Fononska svojstva poluvodiča *Si* i *BN*

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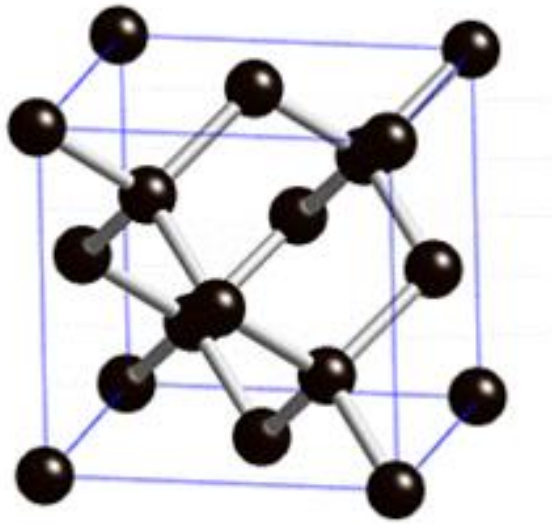
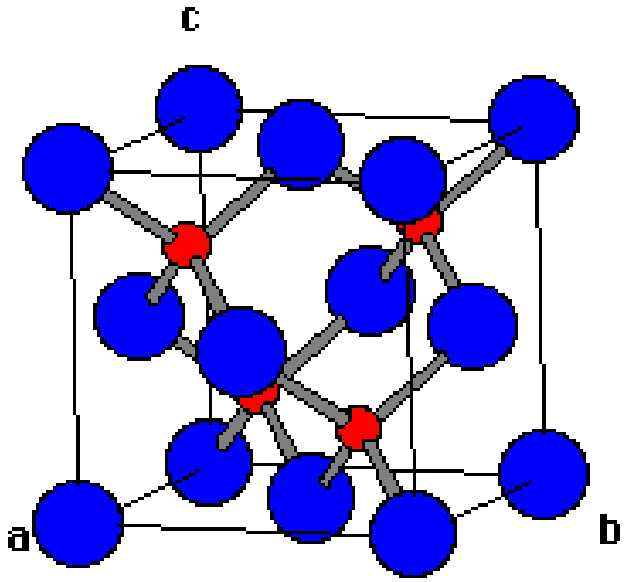
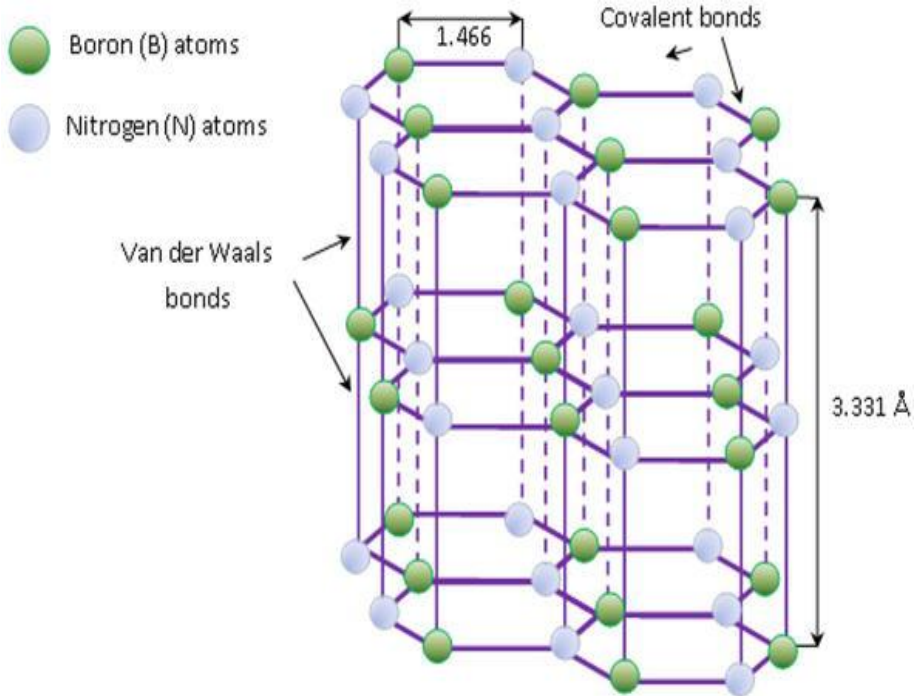
Silicij



cBN



hBN



$$\mathcal{D}_{s\alpha,s\prime\alpha\prime}(\vec{q})$$

$$D(\vec{q})_{ij} = \frac{1}{\sqrt{M_i M_j}} C(\vec{q})_{ij}$$

$$\tilde{D}(\vec{q}) = \frac{1}{N} \sum_{\vec{R}} F(\vec{R}) e^{-i\vec{q}\vec{R}}$$

Mnogočestični elektronski problem

$$H\Psi(\vec{r}_1,\ldots,\vec{r}_N) = \varepsilon\Psi(\vec{r}_1,\ldots,\vec{r}_N)$$

$$H = \sum_{i=1}^{N}\left[-\frac{\hbar^2\nabla_i^2}{2m} + V_{\text{ext}}(\vec{r}_i)\right] + \sum_{i>j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Cilj je mnogočestični kvatni problem svesti na funkciju gustoće $n(r)$, umjesto računa s valnom funkcijom $\Psi(\overrightarrow{r_1},\ldots,\overrightarrow{r_2})$. Prednosti ovoga pojednostavljenja su znatne:

- radimo s funkcijom 3 prostorne koordinate, umjesto 3N prostornih varijabli
- gustoća je mjerljiva veličina
- $n(r)$ je moguće povezati s v. funkcijom i povezati s raznim fizikalnim veličinama

$$n(\vec{r}) = \langle\Psi|\sum_{i=1}^{N}\delta(\vec{r}-\vec{r}_i)|\Psi\rangle = N\int d^3r_2\ldots\int d^3r_N\,|\Psi(\vec{r},\vec{r}_2,\ldots,\vec{r}_N)|^2$$

Hohenberg-Kohn teoremi

1)Ako je osnovno stanje nedegerirano: postoji relacija ekvivalencije između hamiltonijana H i gustoće u osnovnom stanju $n_0(r)$:

Energija osnovnog stanja je funkcional $n(r)$: $E = E[n]$

2)Među svim mogućim elektronskim gustoćama $n(r)$; $E[n]$ je minimalan kad je $n(r)$ egzaktna gustoća osnovnog stanja $n_0(r)$:

$$\min E[n] = E[n_0]$$

Moramo dakle minimizirati funkcijonal energije:

$$E[n] = T[n] + E_{\text{ext}}[n] + U[n]$$

DFT računi (Density functional theory)

$$E[n] = T[n] + E_{\text{ext}}[n] + U[n]$$

$$U[n] = E_{\text{H}}[n] + \Delta U[n]$$

$$T[n] = T_s[n] + T_c[n]$$

$$E_{\text{xc}}[n] = T_c[n] + \Delta U[n]$$

$$E_{\text{ext}}[n] = \int d^3r \, V_{\text{ext}}(\vec{r}) \, n(\vec{r})$$

$$E_{\text{H}}[n] = \frac{e^2}{2} \int d^3r \int d^3r' \, \frac{n(\vec{r}) n(\vec{r'})}{|\vec{r} - \vec{r'}|}$$

$$E[n] = T_s[n] + \int d^3r \, V_{\text{ext}}(\vec{r}) \, n(\vec{r}) + E_{\text{H}}[n] + E_{\text{xc}}[n]$$

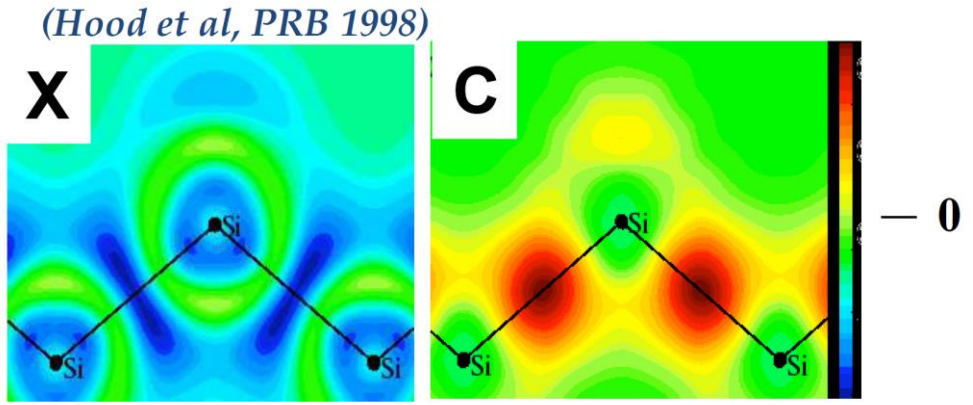
$$E_{xc}[n] = T_c[n] + \Delta U[n]$$

- **Član razlike kinetičkih energija interagirajućeg i neinteragirajućeg sustava za istu gustoću $n(r)$**
- **Kvantni učinci pri elektron-elektron interakciji: član izmjene (Fock), kulonske korelacije, popravke vlastitoj energiji**

LDA (local density approximation)

$$\varepsilon_{XC} = \varepsilon_X + \varepsilon_C$$

Član XC, rastavimo na član izmjene (X - exchange) i član koji opisuje korelacije (C).
Vrijednosti ta dva člana u ovisnosti o $\vec{r}$ možemo računati uz zadani $\boldsymbol{n(r)}$, kao u slobodnom plinu iste gustoće: nehomogen sustav pretpostavljamo lokalno homogenim.



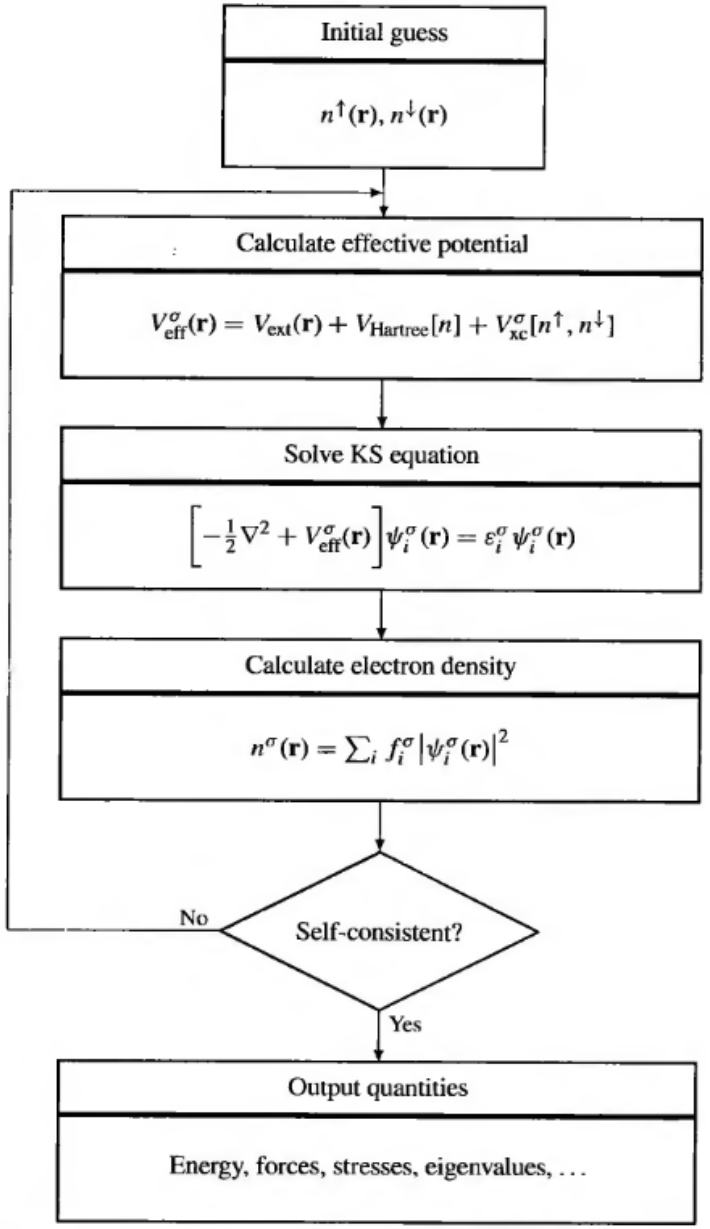
Razlika točne XC energije i LDA energije u c-SI

Kohn-Sham ansatz i samosuglasni račun

$$
\begin{array}{ccccccc}
V_{\text{ext}}(\mathbf{r}) & \overset{\text{HK}}{\Longleftarrow} & n_0(\mathbf{r}) & \overset{\text{KS}}{\Longleftrightarrow} & n_0(\mathbf{r}) & \overset{\text{HK}_0}{\Longrightarrow} & V_{\text{KS}}(\mathbf{r}) \\
\Downarrow & & \Uparrow & & \Uparrow & & \Downarrow \\
\Psi_i(\{\mathbf{r}\}) & \Rightarrow & \Psi_0(\{\mathbf{r}\}) & & \psi_{i=1..N_e}(\mathbf{r}) & \Leftarrow & \psi_i(\mathbf{r})
\end{array}
$$

Zamjeniti teško rješivi mnogočestični sustav s interakcijom s jednostavnijim sustavom.

Osnovno stanje **izvornog interagirajućeg** sustava je jednako osnovnom stanju **izabranog neinteragirajućeg** problema koji možemo egzaktno riješiti preko efektivnih nelokalnih interakcija.



DFT račun za fonone

Kako bismo došli do energija vibracija fonona, odnosno kako bismo modelirali ovisnost o pomacima atoma, koristimo **Born-Oppenheimer aproksimaciju** te za zadanu konfiguraciju λ_i gdje se atomi nalaze **u položajima $\vec{R}_{\lambda_i}$ računamo energiju osnovnog stanja elektrona.**

Koristeći Hellmann-Feynman teorem dolazimo do izraza za silu:

$$\frac{\mathrm{d}E_\lambda}{\mathrm{d}\lambda} = \langle\psi_\lambda|\frac{\mathrm{d}\hat{H}_\lambda}{\mathrm{d}\lambda}|\psi_\lambda\rangle = \int \psi_\lambda^* \frac{\mathrm{d}\hat{H}_\lambda}{\mathrm{d}\lambda}\psi_\lambda \,\mathrm{d}V \quad \Rightarrow \quad \frac{\partial^2 E}{\partial\lambda_i\partial\lambda_j} = \int \frac{\partial^2 V_\lambda(\mathbf{r})}{\partial\lambda_i\partial\lambda_j} n_\lambda(\mathbf{r})d\mathbf{r} + \int \frac{\partial n_\lambda(\mathbf{r})}{\partial\lambda_i}\frac{\partial V_\lambda(\mathbf{r})}{\partial\lambda_j}d\mathbf{r}$$

Nova iterativna jednadžba za potencijal, koju moramo riješiti samosuglasno, je dana s:

$$\Delta V_{SCF}(\mathbf{r}) = \Delta V(\mathbf{r}) + e^2\int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \left.\frac{dv_{xc}(n)}{dn}\right|_{n=n(\mathbf{r})} \Delta n(\mathbf{r})$$

Novi član koji zahtjeva samosuglasni iterativni račun

Translacijska invarijantnost kristalne rešetke – energija fonona ovisi o valnom vektoru

Rješavanje fonoske jedadžbe oko $q \to 0$

$$\begin{bmatrix} (\mathcal{C}_z)_{11} & (\mathcal{C}_z)_{12} \\ (\mathcal{C}_z)_{21} & (\mathcal{C}_z)_{22} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \omega^2 \begin{bmatrix} m_1 v_1 \\ m_2 v_2 \end{bmatrix}$$

Koristimo svojstvo simetrije :

$$\frac{\partial^2 \epsilon}{\partial v_1 \partial v_2} = \frac{\partial^2 \epsilon}{\partial v_2 \partial v_1}$$

Translatorni mod ima frekvenciju nula :

$$\begin{bmatrix} (\mathcal{C}_z)_{11} & -a \\ -a & (\mathcal{C}_z)_{22} \end{bmatrix} \begin{bmatrix} v \\ v \end{bmatrix} = 0$$

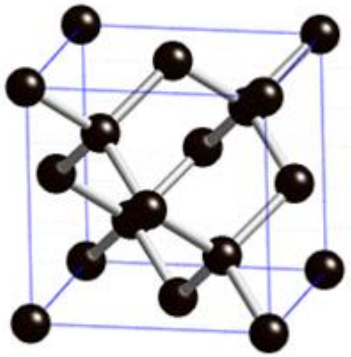
$$\begin{bmatrix} (\mathcal{C}_z)_{11} & (\mathcal{C}_z)_{12} \\ (\mathcal{C}_z)_{21} & (\mathcal{C}_z)_{22} \end{bmatrix} = \begin{bmatrix} a & -a \\ -a & a \end{bmatrix}$$

U slučaju cBN-a DFT račun daje :

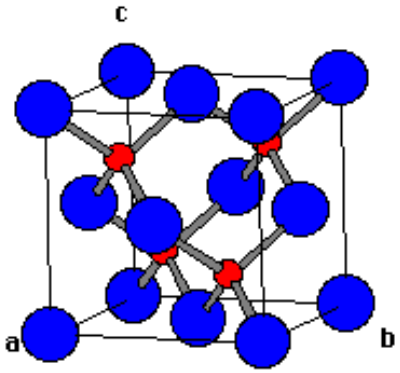
$$\begin{bmatrix} (\mathcal{C}_z)_{11} & (\mathcal{C}_z)_{12} \\ (\mathcal{C}_z)_{21} & (\mathcal{C}_z)_{22} \end{bmatrix}_{BN} = \begin{bmatrix} 0.52144 & -0.52110 \\ -0.52111 & 0.52280 \end{bmatrix}$$

Koristeći dinamičku matricu: $1062\ \mathrm{cm}^{-1}$

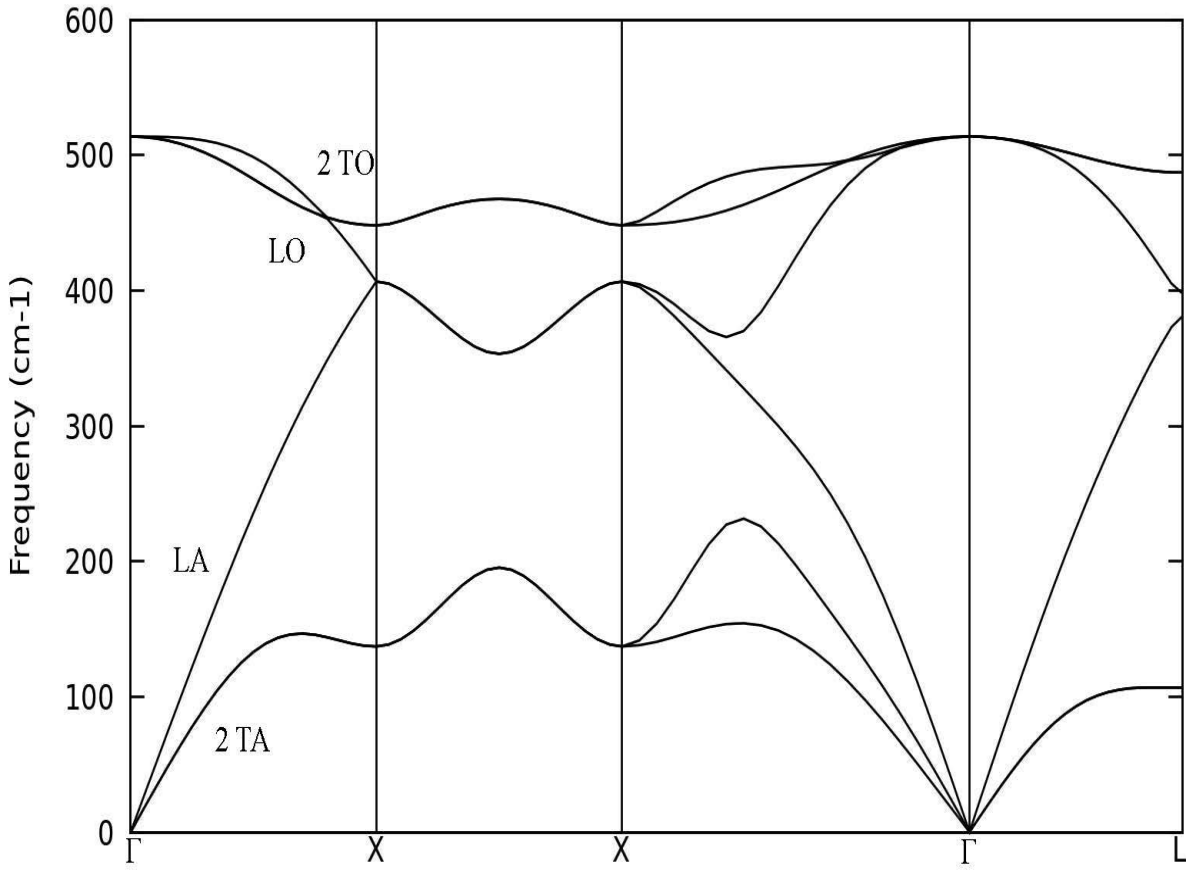
Quantum espresso: $1078\ \mathrm{cm}^{-1}$



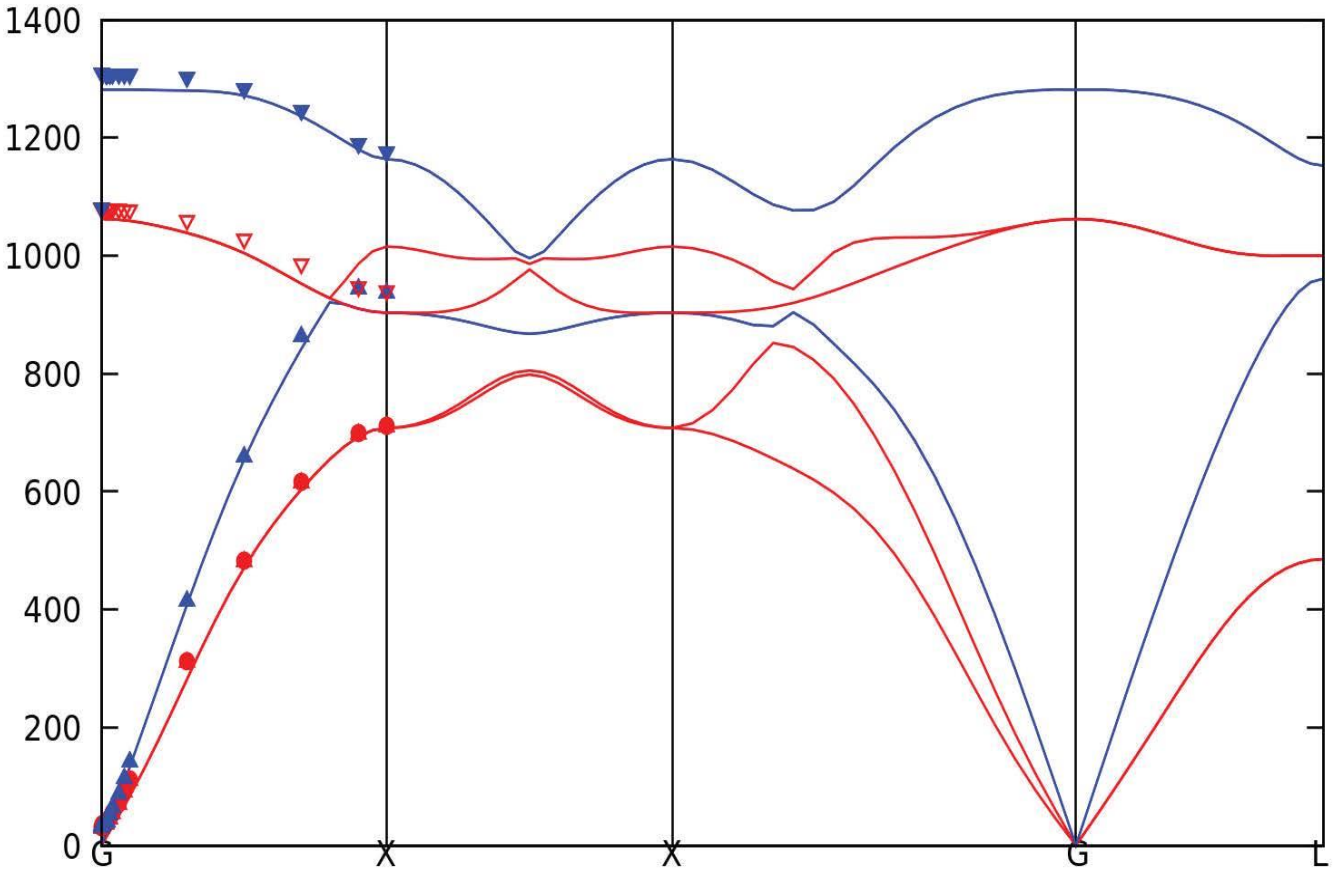
LO/TO splitting u *cBN-u*



Si phonon dispersion



BN phonon dispersion



Teoretska pozadina

Pošto nemamo slobodnih naboja
Maxwellove jednadžbe glase :

$$\vec{\nabla}\vec{D} = 0 \quad \Rightarrow \quad \vec{q}\vec{D}_q = 0$$
$$\vec{\nabla} \times \vec{E} = 0 \quad \Rightarrow \quad \vec{q} \times \vec{E}_q = 0$$

LO: $\vec{D}_q \parallel \vec{q}$ $\qquad \vec{D}_q = 0 = \vec{E}_q + 4\pi\vec{P}_q$

TO: $\vec{q} \perp \vec{E}, \vec{P}$ $\qquad \vec{E} = 0$

$$\omega_{LO}^2 = \omega_{TO}^2 + \mathcal{W}_c(\vec{q}) \frac{e^2|\vec{q}|^2}{\Omega} \left(\sum_n \frac{\vec{e}\vec{q} \cdot \mathcal{Z}_n \cdot \vec{e}_{LO}^n}{M_n} \right)^2$$

$$\mathcal{D}_{s\alpha,s\prime\alpha\prime}(\vec{q} \to 0) = \mathcal{D}_{s\alpha,s\prime\alpha\prime}(\vec{q} = 0) + \mathcal{W}_c(\vec{q}) \frac{4\pi e^2}{\Omega} \left(\frac{(\vec{\mathcal{Z}}_{s\alpha} \cdot \vec{q})(\vec{\mathcal{Z}}_{s\prime\alpha\prime} \cdot \vec{q})}{\vec{q} \cdot \hat{\epsilon} \cdot \vec{q}} \right)^2$$

$$\mathcal{D}_{s\alpha,s'\alpha'}(\vec{q}\to 0)=\mathcal{D}_{s\alpha,s'\alpha'}(\vec{q}=0)+\mathcal{W}_c(\vec{q})\frac{4\pi e^2}{\Omega}\left(\frac{(\vec{Z}_{s\alpha}\cdot\vec{q})(\vec{Z}_{s'\alpha'}\cdot\vec{q})}{\vec{q}\cdot\hat{\epsilon}\cdot\vec{q}}\right)^2$$

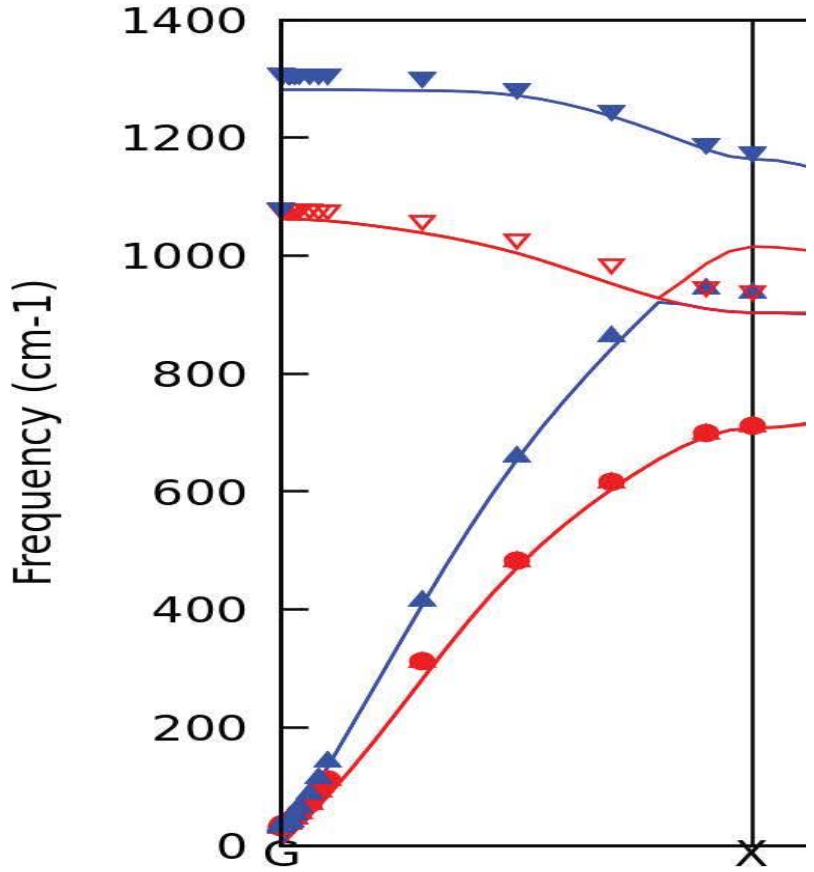
$$\hat{\epsilon}=\begin{bmatrix}4.538 & 0 & 0\\ 0 & 4.538 & 0\\ 0 & 0 & 4.538\end{bmatrix}\qquad \vec{Z}_B=-\vec{Z}_N=\begin{bmatrix}1.864 & 0 & 0\\ 0 & 1.864 & 0\\ 0 & 0 & 1.864\end{bmatrix}$$

	average m.e.	QE
$\mathcal{D}_{s\alpha,s'\alpha'}(\vec{q}=0)$	1062 cm^{-1}	1078 cm^{-1}
$\mathcal{D}_{s\alpha,s'\alpha'}(\vec{q}\to 0)$	1290 cm^{-1}	1307 cm^{-1}

Fourier interpolacija

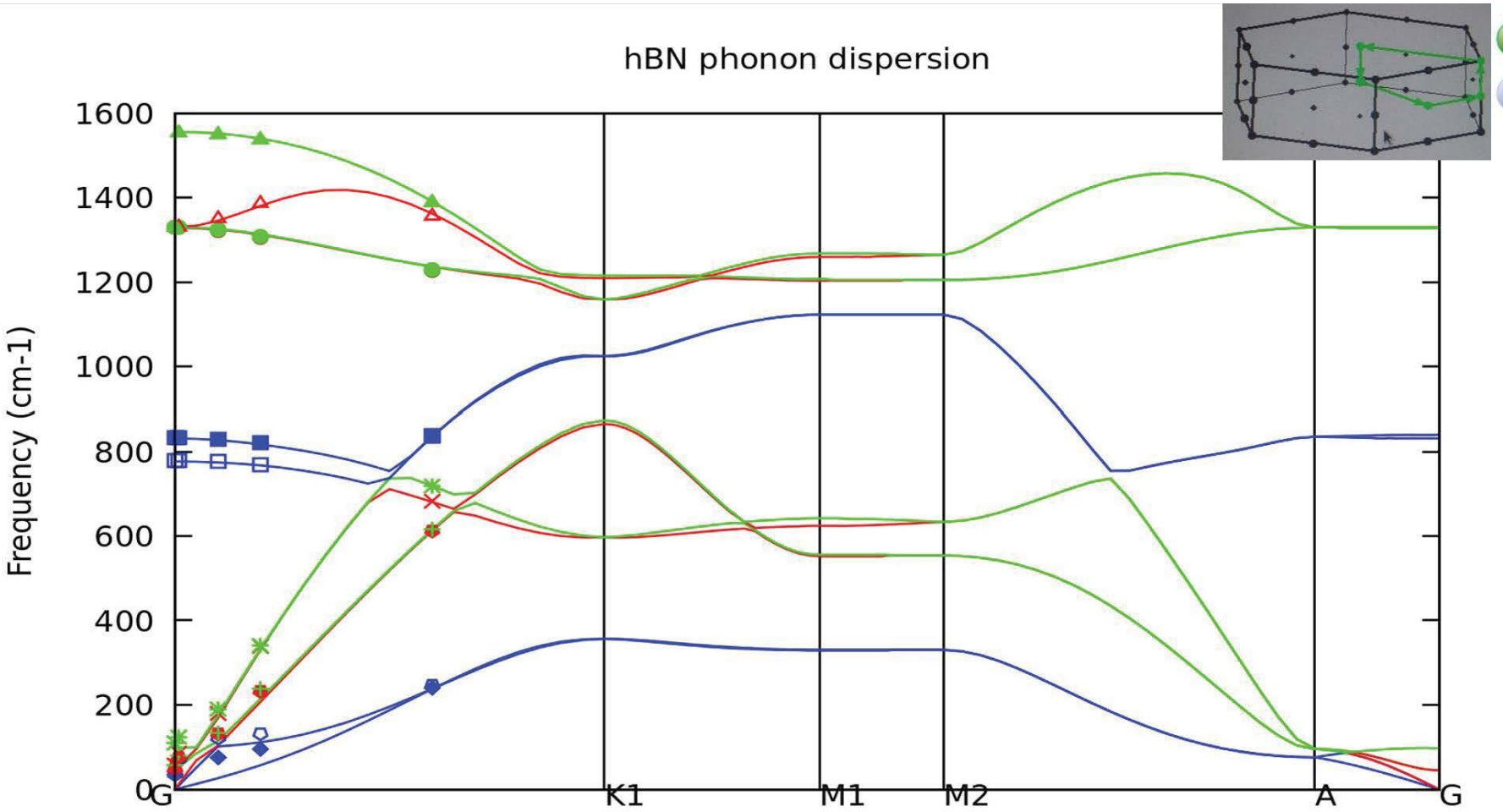
$$\tilde{D}(\vec{q}) = \frac{1}{N}\sum_{\vec{R}} F(\vec{R})e^{-i\vec{q}\vec{R}}$$

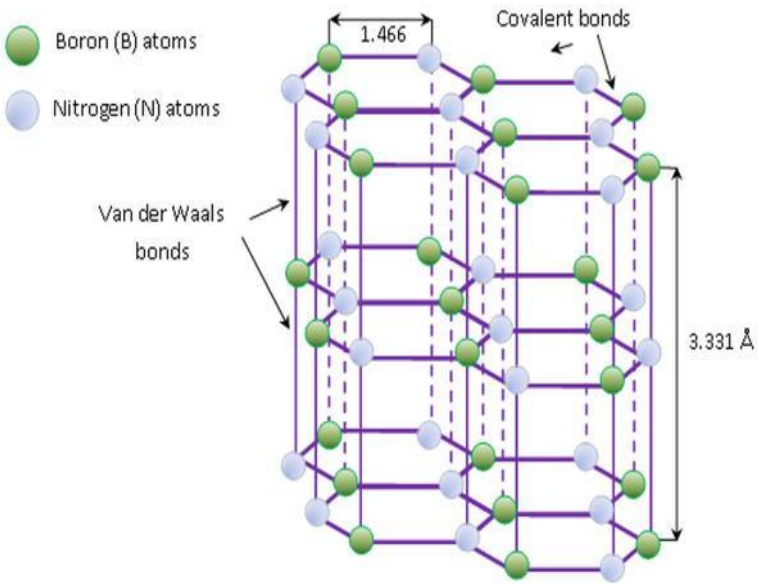
$$F(\vec{R}) = \sum_{\vec{q}\in grid} D(\vec{q})e^{i\vec{q}\vec{R}}$$



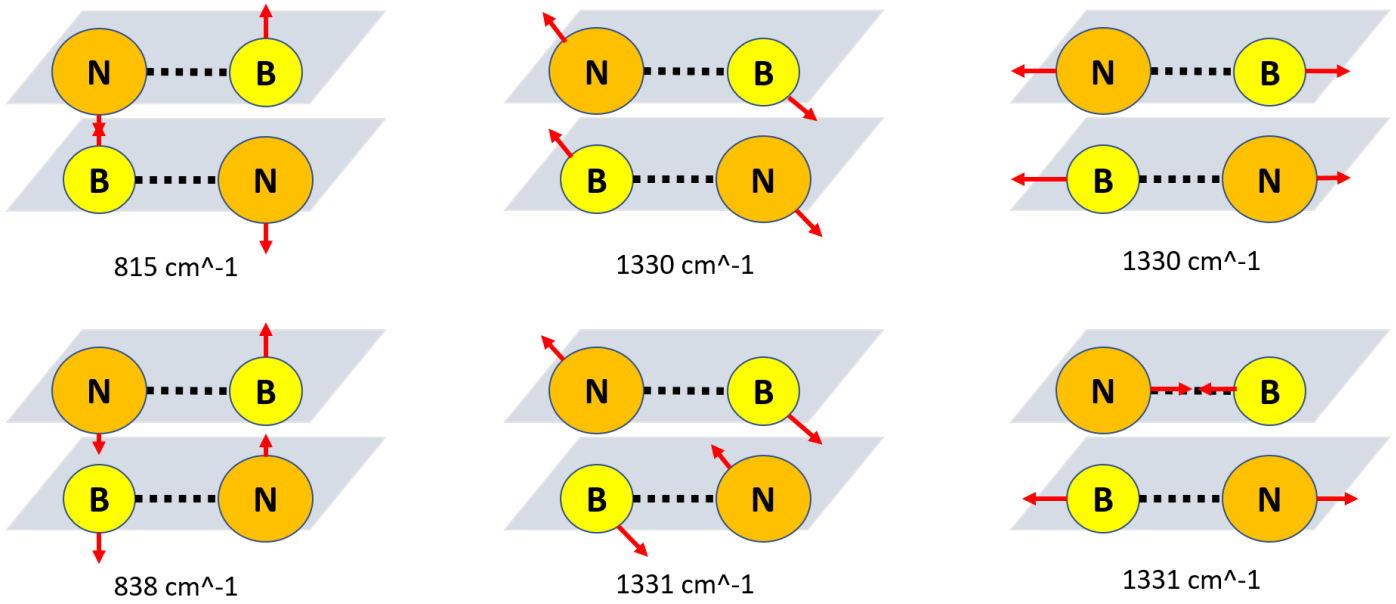
$$\tilde{N}(\vec{q})_{\beta s\beta\prime s\prime} = \sum_{\vec{G}\neq 0} \frac{4\pi}{\Omega} \frac{(q+G)_\alpha Z_{\alpha,\beta s}(q+G)_{\alpha\prime} Z_{\alpha\prime,\beta\prime s\prime}}{(q+G)_\alpha \epsilon_{\alpha\alpha\prime}(q+G)_{\alpha\prime}}$$

hBN – fonon disperzija

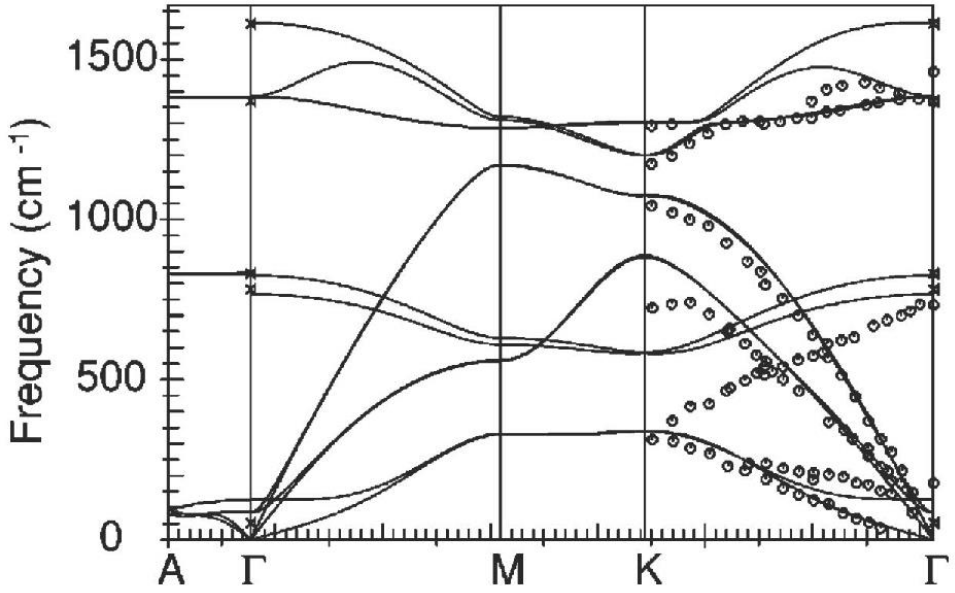




Rezultati dobiveni DFT računom za hBN

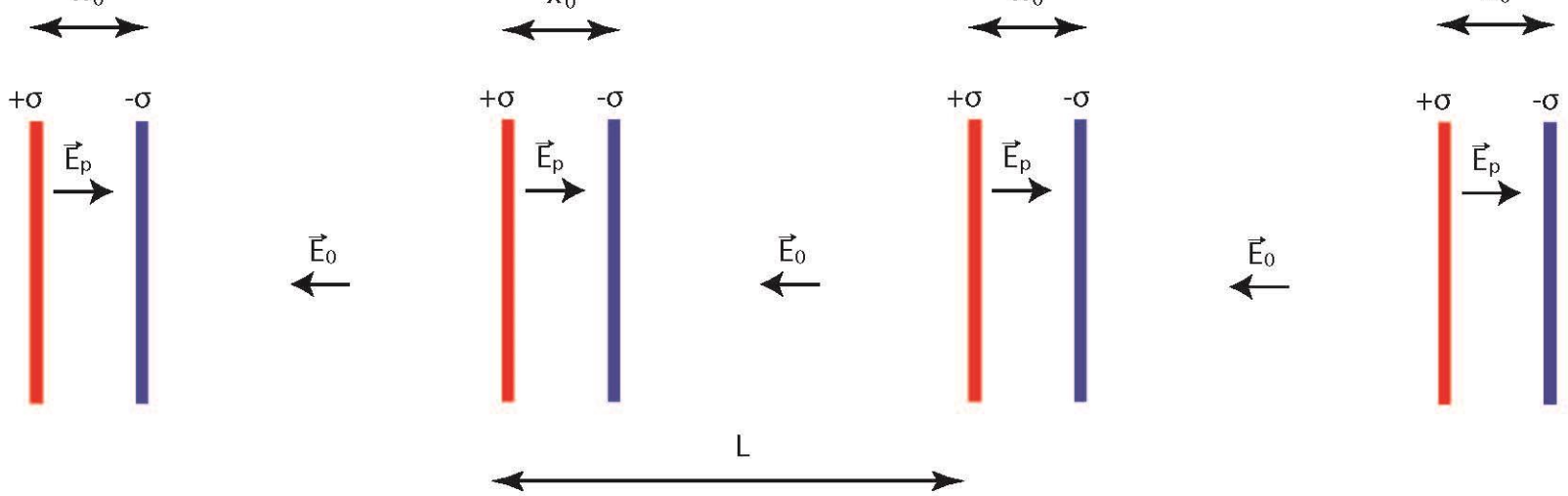


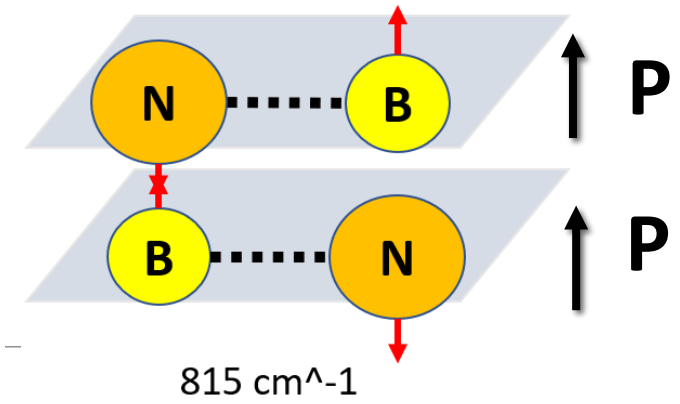
Optički modovi

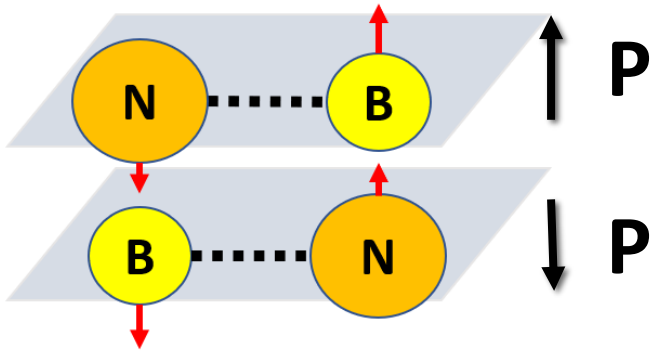


Eksperimentalni podatci:

- Infra crveno zračenje
- Raman
- HREELS







Kako bi dobili periodički potencijal potrebno je dodati vanjsko električno polje :

$$E_0 = -\sigma\ x_0/L$$

Makroskopsko polje u jednom sloju hBN-a:

$$P = \sigma\ x_0/L$$

Linearni odziv: $P = \chi\, E$

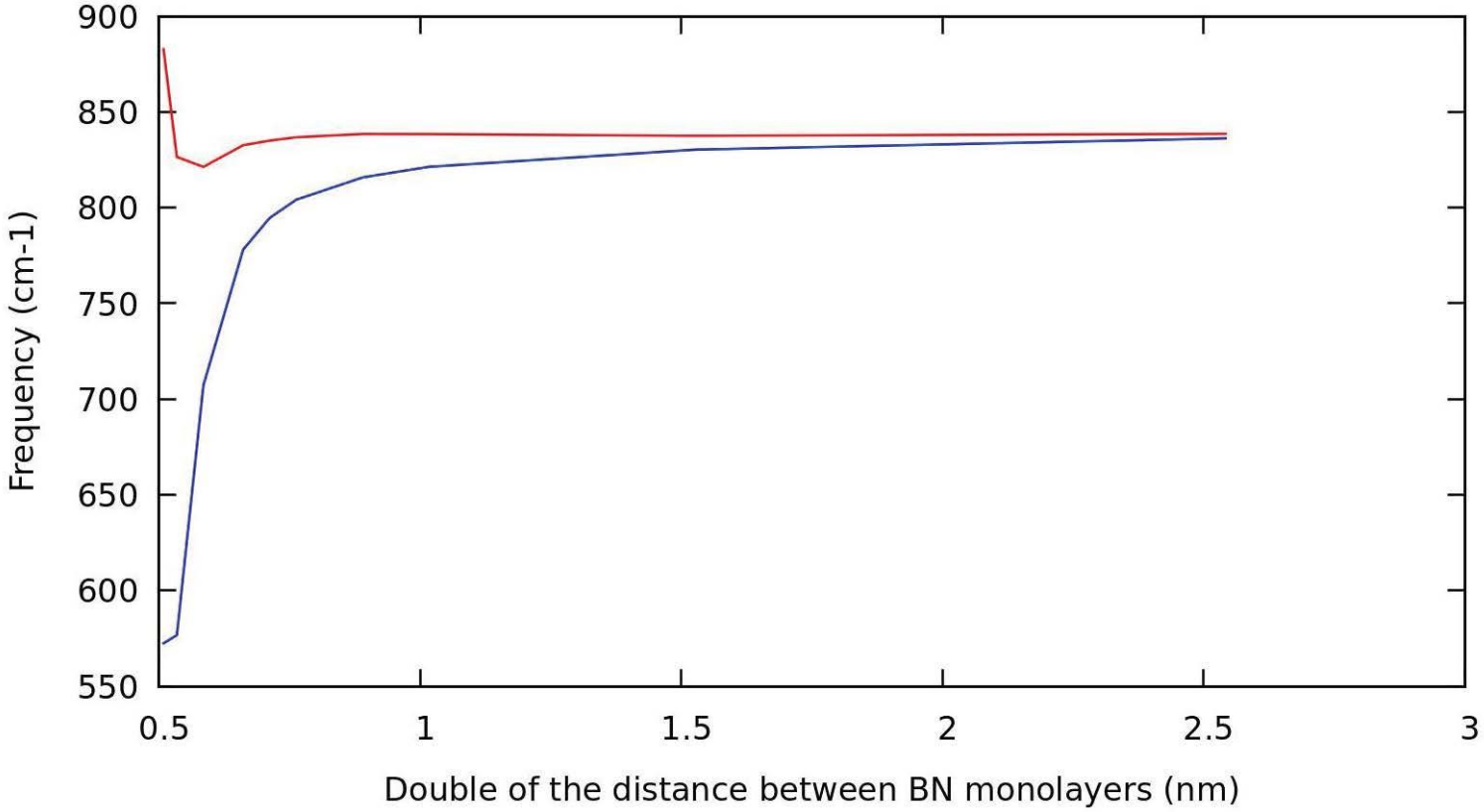
External filed in relation to mean electric field:

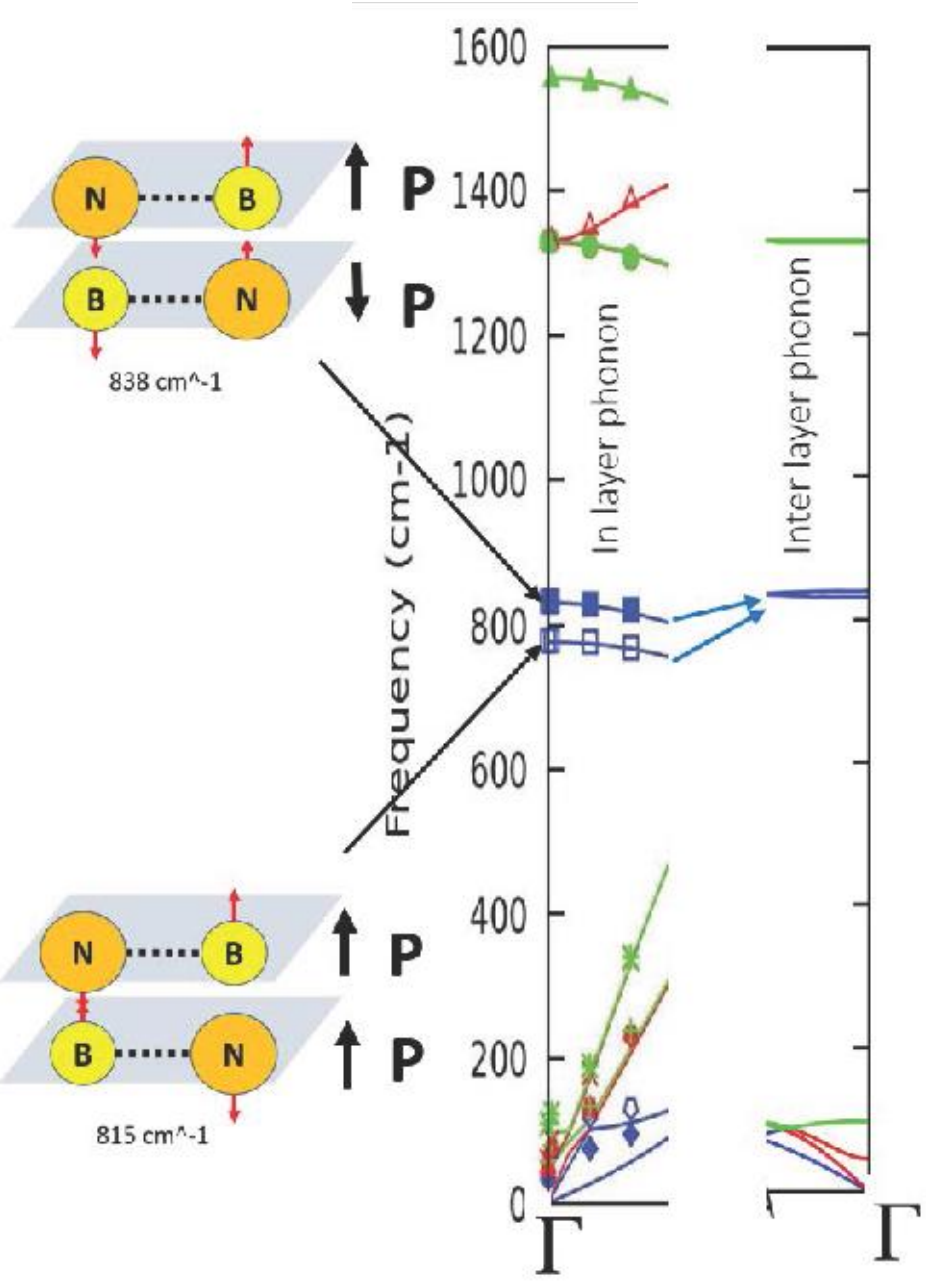
$$E_0 = (1 + 4\pi\chi)E = D = \epsilon E$$

U slučaju LO moda s paralelnim P:

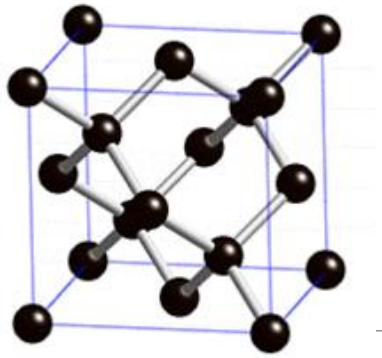
$$q \parallel E, D,\ E = -4\pi P$$

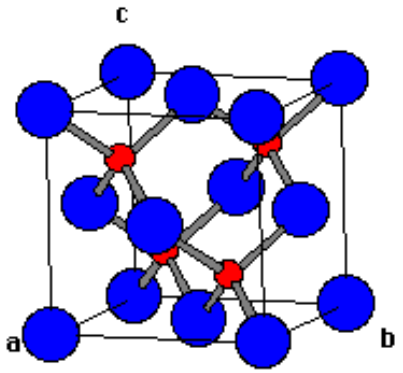
Optički modovi u z smjeru

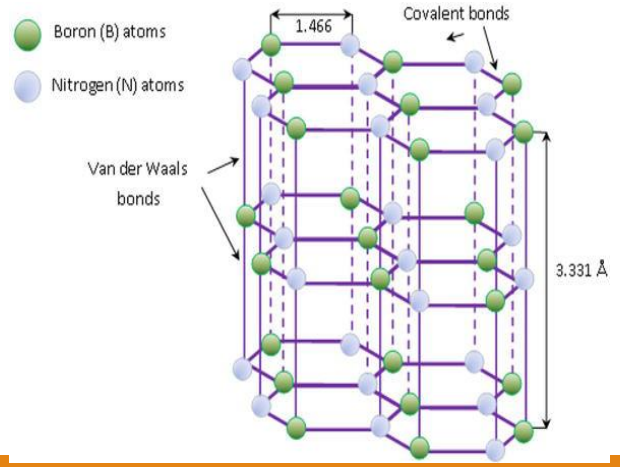


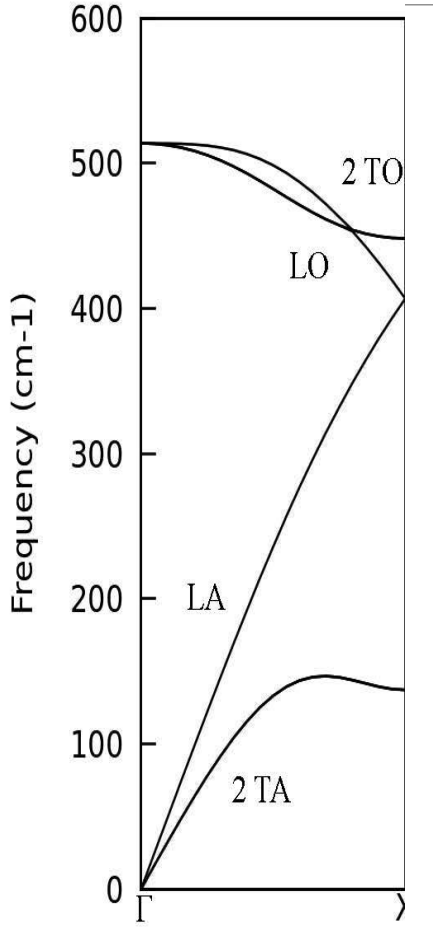


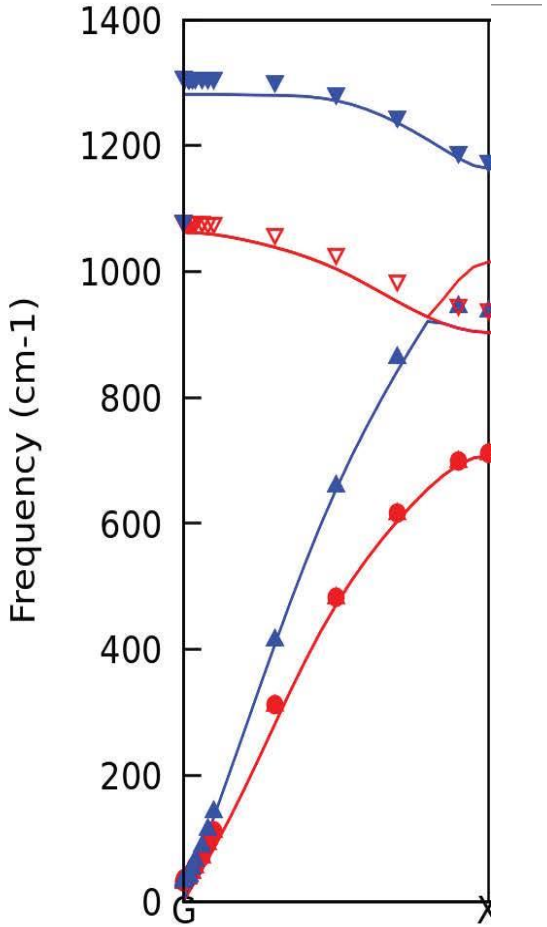
Zaključak

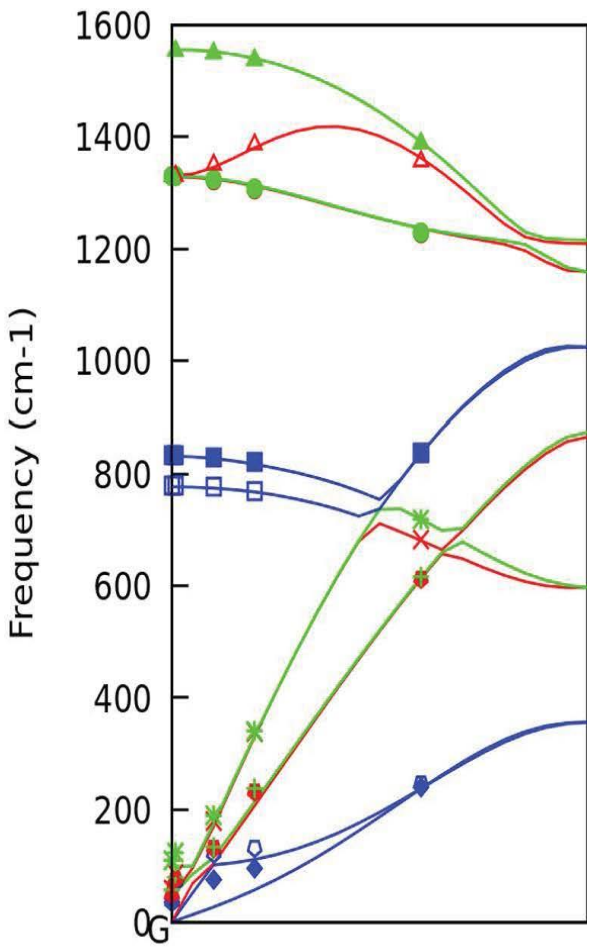



c
a
b


Boron (B) atoms
Nitrogen (N) atoms
1.466
Covalent bonds
Van der Waals bonds
3.331 Å


Frequency (cm-1)
600
500
400
300
200
100
0
2 TO
LO
LA
2 TA
Γ
X


Frequency (cm-1)
1400
1200
1000
800
600
400
200
0
G
X


Frequency (cm-1)
1600
1400
1200
1000
800
600
400
200
0
G