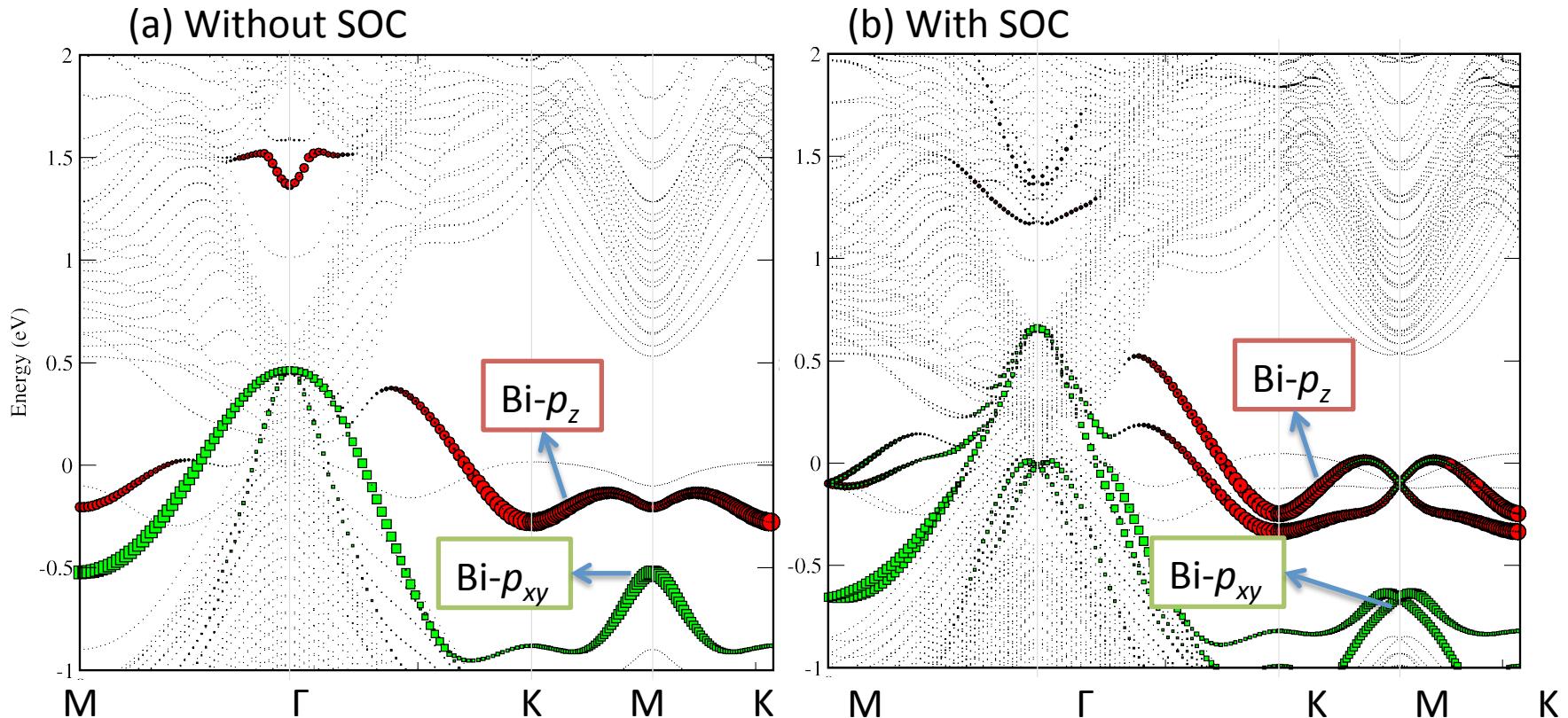
$$\mathbf{B} = \frac{1}{c^2} \mathbf{E} \times \mathbf{v}.$$

$v_{ij} = +1$  (-1) for left (right) turn hopping

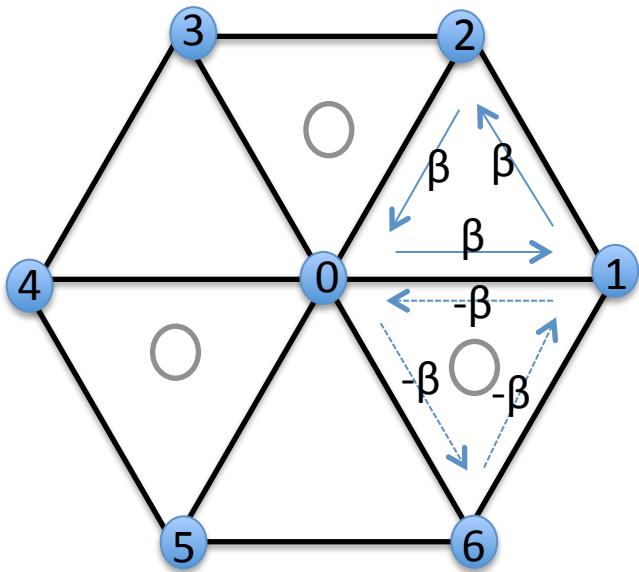


$$\mathcal{H} = \sum_{\langle ij \rangle \alpha} t c_{i\alpha}^\dagger c_{j\alpha} + \sum_{\langle\langle ij \rangle\rangle \alpha\beta} it_2 v_{ij} s_{\alpha\beta}^z c_{i\alpha}^\dagger c_{j\beta}.$$

# More general than graphene



We confirm that the surface state near -100 meV is indeed the Bi- $p_z$  state.  
Next, we will fit above ab initio results using a simple TB model in the 2D triangular lattice.



- Top Bi atoms form a triangular lattice.
- The underlying Pt atom.

The Bi layer exhibits  $C_3$  symmetry, rather than  $C_6$ , due to the Pt layer below it.

Lattice constant:  $a = 4.6513 \text{ \AA}$

Besides the common Rashba effect, there is a spin-dependent hopping term along a Bi-Bi bond, like the Kane-Mele term in graphene.

The Hamiltonian can be written as

$$H = H^0 + H^R + H^{KM}$$

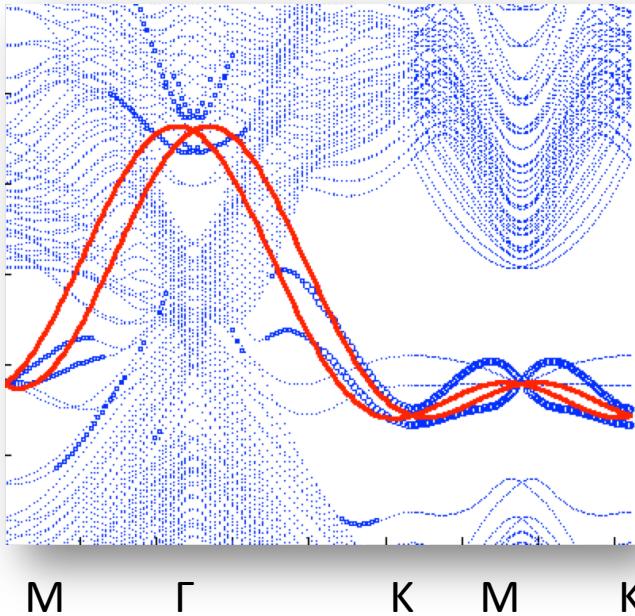
$$H^0 = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^+ c_{j\sigma}$$

$$H^R = \frac{\alpha}{2} \sum_{\langle ij \rangle \sigma\sigma'} \left( \boldsymbol{\sigma} \times \frac{\hat{\mathbf{e}}_{ij}}{i} \right)_{z,\sigma\sigma'} c_{i\sigma}^+ c_{j\sigma'}$$

$$H^{KM} = \frac{\beta}{2i} \sum_{\langle ij \rangle \sigma\sigma'} v_{ij} \sigma_z c_{i\sigma}^+ c_{j\sigma'}$$

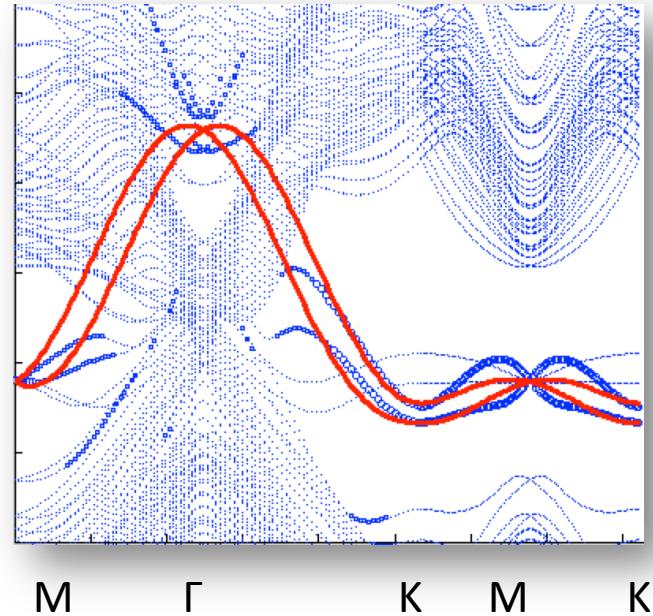
Where,  $v_{ij} = -v_{ji} = 1$ , depends on the relative hopping direction with respect to the underlying Pt neighbor.

Fitting without  $H^{KM}$  term



$t=0.35$   
 $\alpha = 0.5$   
 $\beta = 0$

Fitting with  $H^{KM}$  term



$t=0.35$   
 $\alpha = 0.5$   
 $\beta = 0.1$

More examples:

- ZK Liu, B. Yan et al, arXiv:1602.05633, Nature Comm. in press  
K. Nakajin and S. Murakami, Physical Review B **91**, (2015).  
X. Zhang, et al, Nature Physics **10**, 387 (2014).

## Outline

### Spin-orbit coupling in an atom

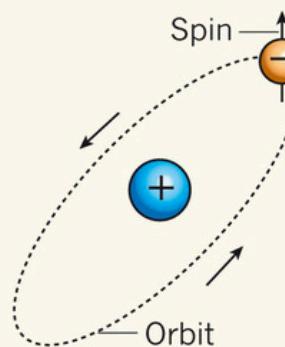
- Atom SOC
- Contraction of s and p shells

### Spin-orbit coupling in solids

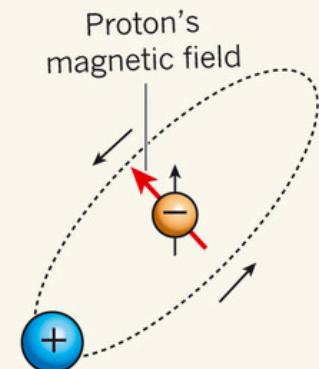
- Atomic SOC, such as HgTe
- Rashba effect
- Dresselhaus effect
- SOC in graphene

### a Electron in an atom

Proton's point of view

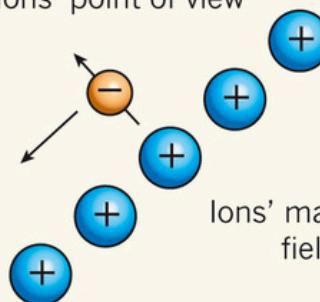


Electron's point of view



### b Free electron

Ions' point of view



Electron's point of view

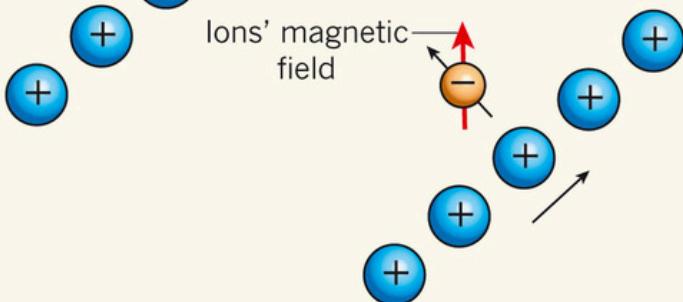
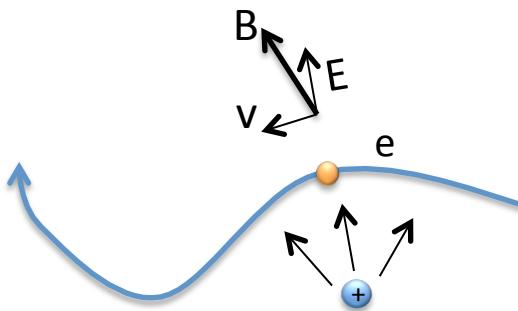


Figure credit: M. Chapman & C. Sá de Melo,  
Nature 471, 41–42 (2011)

# Spin-orbit coupling: a general relativistic effect in solids



$$\mathbf{B} = \frac{1}{c^2} \mathbf{E} \times \mathbf{v}.$$

Thanks for your attention!