UNIVERSAL INFRARED ABSORBANCE IN GRAPHENE, SILICENE AND GERMANENE

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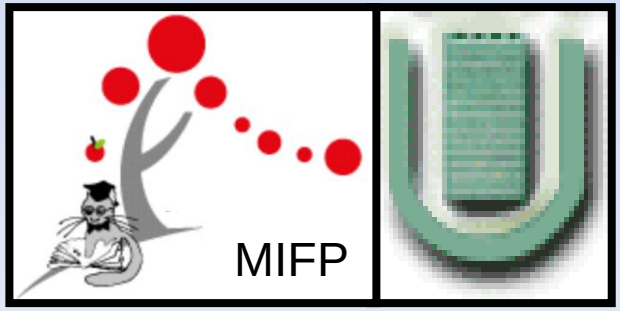

Fine Structure Constant Defines Visual Transparency of Graphene

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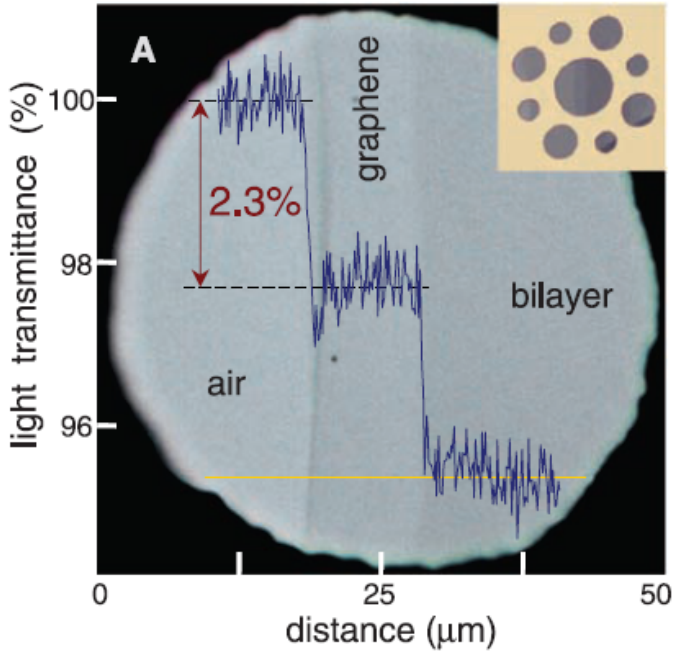
$\alpha = e^2/\hbar c \sim 1/137$



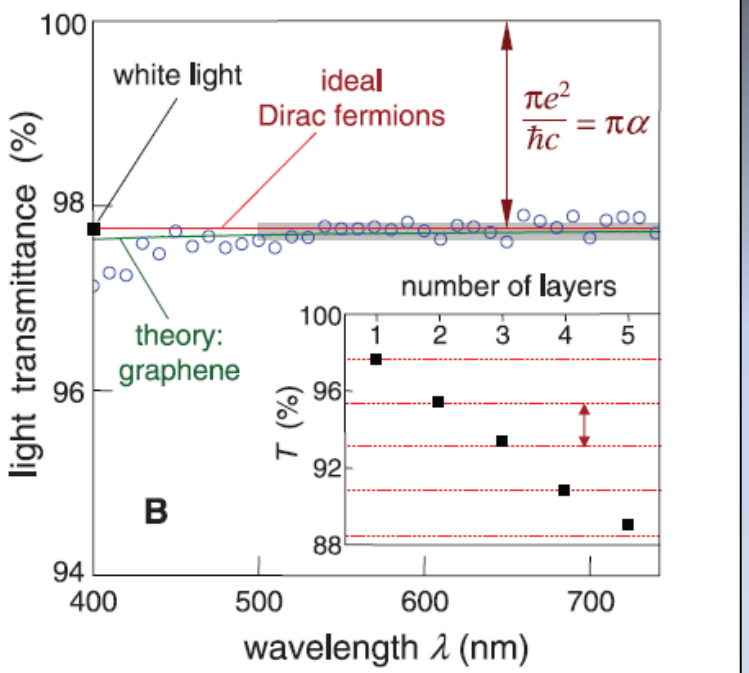
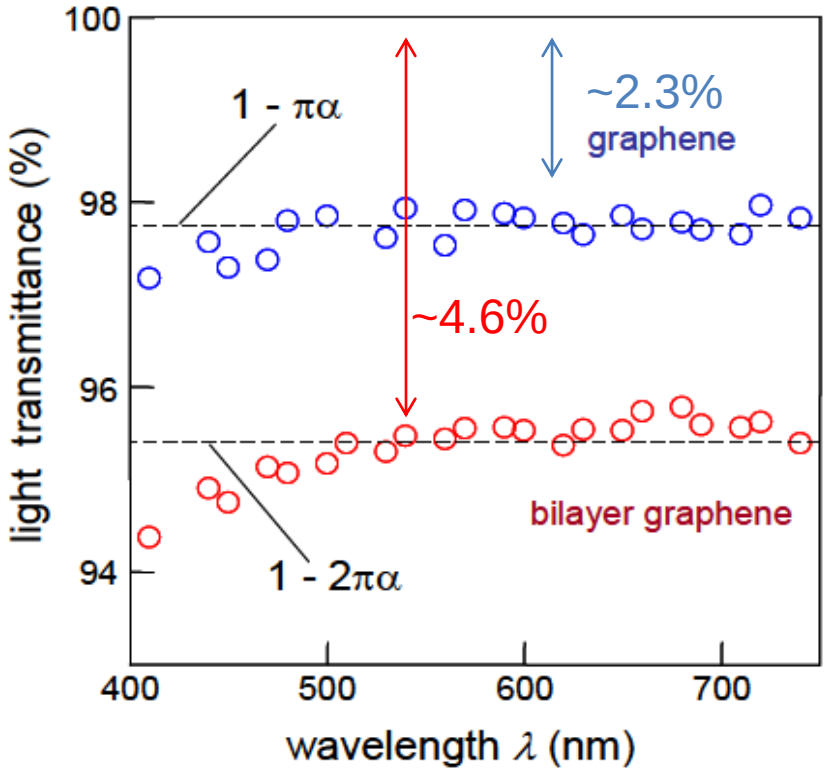


Fig. 1. Looking through one-atom-thick crystals. (**A**) Photograph of a 50-μm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of transmitted white light along the yellow line. (Inset) Our sample design: A 20-μm-thick metal support structure has several apertures of 20, 30, and 50 μm in diameter with graphene crystallites placed over them. (**B**) Transmittance spectrum of single-layer graphene (open circles). Slightly lower transmittance for $\lambda < 500$ nm is probably due to hydrocarbon contamination (*5*). The red line is the transmittance $T = (1 + 0.5\pi\alpha)^{-2}$ expected for two-dimensional Dirac fermions, whereas the green curve takes into account a nonlinearity and triangular warping of graphene's electronic spectrum. The gray area indicates the standard error for our measurements (*5*). (Inset) Transmittance of white light as a function of the number of graphene layers (squares). The dashed lines correspond to an intensity reduction by $\pi\alpha$ with each added layer.

Graphene: experimental findings



Graphene Absorbance A~1-T~2.3%

$$\hat{H} = v_F \vec{\sigma} \cdot \vec{p} = v_F \vec{\sigma} \cdot (\hat{p} - \frac{e}{c}\vec{A}) = \hat{H}_0 + \hat{H}_{\text{int}}$$

$$A = W_a / W_i = \pi e^2/\hbar c = \pi\alpha = 0.023$$

α= 1/137.036=fine structure constant

What about other 2D systems?

Silicene: does it exist!?

Silicene: The discovery of graphene-like two-dimensional silicon

Patrick Vogt[a,b,*] Paola De Padova[c,†] Claudio Quaresima[a], Jose Avila[d], Emmanouil Frantzeskakis[d], Maria Carmen Asensio[d], Andrea Resta[a], Bénédicte Ealet[a], and Guy Le Lay[a,c]

PRL2012 (in press)

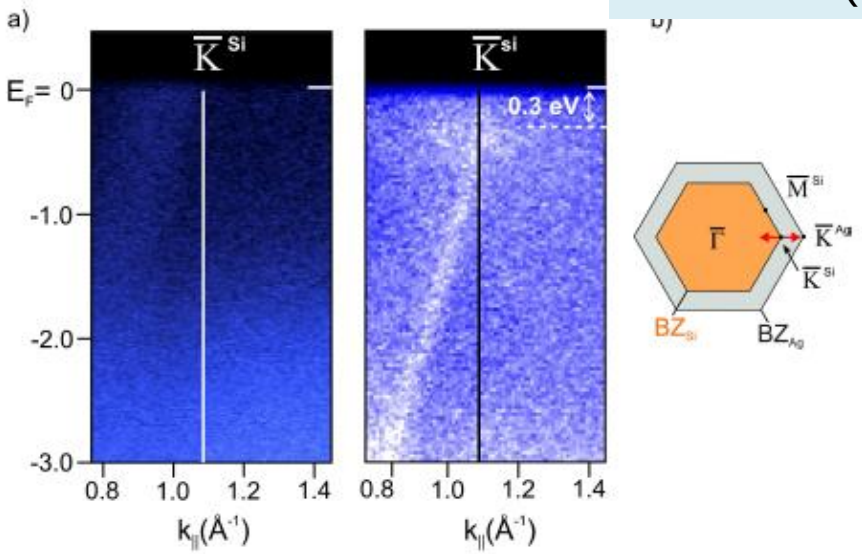


FIG. 3. a) ARPES intensity map for the clean Ag surface (left) and after formation of the 2D Si ad-layer, taken along the Ag $\overline{\Gamma}$-$\overline{K}$ direction through the silicene $\overline{K}$ point.b) Brillouin-zone (BZ) scheme of the 2D Si layer with respect to the Ag(111) 1 × 1 surface. The red arrow indicates the ARPES measurement direction.

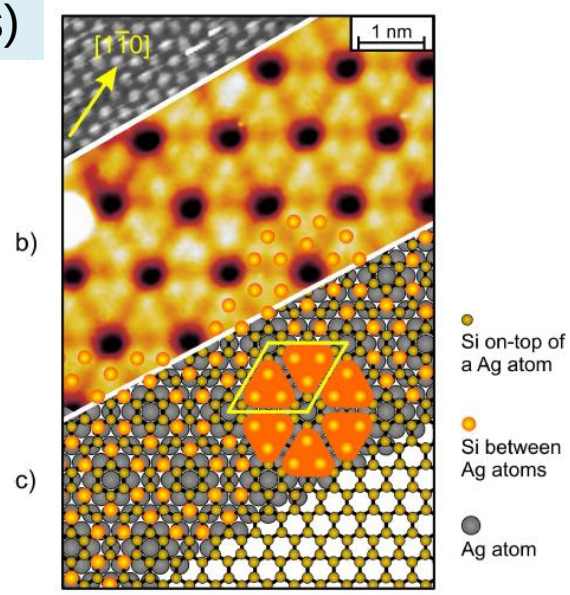
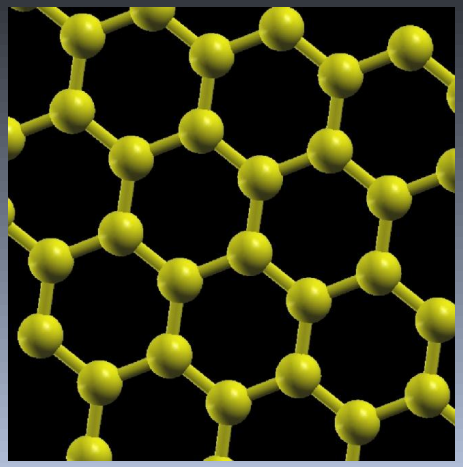
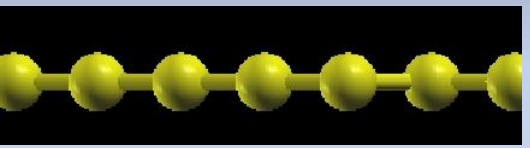


FIG. 4. Construction of the atomic structure model for the 2D Si ad-layer. Filled states STM images of a) the initial clean Ag(111)1 × 1 surface ($U_{bias} = -0.2$ V, $I = 1.93$ nA) and b) the (4 × 4) silicene sheet ($U_{bias} = -1.4$ V, $I = 0.29$ nA). c) Model of silicene on Ag(111), Si-atoms sitting on top of Ag-atoms are highlighted as bigger orange balls, resembling the measured STM image. In the bottom right corner the ball-and-stick model for the free-standing silicene layer is shown with a Si-Si distance of 0.22 nm.

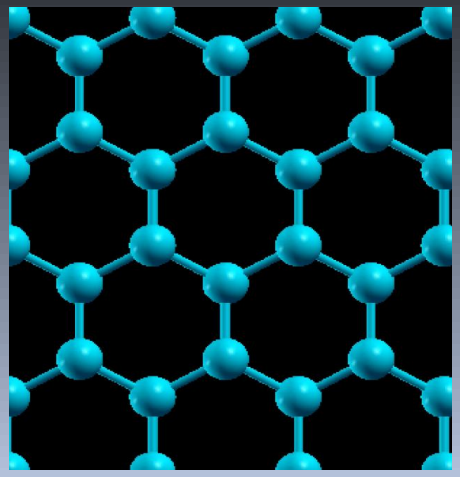
Graphene!

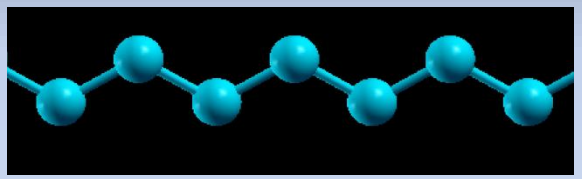




No buckling

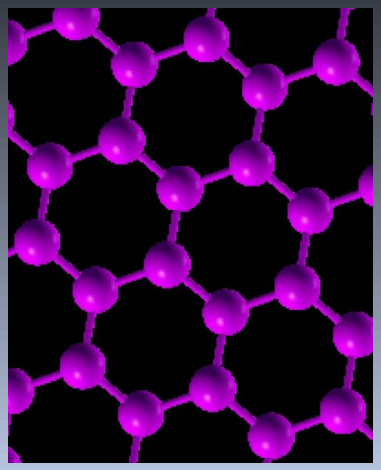
silicene

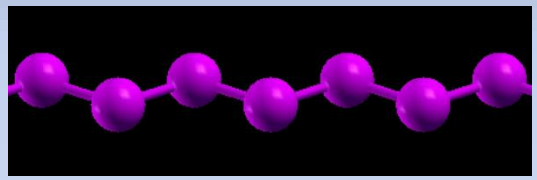




Buckling Δ= 0.45 A

germanene





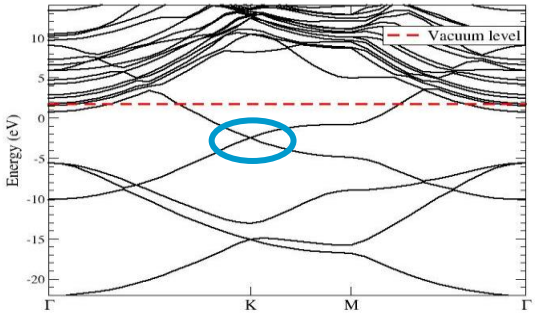
Buckling Δ= 0.69 A

TABLE I. Bond lengths d and buckling amplitude Δ for group-IV honeycomb crystals. The Fermi velocity v_F is also listed.

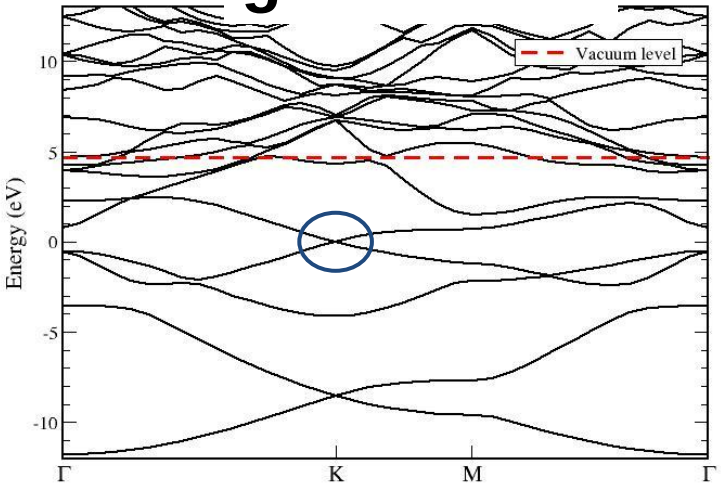
	C	Si	Ge
d (Å)	1.424	2.232	2.341
Δ (Å)	0.00	0.45	0.69
v_F (10^6m/s)	0.829	0.532	0.517

ELECTRONIC BAND STRUCTURES

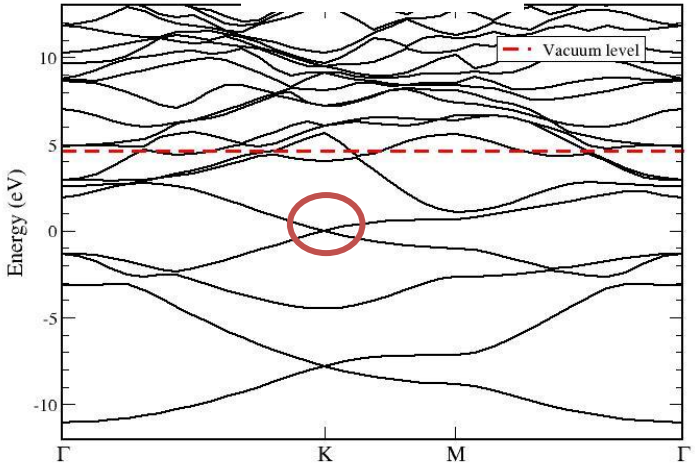
graphene



germanene



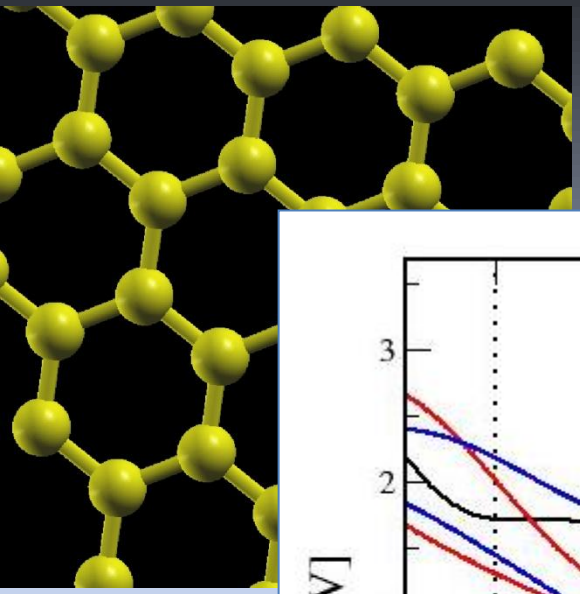
silicene

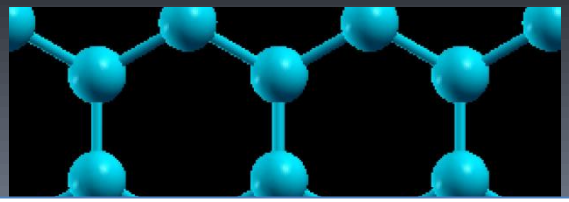


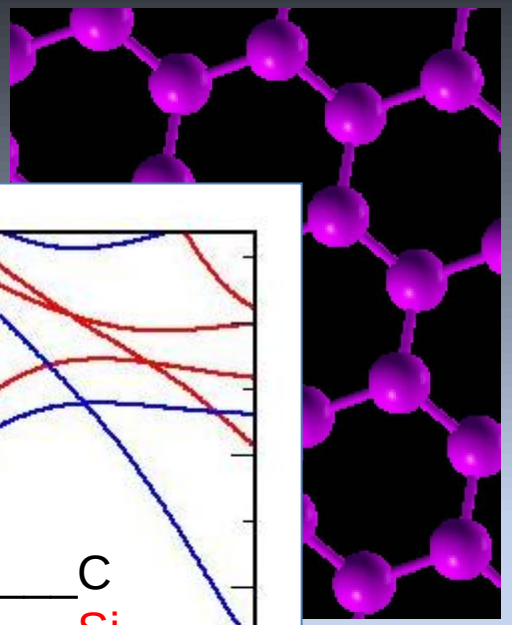
Graphene!

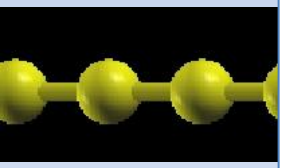
silicene

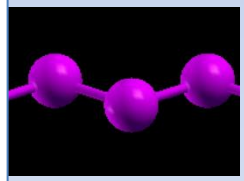
germanene



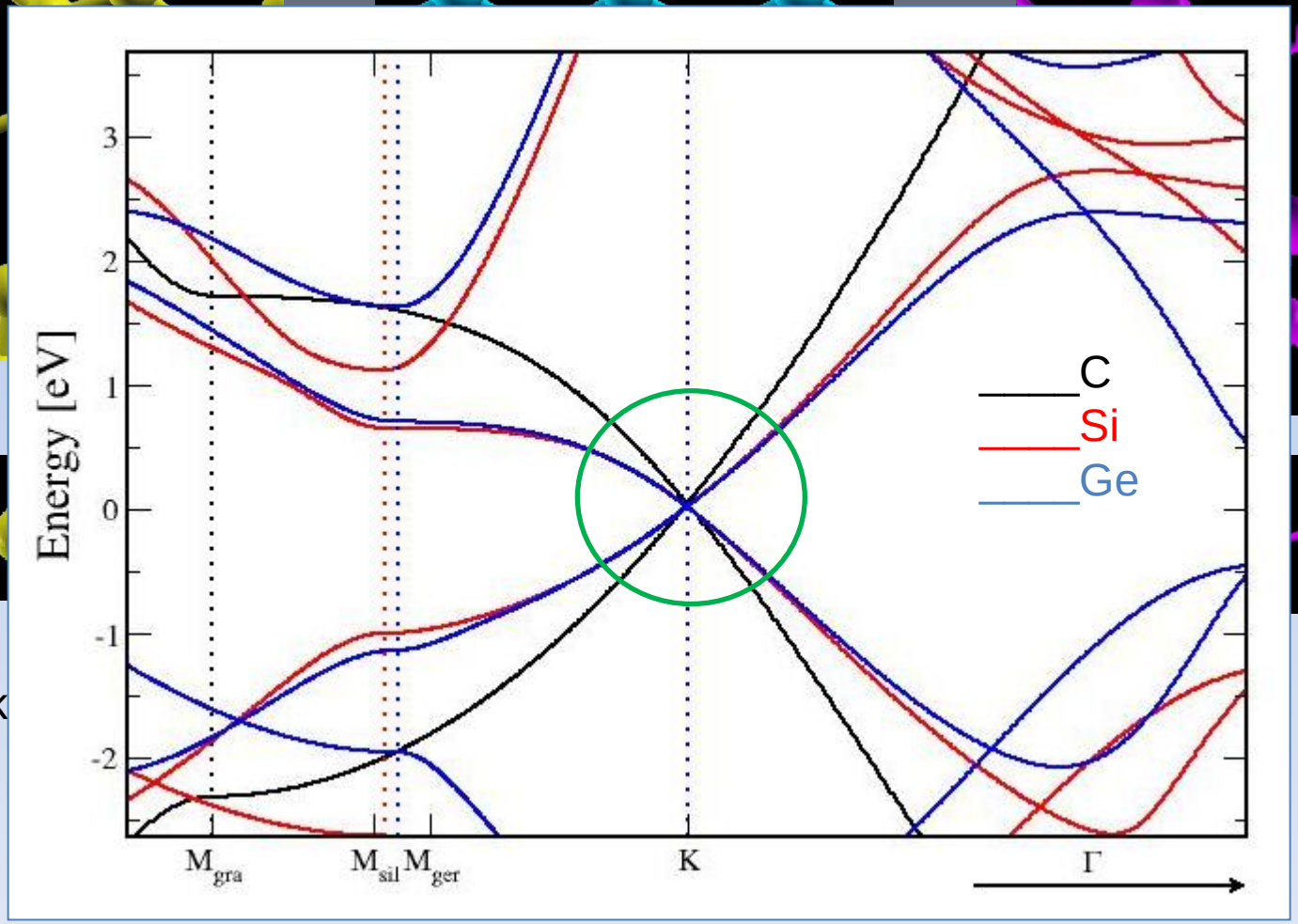






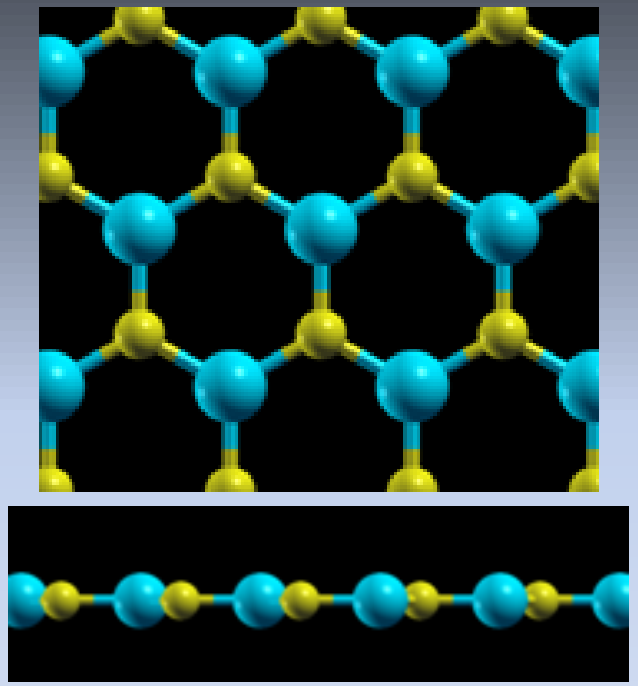


No buck

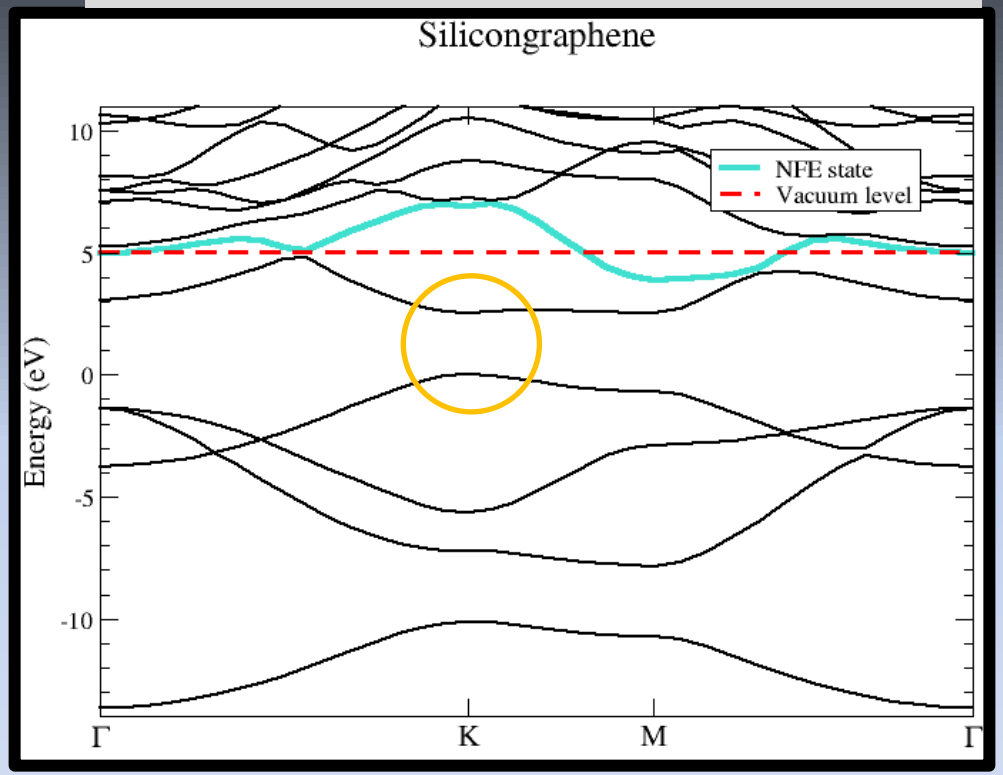


Silicongraphene (2D SiC)

P. Gori, O. Pulci, M. Marsili, F. Bechstedt, APL 2012



No buckling….



No Dirac cone **at K, a gap opens due to different electronegativity of C and Si**

(see the talk of Paola Gori this afternoon…)

ABSORBANCE A(ω)

- $A(\omega)=W_{abs}/W_{in}$

- $A(\omega)$ related to $\varepsilon_2(\omega)$: $A(\omega)=\omega/c * L * \varepsilon_2(\omega)$

with L distance between graphene layers

- $\varepsilon_2(\omega)$ Ab-initio: no experimental input
- no a-priori knowledge of the band dispersion

Our (numerical) method

- Density Functional Theory

Hohenberg Kohn 1964, Kohn and Sham 1965

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{e-ion}(r) + \int d^3r' \frac{e^2}{|r-r'|} n(r') + V_{xc}(r)\right)\varphi_{nk}(r) = \varepsilon_{nk}\varphi_{nk}(r)$$

- Fermi Golden Rule

$$A(\omega) = \frac{\omega}{c} L \cdot Im\epsilon(\omega) = \frac{8\pi^2\omega}{c}\frac{1}{A}\sum_{c,v}\sum_{\boldsymbol{k}} |M_{cv}(\boldsymbol{k})|^2 \delta(\varepsilon_c(\boldsymbol{k}) - \varepsilon_v(\boldsymbol{k}) - \hbar\omega)$$

$$M_{cv} = \frac{< c\vec{k} \,|\, \hat{e}\cdot\vec{p} \,|\, v\vec{k} >}{\varepsilon_c(\vec{k}) - \varepsilon_v(\vec{k})}$$

Ingredients: ab-initio single particle eigenvalues and eigenstates

optical properties: challenging numerical treatment

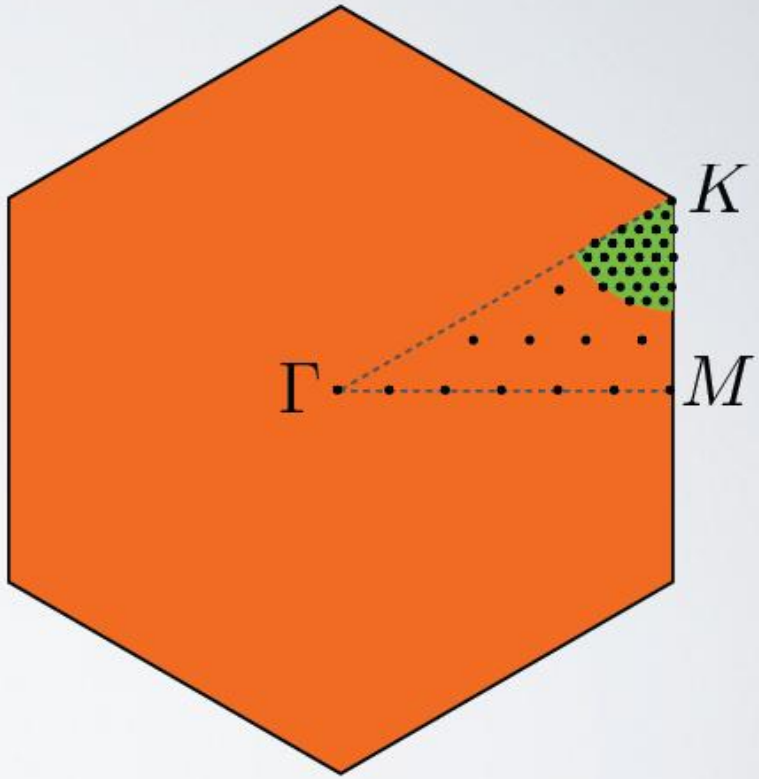
high accuracy for low transition energies = many **k**-points close to Diracpoints

hybrid mesh strategy:

1) 400x400 **k**-points in Brillouin zone
   for optical spectra above 0.5 eV

2) refined grid close to Diracpoint
   (≈ 13k **k**-points)
   for optical spectra below 0.5 eV

→ low energy limit of absorbance
converged to 4 digits



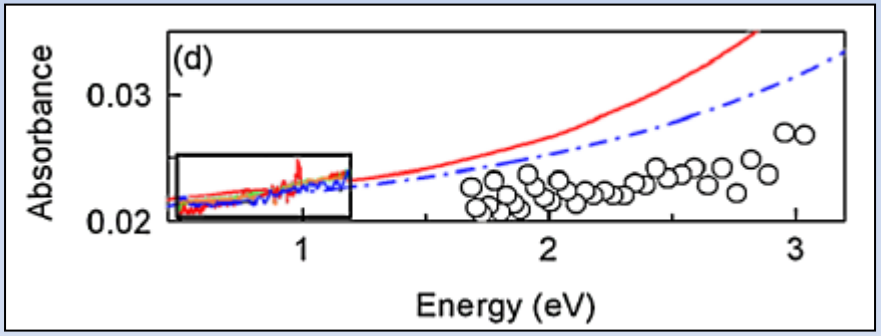
~13000 k points in IBZ!!!!

What we neglect:

- Many body effects in the band structure
- Excitonic effects in the optical properties

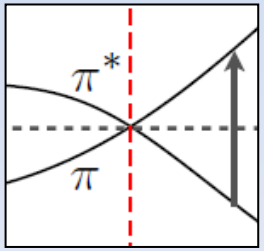
But: for $\omega \rightarrow 0$ negligible!

See Louie PRL 2009



with and without e-h interaction

- Only vertical transitions

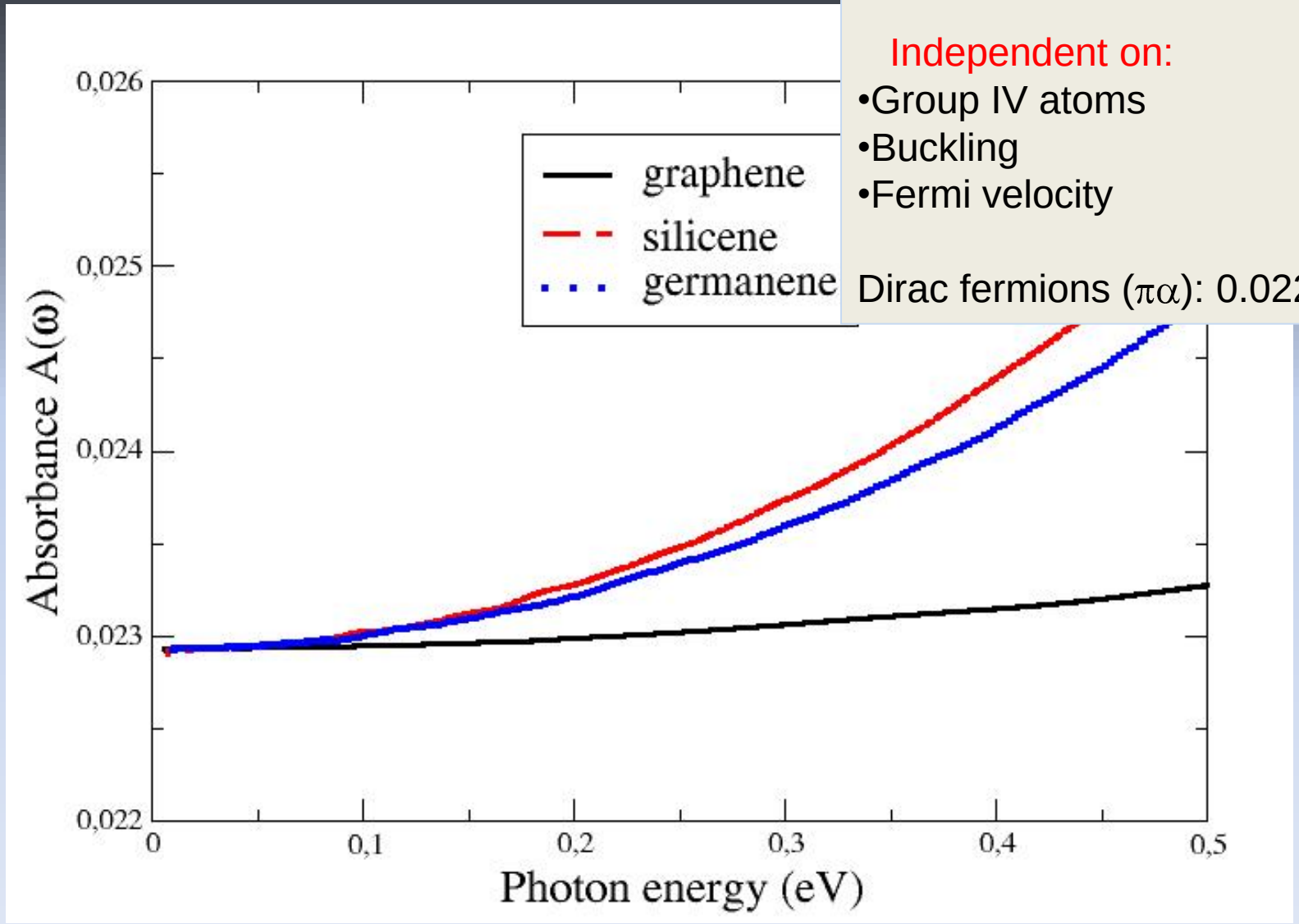


RESULTS

Graphene: 0.02293
Silicene : 0.02290
Germene: 0.02292

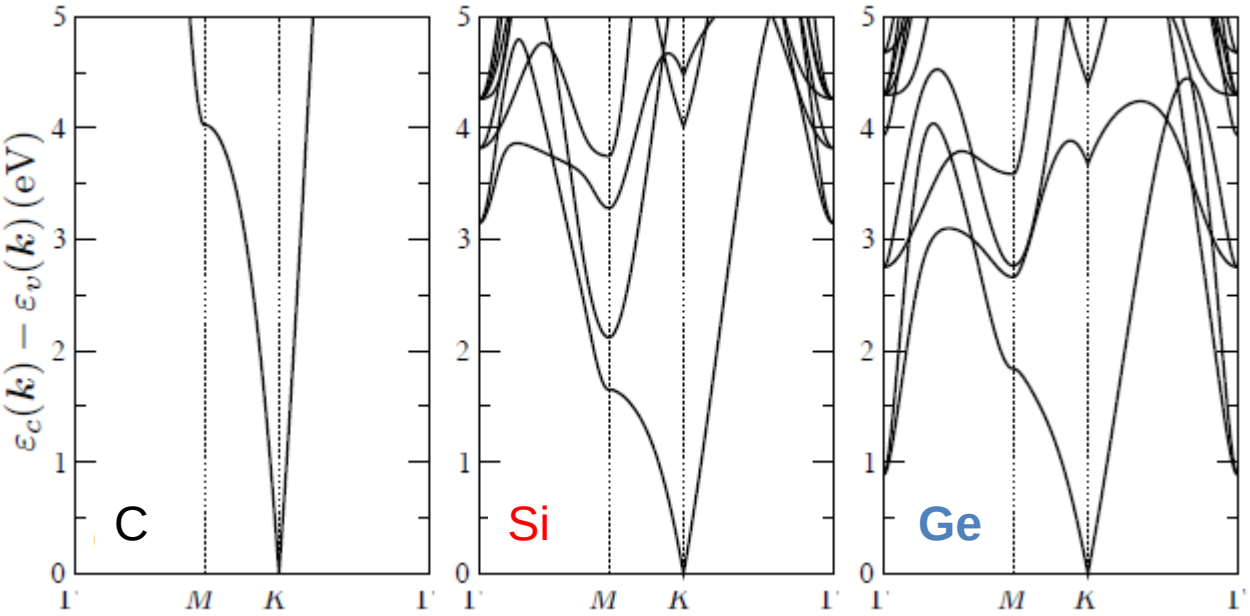
Independent on:
- Group IV atoms
- Buckling
- Fermi velocity

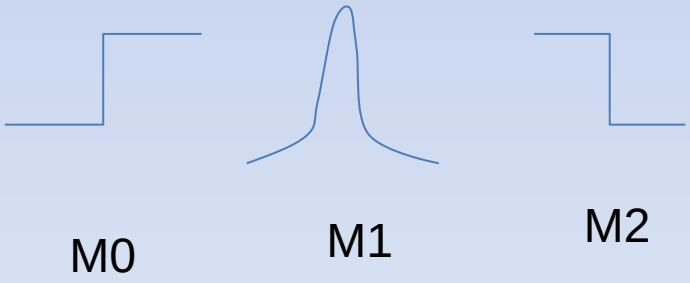
Dirac fermions ($\pi\alpha$): 0.022925

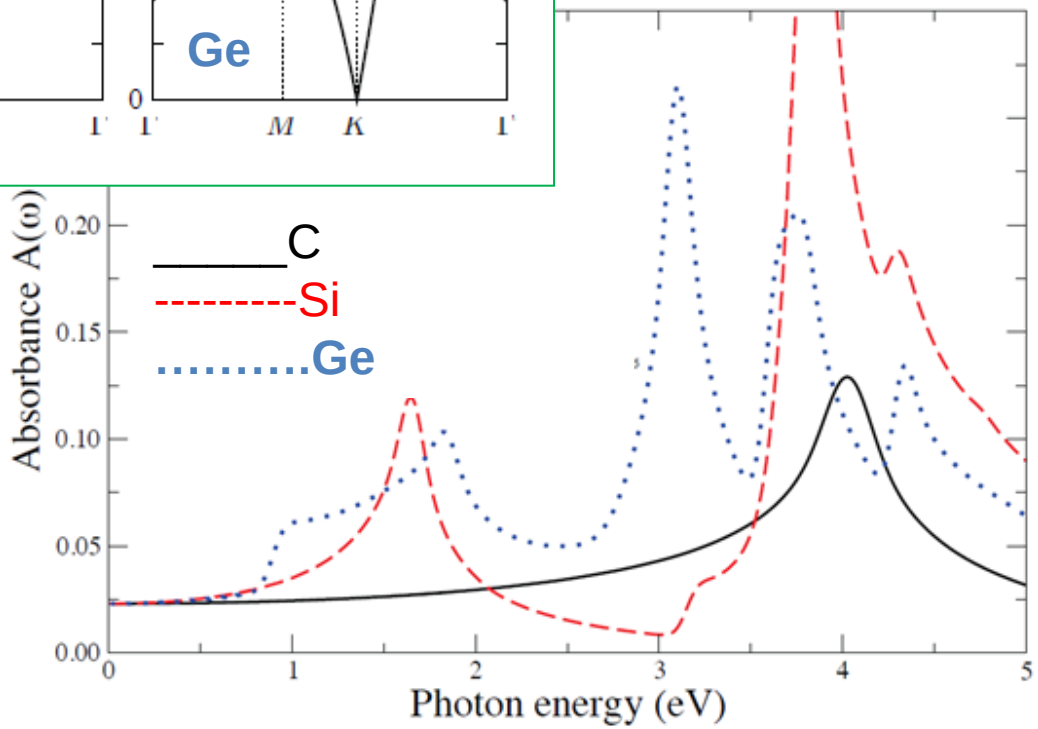


F. Bechstedt, L. Matthes, P. Gori, O. Pulci, submitted

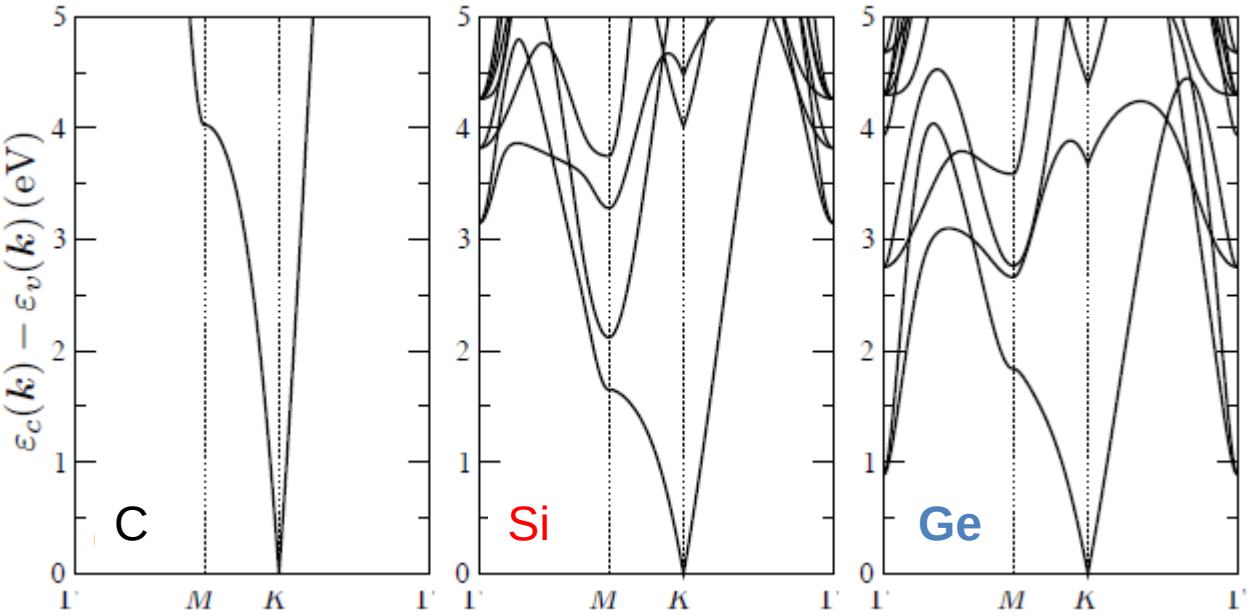
Van Hove singularities:

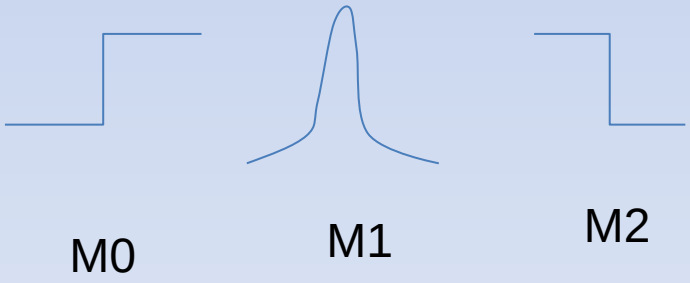


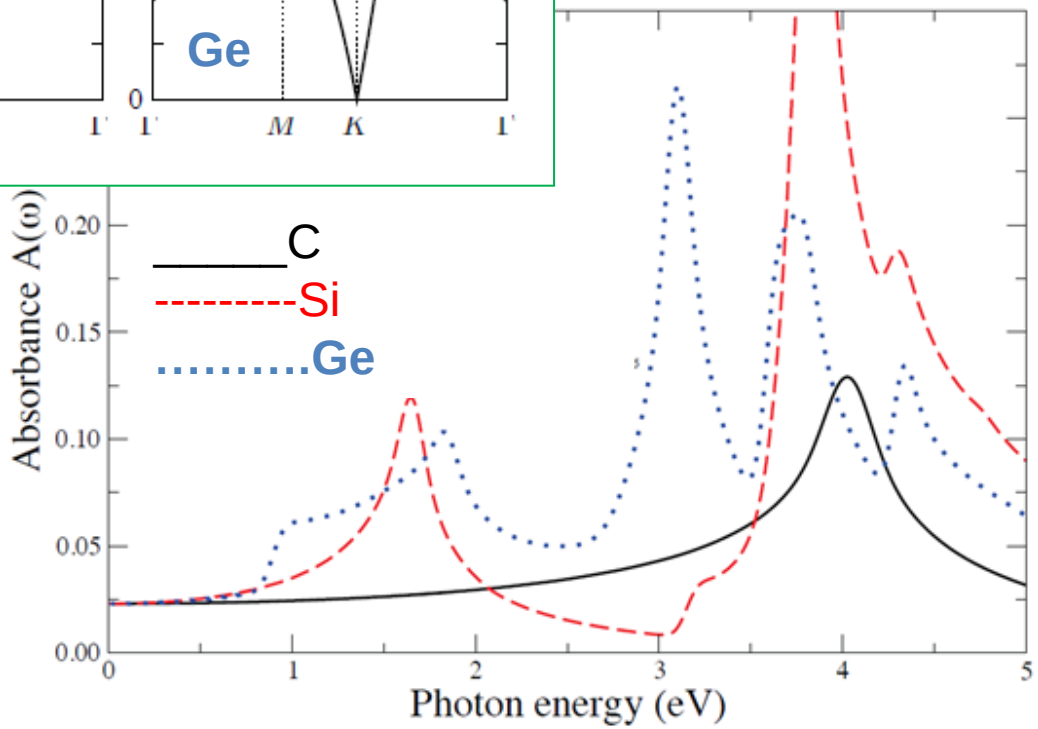




Van Hove singularities:







Analytic derivation

$$\langle c;\boldsymbol{k}|\boldsymbol{p}|v;\boldsymbol{k}\rangle \approx \langle v;\boldsymbol{k}|\boldsymbol{p}|v;\boldsymbol{k}\rangle = \frac{m}{\hbar}\nabla_{\boldsymbol{k}}\epsilon_v(\boldsymbol{k})$$

$$\approx m v_F$$

→ independent of **k** near K, K'

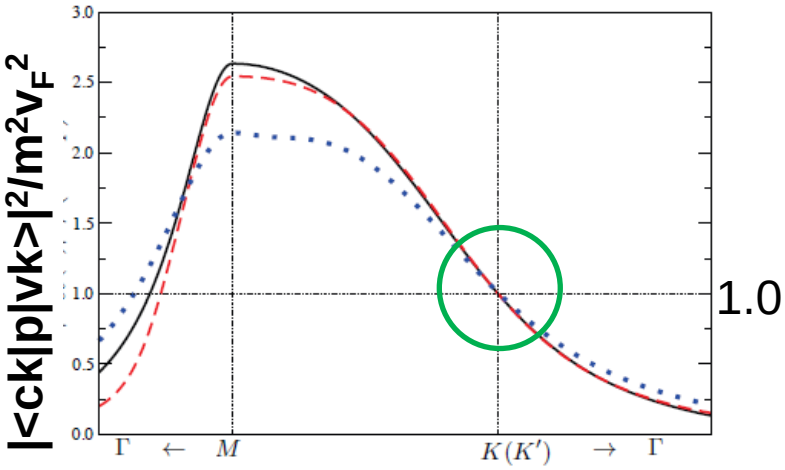
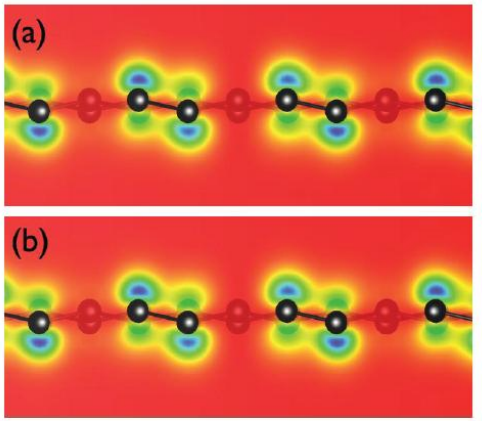


FIG. 3. (Color online) Transition matrix elements of the pure $\pi - \pi^*$ transition along high-symmetry lines in the BZ for graphene (black solid line), silicene (red dashed line), and germanene (blue dotted line). The longitudinal representation[18] has been used in the calculations.



v

c

FIG. 4. (Color online) Wave-function squares in silicene for the highest occupied state (a) and the lowest unoccupied state (b) at K. The atomic positions in the isolated Si sheet are indicated.

$$|\varphi_{n,k}(\boldsymbol{r})|^2$$

Analytic derivation

$$A(\omega) = \frac{8\pi^2\omega}{cA}\sum_{c,v}\sum_{\mathbf{k}} |M_{cv}(\mathbf{k})|^2\,\delta\left(\varepsilon_c(\mathbf{k}-\varepsilon_v(\mathbf{k})-\hbar\omega\right)$$

Fermi Golden rule

$$A(\omega) = \frac{\alpha\hbar}{m^2\omega}\int_{\mathrm{BZ}} d^2\mathbf{k}\sum_{j=x,y} |\langle +\mathbf{k}|p_j|-\mathbf{k}\rangle|^2 \times \delta\left(\varepsilon_+(\mathbf{k})-\varepsilon_-(\mathbf{k})-\hbar\omega\right).$$

\+ =conduction band
\- =valence band

$$\sum_{j=x,y} |\langle +\mathbf{k}_0|p_j|-\mathbf{k}_0\rangle|^2 = (mv_F)^2$$

around K, K’

$$A(\omega) = 2\frac{\hbar v_F^2}{\omega}\alpha\int d^2(\Delta\mathbf{k})\delta(2\hbar v_F|\Delta\mathbf{k}|-\hbar\omega)$$

Simple integral

$$A(\omega) = 2\frac{\hbar v_F^2}{\omega}\alpha\frac{\pi\omega}{2\hbar v_F^2} = \pi\alpha.$$

Universal behavior

Gauge invariance

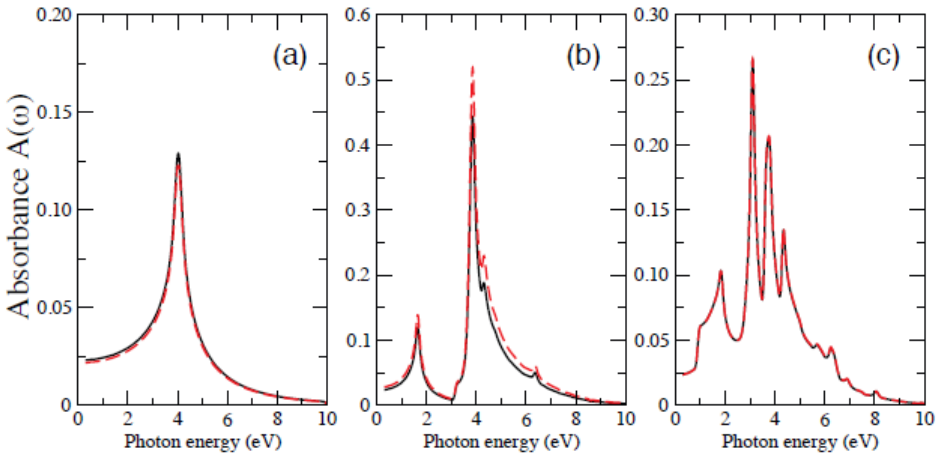


FIG. 5. (Color online) The frequency-dependent absorbance for (a) graphene, (b) silicene, and (c) germanene. Besides the longitudinal gauge (2) (black solid line) also the transversal gauge (3) (red dashed line) has been used.

$$M_{cv}(\mathbf{k}) = \lim_{\mathbf{q}\to 0} \frac{e}{|\mathbf{q}|} \langle c;\mathbf{k} \left| e^{i\mathbf{q}\cdot\mathbf{r}} \right| v;\mathbf{k}+\mathbf{q}\rangle$$

Longitudinal gauge

$$M_{cv}(\mathbf{k}) = \frac{e\hbar}{m} \frac{\left\langle c;\mathbf{k} \left| \frac{\mathbf{q}}{|\mathbf{q}|}\mathbf{p} \right| v;\mathbf{k} \right\rangle}{\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k})}.$$

Transverse gauge

Conclusions

- **"Opacity" of the 2D honeycomb crystals graphene, silicene, and germanene *ab-initio calculations within the independent particle* approach.**
- **ω->0 *A(0) = $\pi\alpha$ as predicted for massless Dirac* fermions.**
- **isotropic linear band structure (*K, K'*) *Dirac points* +optical interband matrix elements related to the Fermi velocity v_F of the 2D material**
- **Independent of the longitudinal or transverse gauge of the electromagnetic field and *universal* for all group-IV crystals independent of the value of v_F , *the* degree of sp^2 *and* sp^3 *hybridization, and the sheet buckling.***
- **For higher frequencies the absorbance spectra start to deviate significantly with the group-IV material.**

Future work

- Inclusion of Many-Body (GW) effects for a refined calculation of the Fermi velocity in silicene and germanene

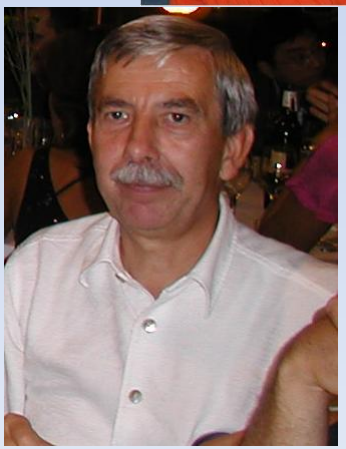
- Effect of substrate (silicene on Ag(111))

Thanks to:

- Lars Matthes (Clermont4 PhD Roma-Jena)

- Paola Gori (CNR-ISM, Roma)

- Friedhelm Bechstedt
  (IFTO Jena, Germany)



European Theoretical Spectroscopy Facility

an initiative of the Nanoquanta Network of Excellence

Next call for projects: deadline 19 April

Thank you for your attention

http://www.etsf.eu

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