# First-principles calculation of many-body effects in graphene

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# Acknowledgments

Collaborators

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# Outline

- Preliminaries
  - Graphene
  - Electron self energy / ARPES
  - Migdal approximation
  - *GW* approximation

- Electron self energy in graphene
  - Contribution from electron-phonon (*e*-ph) interactions
  - Contribution from electron-electron (*e*-*e*) interactions
  - Combining the effects of *e*-ph and *e*-*e* interactions

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# Graphene

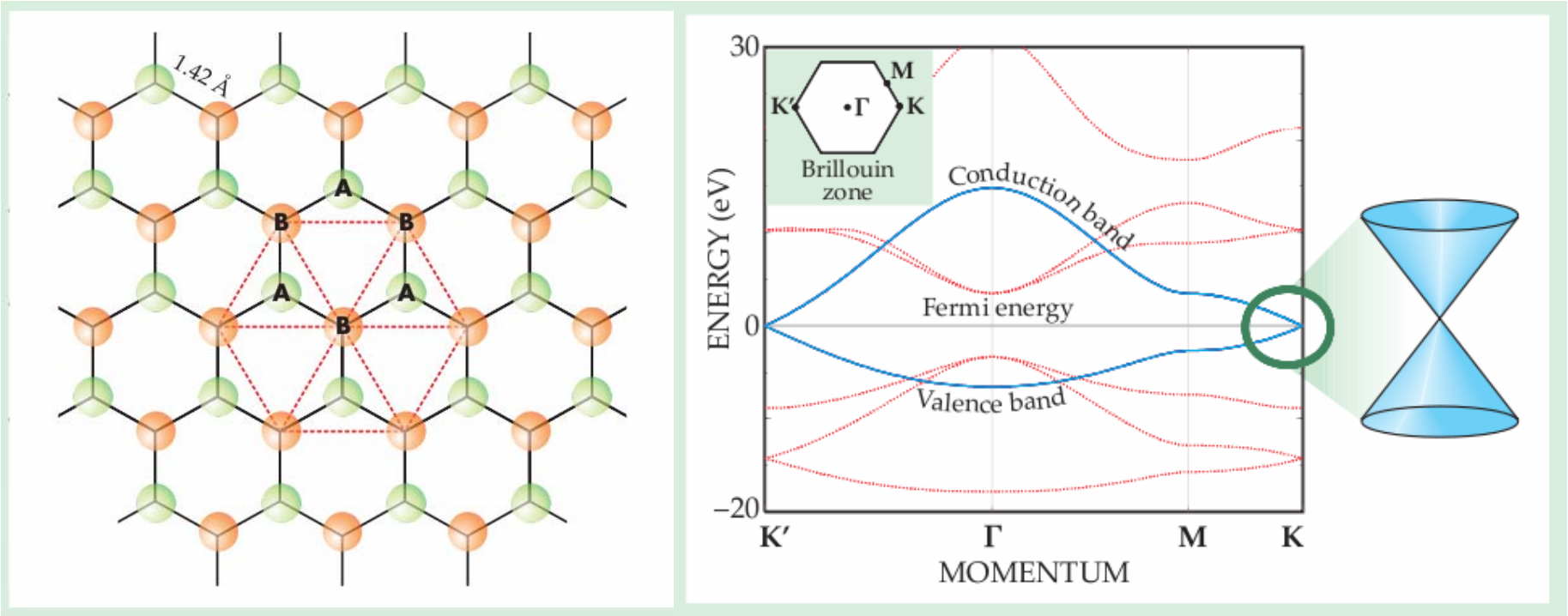
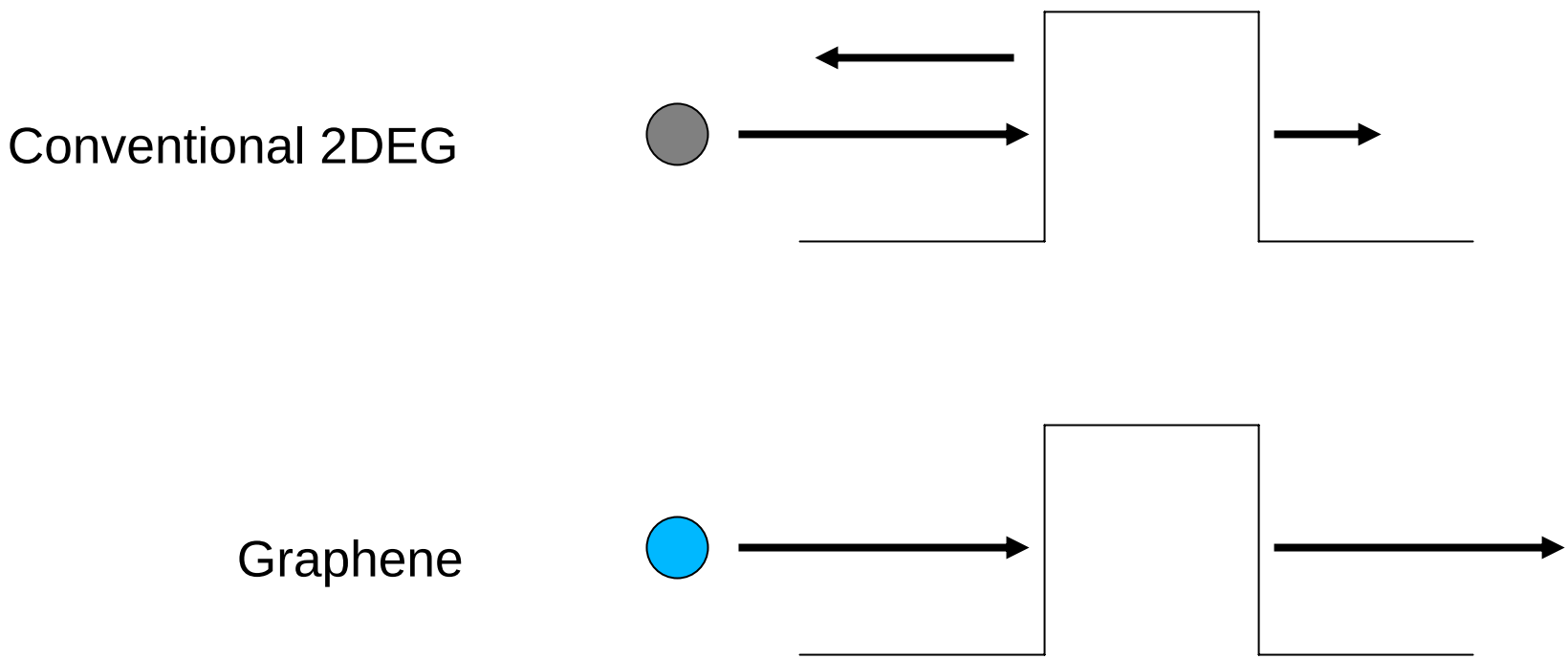



Figure: Geim and McDonald, Phys. Today (2008)

Charge carriers in graphene are 2D massless Dirac fermions

# Klein tunneling in graphene



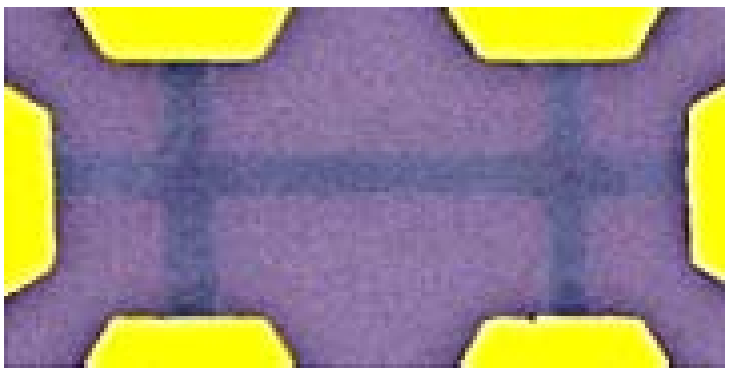

The most spectacular phenomenon of 2D massless Dirac fermions

Katsnelson, Novoselov & Geim, Nature Physics 2, 620 (2006)

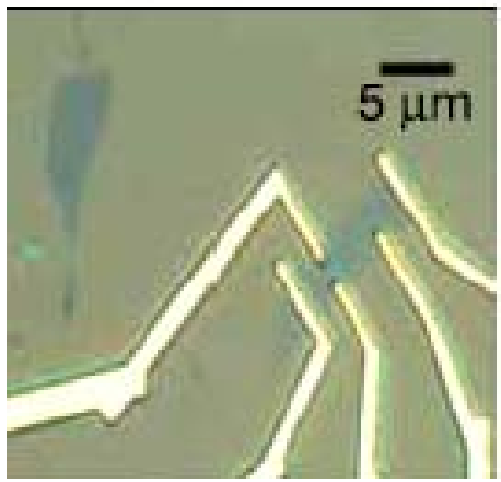
# Scotch tape separated graphene

Isolation of single-layer graphene and observation of new integer quantum Hall effect

A. K. Geim Group at Manchester
K. S. Novoselov *et al*, Nature **438**, 197 (2005)



P. Kim Group at Columbia
Y. Zhang *et al*, Nature **438**, 201 (2005)

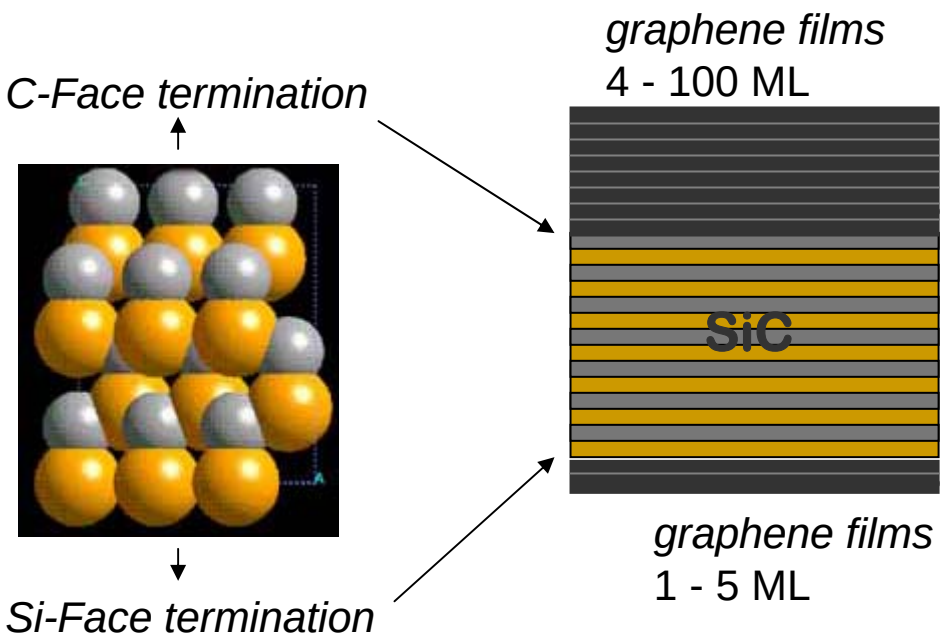


# Epitaxial growth of graphene layers on SiC

Thermal decomposition of SiC at high temperature (>1400°C)

⟶ Sublimation of Si

C. Berger *et al.*, *J Phys Chem B* 108, 19912 (2004)




**By controlling temperature, growth of 1 to ~100 graphene layers (tens of microns)**

(Slide courtesy of Walter de Heer)

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# Electron self energy due to many-body effects

$\Sigma_{\mathbf{k}}$ ←

**Many-body effects:**
*e*-*e* interactions (*e*-*h* pair generation, plasmon emission)
*e*-ph interactions
impurity scattering
…

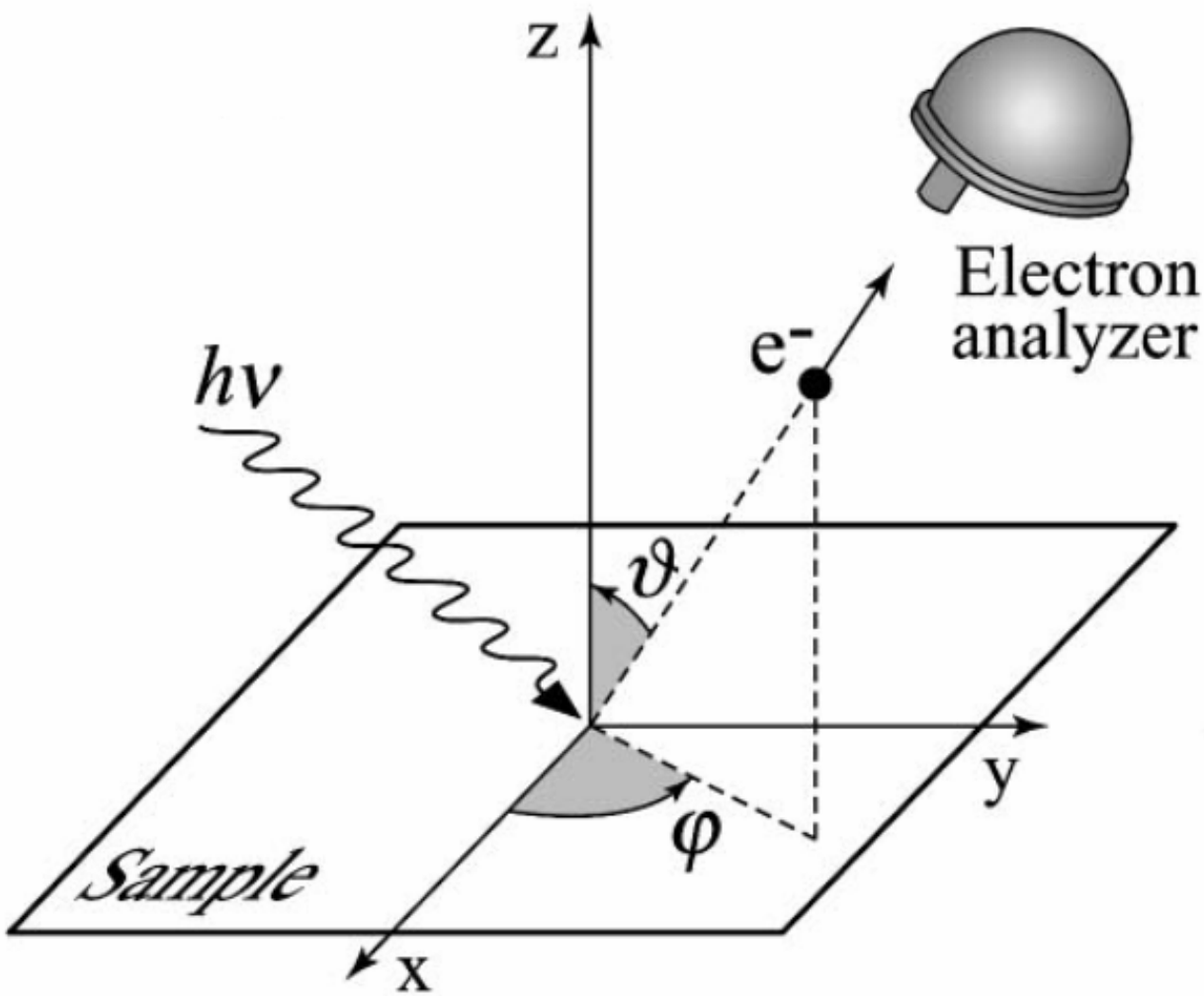
$$\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}}^{0} + \mathrm{Re}\,\Sigma_{\mathbf{k}}$$

Quasiparticle energy

$$\tau_{\mathbf{k}} = \frac{\hbar}{2\,\mathrm{Im}\,\Sigma_{\mathbf{k}}}$$

Quasiparticle lifetime

# Angle-resolved photoemission spectroscopy (ARPES)




A. Damascelli, Z. Hussain, and Z.-X. Shen, Rev. Mod. Phys. 75, 473 (2003)

# Angle-resolved photoemission spectroscopy (ARPES)

$$I(\mathbf{k},\omega,\hat{e}_\nu,h\nu) = I_0(\mathbf{k},\omega,\hat{e}_\nu,h\nu)\, f_{\mathrm{FD}}(\omega)\, A(\mathbf{k},\omega)$$

$$A(\mathbf{k},\omega) = \frac{2}{\pi}\frac{-\mathrm{Im}\,\Sigma(\mathbf{k},\omega)}{\left[\omega-\varepsilon_{\mathbf{k}}-\mathrm{Re}\,\Sigma(\mathbf{k},\omega)\right]^2+\left[\mathrm{Im}\,\Sigma(\mathbf{k},\omega)\right]^2}$$

ARPES → electron self energy

# Width of the momentum distribution curve (MDC)

$$\varepsilon_{\mathbf{k}} = \hbar v_F \, k \quad \text{(graphene or doped cuprates)}$$

$$A(\mathbf{k},\omega) = \frac{2}{\pi} \frac{-\operatorname{Im}\Sigma(\mathbf{k},\omega)}{\left[\omega - \hbar v_{\mathbf{k}} \, k - \operatorname{Re}\Sigma(\mathbf{k},\omega)\right]^2 + \left[\operatorname{Im}\Sigma(\mathbf{k},\omega)\right]^2}$$

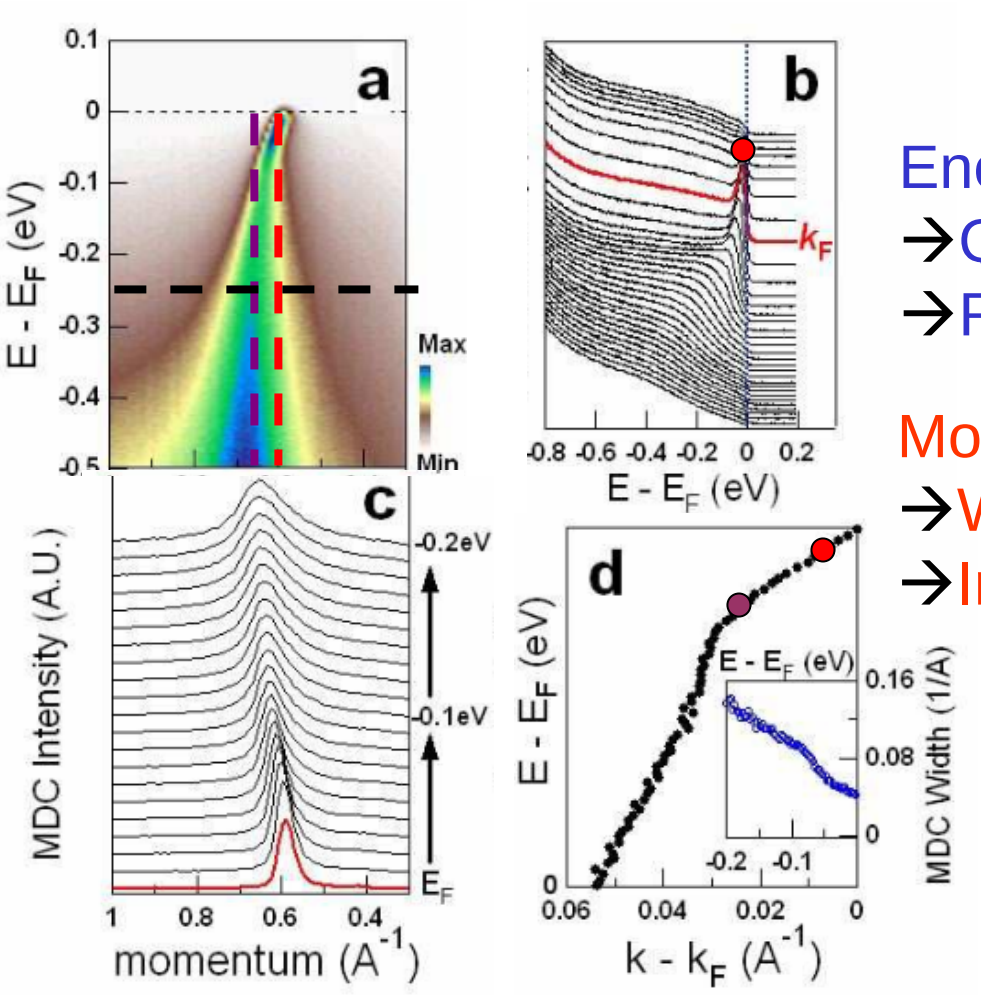
$$\approx \frac{2}{\pi} \frac{-\operatorname{Im}\Sigma(\omega)}{\left[\omega - \hbar v_{\mathbf{k}} \, k - \operatorname{Re}\Sigma(\omega)\right]^2 + \left[\operatorname{Im}\Sigma(\omega)\right]^2}$$

Lorentzian of $k$

$$\Delta k(\omega) = \mathrm{FWHM} \approx 2 \times \frac{\left|\operatorname{Im}\Sigma(\omega)\right|}{\hbar v_F}$$

Imaginary part of the self energy is proportional to the MDC width in graphene, to a good approximation.

# Angle-resolved photoemission spectroscopy (ARPES)



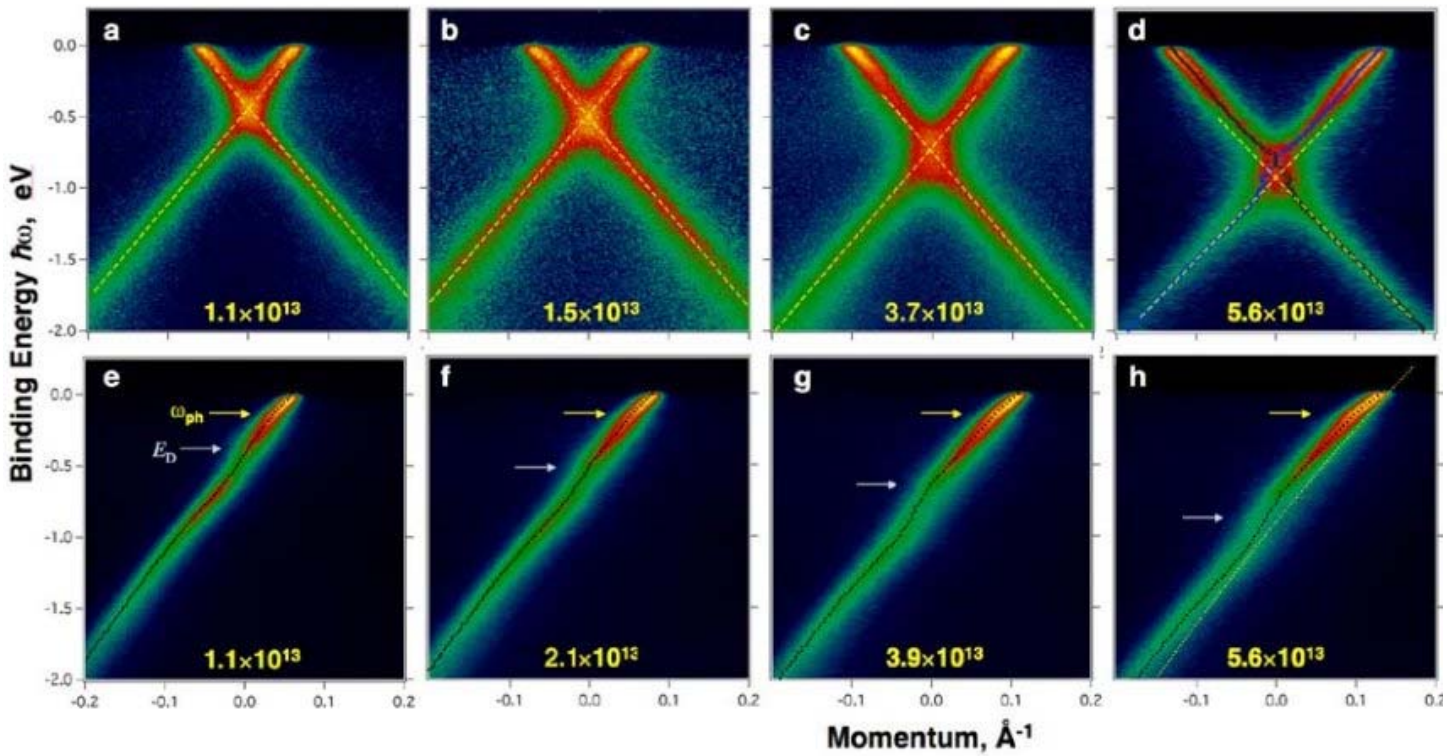

Energy distribution curve (EDC)
→Quasiparticle bandstructure
→Real part of the self energy

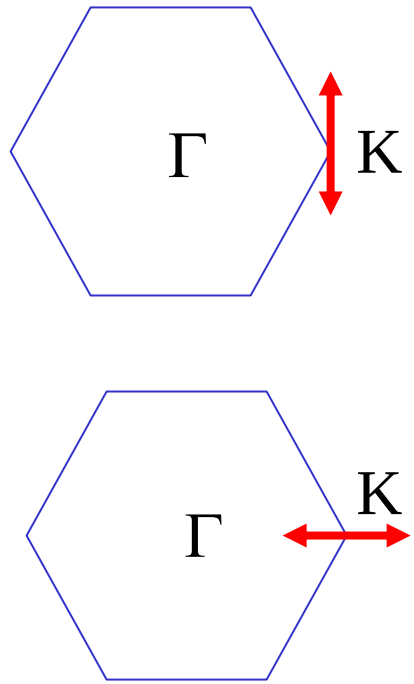
Momentum distribution curve (MDC)
→Width gives lifetime
→Imaginary part of the self energy

Zhou, Cuk, Devereaux, Nagaosa, and Shen, Handbook of High-Temperature Superconductivity: Theory and Experiment, edited by J. R. Schrieffer, (Springer, 2007) / **(arXiv:cond-mat/0604284)**

# Motivation

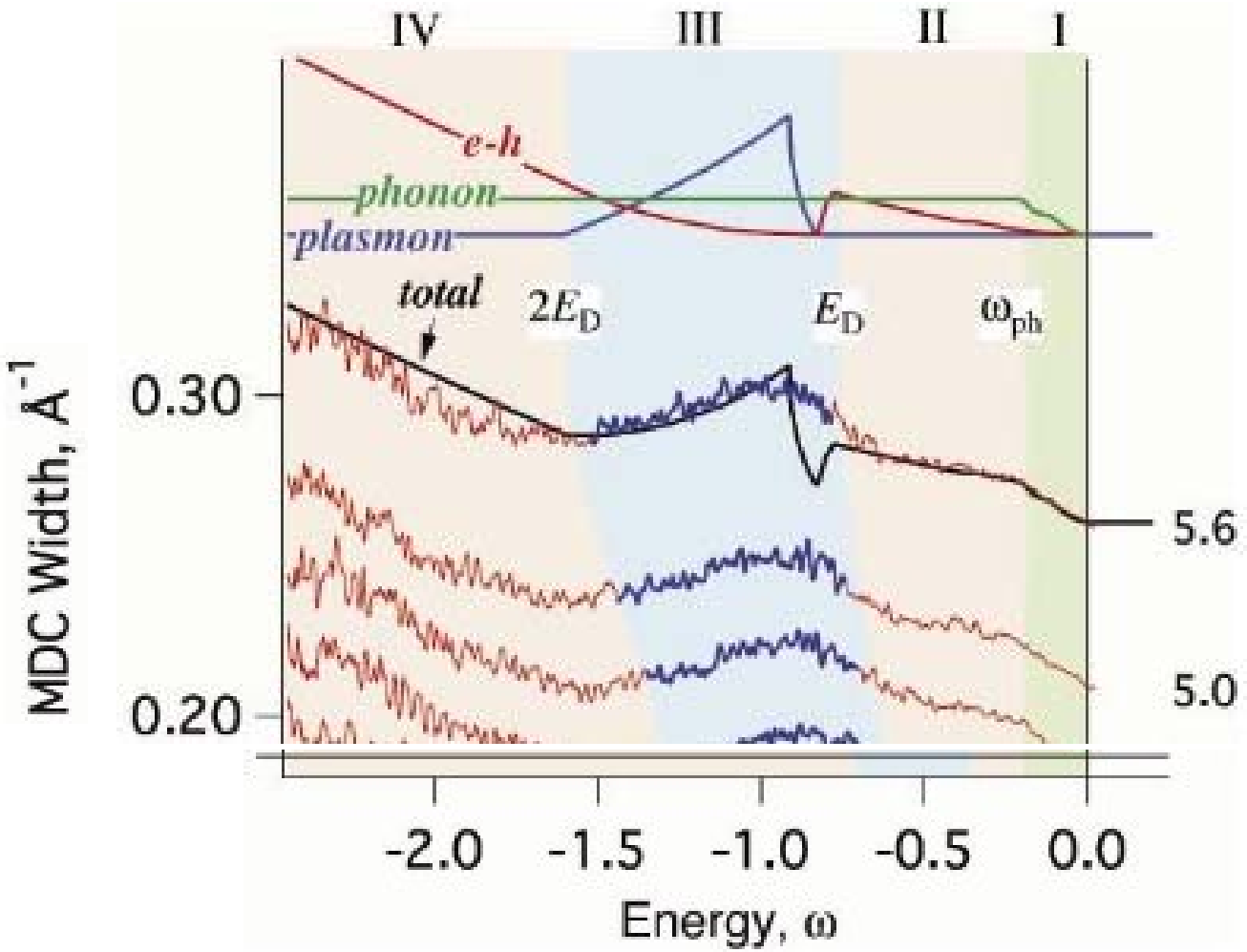
ARPES of epitaxial graphene on (0001) surface of SiC[1]




1) A. Bostwick, *et. al.,* Nature Physics **3**, 36 (2007)

# Motivation




A. Bostwick, *et. al.,* Nature Physics **3**, 36 (2007).

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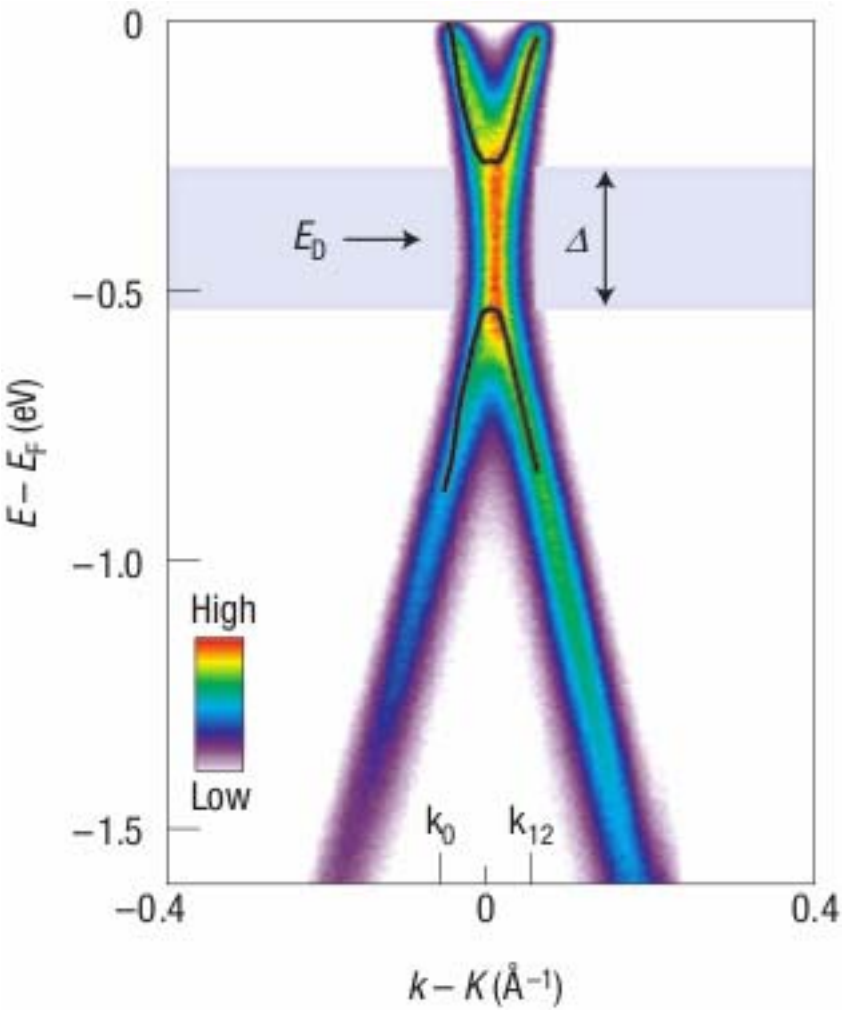
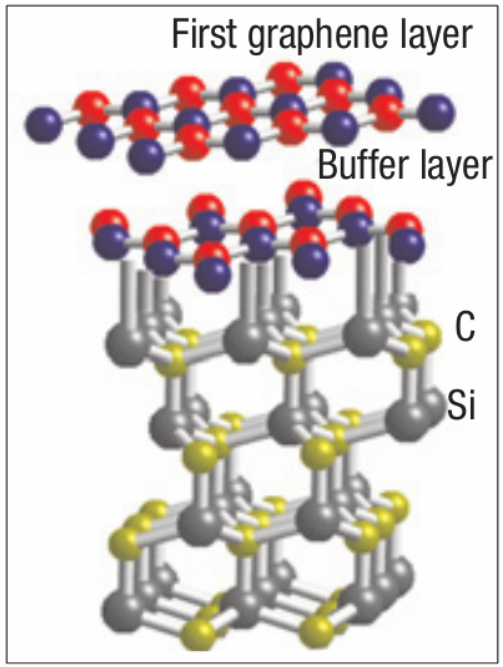
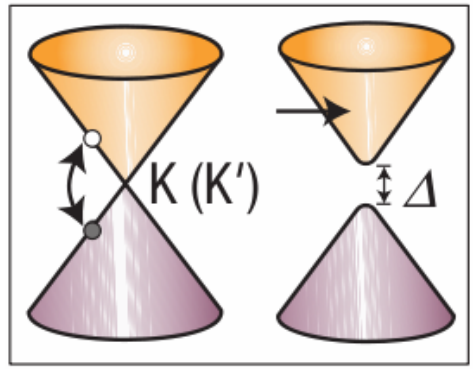



Substrate induced band gap




Important issue for applications

S.Y. Zhou, *et. al.,* Nature Materials **6**, 770 (2007).

# Interpretation of the ARPES spectra of graphene

Q: Self-energy effects[1] or substrate induced band gap[2]?


1) A. Bostwick, *et. al.,* Nature Physics **3**, 36 (2007).

2) S.Y. Zhou, *et. al.,* Nature Materials **6**, 770 (2007).

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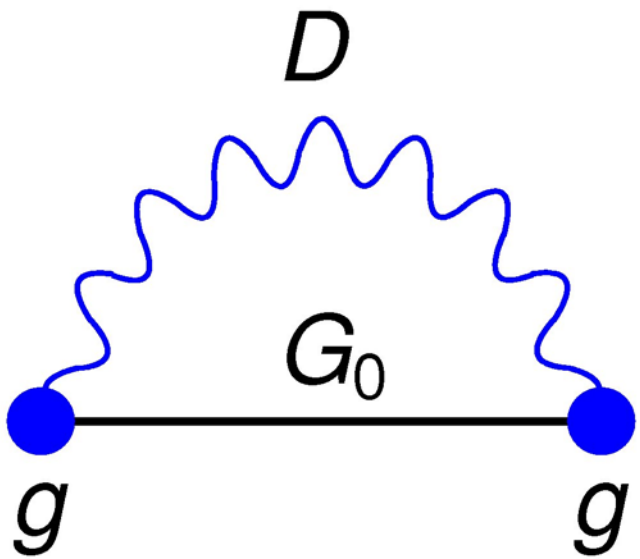
# Migdal approximation




$$\Sigma^{e-\mathrm{ph}} = i\, g^2\, D\, G_0$$

Electron self energy arising from *e*-ph interactions

# Electron self energy arising from *e*-ph interactions

- Step 1. DFT wavefunctions (planewave basis) and energy eigenvalues within LDA using *ab initio* pseudopotentials.[1]

$$\left[-\frac{\nabla^2}{2}+V_{ion}+V_{Hartree}+V_{xc}^{LDA}\right]\psi_{nk}=E_{nk}^{LDA}\psi_{nk}$$

- Step 2. Phonon eigenmodes / frequencies / electron-phonon coupling within DFPT [2]

$$g_{n,n',\lambda}(\mathbf{k},\mathbf{q})=\sqrt{\frac{\mathrm{h}}{2M\omega_{\lambda,\mathbf{q}}}}\left\langle n,\mathbf{k}\left|\Delta V_{SCF}(\lambda,\mathbf{q})\right|n',\mathbf{k}+\mathbf{q}\right\rangle$$


1) W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965)

2) S. Baroni *et al.*, Rev. Mod. Phys. **73**, 515 (2001)

# Electron self energy arising from *e*-ph interactions

- Step 3. Interpolation of the above quantities for q points in a fine grid (500 x 500 irreducible points) using maximally localized Wannier functions.[1-3]

- Step 4. Self-energy of electron within Migdal formalism.[4]

$$\Sigma_n(\mathbf{k},E) = \sum_{n',\lambda}\int \frac{d^2q}{A_{BZ}} g_{n,n',\lambda}(\mathbf{k},\mathbf{q})^2 \left[ \frac{n_B(\omega_{\lambda,\mathbf{q}})+1-n_F(\xi_{n',\mathbf{k}+\mathbf{q}})}{E-\xi_{n',\mathbf{k}+\mathbf{q}}-\omega_{\lambda,\mathbf{q}}+i\delta} + \frac{n_B(\omega_{\lambda,\mathbf{q}})+n_F(\xi_{n',\mathbf{k}+\mathbf{q}})}{E-\xi_{n',\mathbf{k}+\mathbf{q}}+\omega_{\lambda,\mathbf{q}}+i\delta} \right]$$


1) N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997)

2) I. Souza, N. Marzari and D. Vanderbilt, Phys. Rev. B **65**, 035109 (2001)

3) F. Giustino, M.L. Cohen and S.G. Louie, Phys. Rev. B **76**, 165108 (2007)

4) J.R. Schrieffer, Theory of Superconductivity (W.A.Benjamin,Inc., 1964)

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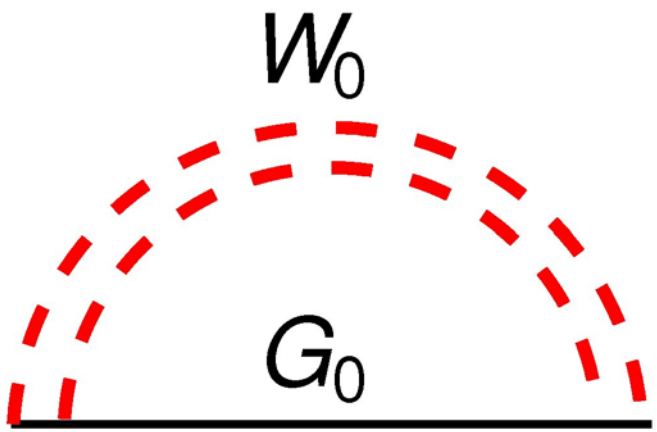
# *GW* approximation




$$\Sigma^{e-e} = i\, G_0\, W_0$$

Electron self energy arising from *e*-*e* interactions

# Electron self energy arising from *e*-*e* interactions

- Step 1. Ground state calculation
  - DFT wavefunctions and eigenvalues within LDA using *ab initio* pseudopotentials. [1]

$$\left[-\frac{\nabla^2}{2}+V_{ion}+V_{Hartree}+V_{xc}^{LDA}\right]\psi_{nk}=E_{nk}^{LDA}\psi_{nk}$$

- Step 2. QP self-energy within *GW* Approximation [2]

$$\left[-\frac{\nabla^2}{2}+V_{ion}+V_{Hartree}+\Sigma(E_{nk})\right]\psi_{nk}=E_{nk}\psi_{nk} \qquad \left(\Sigma=iG_0W_0\right)$$


1) W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965)

2) M.S. Hybertsen and S.G. Louie, Phys. Rev. B **34**, 5390 (1986)

# Electron self energy arising from *e*-*e* interactions

- *GW* calculations performed with BerkeleyGW code[1].
- Full dynamical dielectric screening of graphene was calculated[2].
- Substrate screening was modeled by[3-4] $\boxed{\varepsilon_q(\omega) = \varepsilon_{\text{eff}} - v_q P_q(\omega)}$.

$$\varepsilon_{\text{eff}} = (1 + \varepsilon_{\text{sub}}^{\infty}) / 2$$

$v_q$ bare Coulomb interaction

$P_q(\omega)$ polarizability of graphene


1) J. R. Deslippe et al., computer code BerkeleyGW (2009)
2) L. X. Benedict, C. D. Spataru, and S. G. Louie, PRB 66, 085116 (2002)
3) E. H. Hwang and S. Das Sarma, PRB 75, 205418 (2007)
4) M. Polini et al., PRB 77, 081411 (2008)

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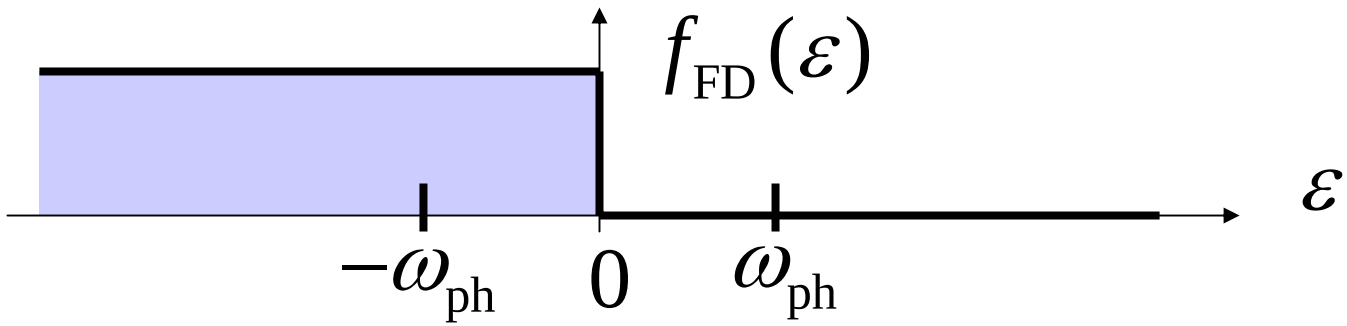
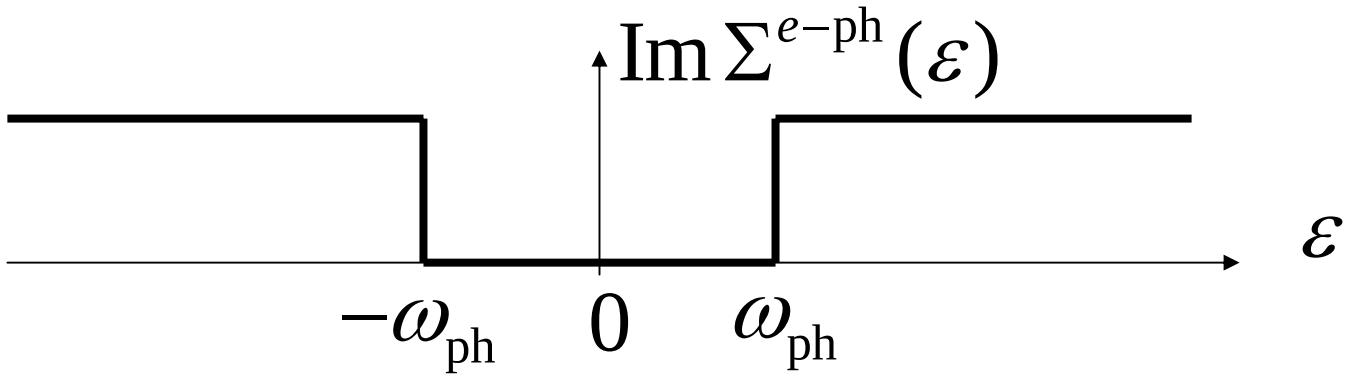
# Imaginary part of the electron self energy (*e*-ph interactions)

Conventional metal: $\mathrm{Im}\,\Sigma^{e-\mathrm{ph}}(\varepsilon)$

(1) Constant DOS near the Fermi level

(2) One effective optical phonon branch (Einstein phonon spectrum)



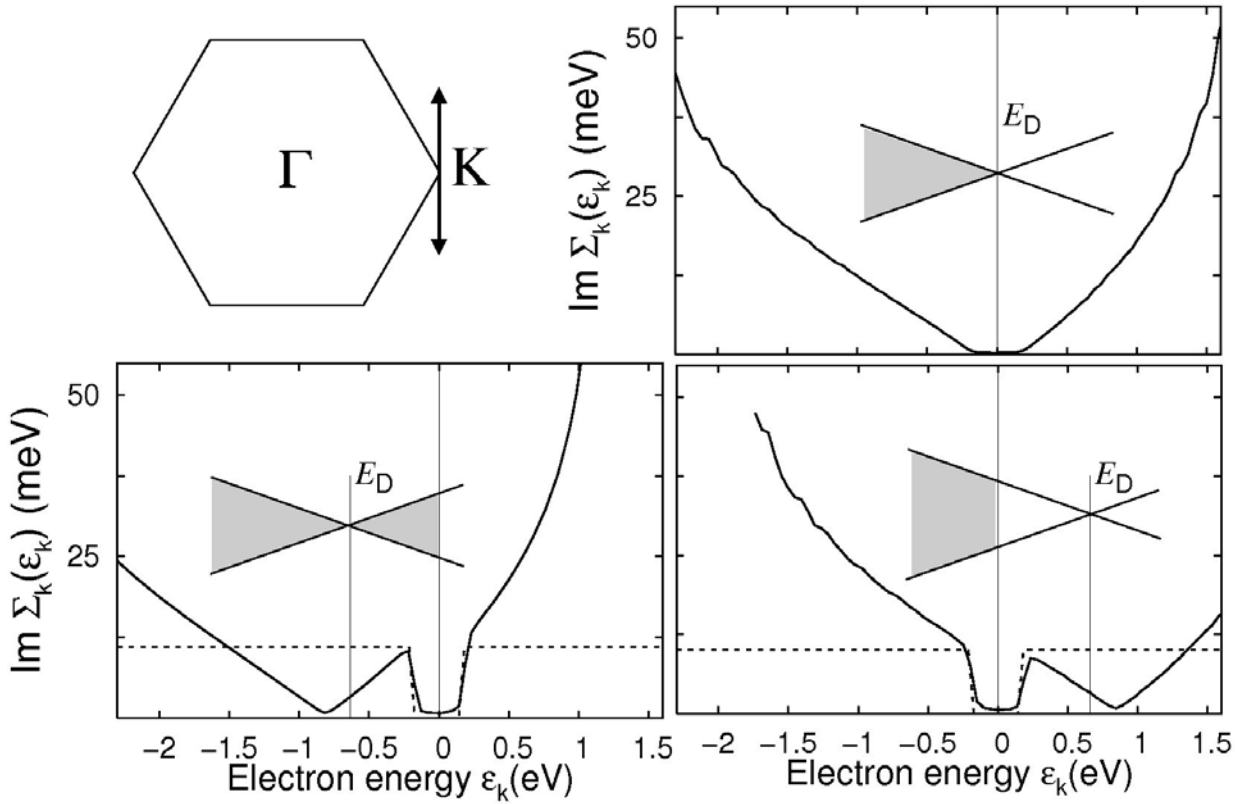



# Imaginary part of the electron self energy (*e*-ph interactions)

$\mathrm{Im}\,\Sigma_{\mathbf{k}}^{e-\mathrm{ph}}(\varepsilon_{\mathbf{k}})$

graphene

conventional metal




Imaginary part of the self energy reflects linear density of states in graphene. Highest optical phonon branches (~ 0.2 eV) are dominant.

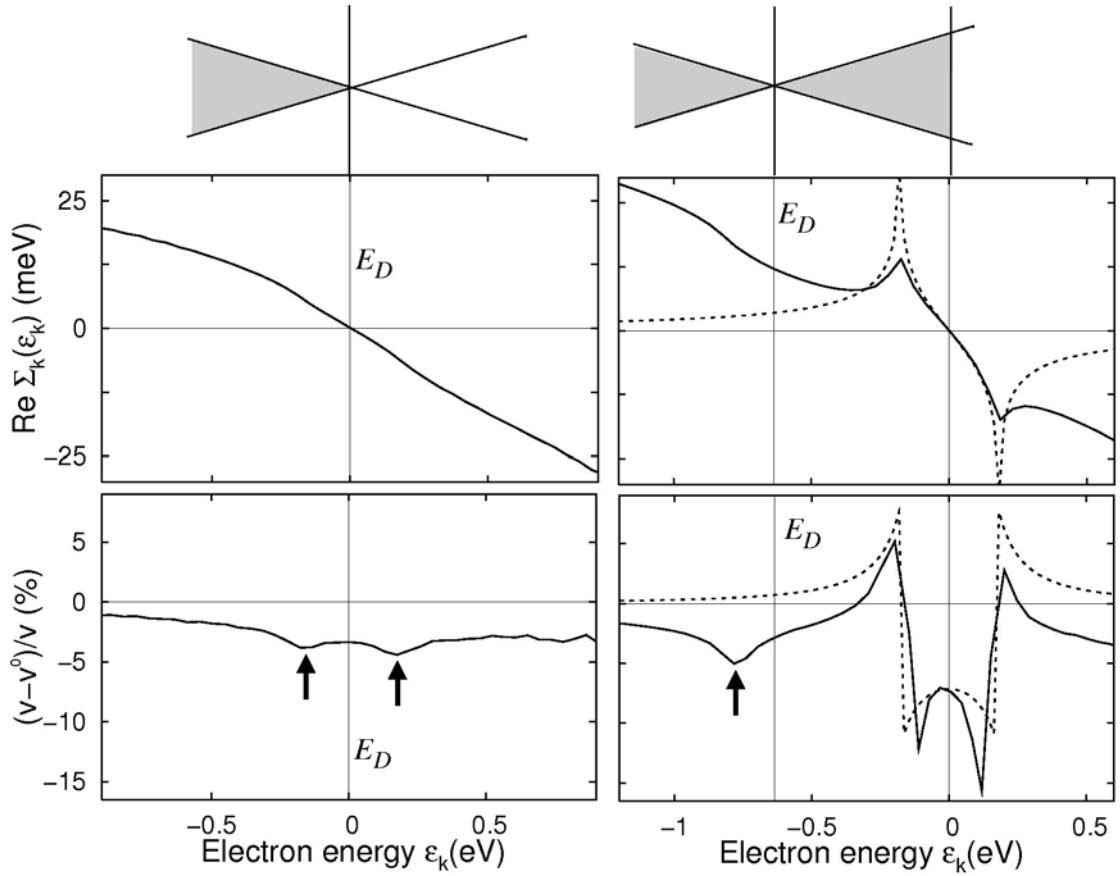
Park, Giustino, Cohen, and Louie, PRL (2007)

# Real part of the electron self energy (*e*-ph interactions)

$$\mathrm{Re}\,\Sigma_{\mathbf{k}}^{e-\mathrm{ph}}(\varepsilon_{\mathbf{k}})$$

graphene

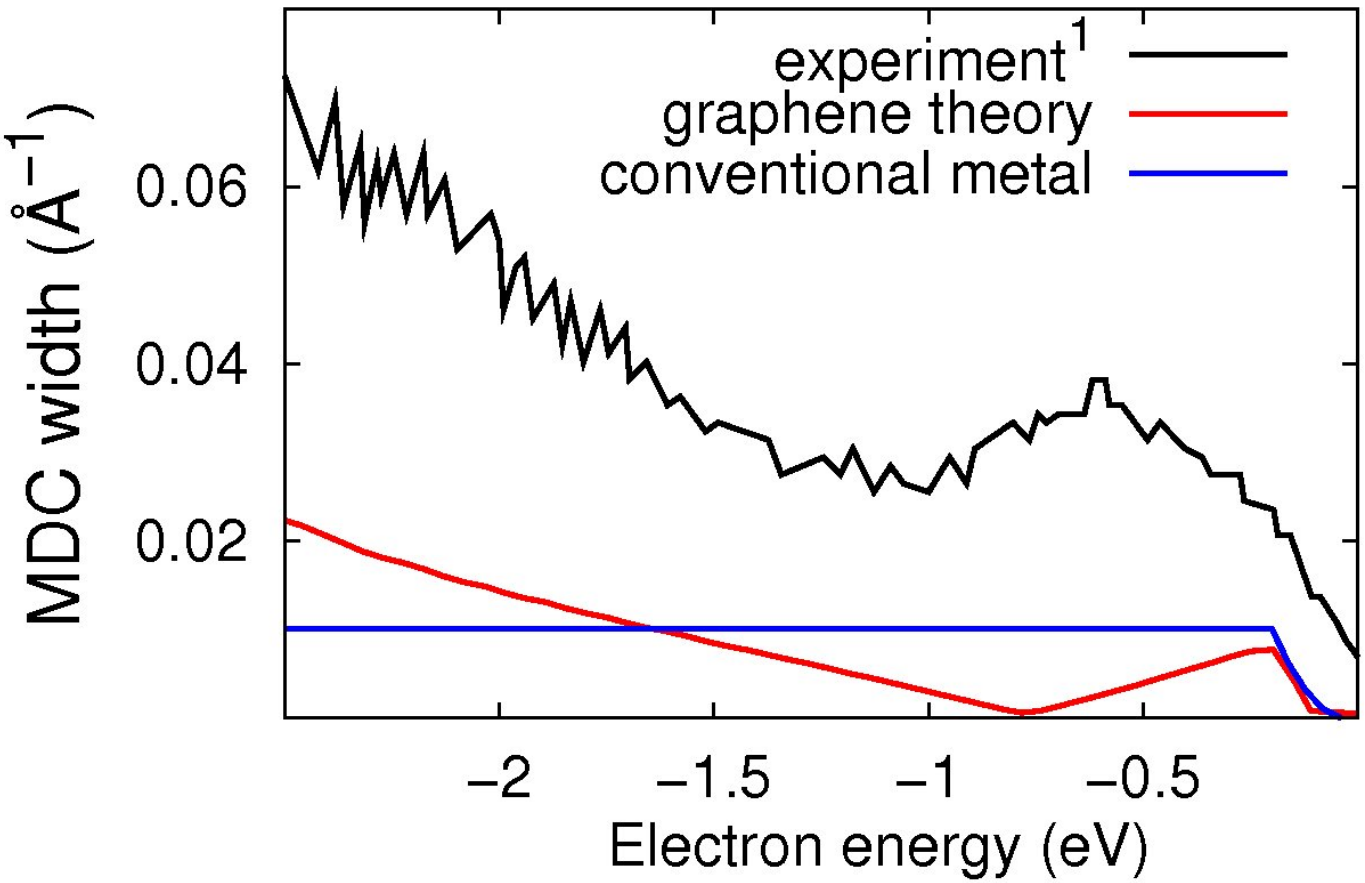
conventional metal




The real part gives rise to 4%~8% reduction in the fermi velocity.

Park, Giustino, Cohen, and Louie, PRL (2007)

# Comparison with experiment (MDC width)




1) A. Bostwick et al., Nature Phys. 3, 36 (2007)

Park, Giustino, Cohen, and Louie, PRL (2007)

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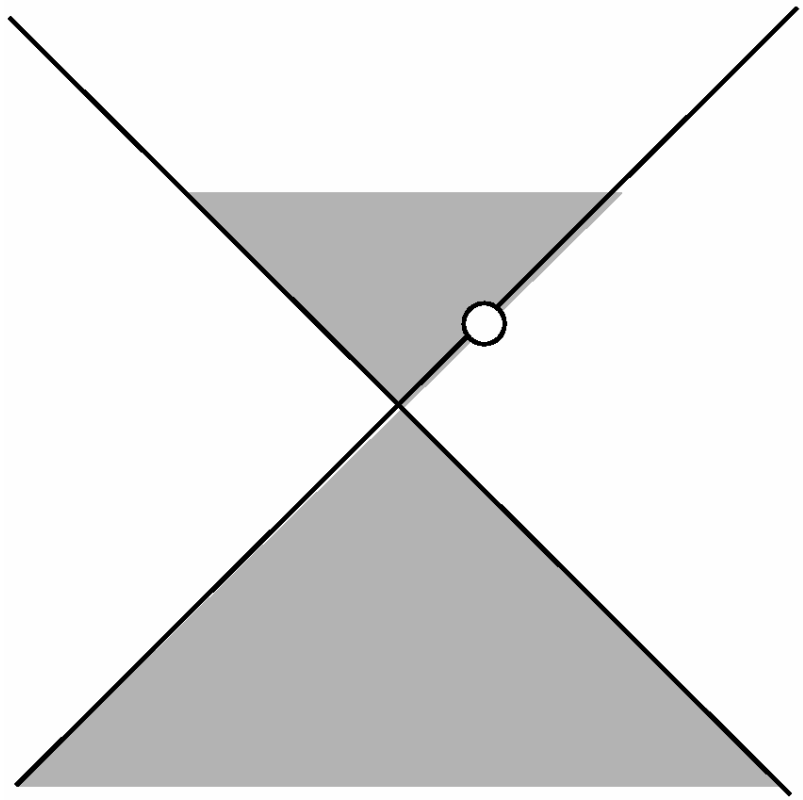
# Imaginary part of the self energy (decay rate)

Decay rate of a hole via e-e interactions?



# Electron energy loss function

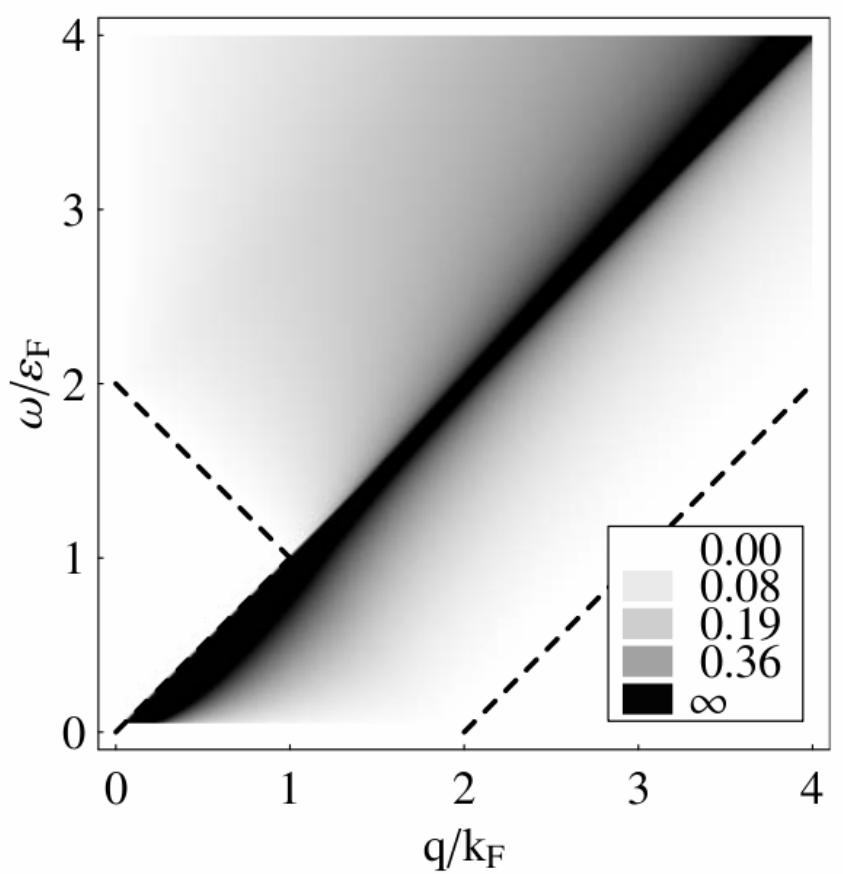
$$\mathrm{Im}\left[\frac{1}{\varepsilon(q,\omega)}\right]$$ is non-zero when

$$\mathrm{Im}\,\varepsilon(q,\omega) \neq 0$$ Electron-hole pair generation

$$\begin{cases} \mathrm{Re}\,\varepsilon(q,\omega) = 0 \\ \mathrm{Im}\,\varepsilon(q,\omega) = 0 \end{cases}$$ Plasmon emission

# Energy loss function of *n*-doped graphene

$$-\operatorname{Im}\,\varepsilon(q,\omega)$$




$$\operatorname{Im}\left[\frac{1}{\varepsilon(q,\omega)}\right]$$

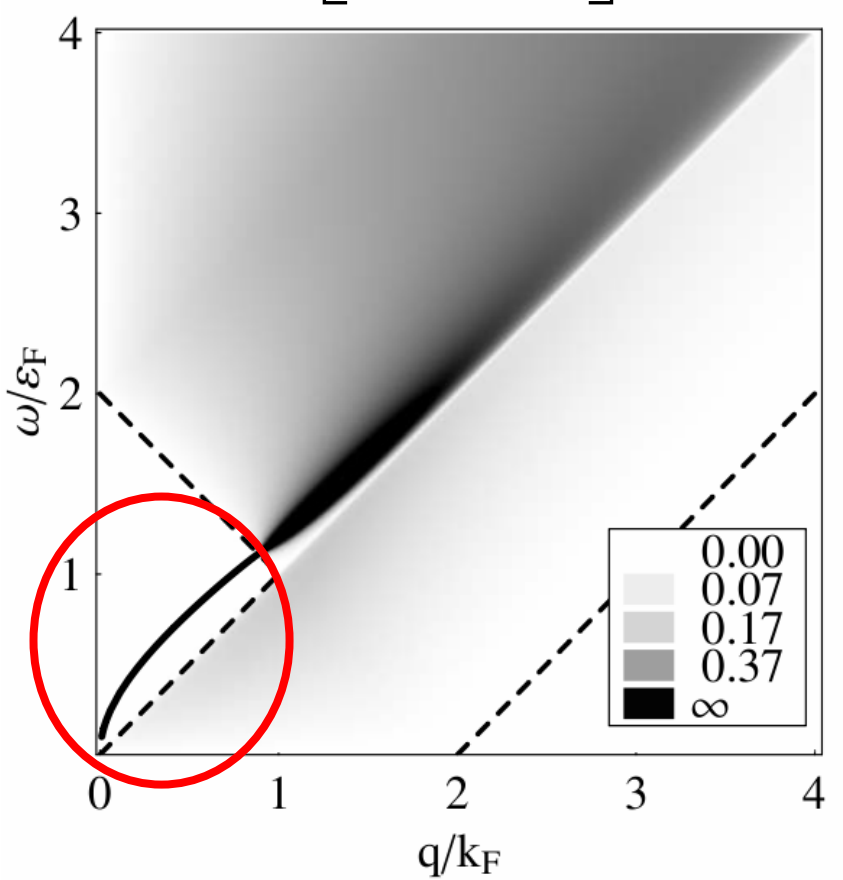


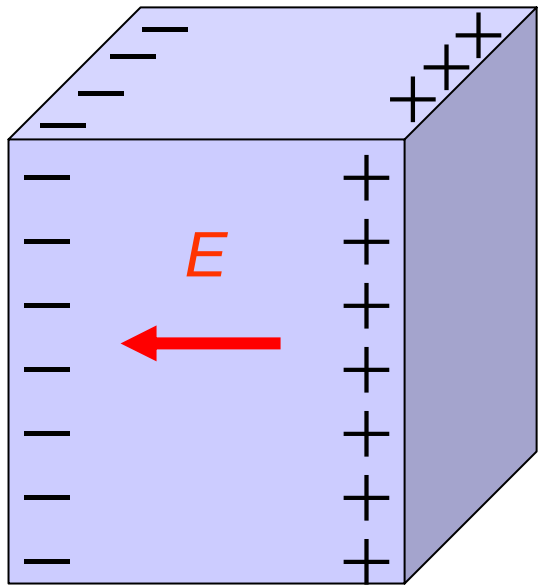

Figure taken from M. Polini *et al.*, PRB 77, 081411 (2008)

# Plasmons (oscillation w/o external field) in 3D & 2D

$$\omega_{\text{plasmon}}(q=0)$$

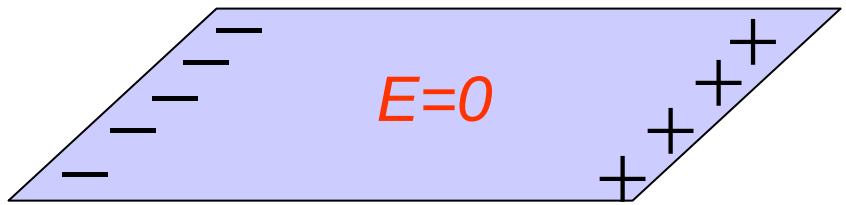
3D: finite restoring force

$$\omega^{\text{3D}}_{\text{plasmon}}(q=0)\neq 0$$




2D: zero restoring force

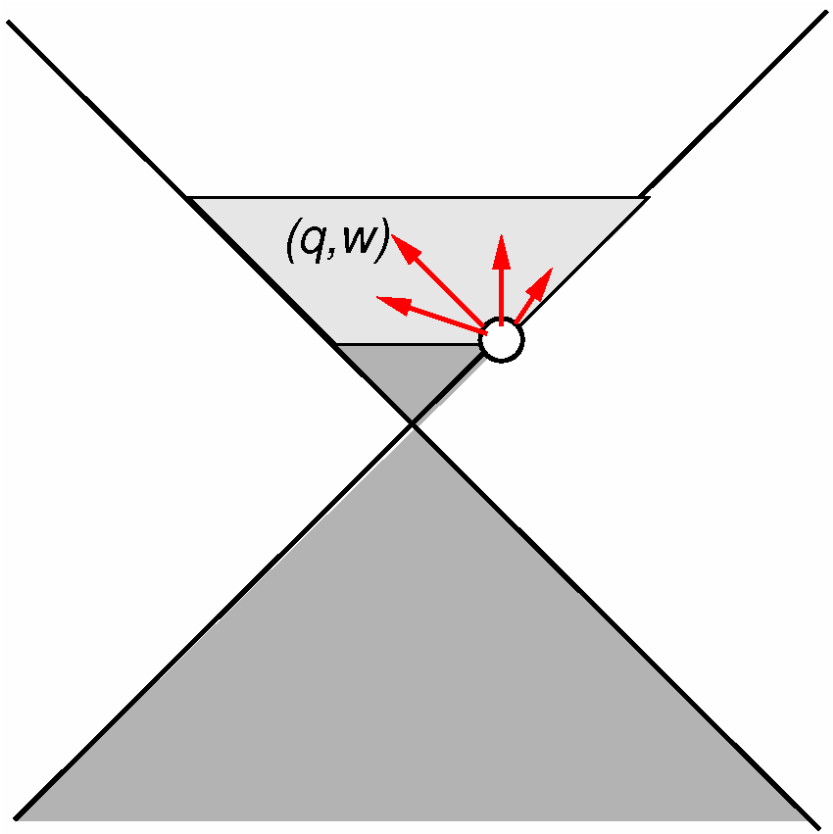
$$\omega^{\text{2D}}_{\text{plasmon}}(q=0)=0$$



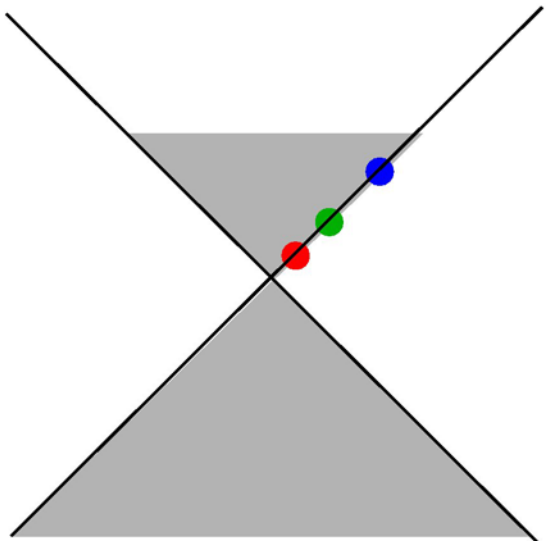
# Imaginary part of the self energy (decay rate)

Decay rate of a hole via e-e interactions?

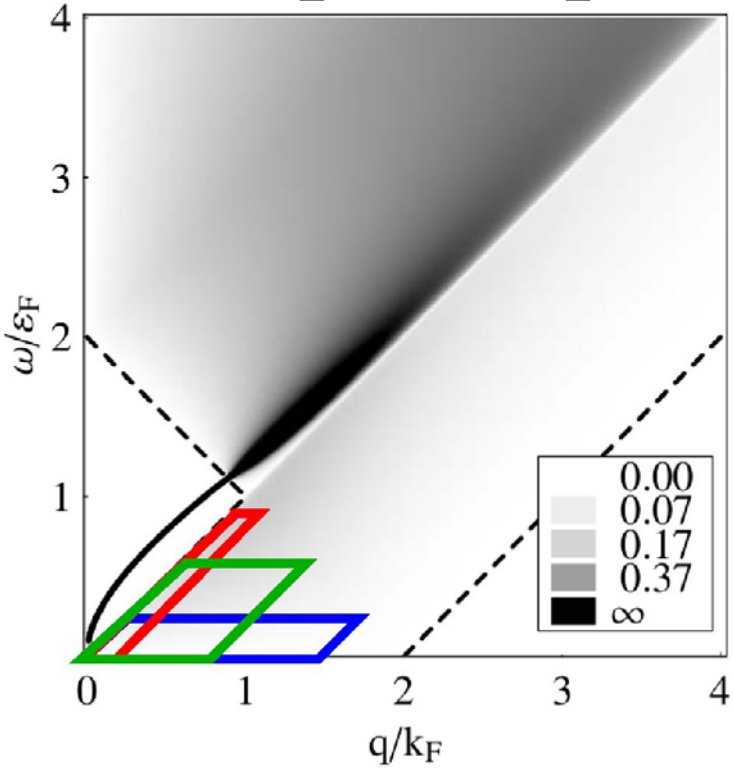
$$\mathrm{Im}\left[\frac{1}{\varepsilon\left(q,\omega\right)}\right]$$



# Energy loss function and decay rate



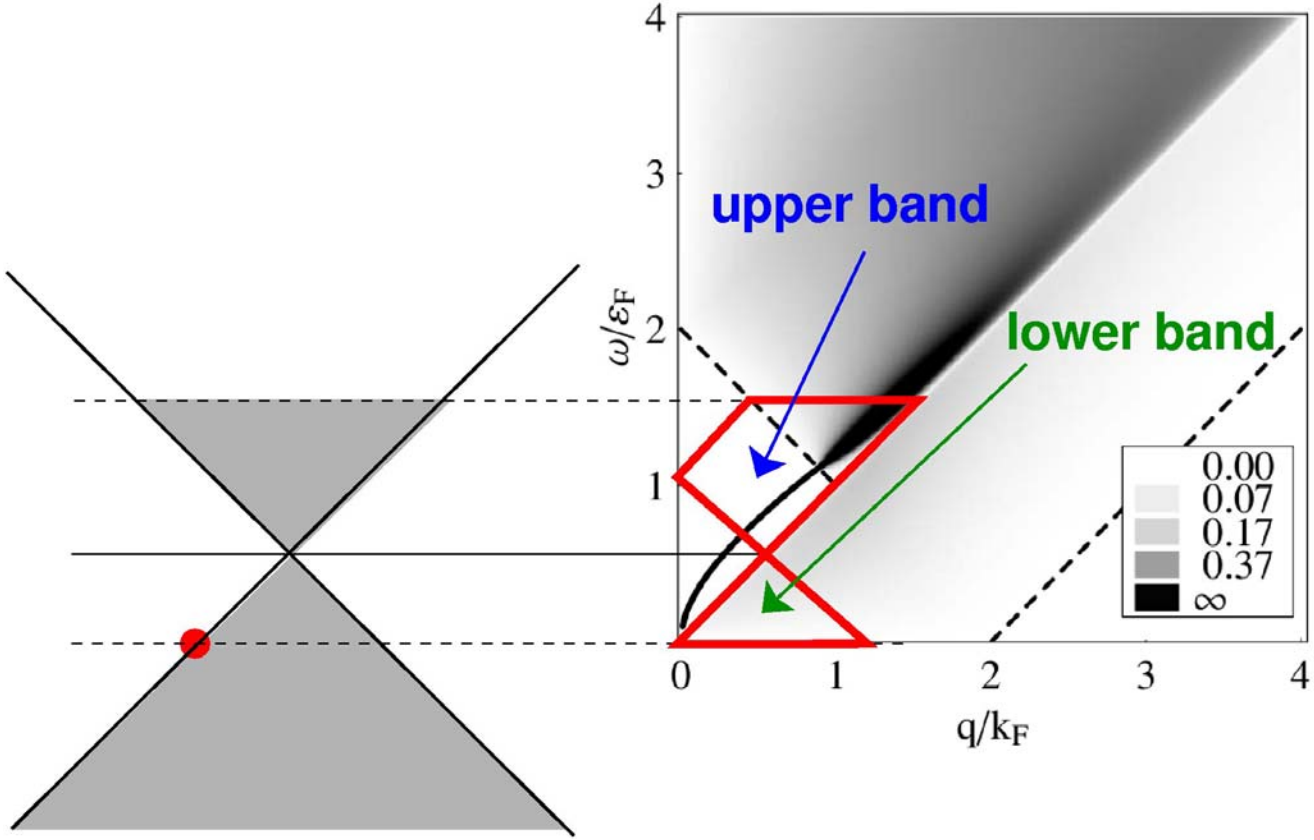
$$\mathrm{Im}\left[\frac{1}{\varepsilon(q,\omega)}\right]$$




- In *n*-doped graphene, a hole above the Dirac point energy do not decay by plasmon emission.

# Energy loss function and decay rate

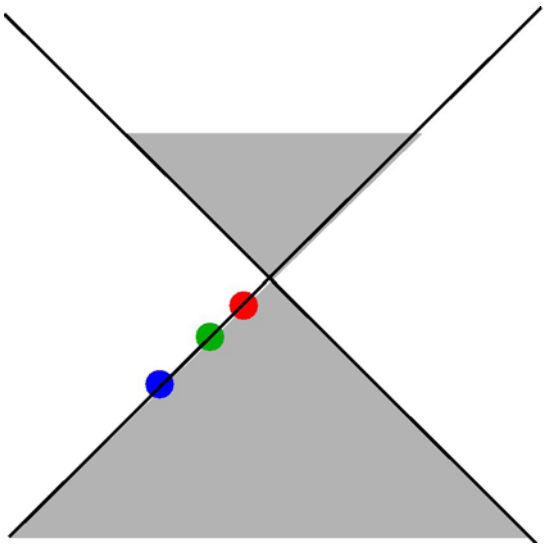
$$\mathrm{Im}\left[\frac{1}{\varepsilon(q,\omega)}\right]$$

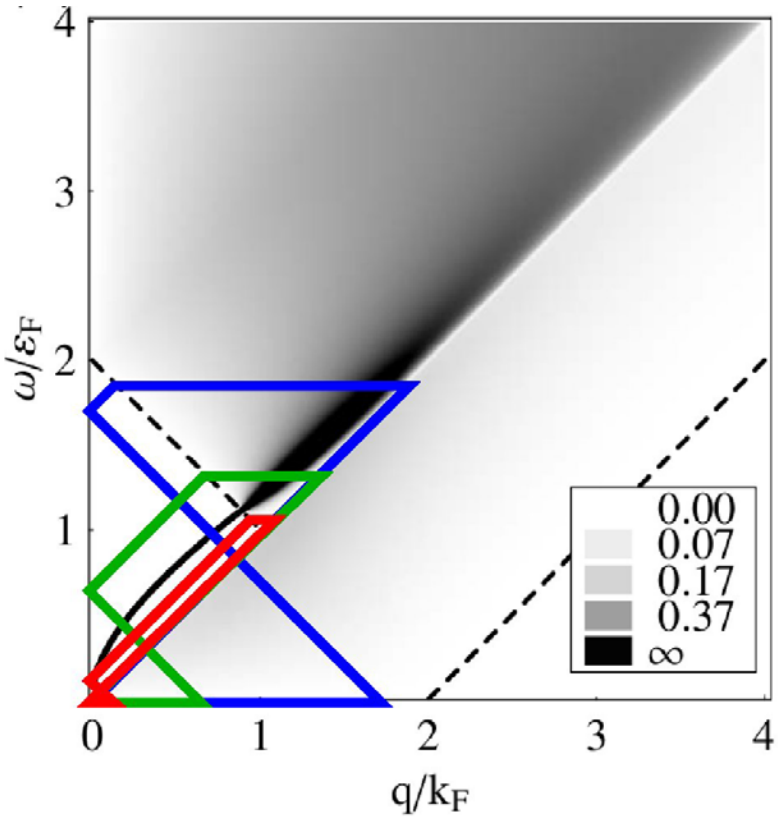



- In *n*-doped graphene, a hole below the Dirac point energy can decay by plasmon emission (transition into upper band).
- Transition into lower band does not involve plasmons.

# Energy loss function and decay rate

$$\mathrm{Im}\left[\frac{1}{\varepsilon(q,\omega)}\right]$$






- An optimal energy exists for transitions into upper band having the largest plasmon contribution.

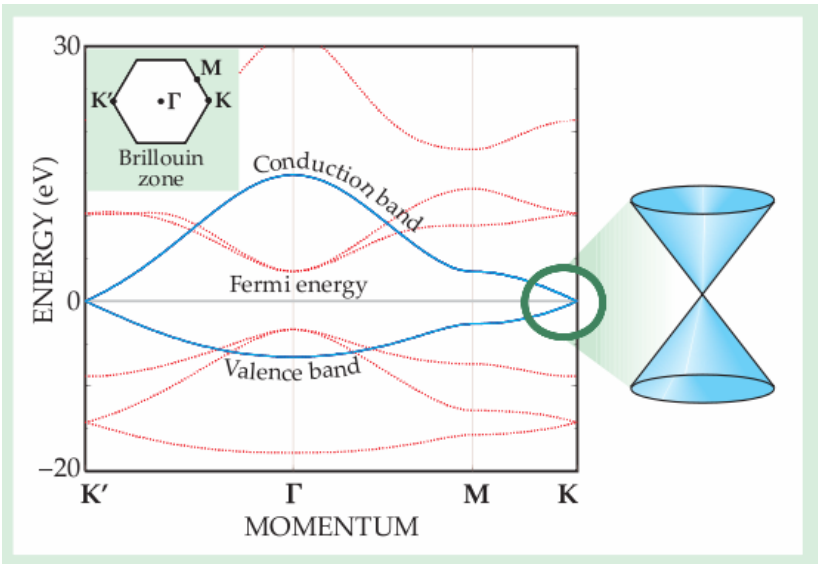
# Imaginary part of the electron self energy (*e*-*e* interactions)

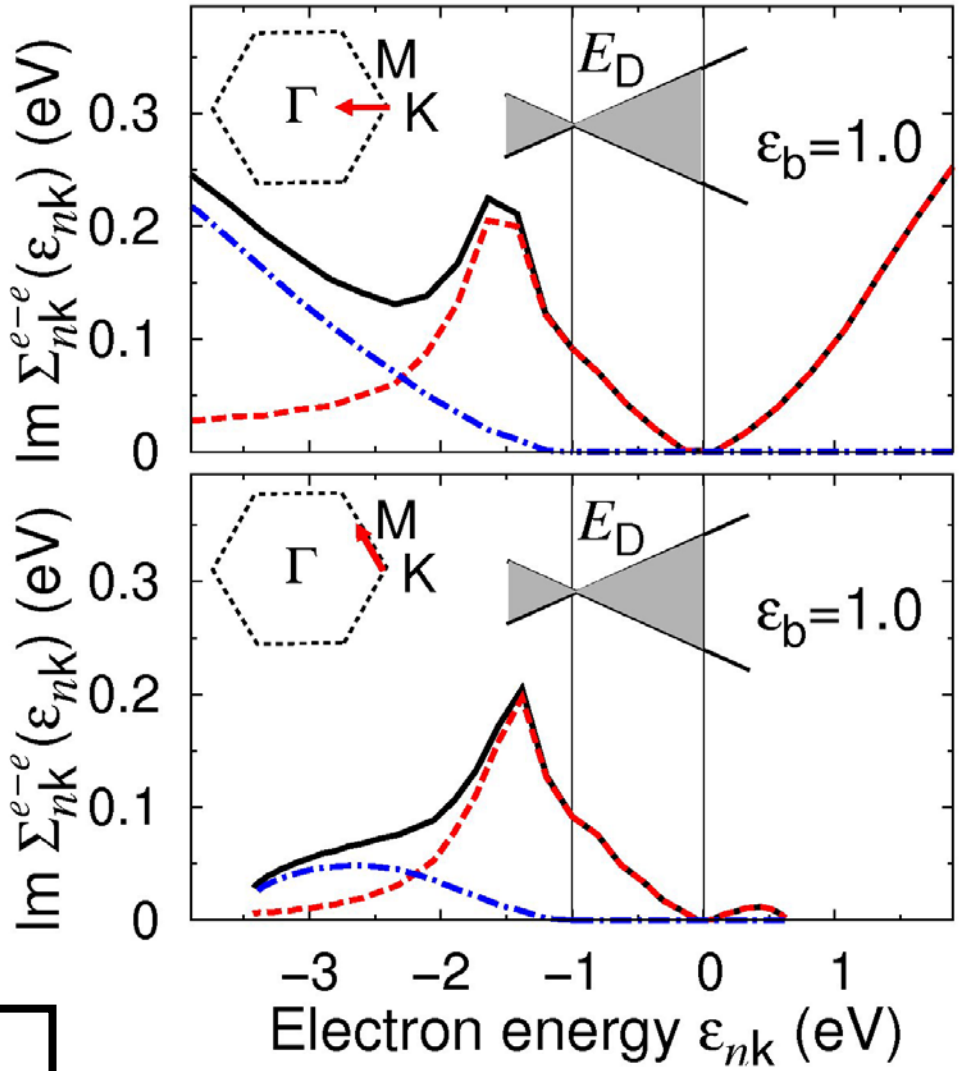
$$\mathrm{Im}\,\Sigma_{\mathbf{k}}^{e-e}(\varepsilon_{\mathbf{k}})$$

Total decay rate

Decay into upper band

Decay into lower band

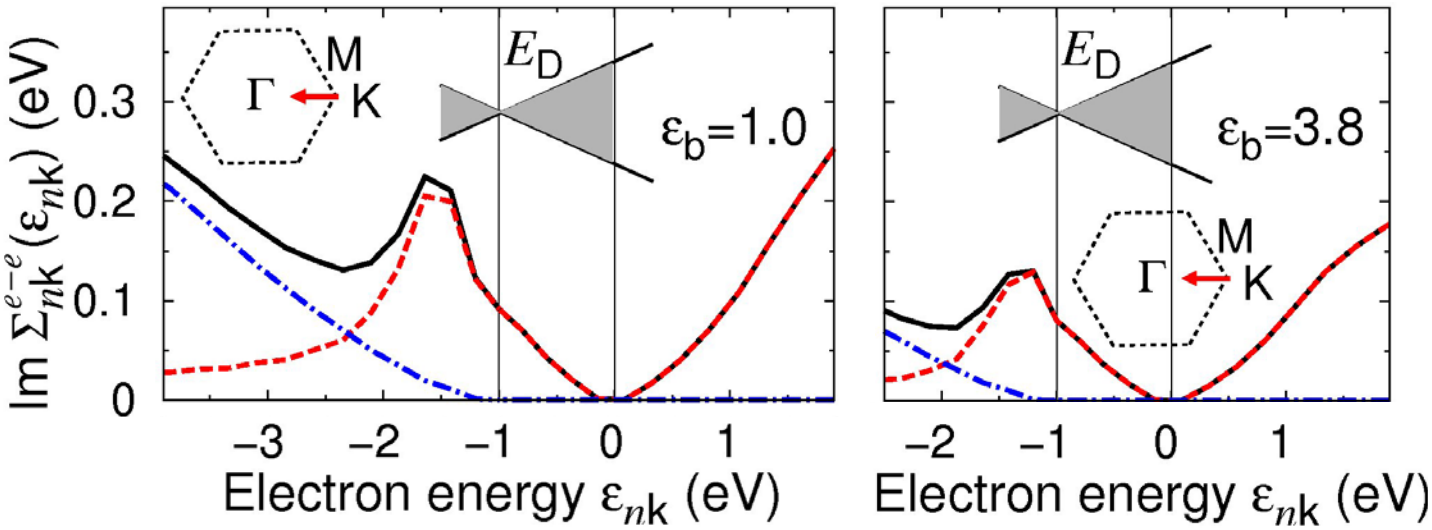



In agreement with previous argument
Strong anisotropy: van Hove singularity

Park, Giustino, Spataru, Cohen, and Louie, PRL (2009)

# Background screening effect




Substrate dielectric screening reduces the decay rate.
Also, the plasmon induced peak position is shifted.

Park, Giustino, Spataru, Cohen, and Louie, PRL (2009)

# Outline

- Preliminaries
  - Graphene
  - ARPES / electron self energy
  - Migdal approximation
  - *GW* approximation

- Electron self energy in graphene
  - Contribution from electron-phonon (*e*-ph) interactions
  - Contribution from electron-electron (*e*-*e*) interactions
  - Combining the effects of *e*-ph and *e*-*e* interactions

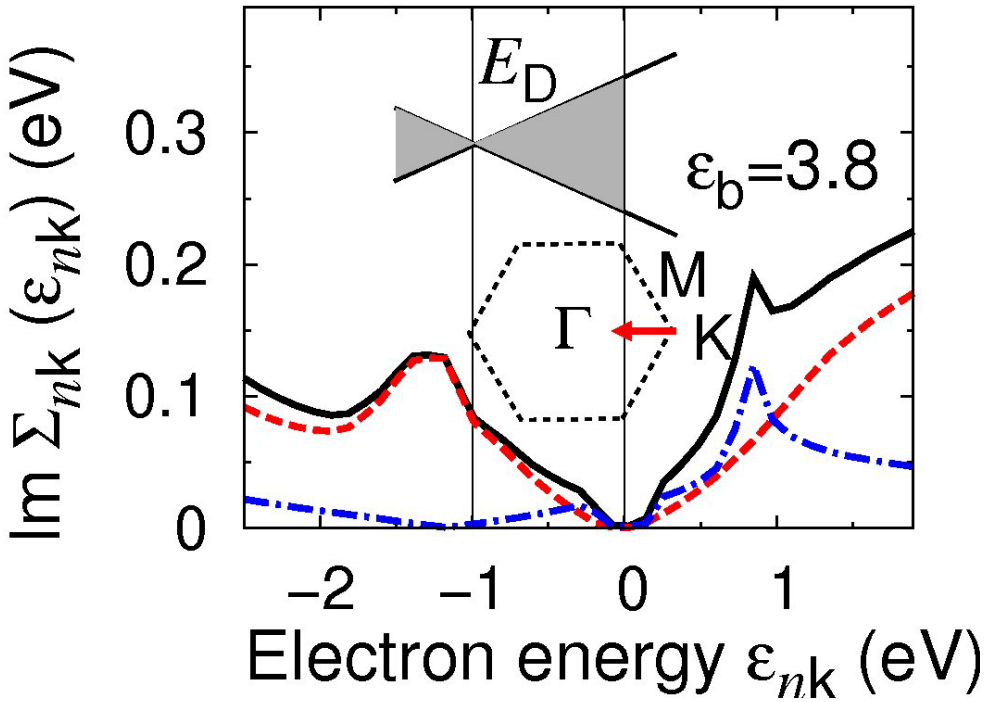
# Electron self energy arising from *e*-*e* and *e*-ph interactions

$\mathrm{Im}\,\Sigma_{\mathbf{k}}(\varepsilon_{\mathbf{k}})$

Total self energy

Self energy arising from *e*-*e* interactions

Self energy arising from *e*-ph interactions




The two interactions are comparable near the Fermi energy.

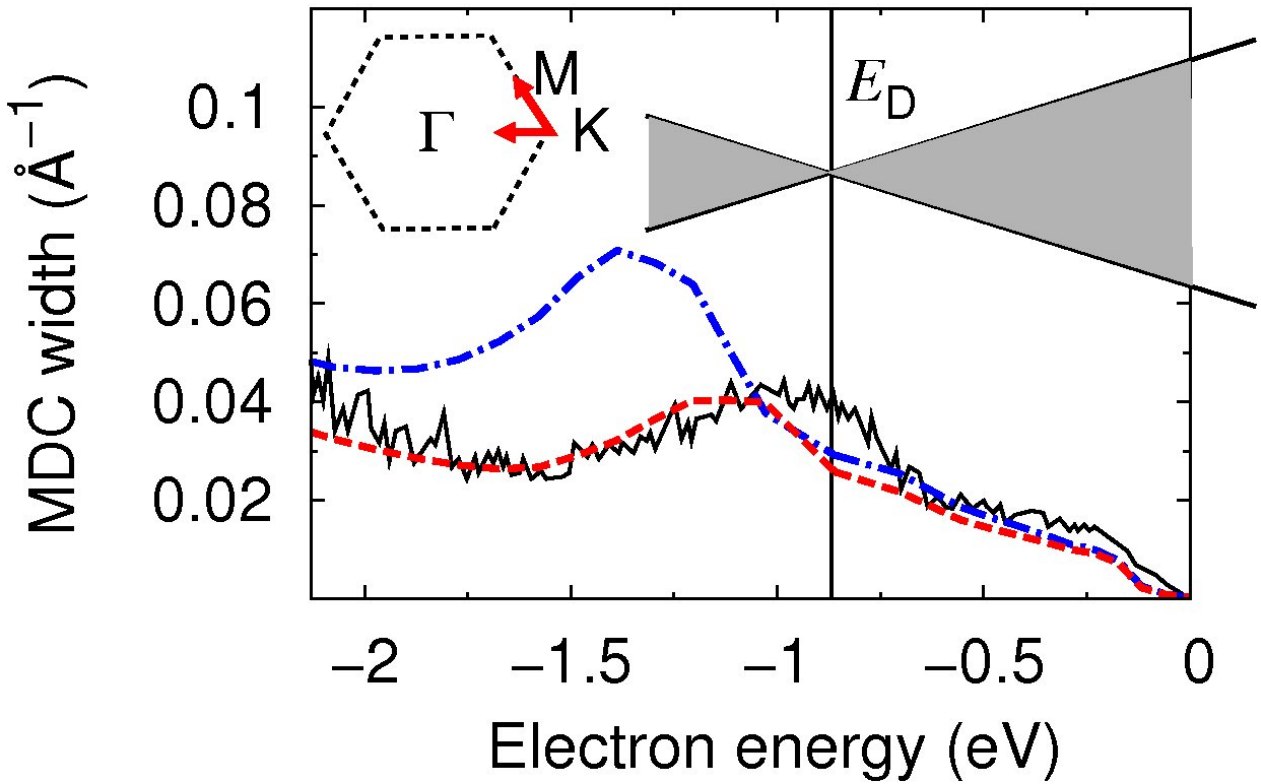
Park, Giustino, Spataru, Cohen, and Louie, PRL (2009)

# MDC width arising from *e*-*e* and *e*-ph interactions

Bostwick et al., Nature Phys. 3, 36 (2007)

Graphene with model substrate screening

Suspended graphene




Reasonable agreement between theory (substrate screening) and experiment
Lower than measurements near the Dirac point energy: midgap states?

Park, Giustino, Spataru, Cohen, and Louie, PRL (2009)

# Interpretation of the ARPES spectra of graphene

Q: Self-energy effects[1] or substrate induced band gap[2]?

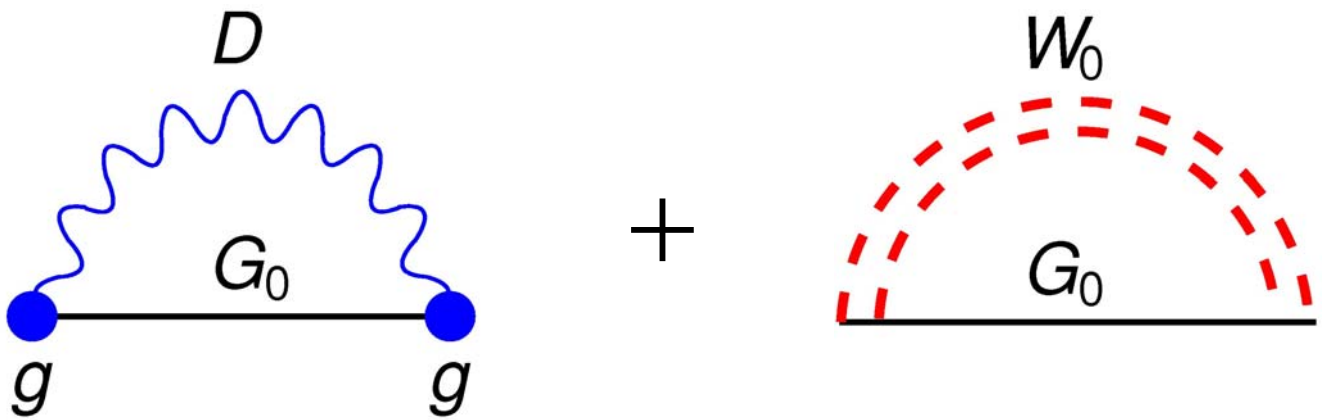
A: Both are important.

1) A. Bostwick, *et. al.,* Nature Physics **3**, 36 (2007).

2) S.Y. Zhou, *et. al.,* Nature Materials **6**, 770 (2007).

# Summary

First-principles calculations




→ Insights to interpret ARPES spectra of graphene