

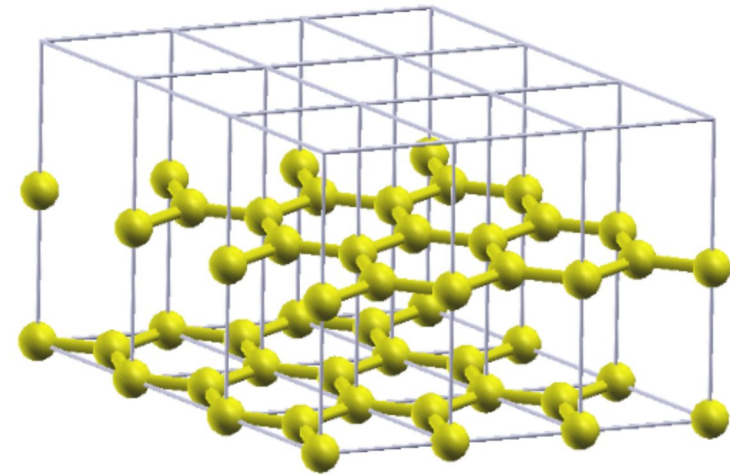
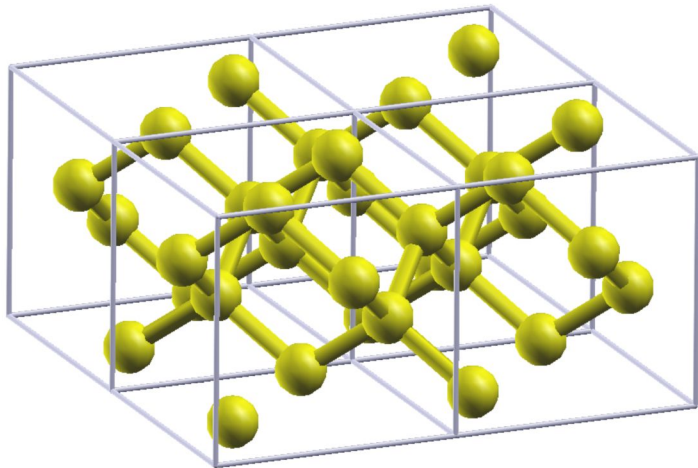
Ab-initio analysis of the structural and electronic properties of new carbon allotropes.

Francesco Delodovici

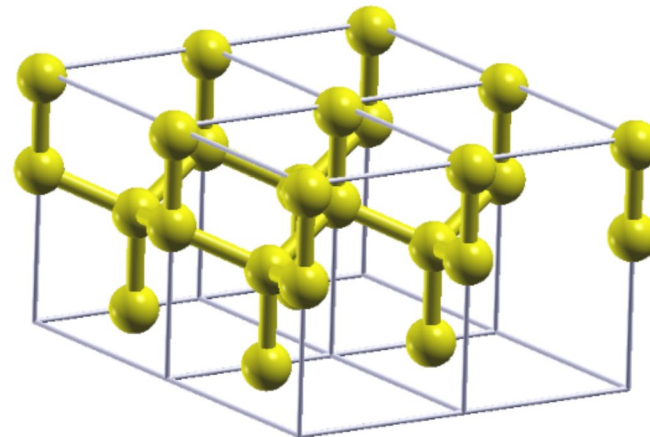
Supervisors: G. Onida
N. Manini

Introduction: known carbon allotropes

- **Graphite**
- **Diamond**
- **Hexagonal diamond**



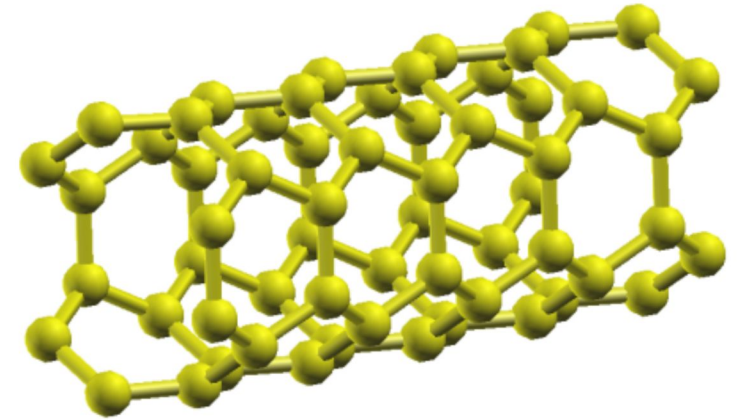
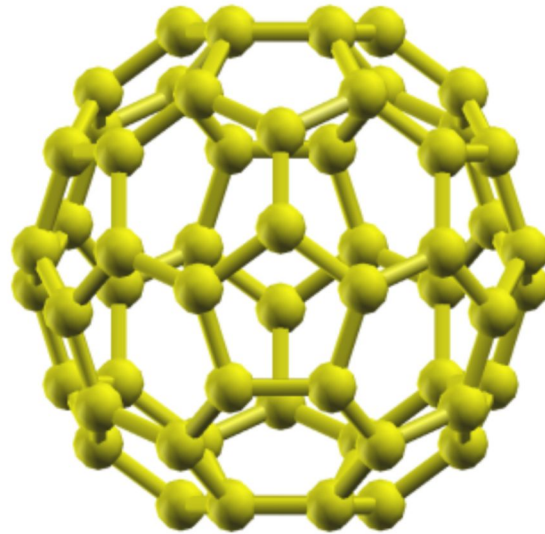
$sp^2 \rightarrow$ conductor



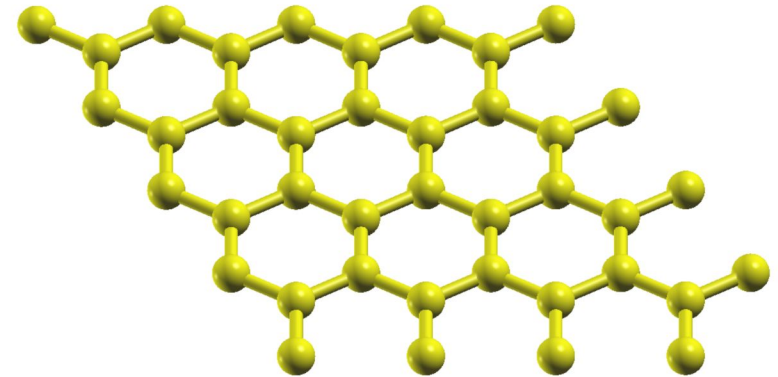
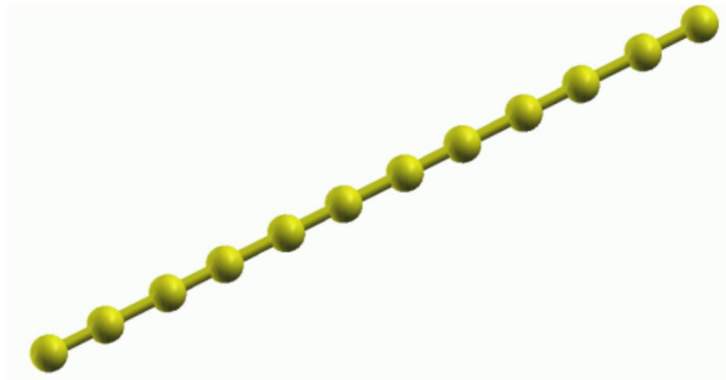
$sp^3 \rightarrow$ insulators

Introduction: known “novel” carbon allotropes

- Fullerenes
- Nanotubes
- Graphene
- Carbyne

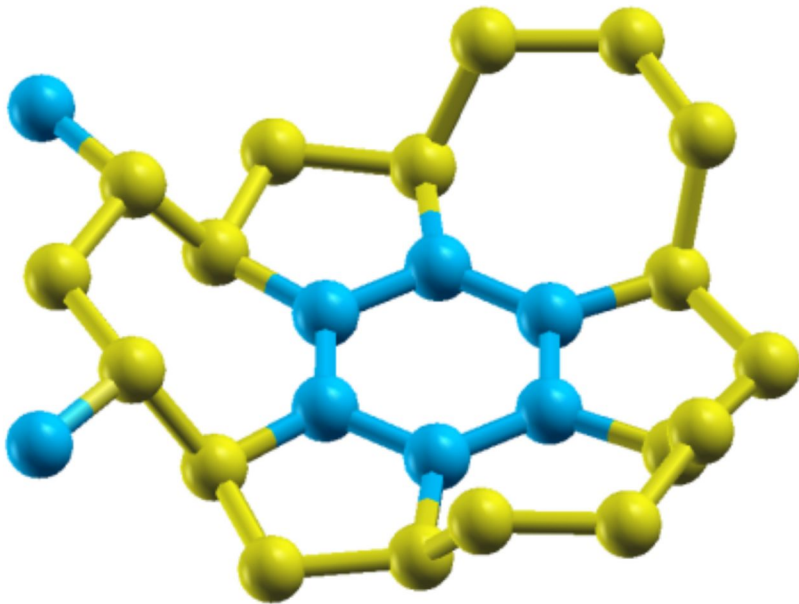


$sp^2 \rightarrow$ conductor

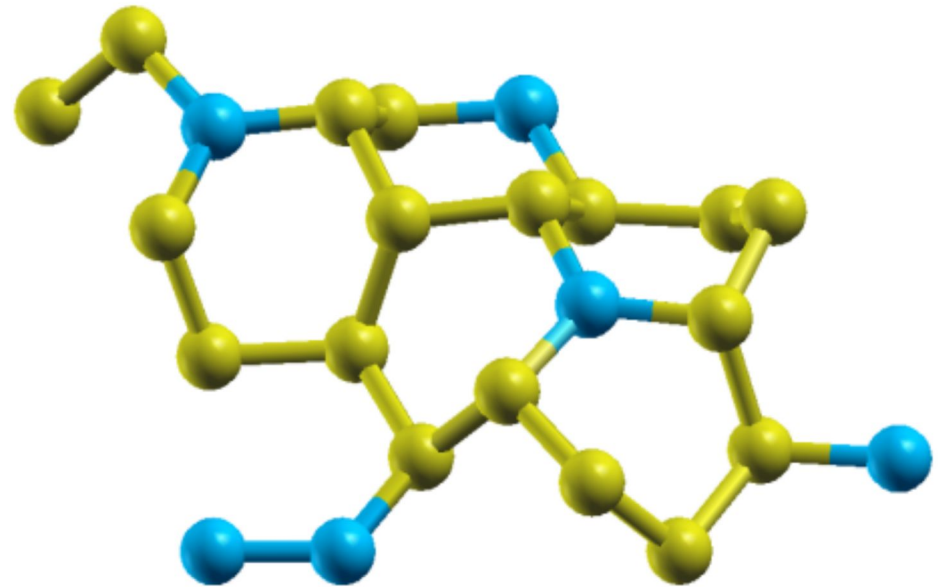


Mixing hybridization

- Possible new allotropes (sacada.sctms.ru)



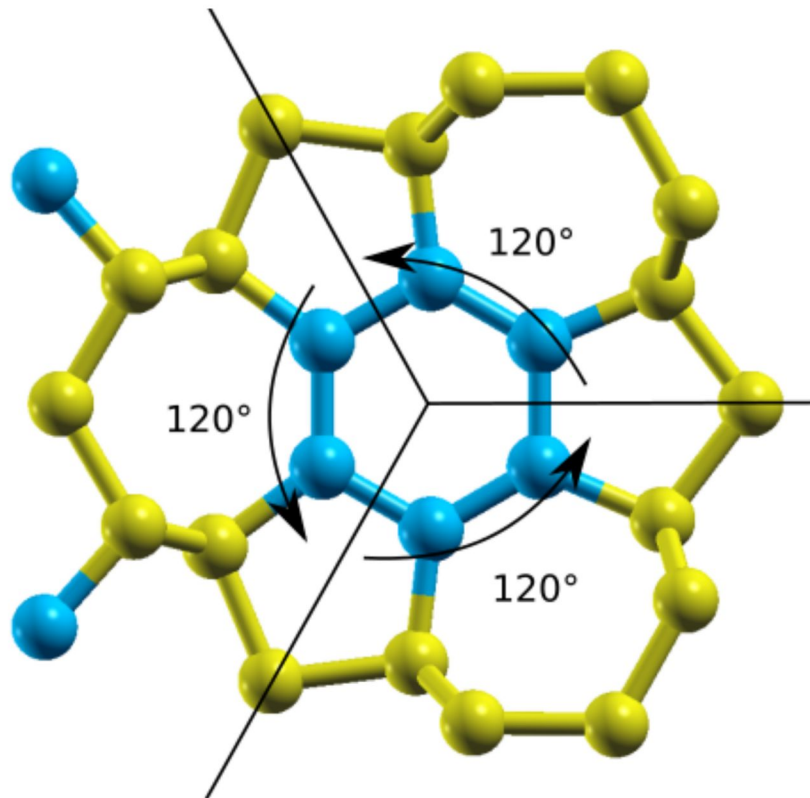
- Novamene



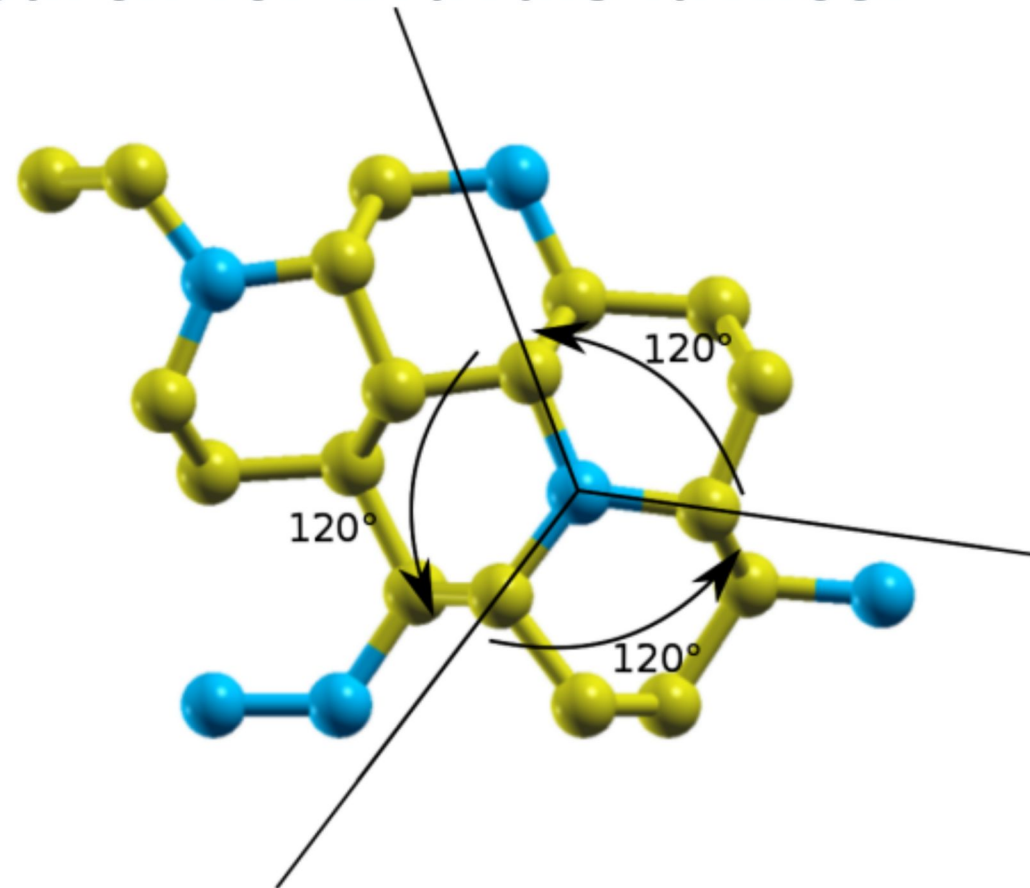
- Protomene

Mixing hybridization

- **Need for periodicity: search for Bravais lattice.**



- Novamene

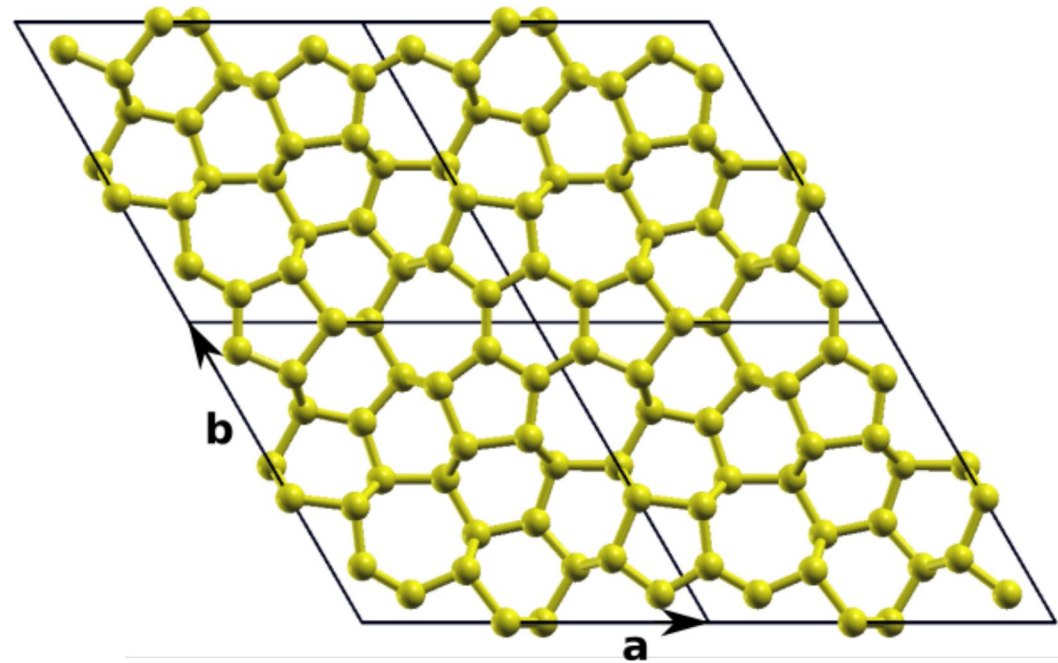
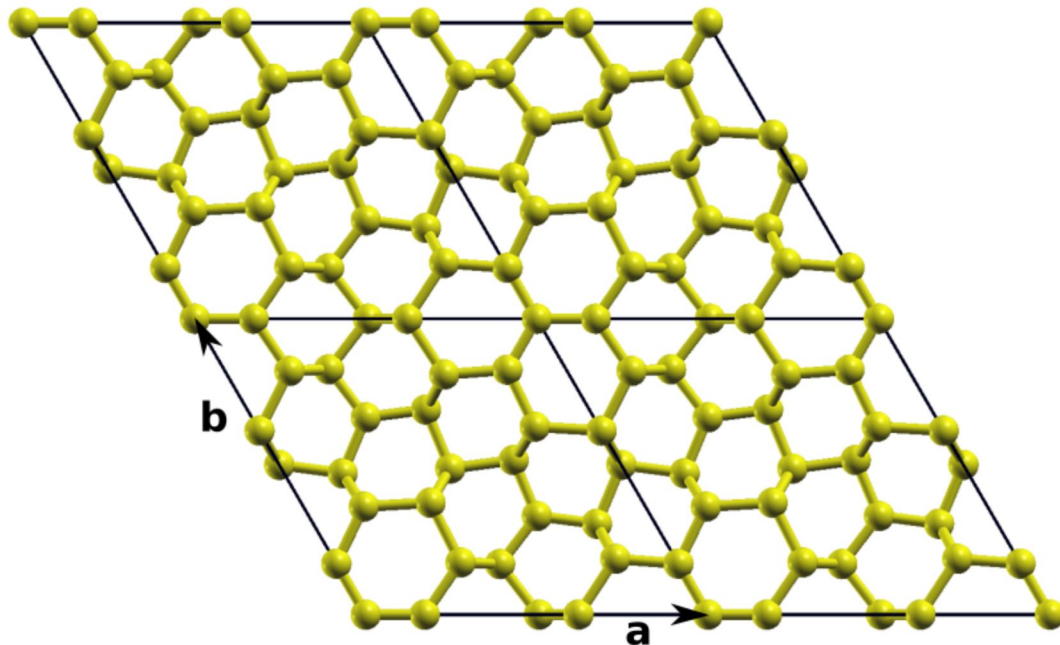


- Protomene

Mixing hybridization

- **Need for periodicity: search for Bravais lattice.**

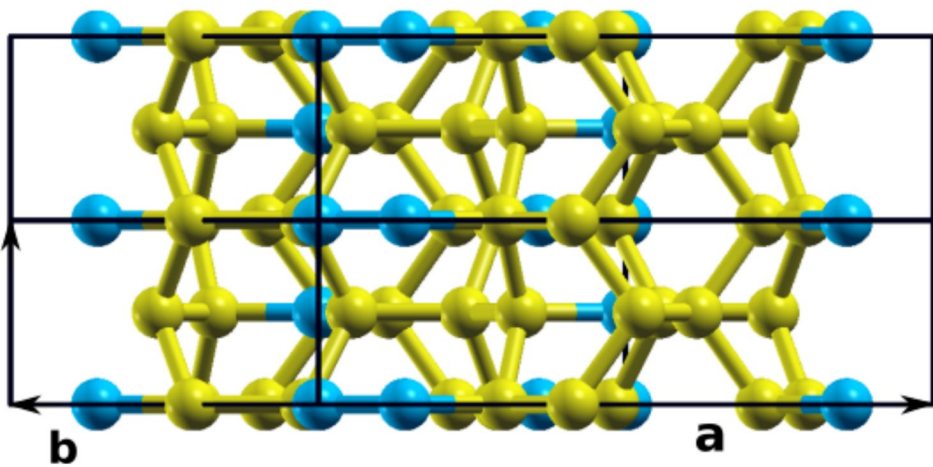
**Novamene: hexagonal lattice
P-62m (#189)**



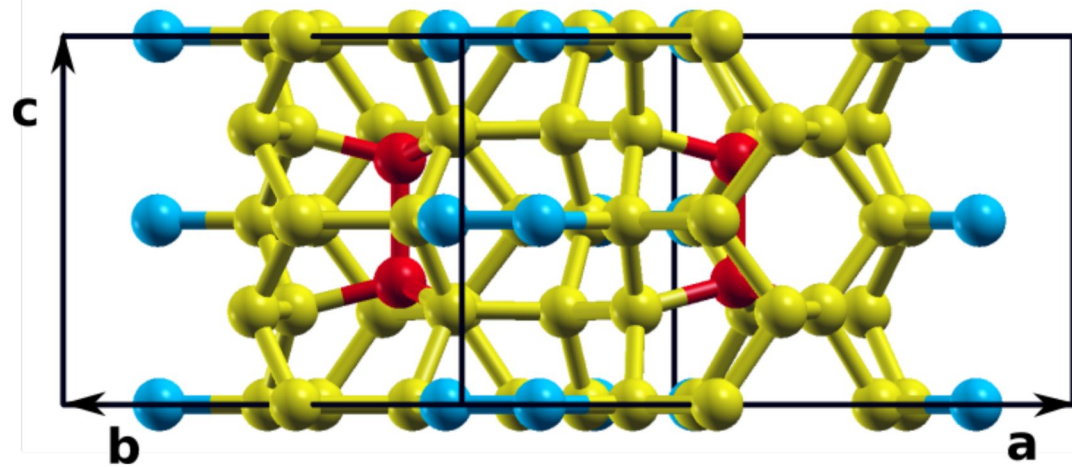
**Protomene: hexagonal lattice
P-31m (#157)**

Dimers formation

- The sp^2 atoms can switch to sp^3



26 atoms

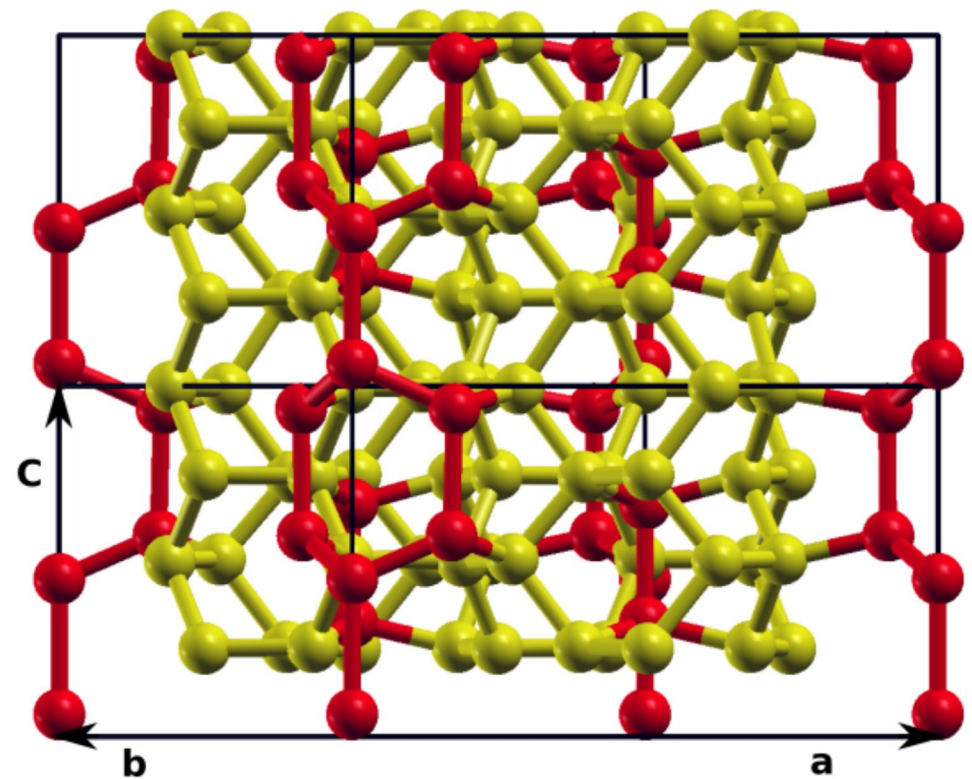
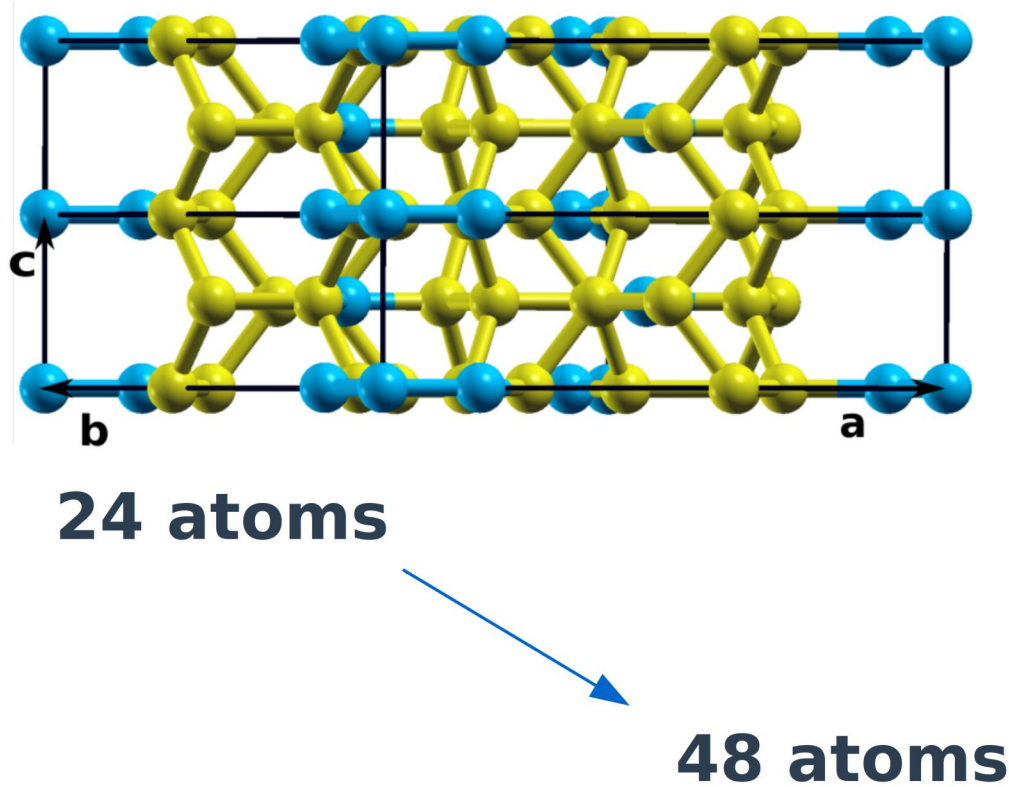


52 atoms

The volume of the primitive doubles

Dimers formation

- The sp^2 atoms can switch to sp^3



Density Functional Theory

- **Ab-initio ground-state theory: no parameters**

$$E[n(\vec{r})] = T[n(\vec{r})] + E_{\text{Nucl}}[n(\vec{r})] + E_{\text{Ha}}[n(\vec{r})] + E_{\text{xc}}[n(\vec{r})]$$

Density Functional Theory

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- **Kohn-Sham equations:**

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{nuc}}(\vec{r}) + V_{\text{Ha}}[n(\vec{r})] + V_{\text{xc}}[n(\vec{r})] \right\} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

Density Functional Theory

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**Approximated
(LDA, GGA etc.)**

Density Functional Theory

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- **Total energy:**

$$E_{\text{tot}} = \sum_j \epsilon_j - E_{\text{Ha}} + \int [\epsilon_{\text{xc}}(n(\vec{r})) - V_{\text{xc}}(n(\vec{r}))] n(\vec{r}) d\vec{r} + E_{\text{ion-ion}}$$

Density Functional Theory

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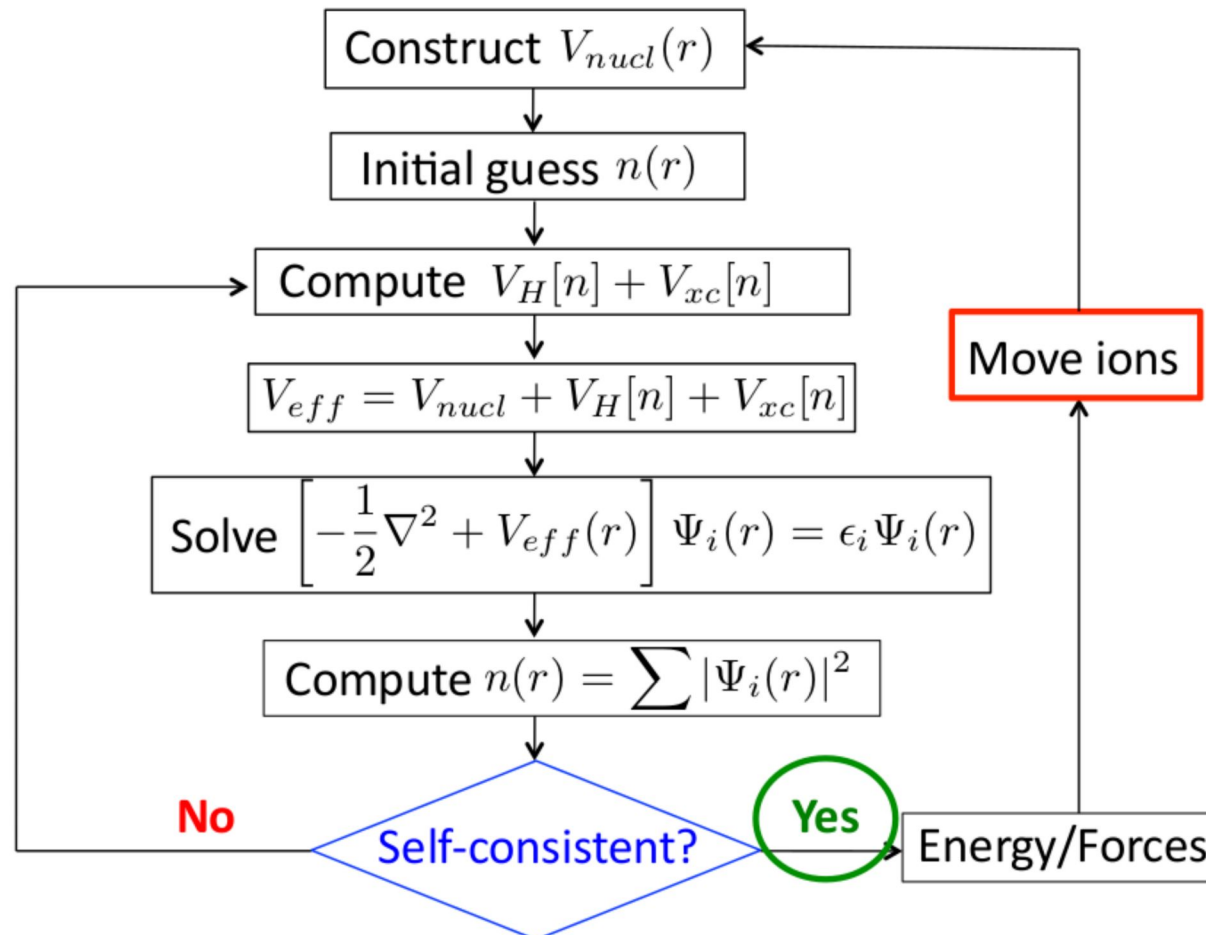
- **Total energy (fixed ions position):**

$$E_{tot} = \sum_j \epsilon_j - E_{Ha} + \int [\epsilon_{xc}(n(\vec{r})) - V_{xc}(n(\vec{r}))] n(\vec{r}) d\vec{r} + E_{ion-ion}$$

Optimized structural equilibrium

Density Functional Theory

Iterative solution of KS equations



Structural research

- **Minimum energy configuration unknown → is any dimer present?**

Structural research

- **Minimum energy configuration unknown → is any dimer present?**
↓
- **Structural optimization of different configurations (DFT relaxation)**
↓
- **Total energy, binding energy**

Structural research

- **Minimum energy configuration unknown → is any dimer present?**



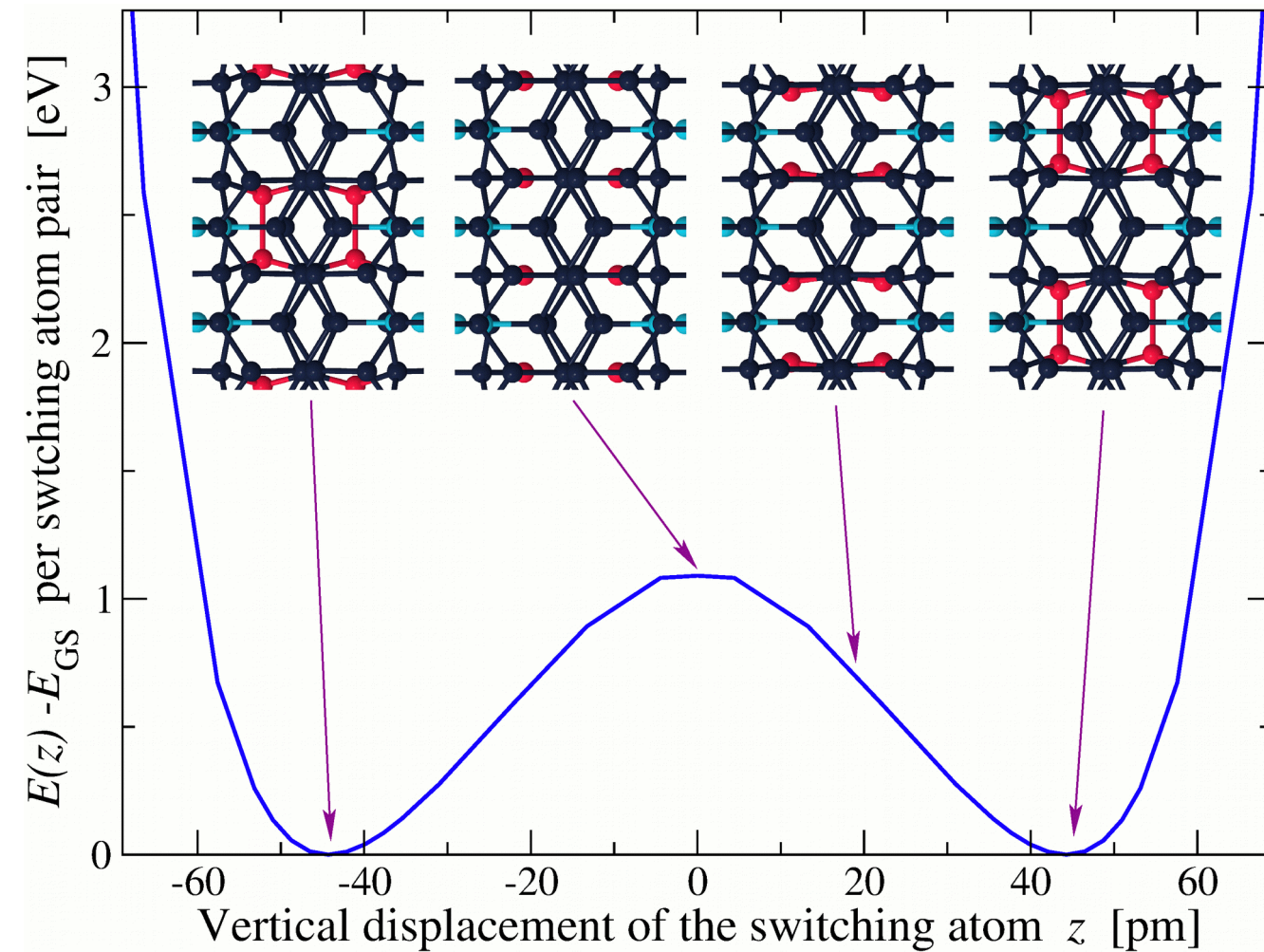
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Total energy, binding energy

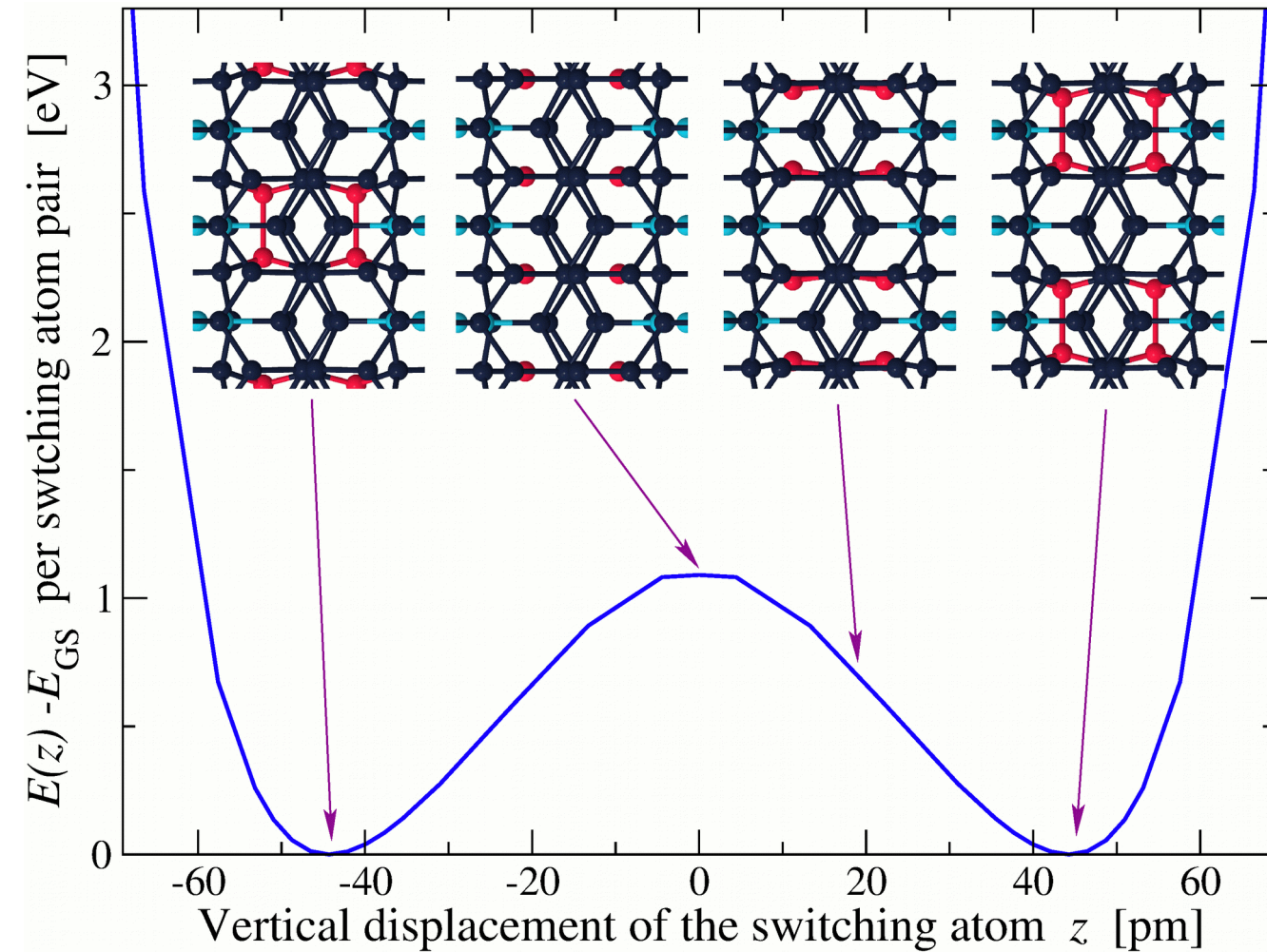
Structural parameter	protomene no-dimer LDA(GGA)	protomene ground state LDA(GGA)	novemene no-dimer LDA(GGA)	novamene ground state LDA(GGA)	diamond LDA (GGA)	graphite LDA (GGA)
N_{atoms} per cell	24	48	26	52	2	4
N_{dimers} corner	–	4	–	–	–	–
N_{dimers} central	–	2	–	2	–	–
ΔE_b per atom [eV]	0.2713 (0.1882)	0.1997 (0.1315)	0.269 –	0.2272 (0.1350)	0 (0)	–0.1460 (–0.3176)

Structural research



- Excitation energy as a function of the displacement of the switching carbons

Structural research



- Excitation energy as a function of the displacement of the switching carbons



- 2 equivalent minima
- No dimer configuration is unstable
- Formation E of one dimer ~ 1 eV (protomene ~ 0.6 eV)

Numerical results

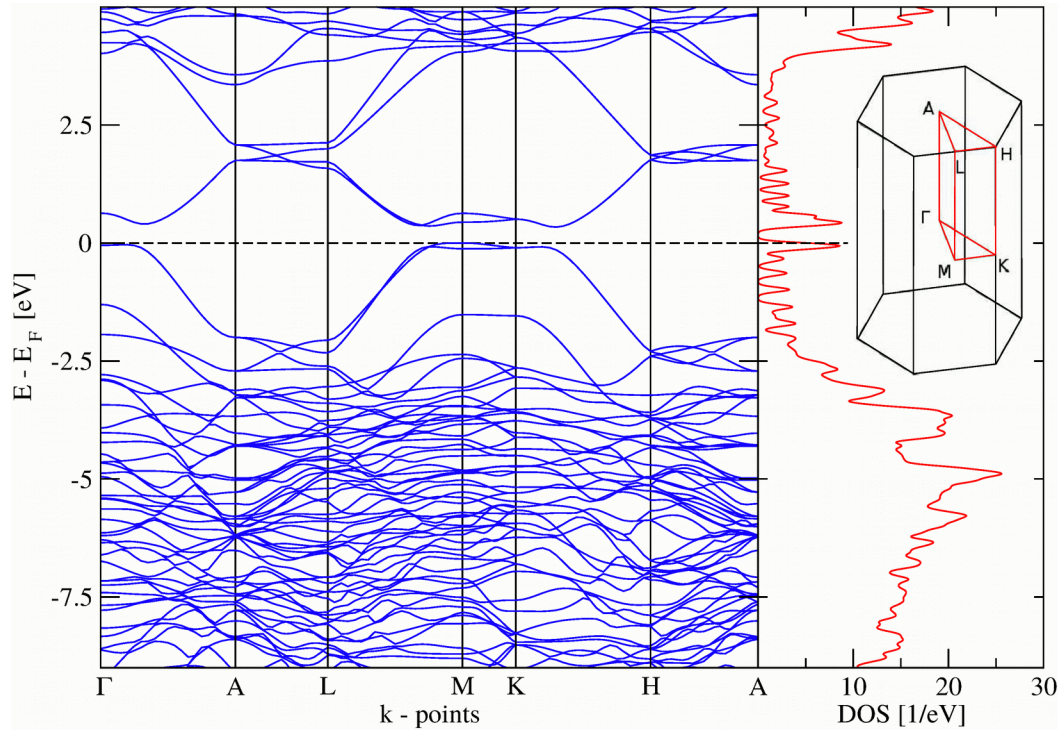
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band gap [eV]	0.000 (0.000)	3.380 (1.274)	0.000	0.336 (0.371)	4.220 (4.445)	0.000 (0.000)
a, b [pm]	807.2 (816.6)	807.4 (815.7)	841.8 –	841.9 (851.0)	352.3 (357.0)	243.3 (245.8)
c [pm]	247.2 (250.9)	482.8 (497.7)	251.9 –	499.8 (509.0)	352.3 (357.0)	589.8 (644.4)
density [kg m ^{–3}]	3432 (3303)	3512 (3338)	3351 –	3381 (3248)	3649 (3504)	2639 (2366)

Comparable stability

$$E_b = \frac{E_{\text{tot}}}{N} - E_{\text{atom}}$$

$$E_b^{\text{diam}} = -8.908 [\text{eV}] \text{ LDA} \\ -8.252 [\text{eV}] \text{ GGA}$$

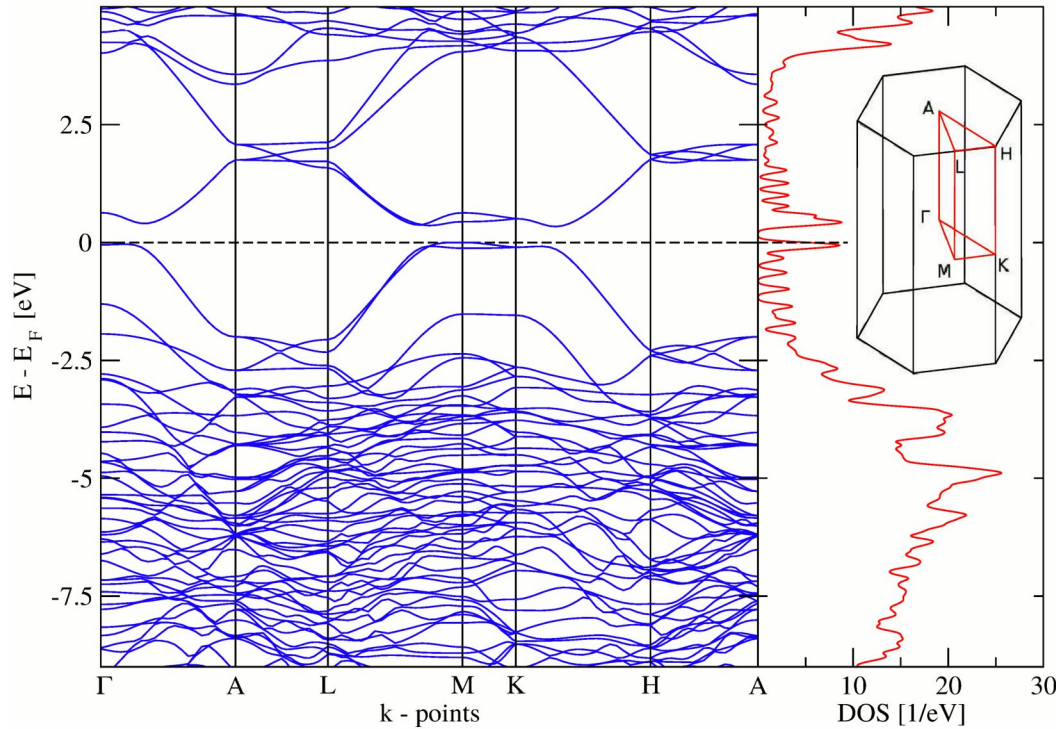
Insulator - metal transition



• **Ground-state novamene**

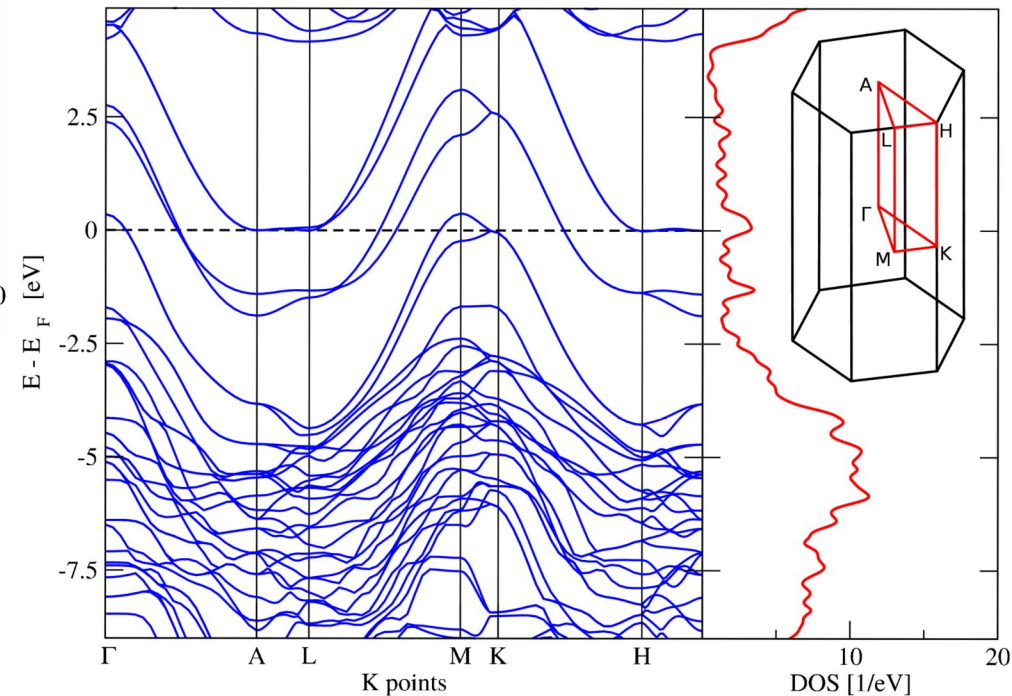
↓
Semiconductor: $E_{\text{gap}} = 0.336$ [eV]
Indirect gap

Insulator - metal transition



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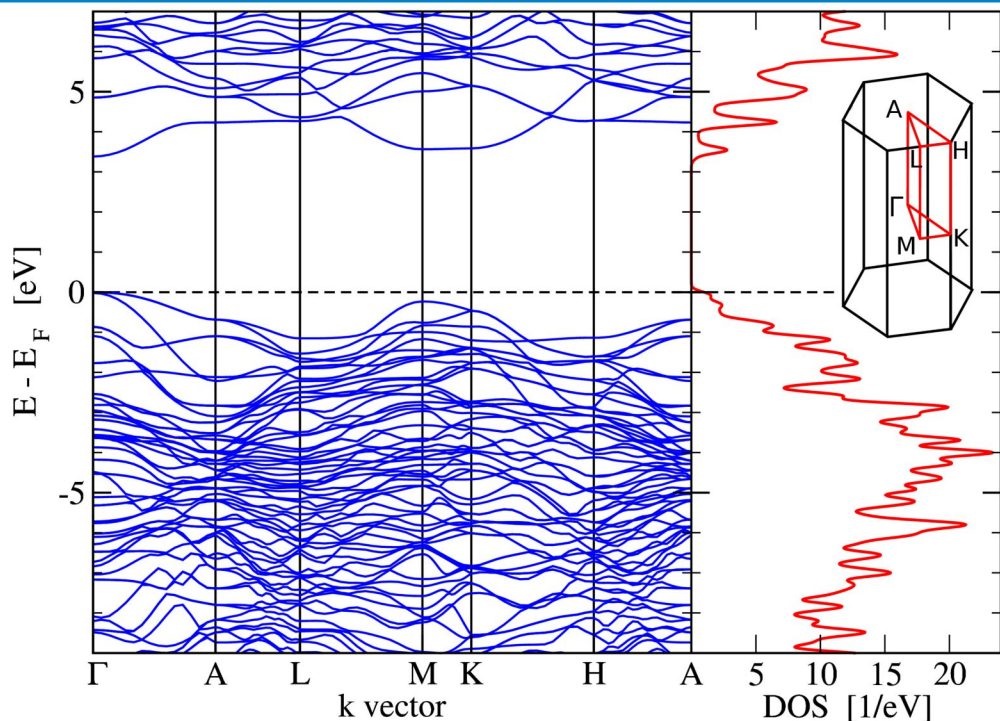
↓
Semiconductor: $E_{\text{gap}} = 0.336$ [eV]
Indirect gap



• **No dimer novamene**

↓
Metal: $E_{\text{gap}} = 0.0$ [eV]

Insulator - metal transition

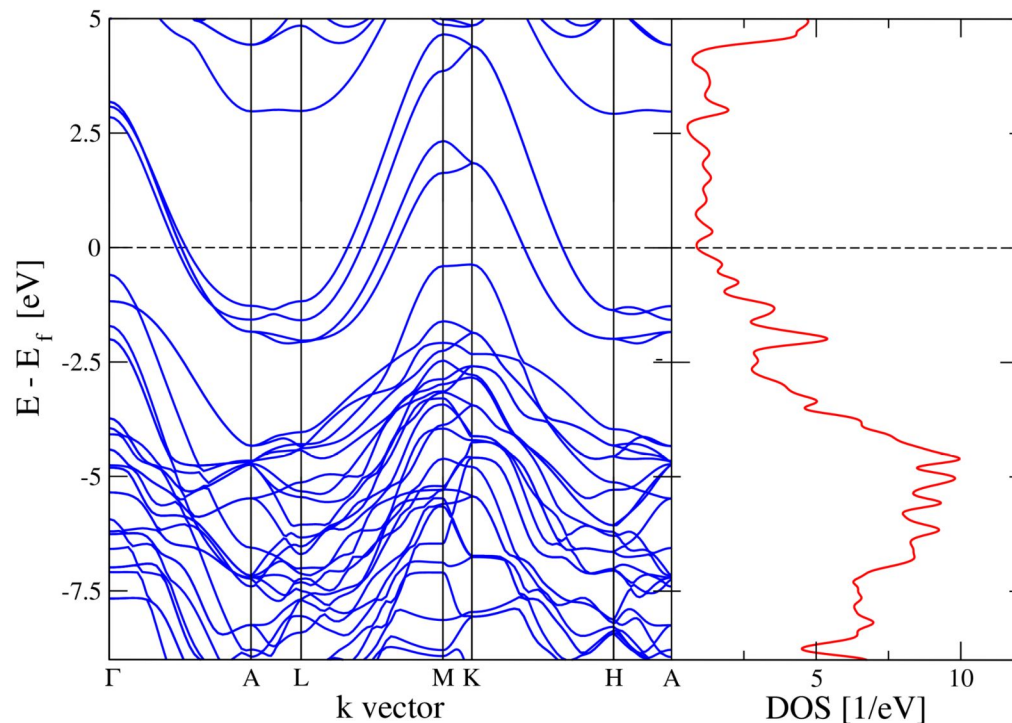


• **No dimer protomene**

↓
Metal: $E_{\text{gap}} = 0.0$ [eV]

• **Ground-state protomene**

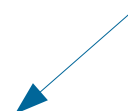
↓
Semiconductor: $E_{\text{gap}} = 3.320$ [eV]
direct gap



Numerical results

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transition



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transition



Phonons dispersion relation: protomene ground state

- **DFPT: density functional perturbation theory**

$$C_{I,J}^{\alpha,\beta} = \frac{\partial E\{\vec{R}\}}{\partial R_I^\alpha \cdot \partial R_J^\beta} \quad \text{Interatomic force constant matrix}$$



- **ω normal modes**

Phonons dispersion relation: protomene ground state

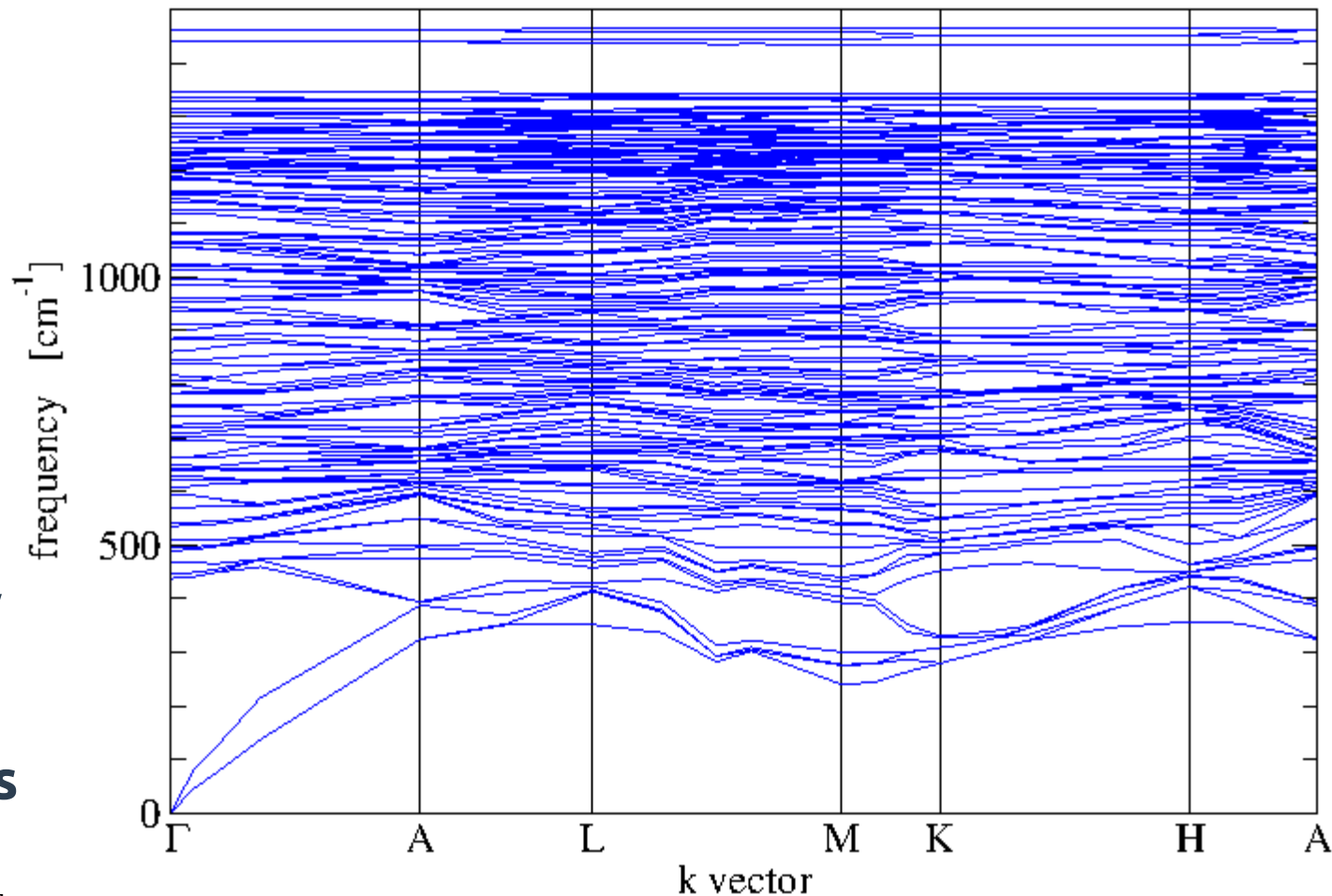
- DFPT

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- ω normal modes
- Mechanical stability
- gap in optical modes

$$\Delta \approx 92 [\text{cm}^{-1}] \approx 2.75 [\text{THz}]$$



Phonons dispersion relation: protomene ground state

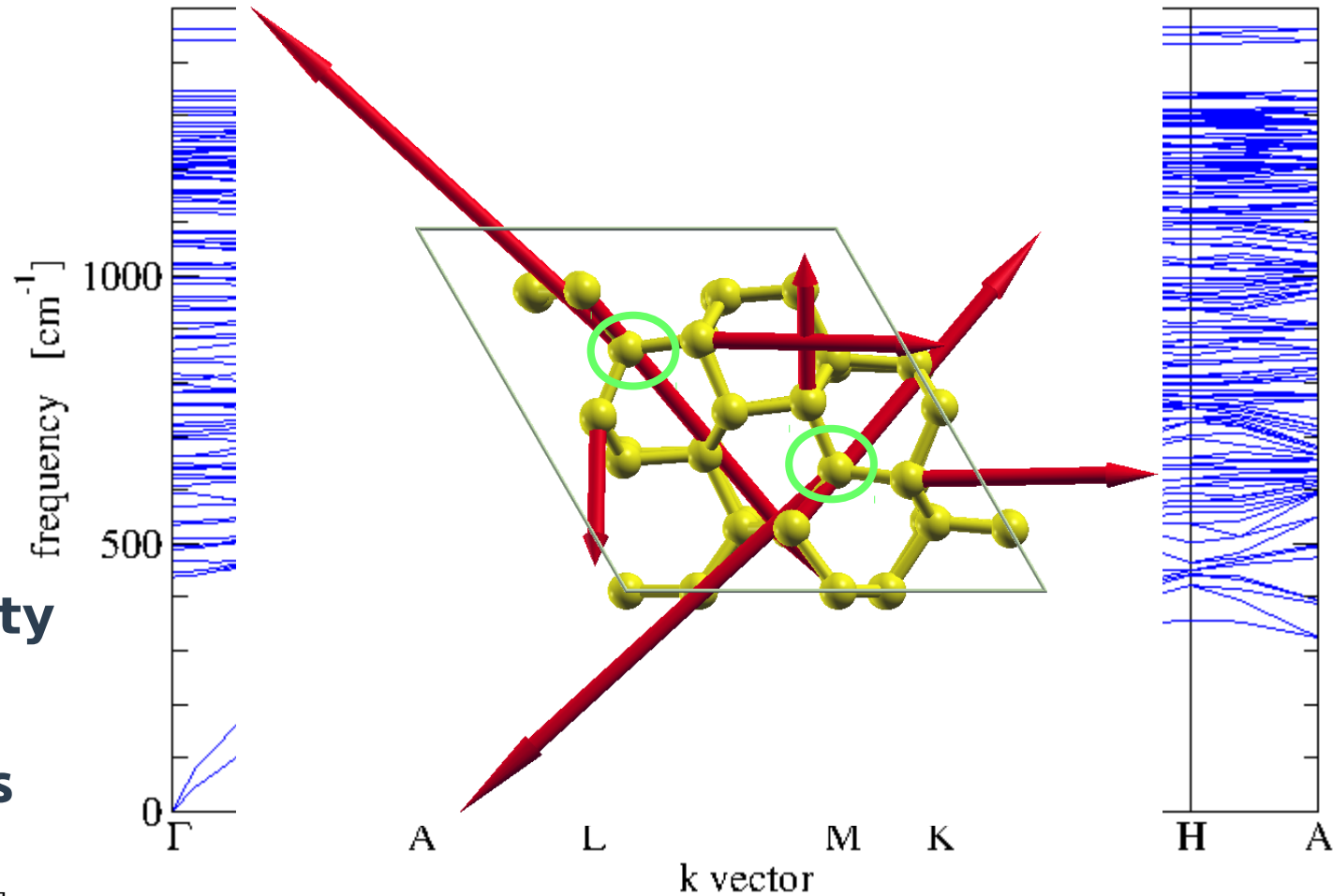
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Conclusions

- **Theoretical design and optimization of mixed sp^2 - sp^3 carbon structures.**
- **Temperature driven switching between insulating and conducting states.**
- **Stability has been checked by phonon spectra calculations.**

Further developments

- **Complete analysis of novamene dimers combination**
- **Understanding optical gap in protomene phonons**
- **Phonons spectra of novamene**
- **Slab configurations**
- **Raman spectrum**

Density Functional Theory

- **Exchange correlation term.**

$$LDA \rightarrow E_{xc}[n(\vec{r})] = \int_V \epsilon_{heg}(n(\vec{r})) n(\vec{r}) d\vec{r}$$

$$\epsilon_{heg} \approx \sum_i [n_i^{2/3} - n_i^{1/3}]$$

HF

QMC

$$V_{xc}[n(\vec{r})] = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} = \epsilon_{heg}(n(\vec{r})) + n(\vec{r}) \frac{\partial \epsilon_{heg}(\vec{r}, n(\vec{r}))}{\partial n(\vec{r})}$$

$$E_{tot} = \sum_j \epsilon_j - E_{Ha} + \int \epsilon_{xc}(n(\vec{r})) n(\vec{r}) d\vec{r} - \int V_{xc}(n(\vec{r})) n(\vec{r}) d\vec{r} + E_{ion-ion}$$

$$E_{Ha} = \frac{e^2}{2} \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

LDA (GGA)

$$E_{ion-ion} = e^2 \sum_{k < l} \frac{Z_k Z_l}{|R_k - R_l|}$$

Density Functional Theory

- **Total energy**

$$E_{tot} = \sum_j \epsilon_j (-E_{Ha}) + \int \epsilon_{xc}(n(\vec{r})) n(\vec{r}) d\vec{r} - \int V_{xc}(n(\vec{r})) n(\vec{r}) d\vec{r} + E_{ion-ion}$$

double counting

$$T_{ks} + E_{ions}(n(\vec{r})) + E_{Ha}$$

$$E_{tot} = T_{ks} + E_{ions} + E_{Ha} + \int \epsilon_{xc}(n(\vec{r})) n(\vec{r}) d\vec{r} + E_{ion-ion}$$

DFT relaxation

- **BFGS algorithm: quasi newtonian algorithm**

$$\vec{x}_{n+1} = \vec{x}_n - [H f(\vec{x}_n)]^{-1} \vec{\nabla} f(\vec{x}_n)$$
$$x_{n+1} = x_n - \frac{f'(x_n)}{f''(x_n)}$$
$$f(\vec{x}'_n) \equiv E_{tot}(\{\vec{R}_{ions}\})$$

**Hessian approximation
(iteratively updated)**

Hellman-Feynman:

$$\vec{F}_I = -\vec{\nabla} E_{tot}(\vec{R}) = -\langle \psi | \vec{\nabla} V(\vec{R}) | \psi \rangle - \vec{\nabla} E_{ions}(\vec{R})$$

Density Functional Perturbation Theory

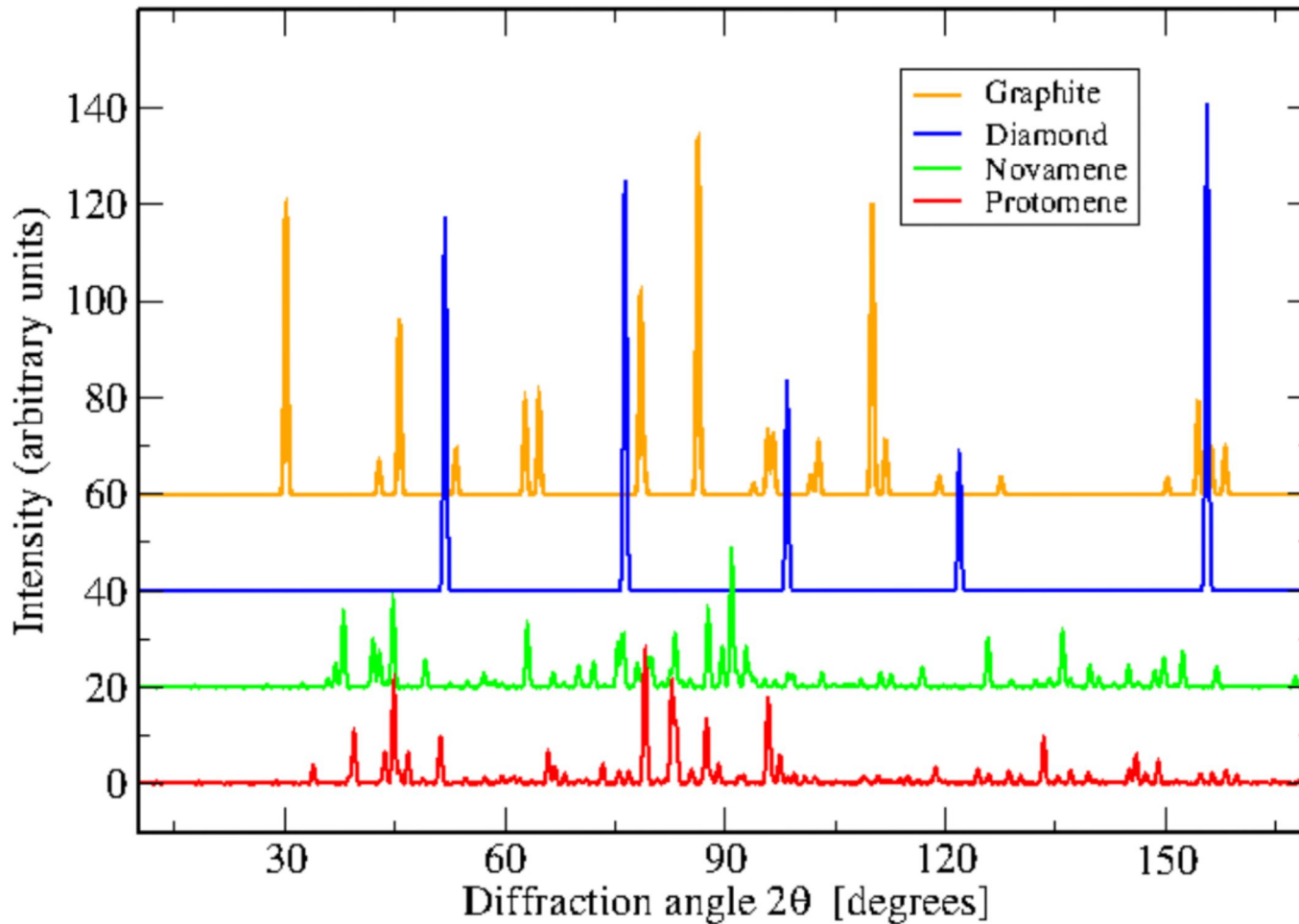
DFPT \longrightarrow ω normal modes: $\sum_{J,\beta} [D_{I,J}^{\alpha,\beta} - \omega^2 \delta_{I,J} \delta_{\alpha,\beta}] u_J^\beta = 0$

$$C_{I,J}^{\alpha,\beta} = \frac{\partial E\{\vec{R}\}}{\partial R_I^\alpha \partial R_J^\beta} \longrightarrow \frac{\partial^2 E}{\partial R_I \partial R_J} = \int \frac{\partial V(r)}{\partial R_I} \frac{\partial n(r)}{\partial R_J} d\vec{r} + \int n(r) \frac{\partial^2 V(r)}{\partial R_I \partial R_J} d\vec{r}$$

Linear response function:

$$\chi_0(r, r') \approx \Re \sum_{v,c} \frac{\tilde{\psi}'_v(r) \psi_c(r) \tilde{\psi}_c(r') \psi_v(r')}{\epsilon_v - \epsilon_c} \longrightarrow \chi = \chi_0 + \chi_0 \left[\frac{\delta V_{el}}{\delta n} \right] \chi$$

X-ray diffraction pattern



- **Powder sample**

$$I(\vec{q}) \propto |\tilde{\rho}(\vec{q})|^2 \cdot \delta_{\Delta\vec{G}, \vec{q}}$$

$$\tilde{\rho}(\vec{q}) \propto S(\vec{q}) = \left| \sum_j f_j(\vec{q}) e^{-i\vec{q}\cdot\vec{r}_j} \right|^2$$

$$f_j(\vec{q}) = \int_{V_{cell}} \rho_j(\vec{q}) e^{-i\vec{q}\cdot\vec{r}} dr$$