Anharmonic energy in periodic systems

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Vibrational properties overview

- Harmonic phonons are a very good approximation.
- Anharmonic phonons: light elements, hydrogen bonds, high temperatures, . . .

- Interacting phonons:
  - Phase stability.
  - Thermal expansion.
- Electron-phonon coupling:
  - Temperature dependence of band gaps.
  - Superconductivity.

Outline

Outline

Condensed matter Hamiltonian

$$\begin{aligned}\hat{H} &= -\frac{1}{2}\sum_i \nabla_i^2 - \frac{1}{2m_\alpha}\sum_\alpha \nabla_\alpha^2 \\ &+\frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \sum_\alpha \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{r}_\alpha|} + \frac{1}{2}\sum_\alpha \sum_{\beta\neq\alpha} \frac{Z_\alpha Z_\beta}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|}\end{aligned}$$

Born-Oppenheimer approximation

- Trial wavefunction:

$$\Psi_m(\{\mathbf{r}_i\},\{\mathbf{r}_\alpha\}) = \psi_m(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\})\Phi(\{\mathbf{r}_\alpha\}) \tag{1}$$

- Equations of motion:

$$\begin{aligned} \hat{H}_e\psi_m(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\}) &= \epsilon_m(\{\mathbf{r}_\alpha\})\psi_m(\{\mathbf{r}_i\};\{\mathbf{r}_\alpha\}) \\ \hat{H}_{\text{vib}}\Phi(\{\mathbf{r}_\alpha\}) &= E\Phi(\{\mathbf{r}_\alpha\}) \end{aligned}$$

- Decoupled Hamiltonians:

$$\begin{aligned} \hat{H}_e &= -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_i\sum_{j\neq i}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_i\sum_\alpha \frac{Z_\alpha}{|\mathbf{r}_i-\mathbf{r}_\alpha|} \\ &\quad + \frac{1}{2}\sum_\alpha\sum_{\beta\neq\alpha}\frac{Z_\alpha Z_\beta}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|} \\ \hat{H}_{\text{vib}} &= -\frac{1}{2}\sum_\alpha \frac{1}{m_\alpha}\nabla_\alpha^2 + \epsilon_m(\{\mathbf{r}_\alpha\}) \end{aligned}$$

Harmonic approximation

- Vibrational Hamiltonian in $\{\mathbf{r}_\alpha\}$ (or $\{\mathbf{u}_\alpha\}$):

$$\hat{H}_{\text{vib}} = -\frac{1}{2}\sum_{\mathbf{R}_p,\alpha}\frac{1}{m_\alpha}\nabla^2_{p\alpha} + \frac{1}{2}\sum_{\mathbf{R}_p,\alpha;\mathbf{R}_{p'},\beta}\mathbf{u}_{p\alpha}\boldsymbol{\Phi}_{p\alpha;p'\beta}\mathbf{u}_{p'\beta}$$

- Normal mode analysis: $\{\mathbf{u}_{p\alpha}\} \longrightarrow \{q_{\mathbf{k}s}\}$

$$\begin{aligned} u_{p\alpha;i} &= \frac{1}{\sqrt{N_0 m_\alpha}}\sum_{\mathbf{k},s} q_{\mathbf{k}s} e^{i\mathbf{k}\cdot\mathbf{R}_p} w_{\mathbf{k}s;i\alpha} \\ q_{\mathbf{k}s} &= \frac{1}{\sqrt{N_0}}\sum_{\mathbf{R}_p,\alpha,i}\sqrt{m_\alpha}\, u_{p\alpha;i} e^{-i\mathbf{k}\cdot\mathbf{R}_p} w_{-\mathbf{k}s;i\alpha} \end{aligned}$$

- Vibrational Hamiltonian in $\{q_{\mathbf{k}s}\}$:

$$\hat{H}_{\text{vib}} = \sum_{\mathbf{k},s}\left(-\frac{1}{2}\frac{\partial^2}{\partial q^2_{\mathbf{k}s}} + \frac{1}{2}\omega^2_{\mathbf{k}s} q^2_{\mathbf{k}s}\right)$$

Principal axes approximation to the BO energy surface

$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k},s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2} \sum_{\mathbf{k},s} \sum_{\mathbf{k}',s'}{}' V_{\mathbf{k}s;\mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \cdots$$

- Static lattice DFT total energy
- DFT total energy along frozen independent phonon
- DFT total energy along frozen coupled phonons

Vibrational self-consistent field equations

- Phonon Schrödinger equation:

$$\left(\sum_{\mathbf{k},s} -\frac{1}{2}\frac{\partial^2}{\partial q_{\mathbf{k}s}^2} + V(\{q_{\mathbf{k}s}\})\right)\Phi(\{q_{\mathbf{k}s}\}) = E\Phi(\{q_{\mathbf{k}s}\})$$

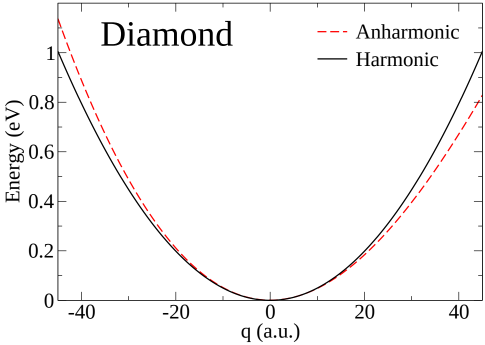
- Ground state ansatz: $\Phi(\{q_{\mathbf{k}s}\}) = \prod_{\mathbf{k},s} \phi_{\mathbf{k}s}(q_{\mathbf{k}s})$
- Self-consistent equations:

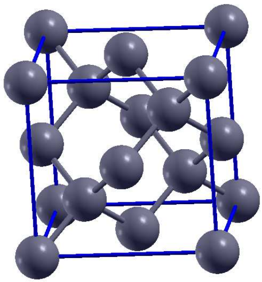
$$\left(-\frac{1}{2}\frac{\partial^2}{\partial q_{\mathbf{k}s}^2} + \overline{V}_{\mathbf{k}s}(q_{\mathbf{k}s})\right)\phi_{\mathbf{k}s}(q_{\mathbf{k}s}) = \lambda_{\mathbf{k}s}\phi_{\mathbf{k}s}(q_{\mathbf{k}s})$$

$$\overline{V}_{\mathbf{k}s}(q_{\mathbf{k}s}) = \left\langle \prod_{\mathbf{k}',s'}{}' \phi_{\mathbf{k}'s'}(q_{\mathbf{k}'s'}) \middle| V(\{q_{\mathbf{k}''s''}\}) \middle| \prod_{\mathbf{k}',s'}{}' \phi_{\mathbf{k}'s'}(q_{\mathbf{k}'s'}) \right\rangle$$

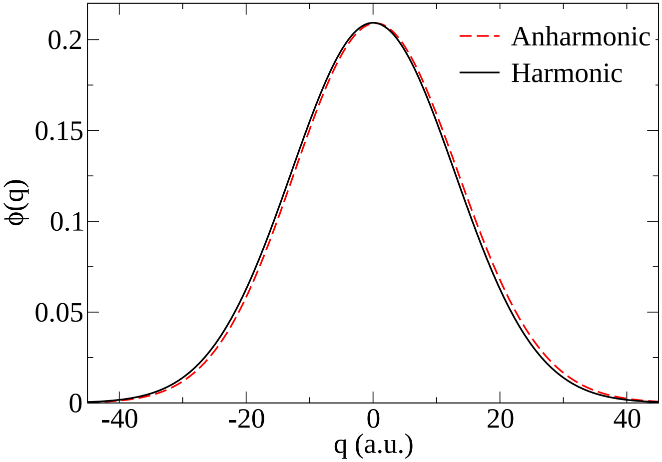
Diamond independent phonon term (I)

$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k},s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2}\sum_{\mathbf{k},s}\sum_{\mathbf{k}',s'}{}' V_{\mathbf{k}s;\mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \cdots$$



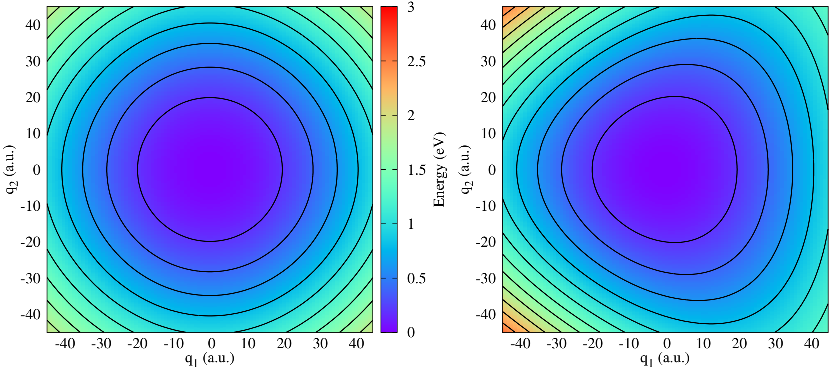


Diamond independent phonon term (II)



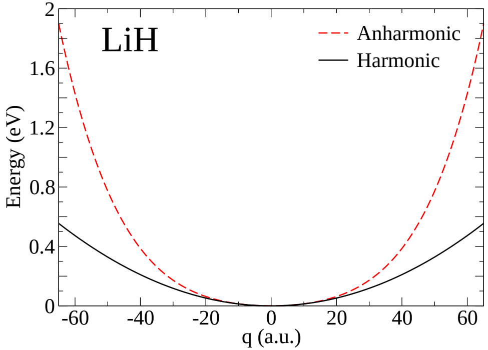
Diamond coupled phonons term

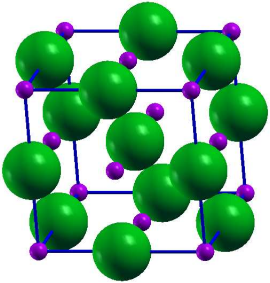
$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k},s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2}\sum_{\mathbf{k},s}\sum_{\mathbf{k}',s'}{}' V_{\mathbf{k}s;\mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \cdots$$



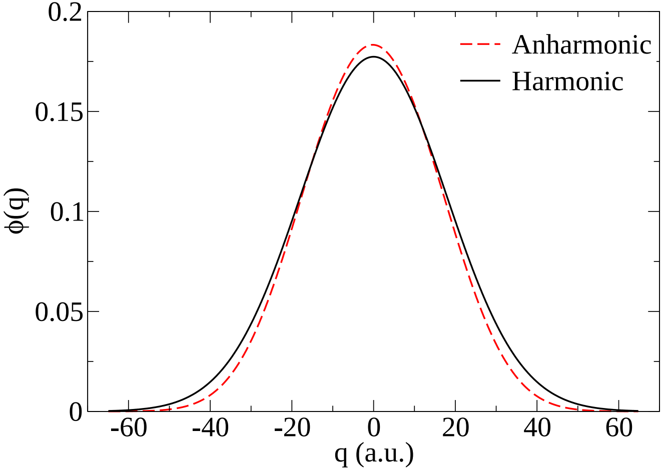
LiH independent phonon term (I)

$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k},s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2}\sum_{\mathbf{k},s}\sum_{\mathbf{k}',s'}{}' V_{\mathbf{k}s;\mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \cdots$$



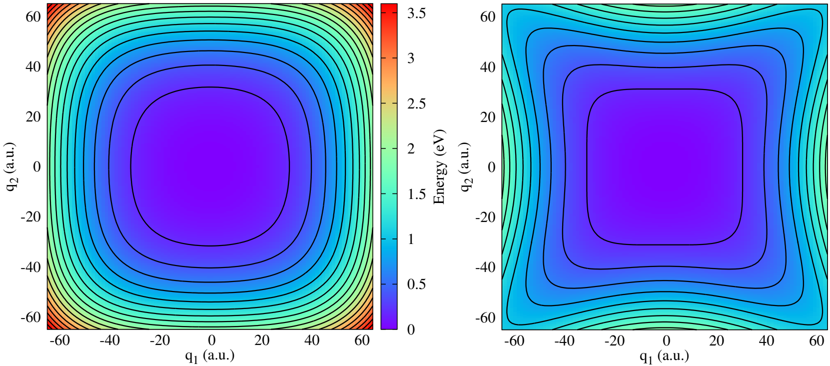


LiH independent phonon term (II)



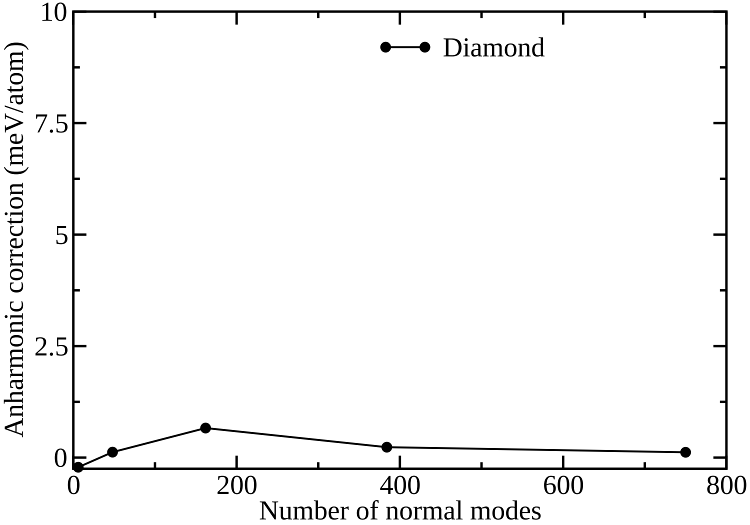
LiH coupled phonons term

$$V(\{q_{\mathbf{k}s}\}) = V(0) + \sum_{\mathbf{k},s} V_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2}\sum_{\mathbf{k},s}\sum_{\mathbf{k}',s'}{}' V_{\mathbf{k}s;\mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \cdots$$

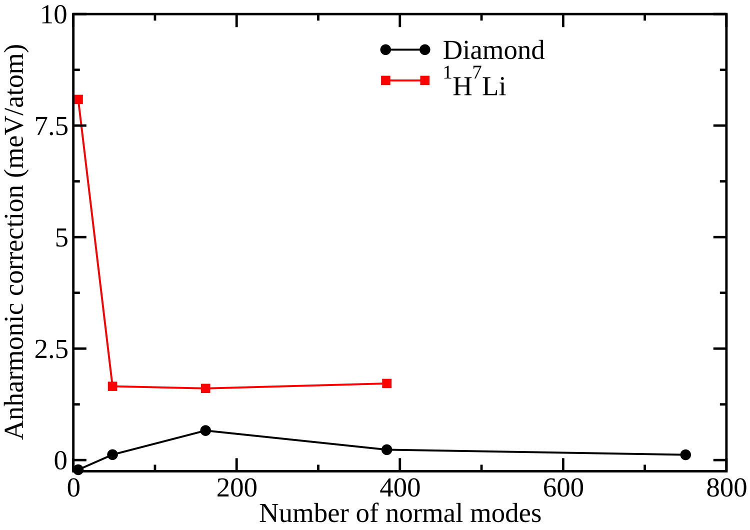


Outline

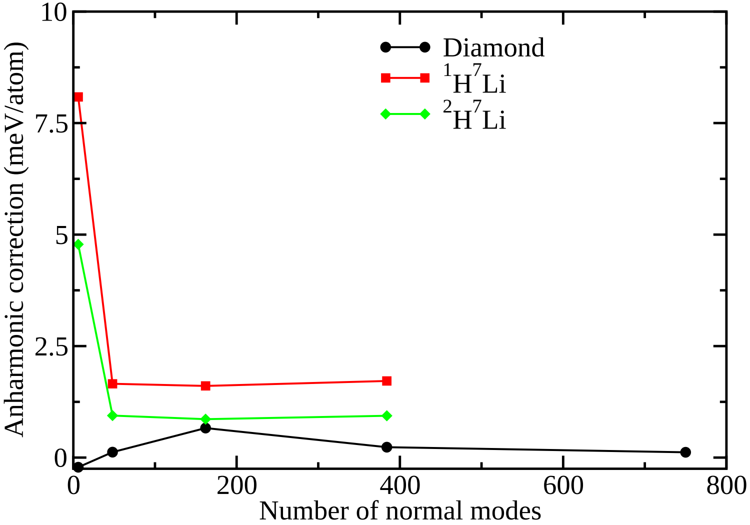
Anharmonic ZPE correction



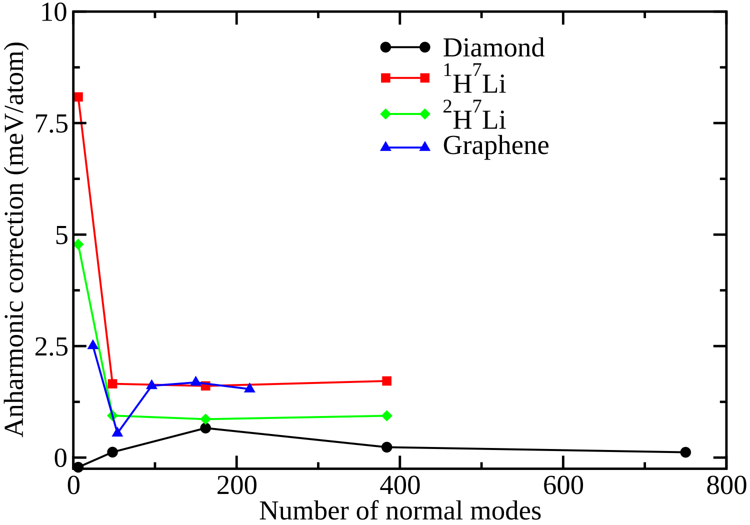
Anharmonic ZPE correction



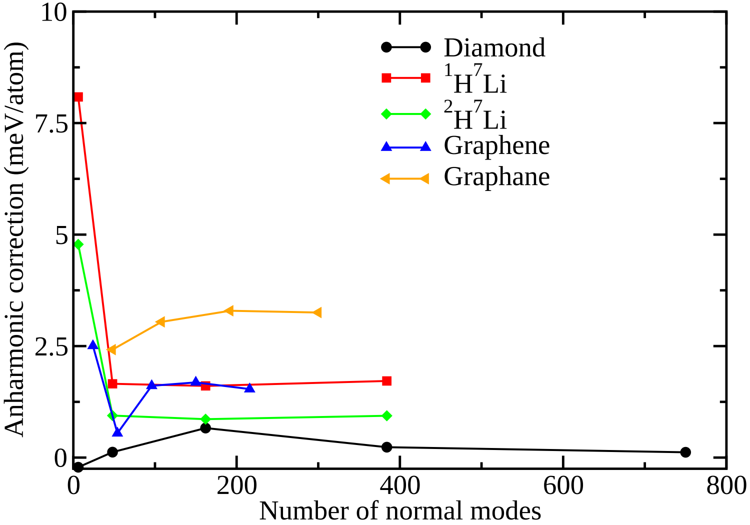
Anharmonic ZPE correction



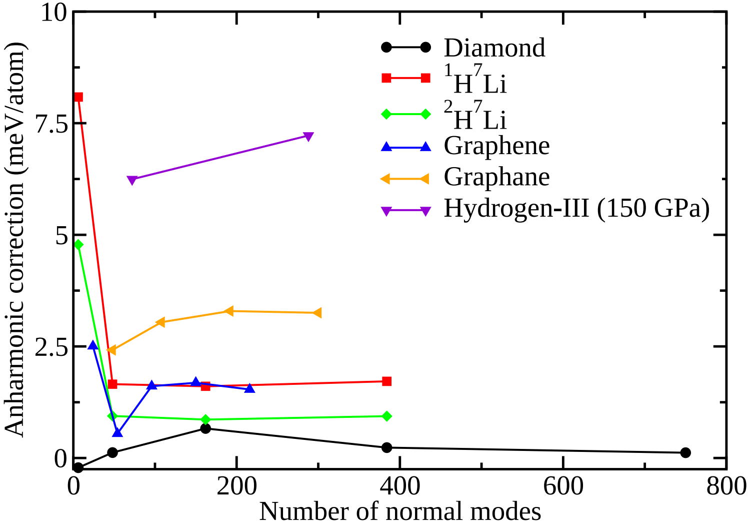
Anharmonic ZPE correction



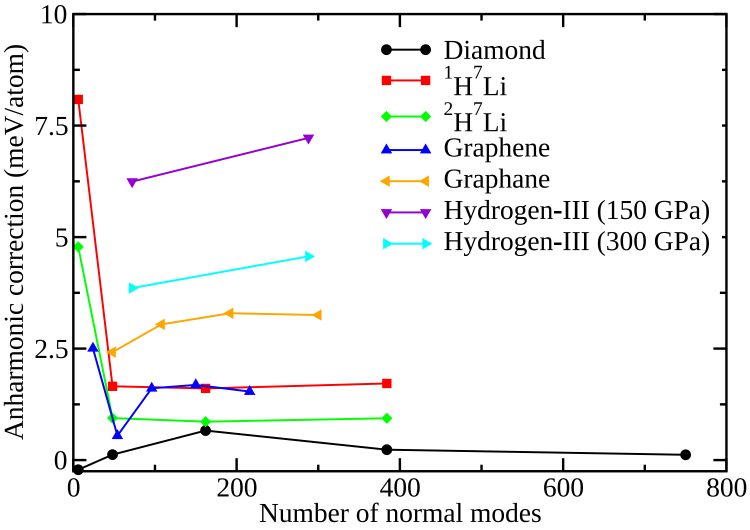
Anharmonic ZPE correction



Anharmonic ZPE correction



Anharmonic ZPE correction



Outline

Theoretical background

Born-Oppenheimer and harmonic approximations

Vibrational self-consistent field

Results

Conclusions

Conclusions

Summary:

- Principal axes approximation to the Born-Oppenheimer energy surface.
- VSCF method for the solution of the vibrational equation.
- Examples of anharmonic energy correction.

Extended framework (see future talk):

- Phonon expectation values for general phonon-dependent operators.
- Electron-phonon interactions, stress tensor, mean atomic positions, hyperfine tensor, . . .

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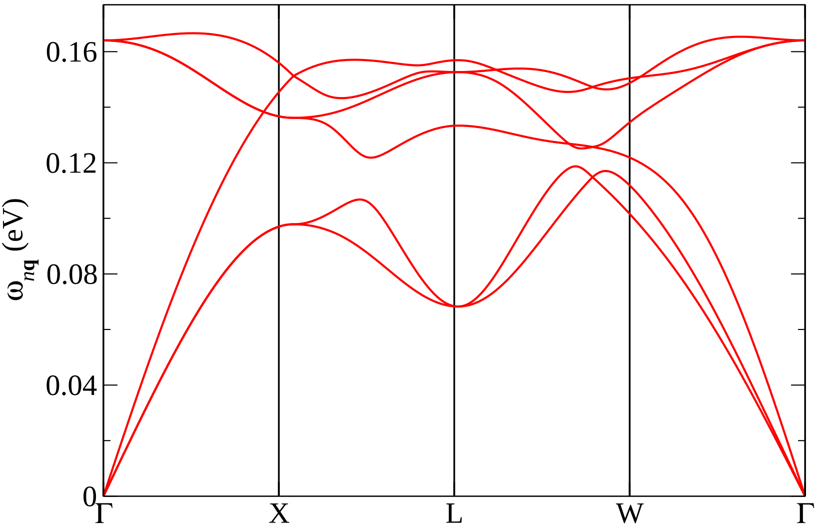
  - TCM group
  - EPSRC

- References:
  - B. Monserrat, N.D. Drummond, R.J. Needs, arXiv:1303.0745

Outline

Additional Material

Additional Material: diamond phonon dispersion



Additional Material: LiH phonon dispersion