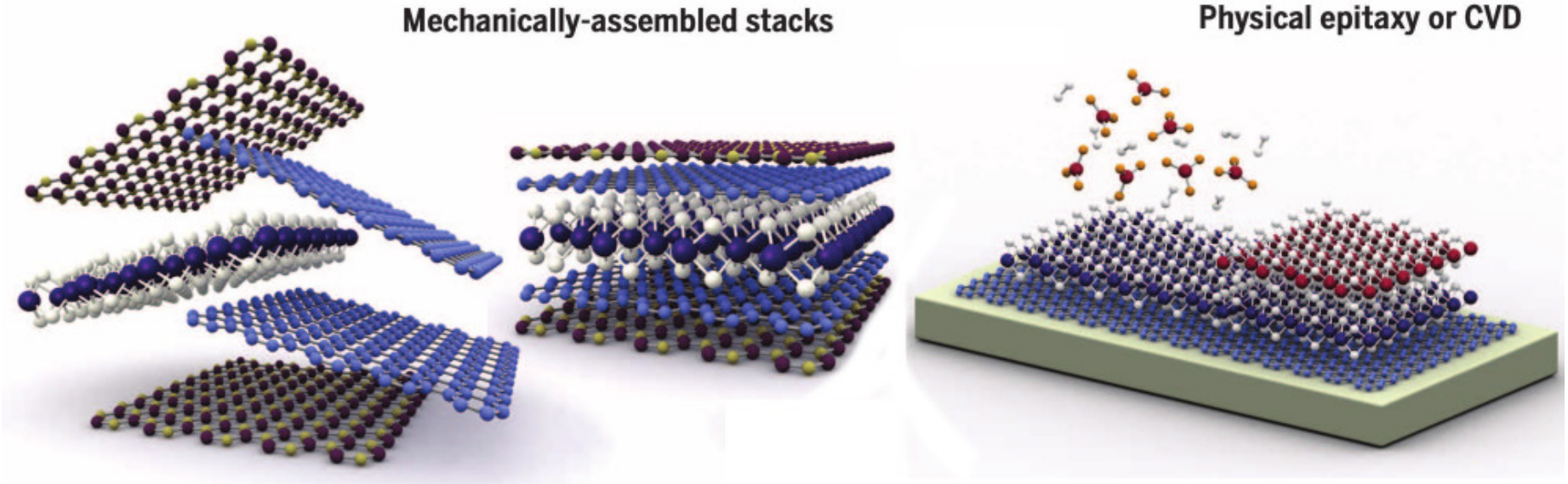
# MTLE-6120: Advanced Electronic Properties of Materials

## Low-dimensional materials

References:

- 2D materials: *Science* **353**, aac9439 (2016)
- Carrier lifetimes: *Adv. Opt. Mat.* **5**, 1600914 (2017)
- Graphene mobility: C. Ullal, J. Shi and R. Sundararaman preprint (2018)

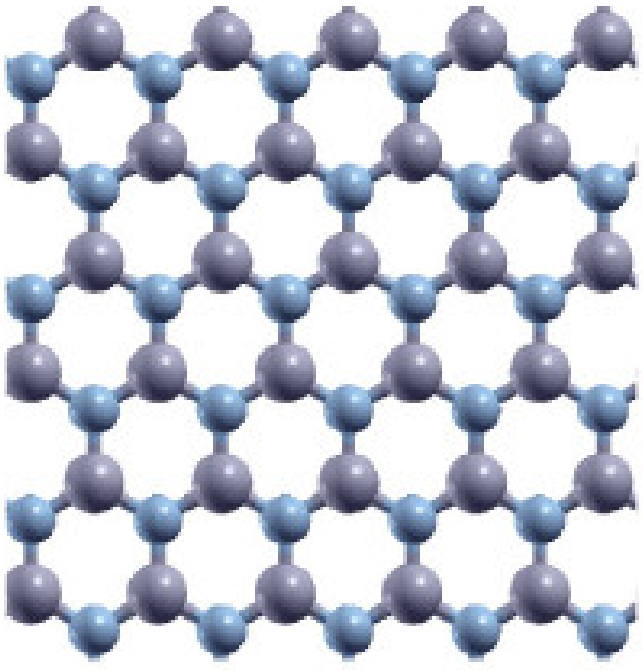
# 2D materials: the new frontier

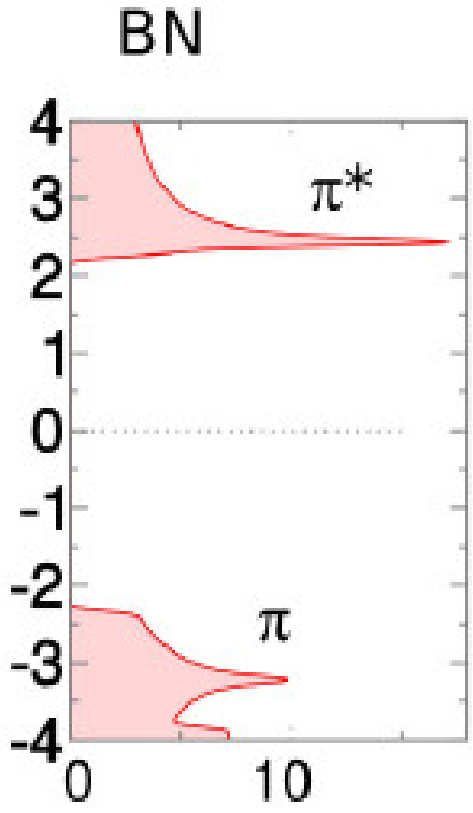


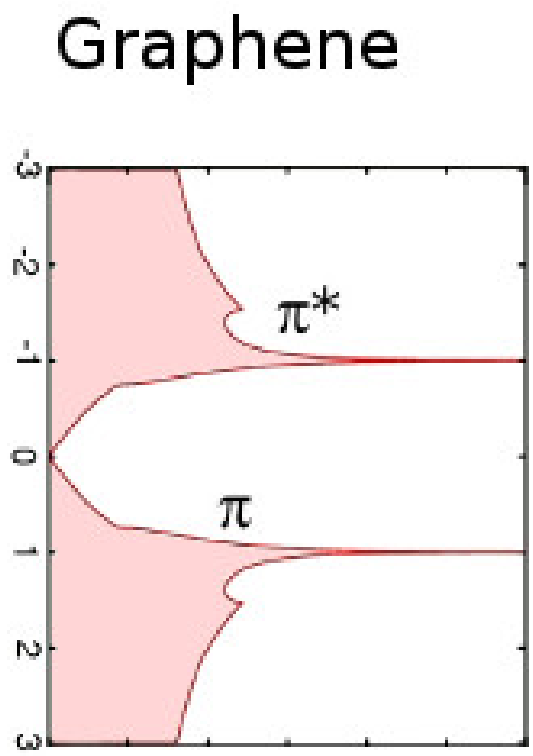

- Design materials at the atomic scale by combining different 2D layers
- Works with many classes of layered materials $\Rightarrow$ tremendous flexibility

Figure adapted from *Science* **353**, aac9439 (2016)

# Graphene and Hexagonal Boron Nitride



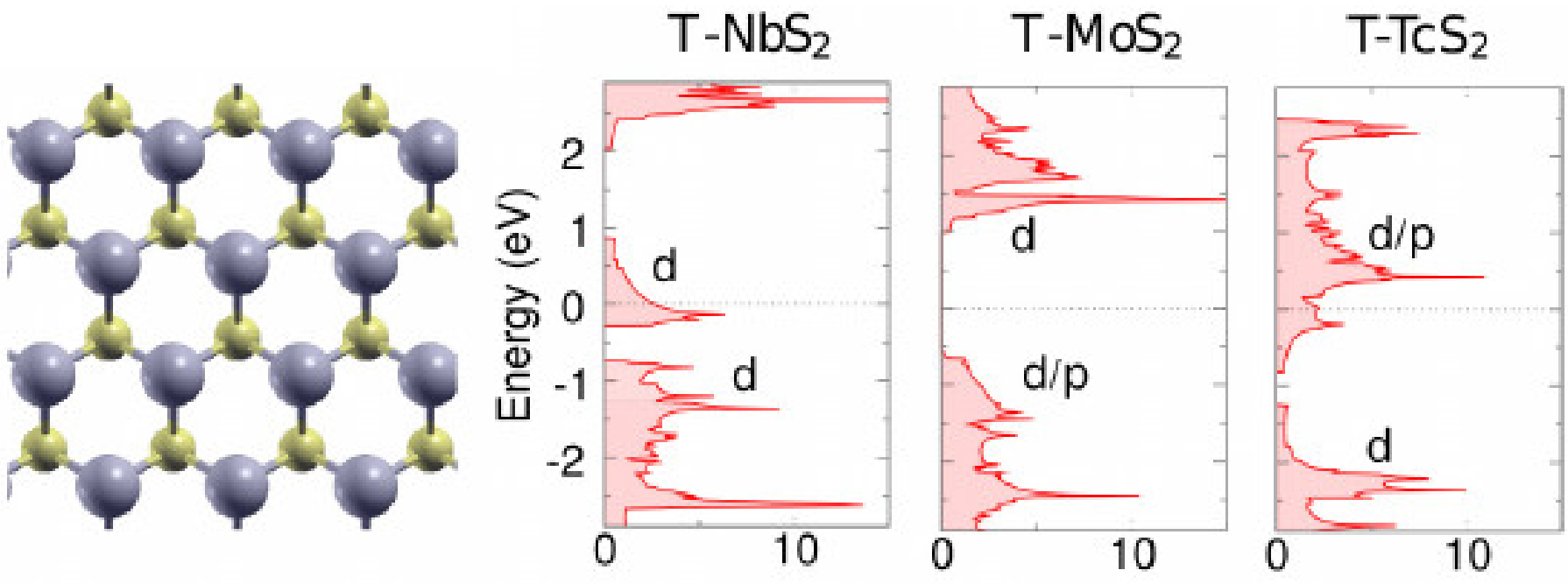



- Planar hexagonal structure ($sp^2$ bonding)
- Graphene semi-metallic (more details later)
- Boron nitride (hBN): insulator which can withstand 0.5 V per atomic layer!
- Graphene/hBN spacing $\approx 3.3$ Å: capacitance?

Figure adapted from *Science* **353**, aac9439 (2016)

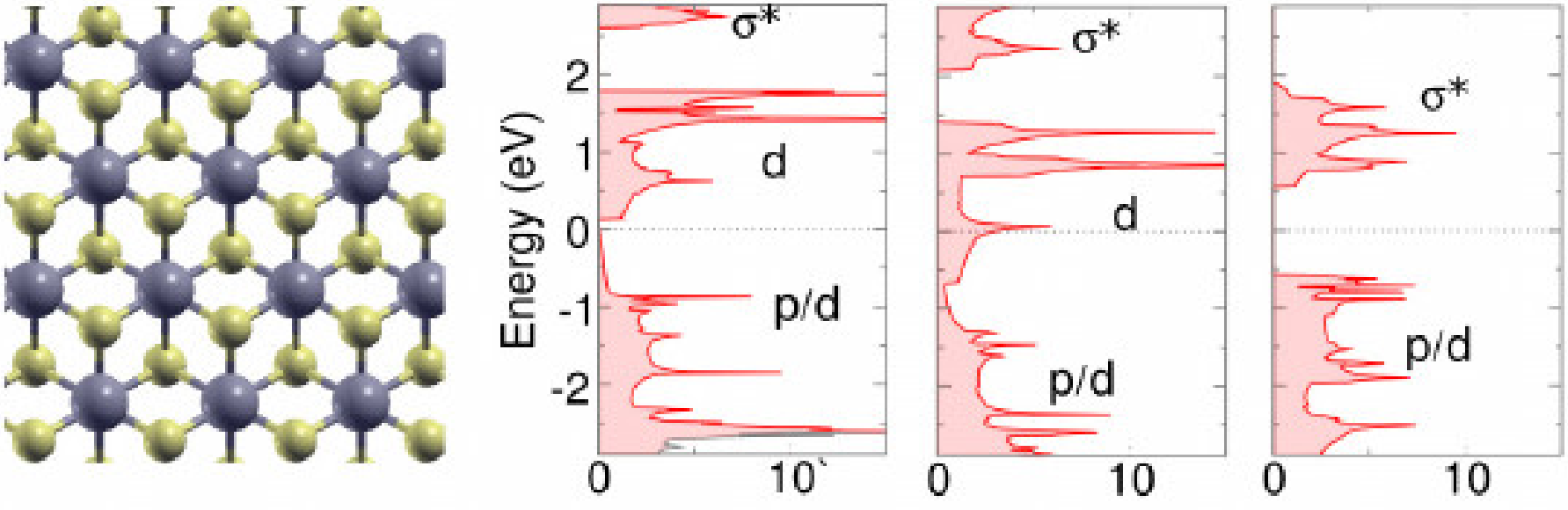
# Transition metal dichalcogenides (TMDC): trigonal




- Non-planar structure: two group VI atoms vertically aligned
- Metallic or semiconducting depending on transition metal group
- Transition metal $\Rightarrow$ $d$ bands play important role
- Low dielectric screening $\Rightarrow$ strongly bound excitons

Figure adapted from *Science* **353**, aac9439 (2016)

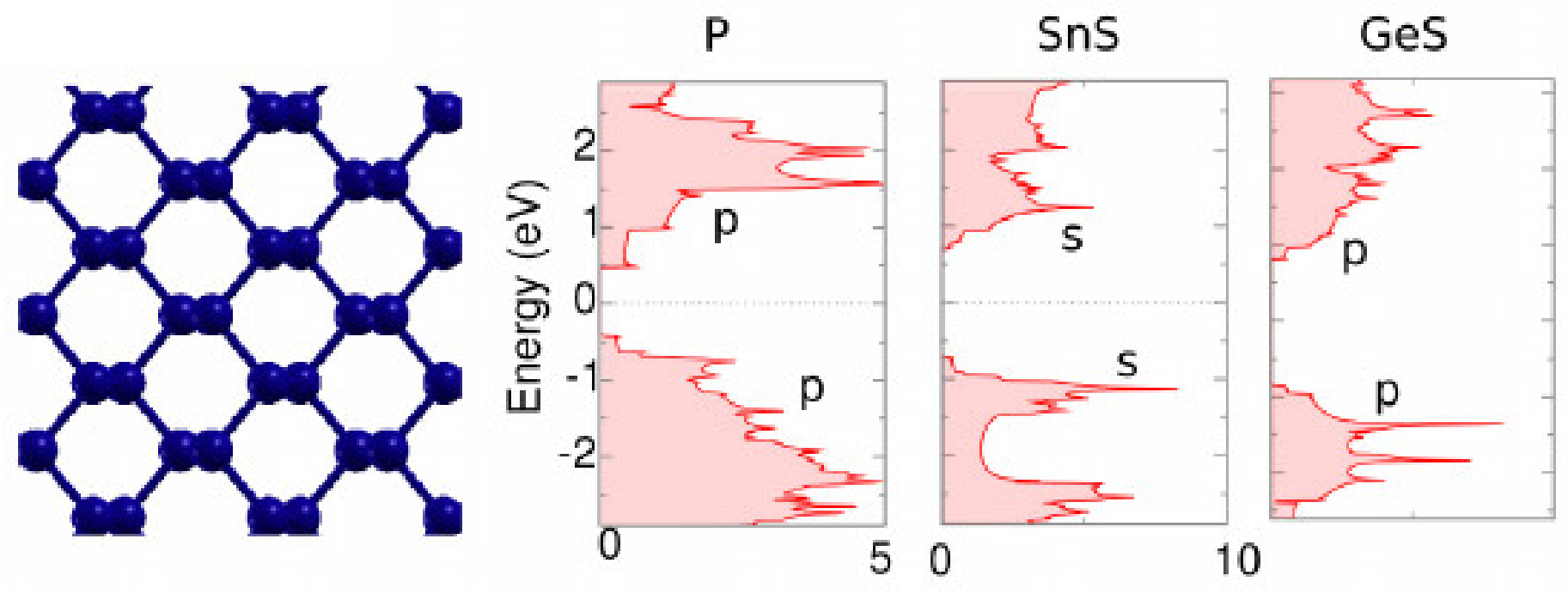
# Transition metal dichalcogenides (TMDC): octahedral




- Non-planar structure: two group VI atoms vertically anti-aligned
- Metallic or semiconducting depending on transition metal group
- Transition metal $\Rightarrow$ $d$ bands play important role
- Low dielectric screening $\Rightarrow$ strongly bound excitons

Figure adapted from *Science* **353**, aac9439 (2016)

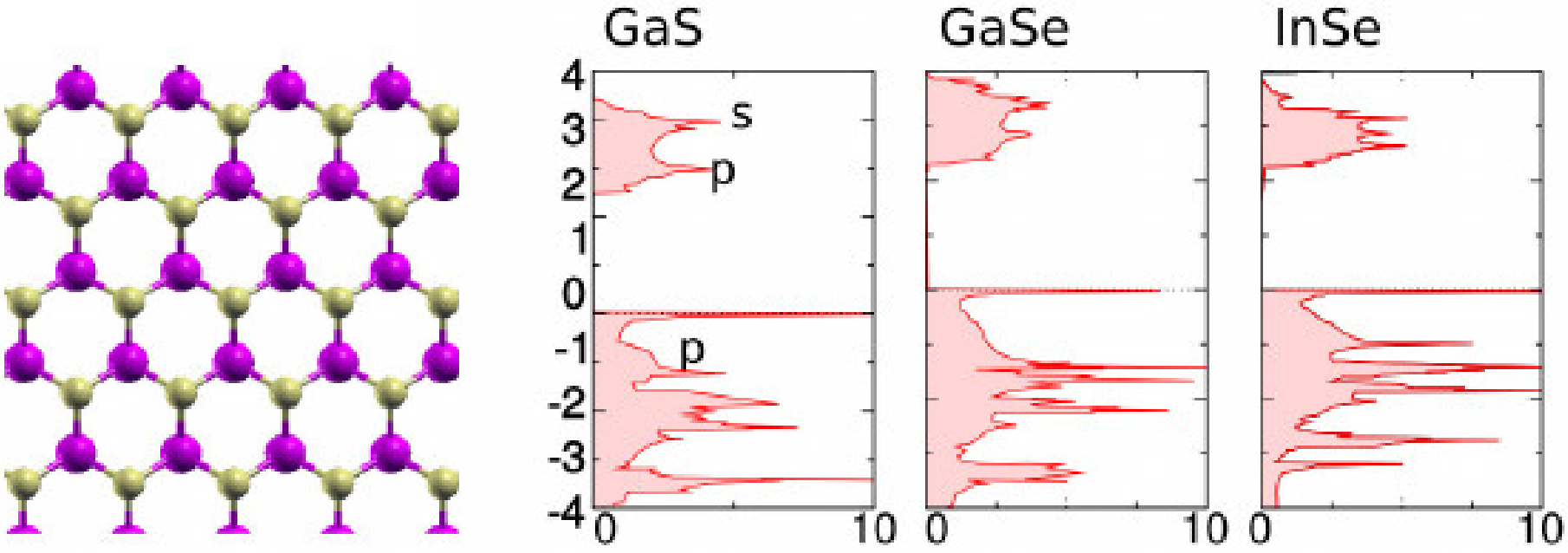
# Phosphorene




- Group V or Group IV-VI
- Distorted hexagons due to higher bond order in one direction
- Anisotropic electronic and optical properties in plane
- IV-VI materials non-centrosymmetric $\Rightarrow$ 2D piezoelectric

Figure adapted from *Science* **353**, aac9439 (2016)

# Group III chalcogenides

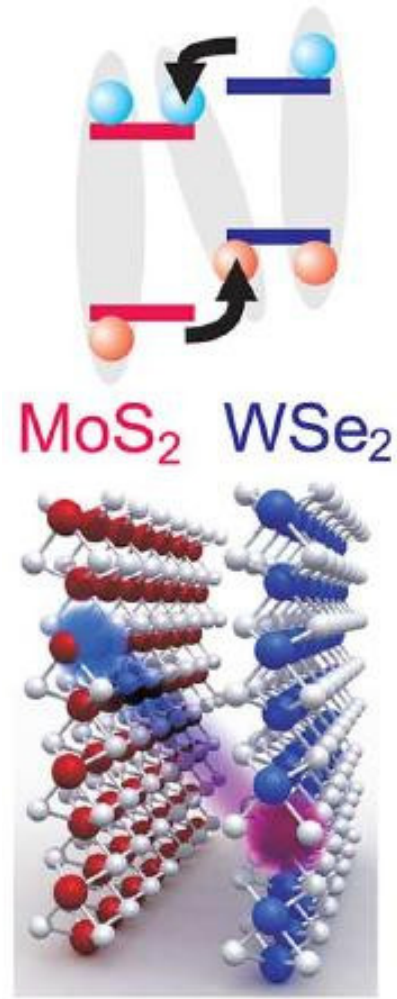



- Structure like trigonal TMDC, but with two metal layers
- Unusual VBM: away from $\Gamma \Rightarrow$ high DOS at VBM
- High DOS $\Rightarrow$ short lifetime $\Rightarrow$ ultrafast response
- Ferromagnetic instability for degenerate $p$-doping

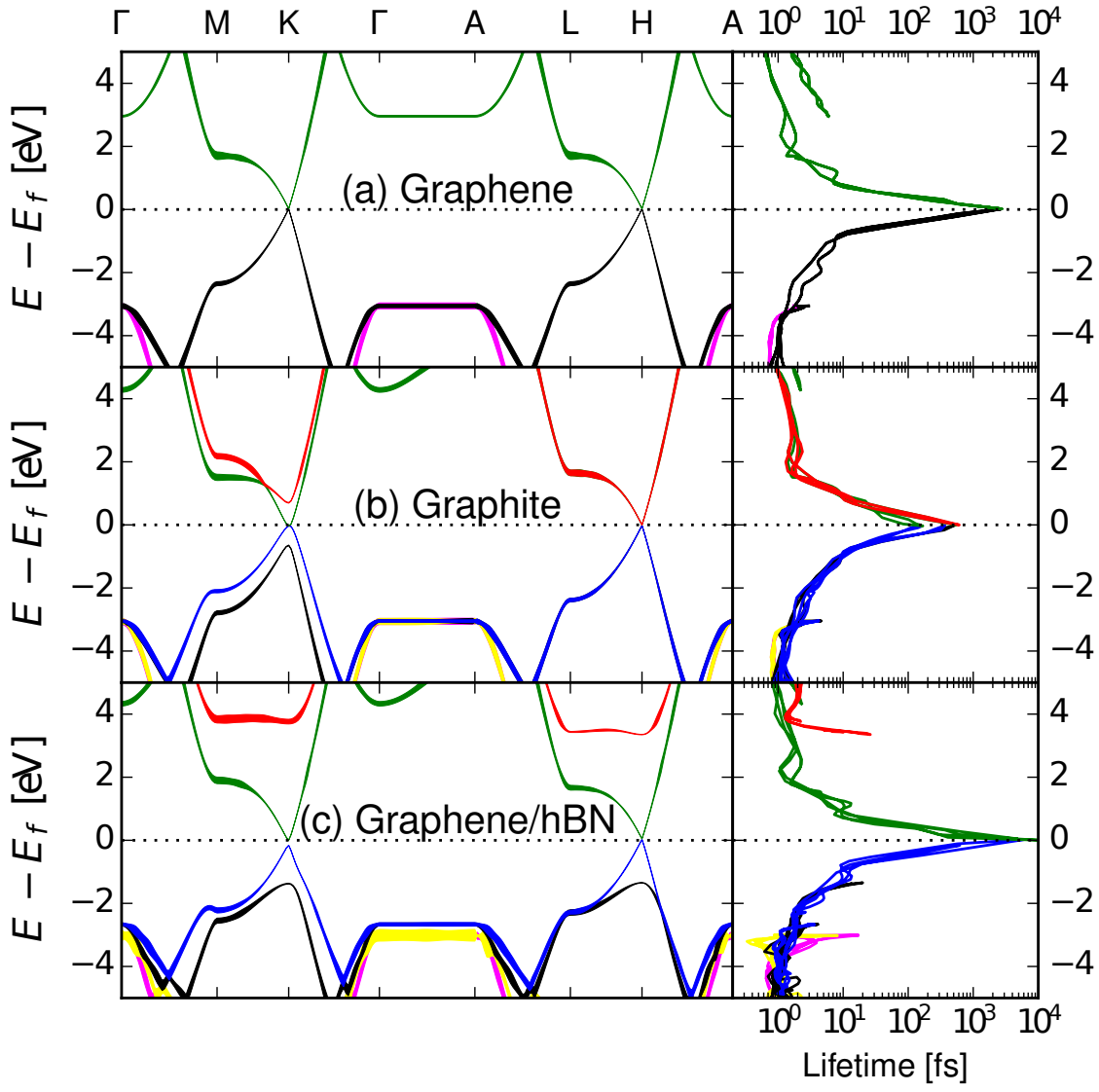
Figure adapted from *Science* **353**, aac9439 (2016)

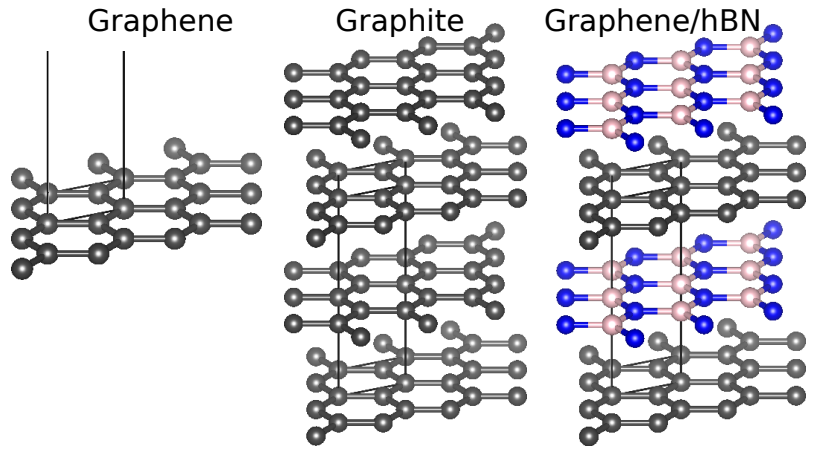
# Summary of properties

- Capacitance: ultra-thin dielectrics
- Tunneling devices: electronic wavefunctions can couple *across* a 2D layer
- Optical properties:
  - Strongly-bound excitons: LEDs (potentially)
  - Indirect (inter-layer) excitions: solar cells
  - Highly-confined plasmons (nano-photonics)
- Electronic properties: high mobility
- Heterostructures: mix and match all of the above!



# Band structure of graphene and heterostructures



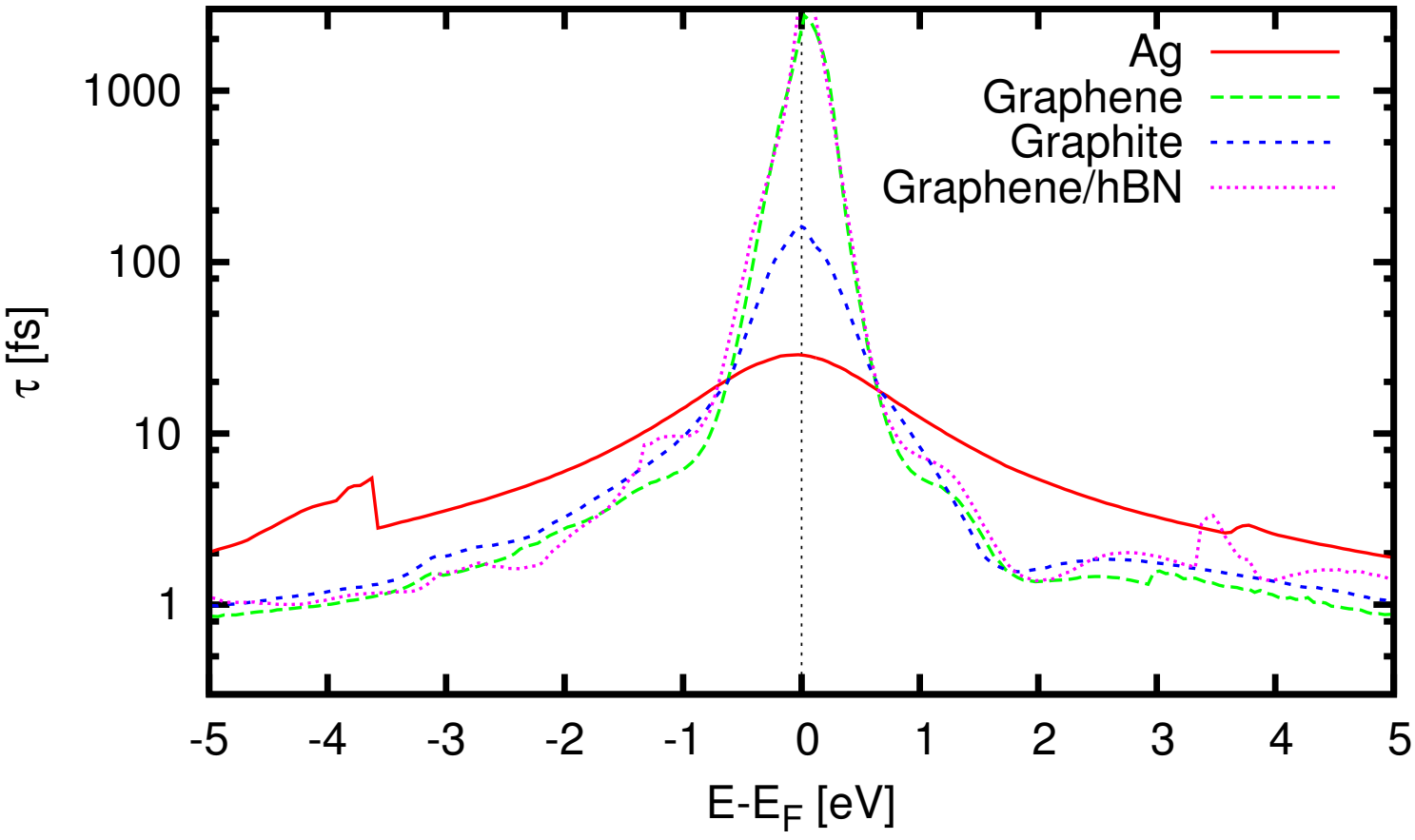




- Dirac point: linear $E$ vs $k$
- Graphite: hybridiztaion across layers breaks this
- hBN spacer reduces coupling; preserves Dirac point
- Dirac point $\Rightarrow$ low DOS $\Rightarrow$ large lifetime $\Rightarrow$ high mobility

Figure adapted from *Adv. Opt. Mat.* **5**, 1600914 (2017)

Rensselaer

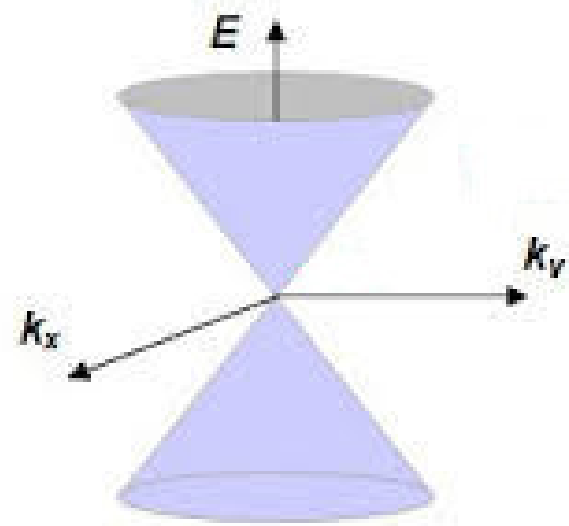
# Carrier lifetimes in graphene




- At Fermi level, graphene lifetime 100× that of silver
- Reduced somewhat by graphite, enhanced slightly by hBN
- Feature of low DOS: drops below Ag once away from Dirac point

Figure adapted from *Adv. Opt. Mat.* **5**, 1600914 (2017)

# Carrier mobility




- Drude formula:

$$\mu = \frac{e\tau}{m^*}$$

- Fermi Golden rule:

$$\tau^{-1} \propto g(E_F)T \qquad (\text{for } T \gg T_D)$$

- Noble metals: $\tau \sim 30$ fs, $m^* \approx m_e \quad \Rightarrow \quad \mu \sim 50$ cm$^2$V/s
- Semiconductors: $\tau \sim 200$ fs, $m^* \approx 0.3m_e \quad \Rightarrow \quad \mu \sim 1000$ cm$^2$V/s
- Graphene: $\tau \sim 2000$ fs, claimed $\mu > 10^5$ cm$^2$V/s $\Rightarrow m^* < 0.02m_e$!
- What is the effective mass for the band structure $E = \hbar v_F |\vec{k}|$ (with $v_F \sim 8.3 \times 10^5$ m/s) near Dirac point?

# Why are carriers massless in graphene?

- In general, define $\dot{\vec{p}} = m^* \dot{\vec{v}}$
- Since $\vec{v} = \nabla_{\vec{p}} E$, this yields $(m^*)^{-1} = \nabla_{\vec{p}} \nabla_{\vec{p}} E$
- Near the Dirac point in graphene, $E = \hbar v_F |\vec{k}| = v_F |\vec{p}|$
- If $\vec{p}$ along $x$, $\vec{v} = \nabla_{\vec{p}} E = v_F \hat{x}$
- $\vec{v}$ follows direction of $\vec{p}$ without changing magnitude!
- What mass does this correspond to?
- Conventional explanation in literature: linear dispersion (Dirac equation) $\Rightarrow$ massless particles in relativity
- Important: this is an analogy: $v_F \sim c/400$; many aspects of relativistic particles like photons do not apply
- Examine mass tensor at more carefully:

$$(m^*)^{-1} = \nabla_{\vec{p}} \nabla_{\vec{p}} v_F |\vec{p}| = \begin{pmatrix} 0 & 0 \\ 0 & v_F/p \end{pmatrix} \qquad \text{at } \vec{p} = p\hat{x}$$

  with eigenvalues $0$ and $v_F/p$, i.e. $\infty$ and $p/v_F$ for $m^*$
- At Dirac point, $p \to 0 \Rightarrow m_T^* \to 0$ while $m_L^* \to \infty$

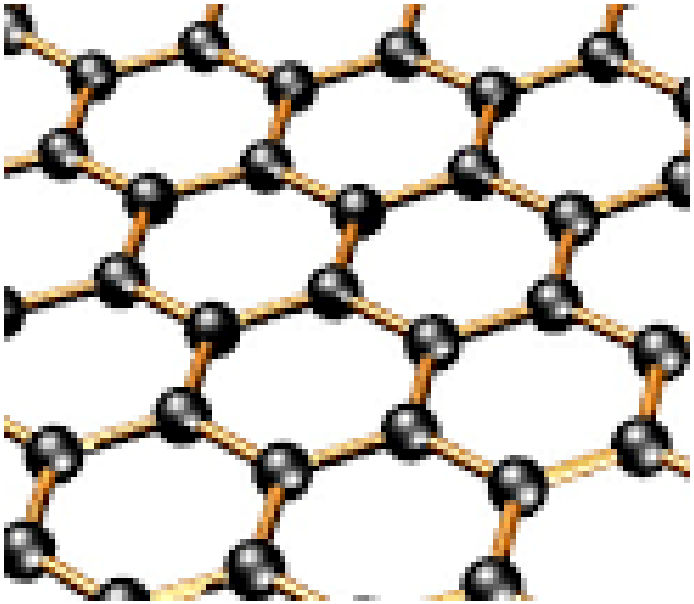
# Mobility of graphene

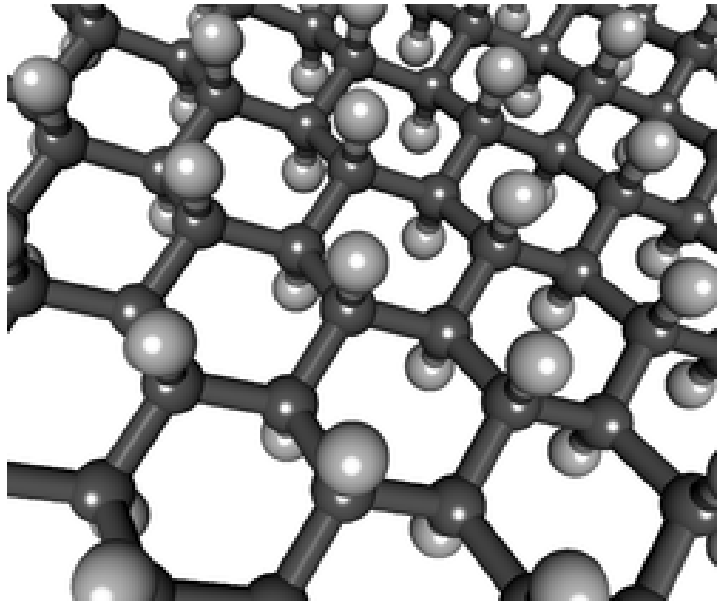
- Derivation outline of usual Drude formula:
  - Momentum $\vec{p} = \vec{p}_0 - e\mathcal{E}t$ where $t =$ time since last collision
  - Average over $\vec{p}_0$ and $t \Rightarrow \langle\vec{p}\rangle = -e\mathcal{E}\tau$
  - Drift velocity $\vec{v}_d = \langle\vec{v}\rangle = \langle\vec{p}\rangle/m^* = -e\mathcal{E}\tau/m^*$
  - Mobility $\mu = v_d/\mathcal{E} = -e\tau/m^*$
- Issue for graphene: $m^*$ strongly dependent on $\vec{p}$ (singular at Dirac point)
- $\vec{p} = \vec{p}_0 - e\mathcal{E}t$ still true, but $\langle\vec{v}\rangle \neq \langle\vec{p}\rangle/m^*$
- True only for an appropriately averaged $m^*$:

$$\langle(m^*)^{-1}\rangle = \frac{\int \mathrm{d}\vec{p}P(\vec{p})(m^*)^{-1}(\vec{p})}{\int \mathrm{d}\vec{p}P(\vec{p})} = \frac{v_F^2}{2k_BT}$$

- At room temperature, this yields $m^*/m_e \approx 0.013$
- At liquid He temperature, $m^*/m_e \approx 3.6 \times 10^{-4}$
- Conduction dominated by the transverse mass i.e. $\vec{v} \perp \vec{p}$!
  (What does that look like?)

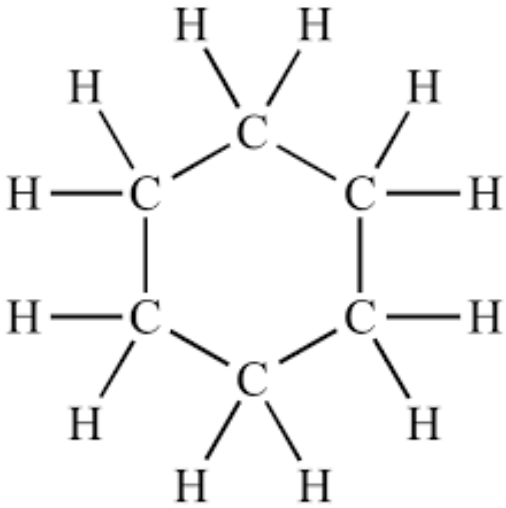
# Graphene vs graphane

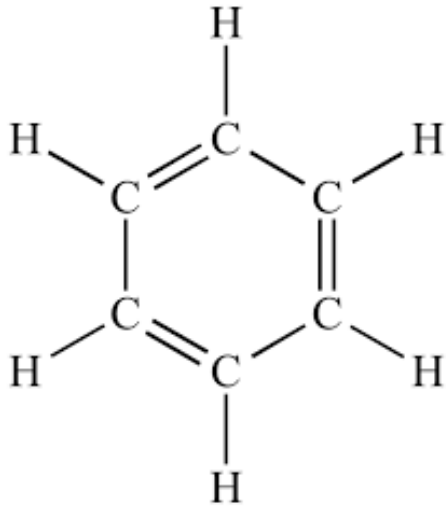


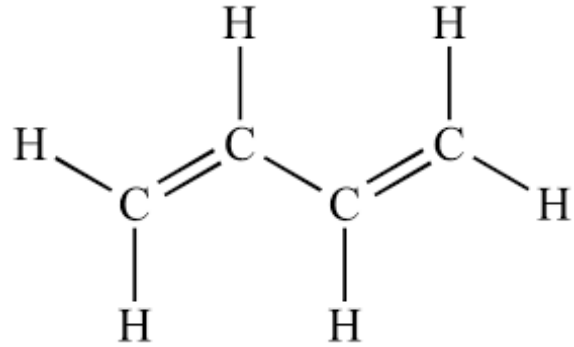


- Graphane = hydrogenated graphene (proposed material)
- Non-planar: $sp^3$ hybridization (like methane, diamond)
- Graphene: $\lim_{\to\infty}$ conjugated benzene rings
- Graphane: $\lim_{\to\infty}$ cyclohexane rings
- Will graphane be a metal, a semi-metal or a semiconductor?

# Band theory of bond conjugation

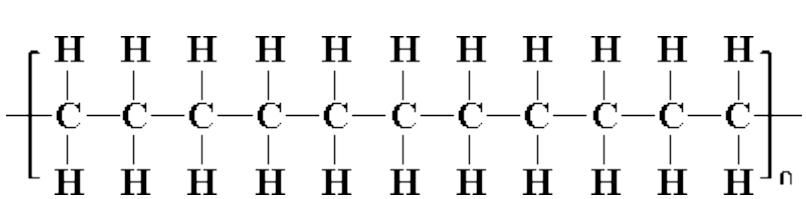


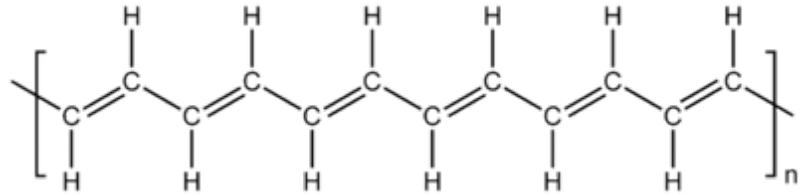




- Alternating single and double bonds $\Rightarrow$ resonance structures
- $\Rightarrow$ symmetry between bonding and antibonding orbitals / energies
- Finite system: discrete levels; always have gap
- Benzene has smaller gap than cyclohexane
- Infinite 2D limit $\rightarrow$ Dirac point in graphene
- What about 1D limit of a linear conjugated hydrocarbon?

# Conductive polymers





- Polyethene (polyethylene): all single bonds, excellent insulator
- Polyethyne (polyacetylene): conjugated bonds, highly conductive!
- Control band structure with functional groups on monomer
- Control Fermi level with occasional functional groups during polymerization (like dopants)
- Conductive polymers and organic semiconductors: 2000 Nobel Prize in chemistry