# Dynamical screening effects in X-ray absorption spectra of graphene and BN

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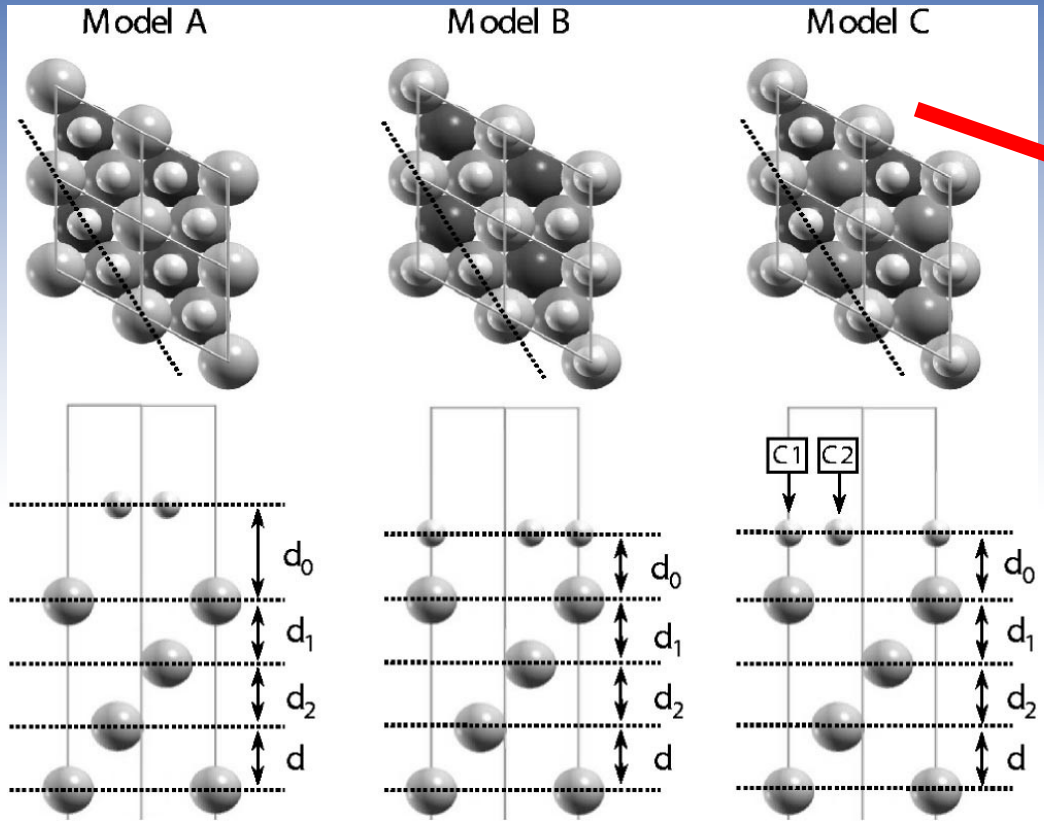
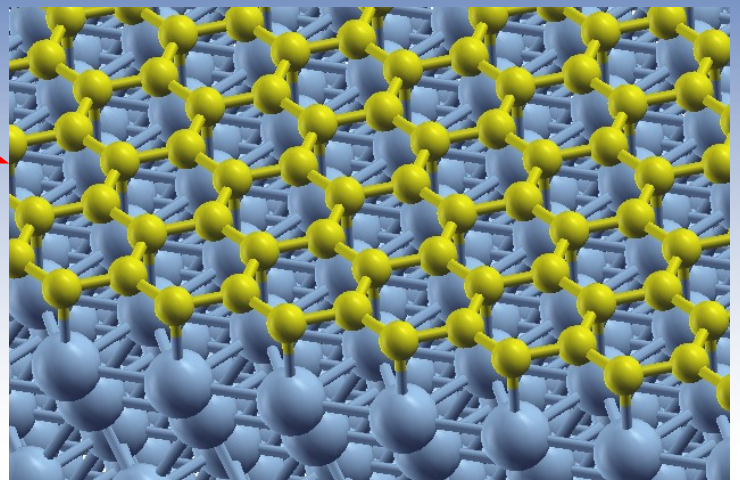
# Outline

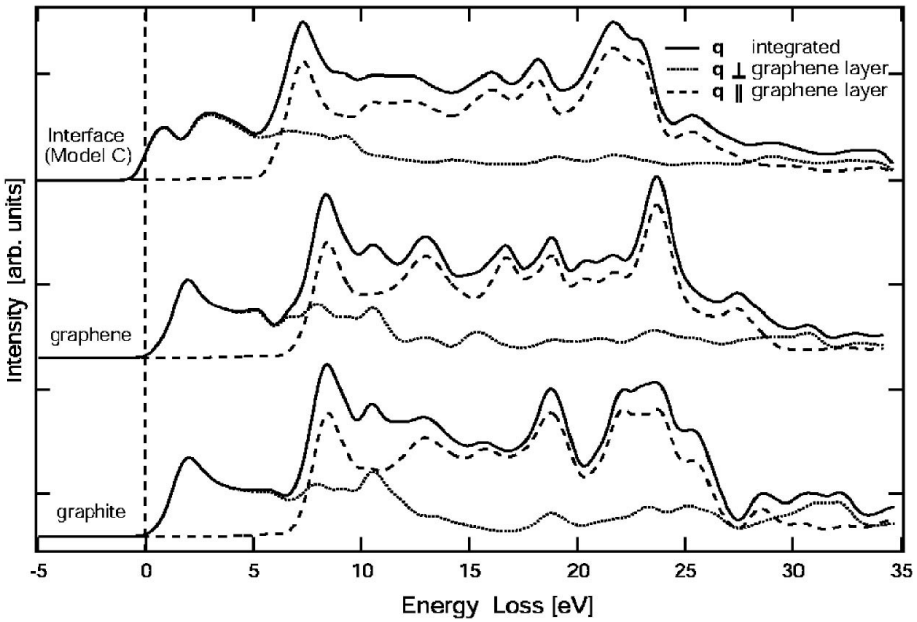
- Graphene on Ni(111)
- BN layer on Ni(111)
- MND theory
- XAS calculations using MND
- Results
  - MG/Ni(111)
  - hBN/Ni(111)
- Conclusions

# Graphene on Ni(111)



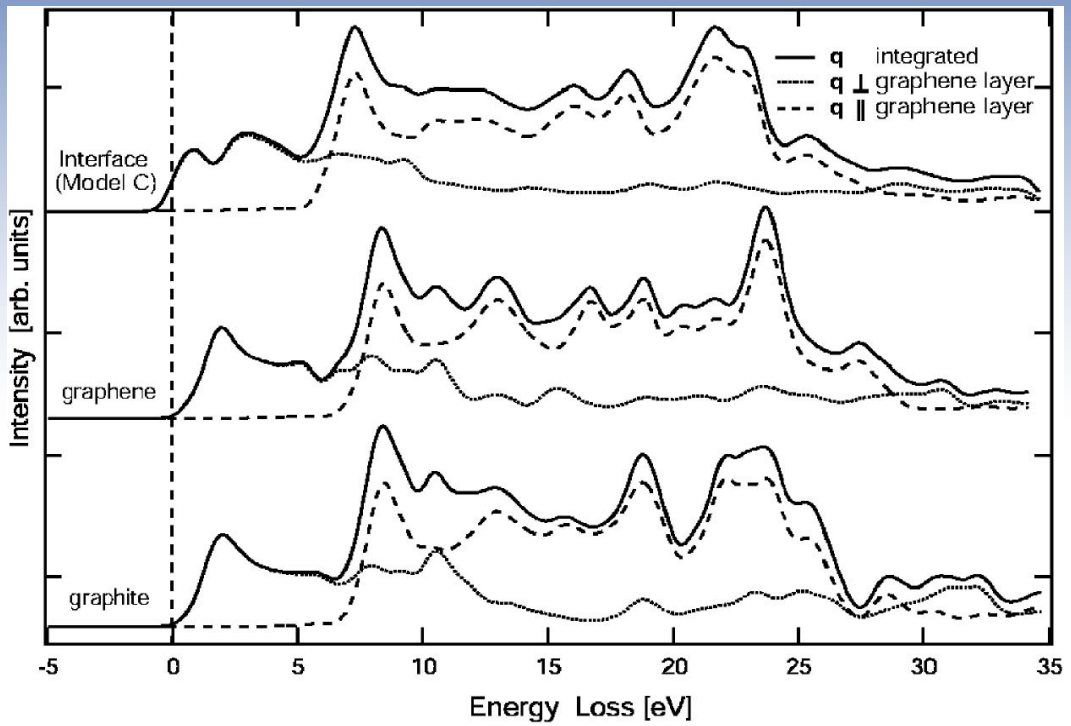



| | Ni(111) | Model A | Model B | Model C |
|---|---|---|---|---|
| $d_0$ (Å) | | 3.050/3.050 | 2.113/2.120 | 2.122/2.130 |
| $d_1$ (Å) | 2.006 | 1.975 | 2.034 | 2.011 |
| $d_2$ (Å) | 2.029 | 1.999 | 2.015 | 2.014 |
| $\Delta E$ (eV) | | +0.062 | +0.066 | 0.000 |
| $m$ ($\mu_B$) | 0.716 | 0.673 | 0.514 | 0.553 |



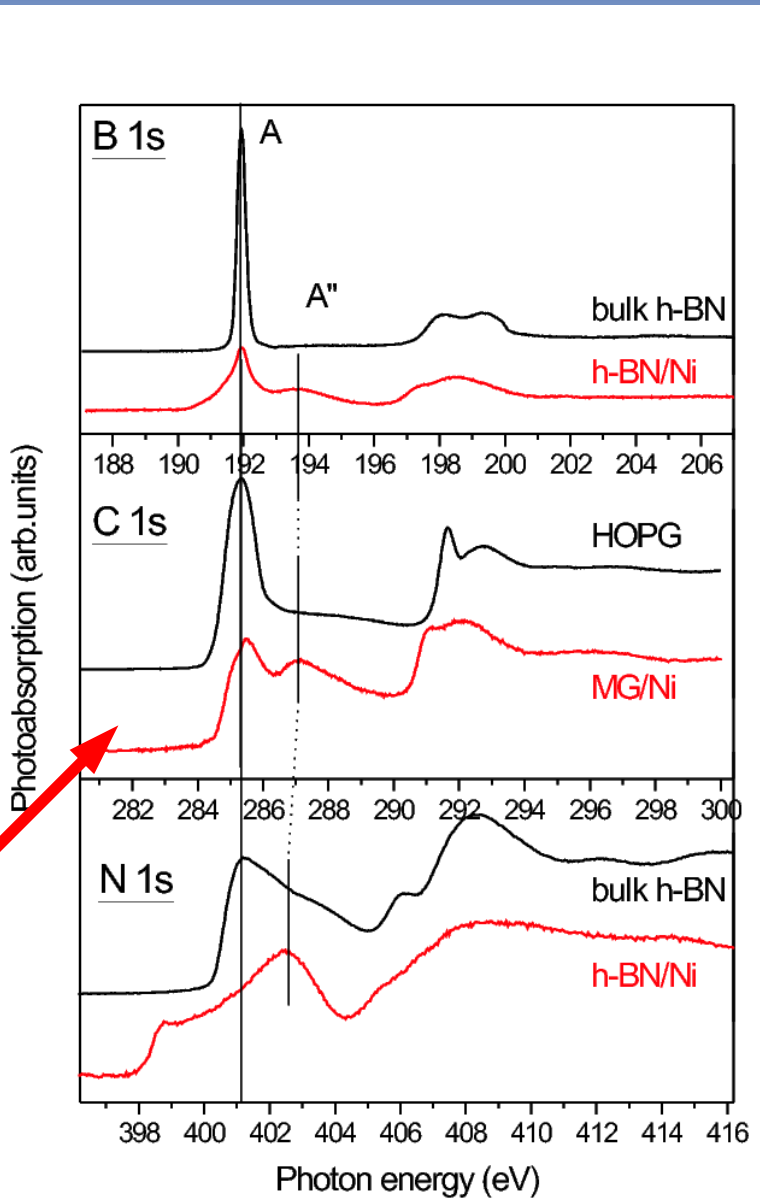

Bertoni et al., PRB71, 075402 (2004)

# Graphene on Ni(111)

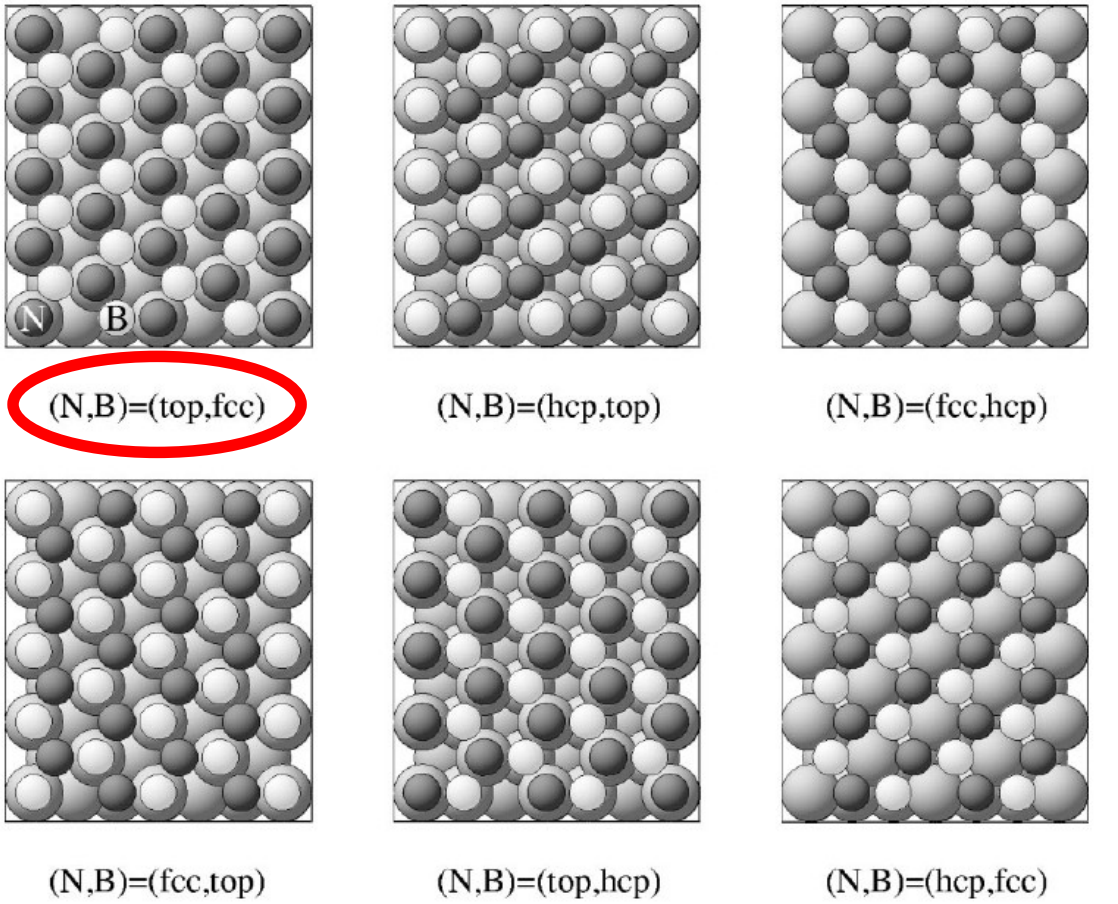


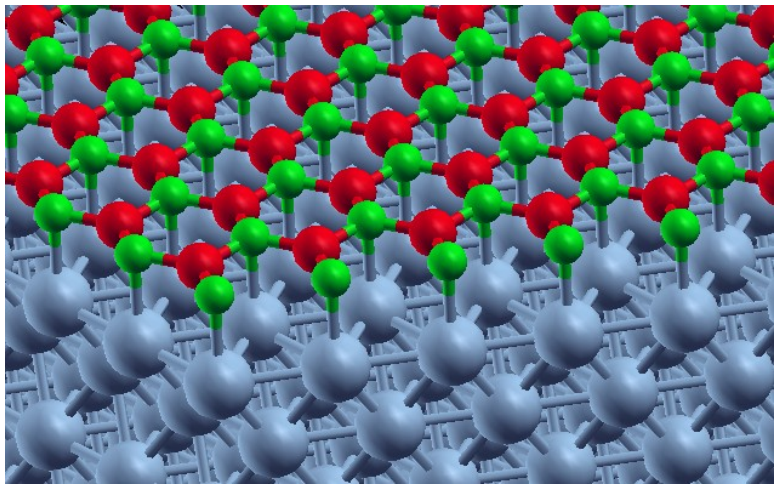

Ground state DFT calculation of ELNES

XAS experiment (A. Preobrajenski)



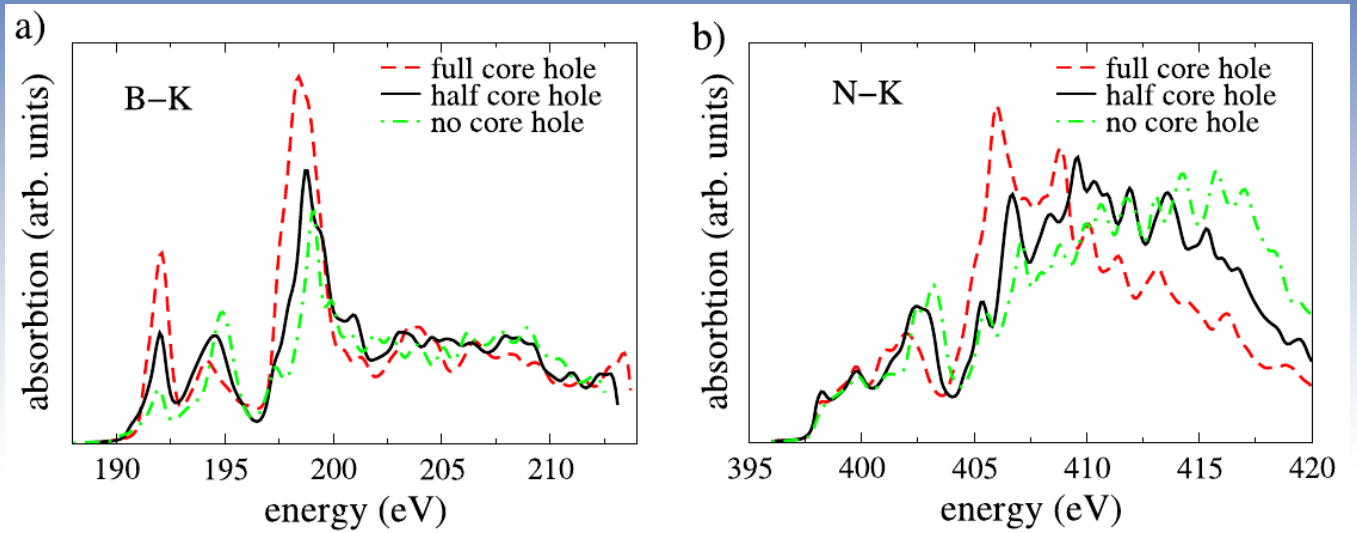
# h-BN on Ni(111)



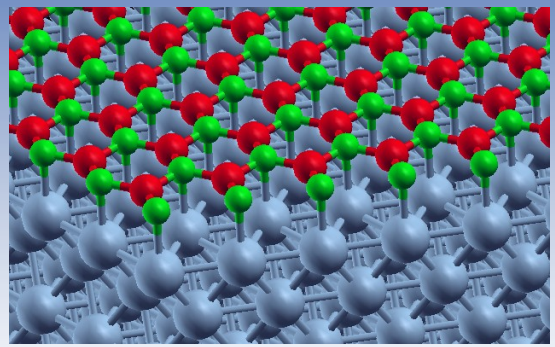
Grad et al., PRB68, 085404 (2003)

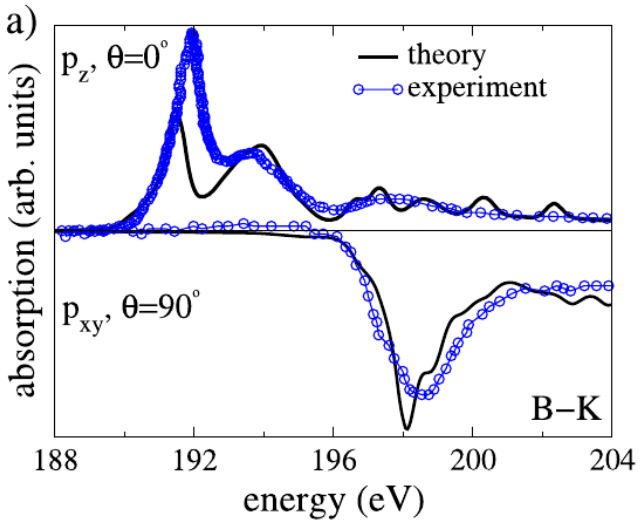
# h-BN on Ni(111)

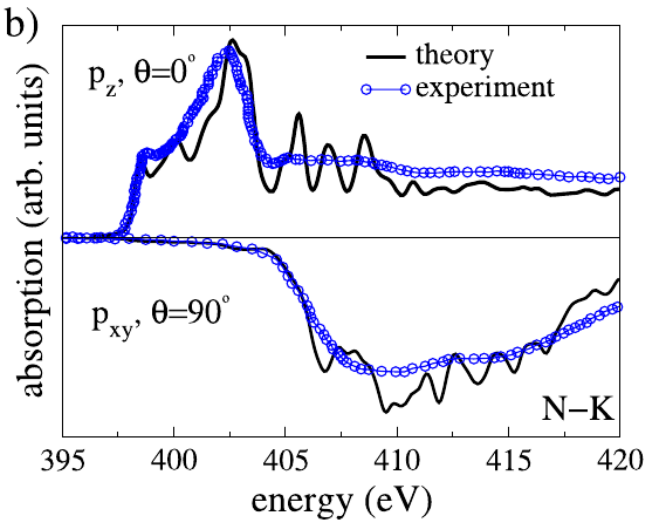


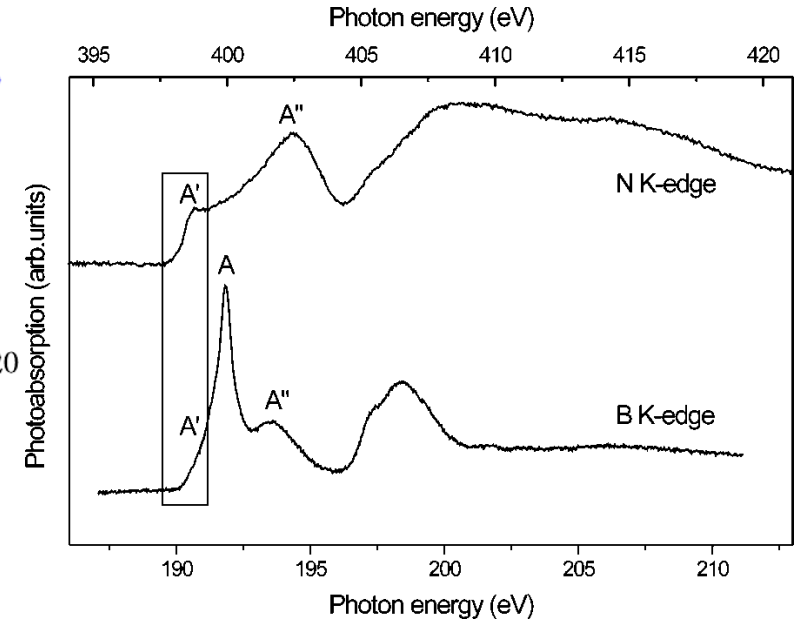









Preobrajenski et al., PRB70, 165404 (2004)
Laskowski et al., JPCM21, 104210 (2009)

# MND theory

- Model

$$H = \sum_{RR'}{}' \varepsilon_{RR'} a_R^+ a_{R'} + E_0 b^+ b - u a_0^+ a_0 b_0 b_0^+$$

- XAS spectrum

$$I(\omega) \sim |W|^2 \,\mathrm{Re} \int_{-\infty}^{\infty} \mathrm{d}t \; K_{00}(t, t) \; \mathrm{e}^{i\omega t}$$

- 2-particle Green's function

$$K_{RR'}(\tau, t) = \frac{1}{i^2} \langle 0 | \; T a_R(\tau) \; b_0^+(t) \; a_{R'}^+(0) \; b_0(0) \; | 0 \rangle$$


Mahan, Phys. Rev. 163, 612 (1967)
Nozieres & de Dominics, Phys. Rev. 178, 1097 (1969)
Grebennikov et al., Phys. Stat. Sol. (b) 79, 423 (1977)

# MND implementation

- Calculate initial and final state Green's func.
- Solve

$$\tilde{\varphi}(\epsilon,t) = \mathbf{1} + \mathbf{V}\int_{\mu}^{\infty} \frac{d\epsilon_1}{\pi} \operatorname{Im} \mathbf{g}^R(\epsilon_1)\mathbf{L}^+(\epsilon,\epsilon_1,t)\tilde{\varphi}(\epsilon_1,t),$$

$$\mathbf{L}^+(\epsilon,\epsilon_1,t) = \frac{\mathbf{I}^*(\epsilon_1,t) - e^{i(\epsilon-\epsilon_1)t}\mathbf{I}^*(\epsilon,t)}{\epsilon_1 - \epsilon},$$

$$\mathbf{I}(\epsilon,t) = \mathbf{1} + \mathbf{V}\int_{-\infty}^{\infty} \frac{d\epsilon_1}{\pi} \frac{e^{i(\epsilon-\epsilon_1)t} - 1}{\epsilon - \epsilon_1} \operatorname{Im} \mathbf{G}^R(\epsilon_1).$$

- Evaluate

$$\Delta(t) = i \operatorname{Tr} \mathbf{V}\int_{0}^{-t} dt_1 \int_{-\infty}^{\mu} \frac{d\epsilon}{\pi} \operatorname{Im} \mathbf{g}^R(\epsilon)\tilde{\varphi}(\epsilon,t_1)$$

- And finally

$$I(\omega) \sim \operatorname{Re}\int_{0}^{\infty} dt \int_{\mu}^{\infty} \frac{d\epsilon}{\pi} e^{it(\omega-\epsilon+\epsilon_c)+\Delta(-t)}$$

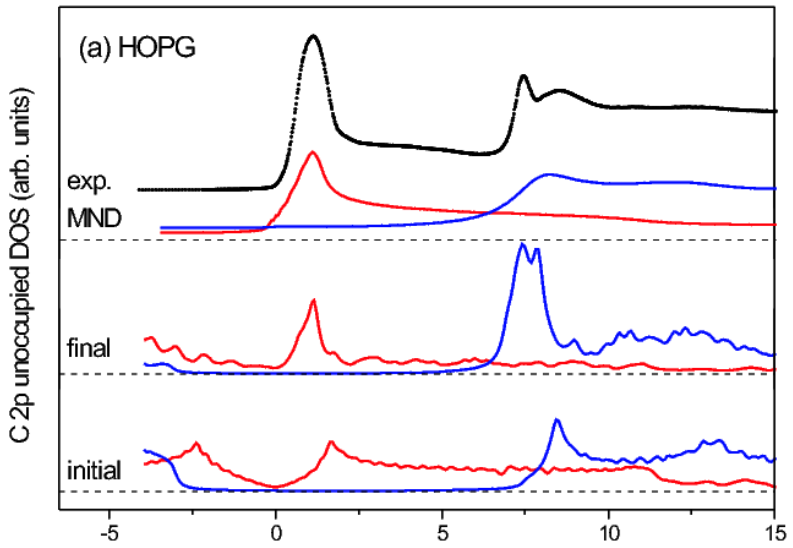
$$\times \sum_{ij} t_i [\operatorname{Im} \mathbf{g}^R(\epsilon)\tilde{\varphi}(\epsilon,t)]_{ij} t_j^*,$$

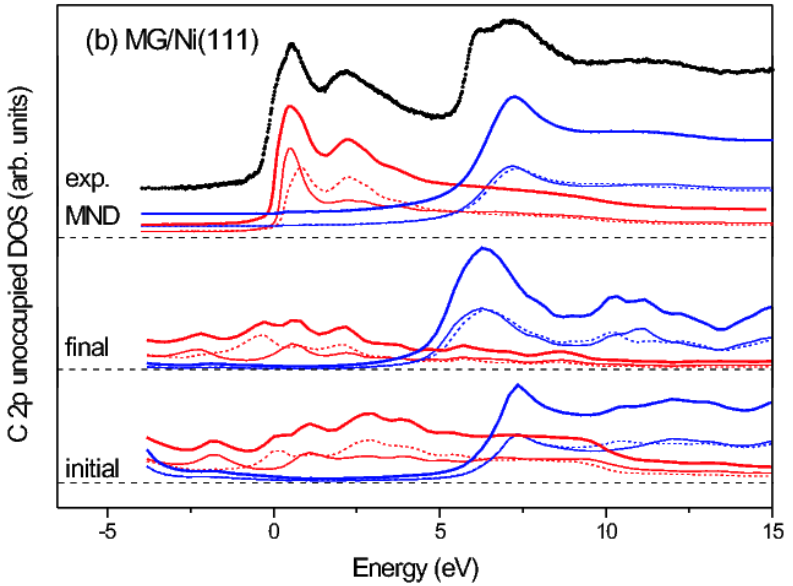
Wessely et al., PRB73, 075402 (2006)

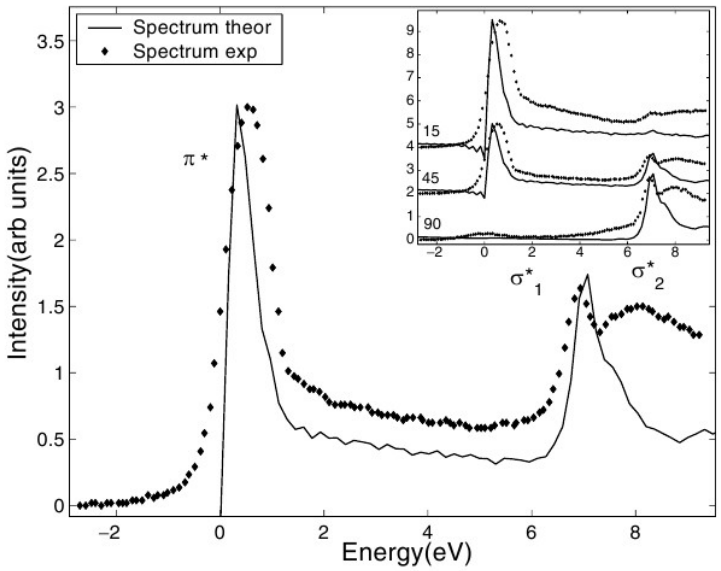
# Computational approach

- Optimization of atom positions with VASP
- 6 layers of Ni, vacuum layer of 18Å
- WIEN2k calculations of the electronic structure
  - initial state
  - final state – supercell 3x3x1 with a core hole
- Evaluation of the local Green's function matrices
- OpenMP implementation of MND equations in fortran

# MND spectra of graphene

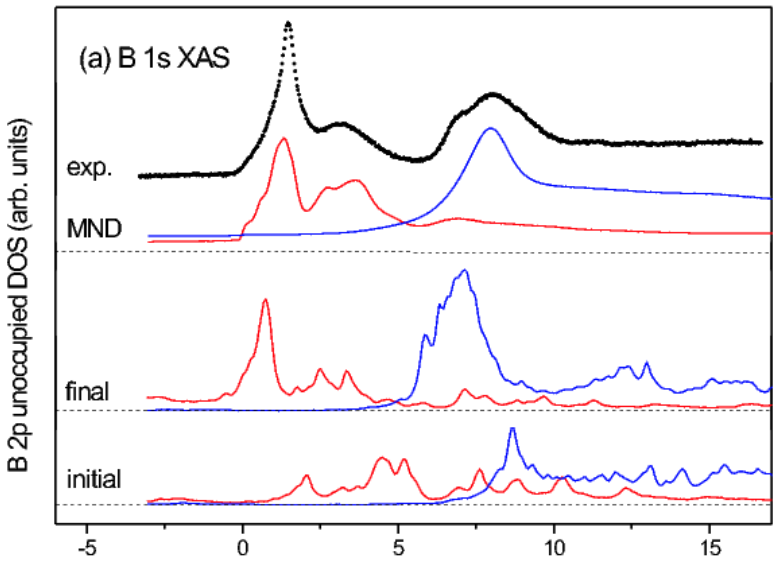


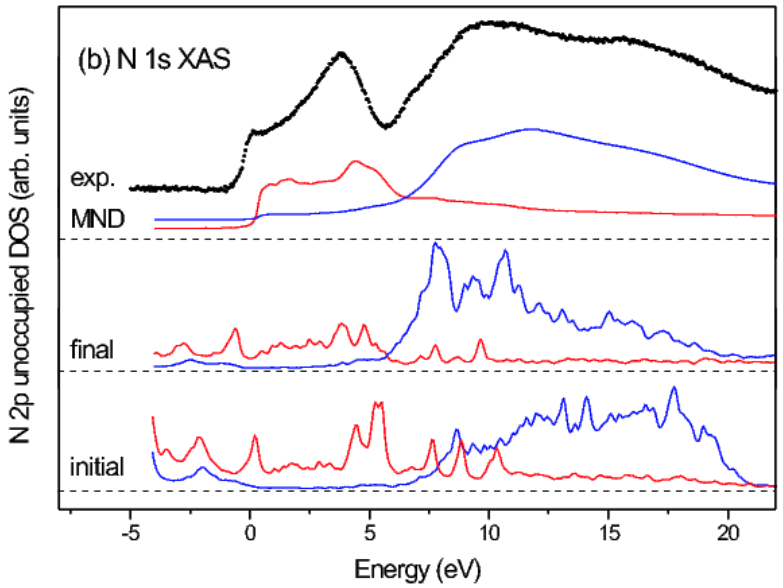




Wessely et al., PRL94, 167401 (2005)

# MND spectra of h-BN



# Conclusions

- Parameter-free calculations of the XAS
- Importance of the dynamical core-hole screening effects
- Good agreement with experiment for all B, C and N K-edge spectra
- Improvement over initial state, final state or Slater transition state XAS calculations