Lattice Dynamics: From Phonons to Thermodynamics

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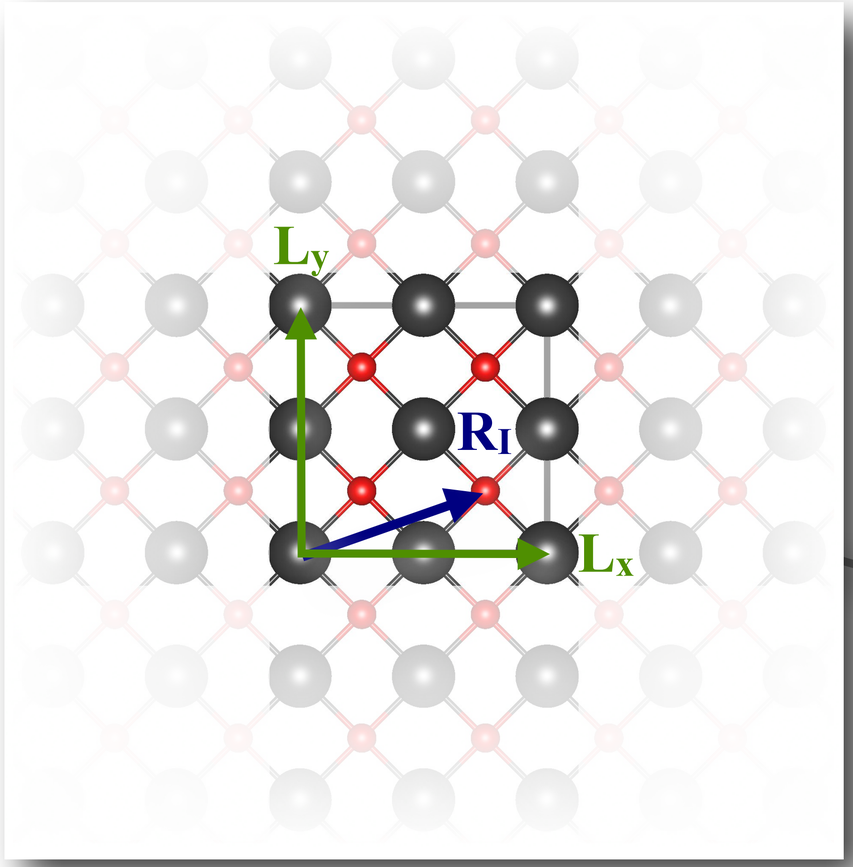
June 12, 2025

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Crystalline Solids

$$\mathbf{R}_{I,lmn} = \mathbf{R}_I + l\,\mathbf{L}_x + m\,\mathbf{L}_y + n\,\mathbf{L}_z \qquad l,m,n \in \mathbb{Z}$$

Idealized Crystal Structure



Infinite grid of **immobile** atoms
with **perfect periodicity**!

```
# Crystal lattice
lattice_vector 5.0   0   0
lattice_vector   0 5.0   0
lattice_vector   0   0 5.0
# Atomic basis
atom   0    0    0   Zr
atom 2.5    0    0   Zr
atom   0  2.5    0   Zr
atom 2.5  2.5    0   Zr
atom 1.25 1.25   0   O
atom 3.75 1.25   0   O
atom 1.25 3.75   0   O
atom 3.75 3.75   0   O
```

Electronic-Structure Theory

Energy, forces, etc.

Crystalline Solids

$$\mathbf{R}_{I,lmn} = \mathbf{R}_I + l\,\mathbf{L}_x + m\,\mathbf{L}_y + n\,\mathbf{L}_z \qquad l, m, n \in \mathbb{Z}$$

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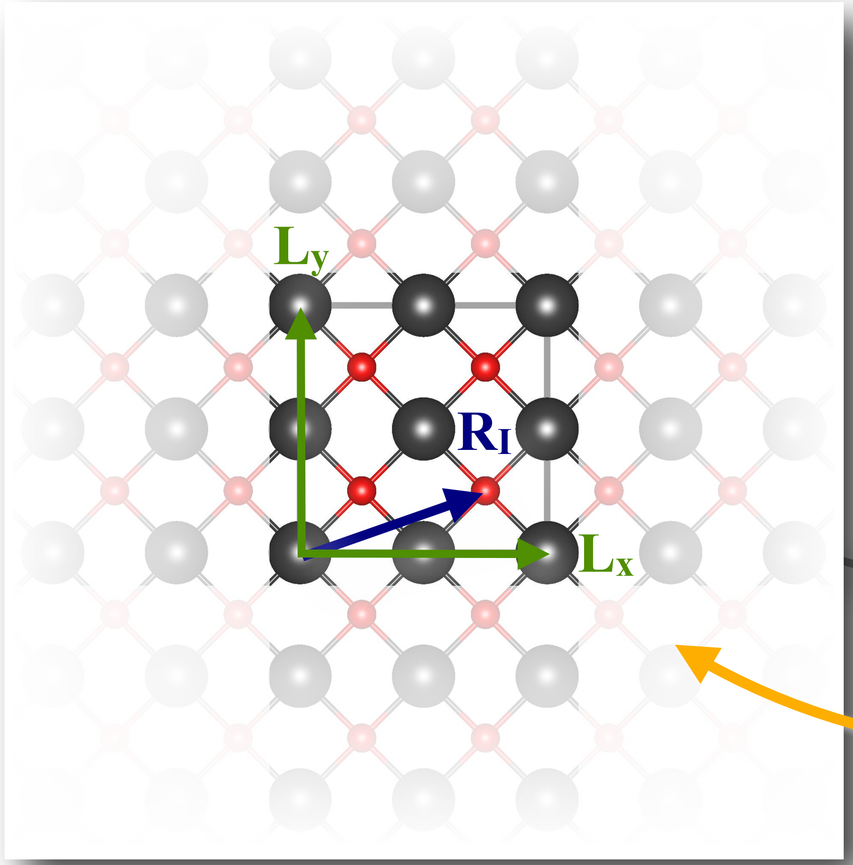

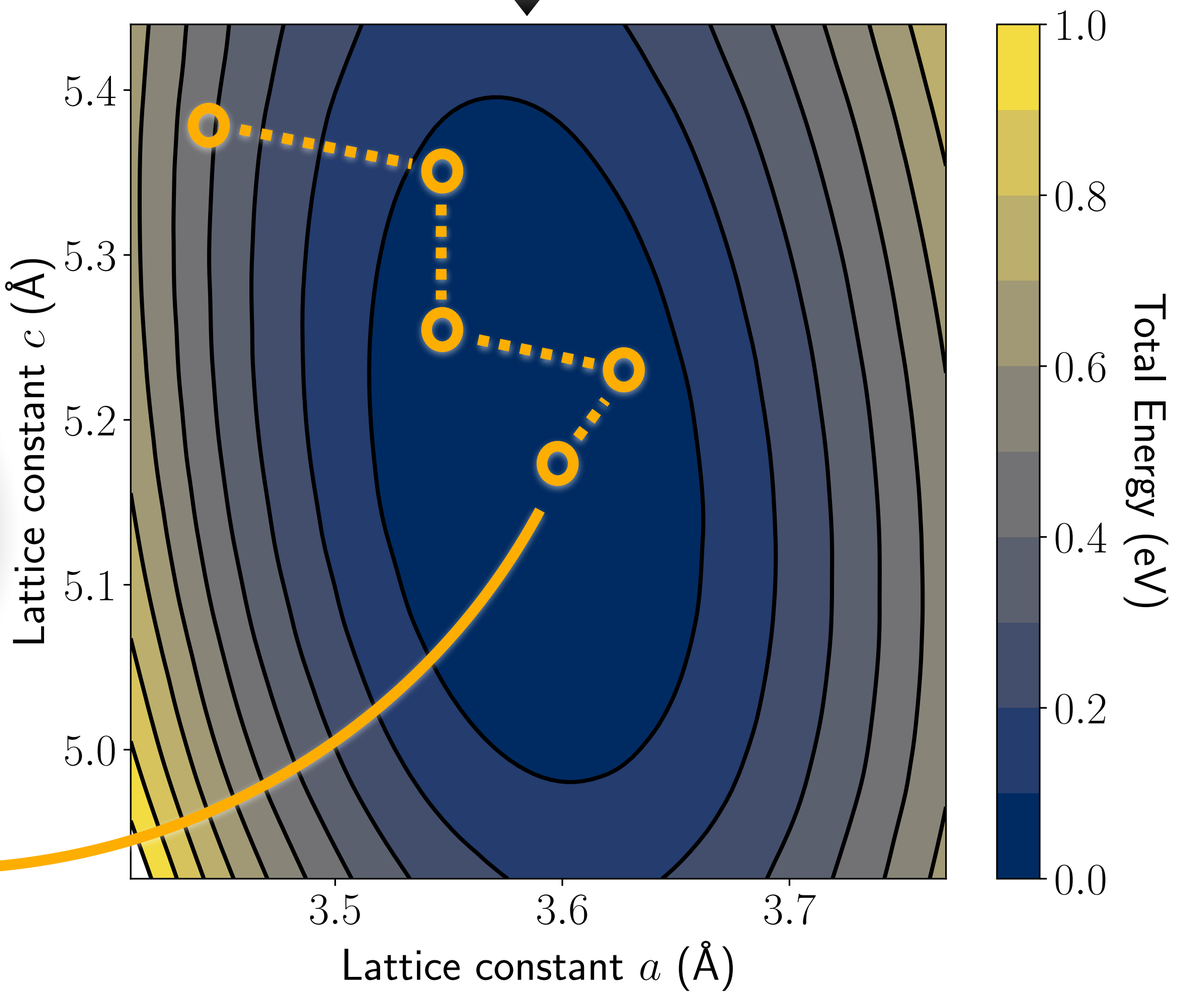

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Crystalline Solids

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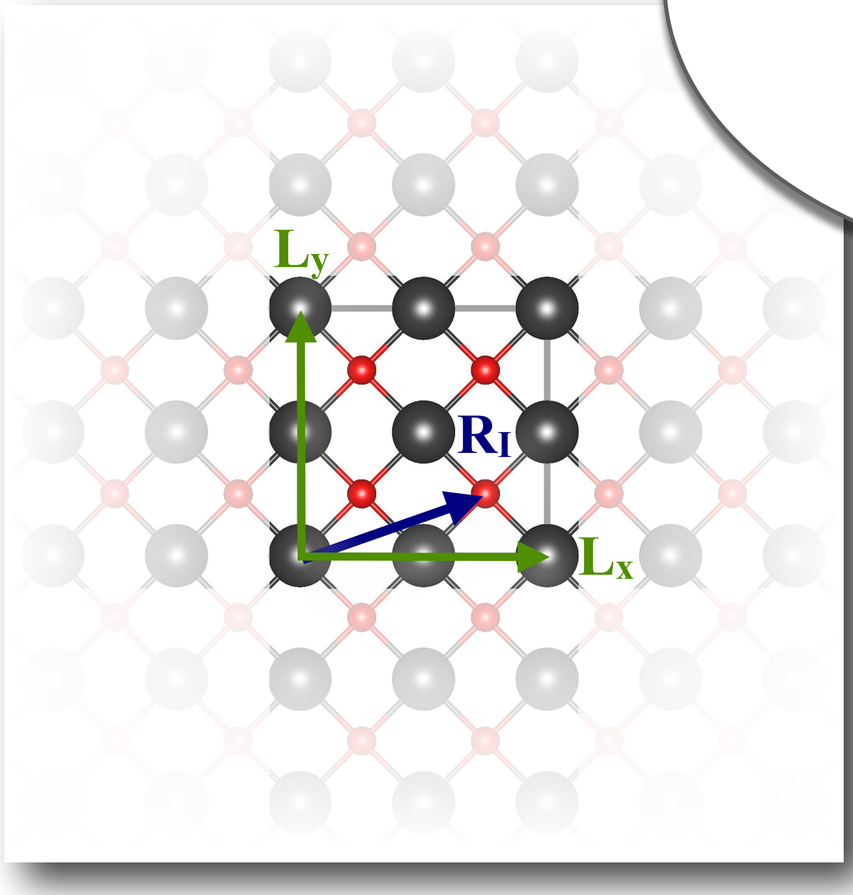


Infinite grid of **immobile** atoms
with **perfect periodicity**!

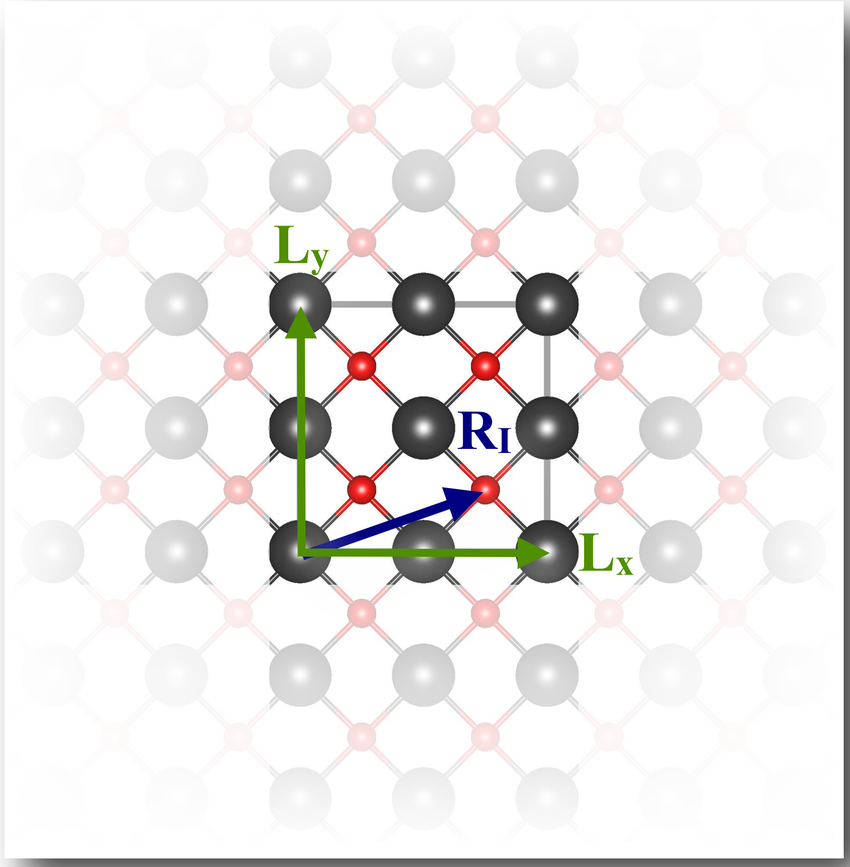
I beg to disagree:

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

Werner Heisenberg

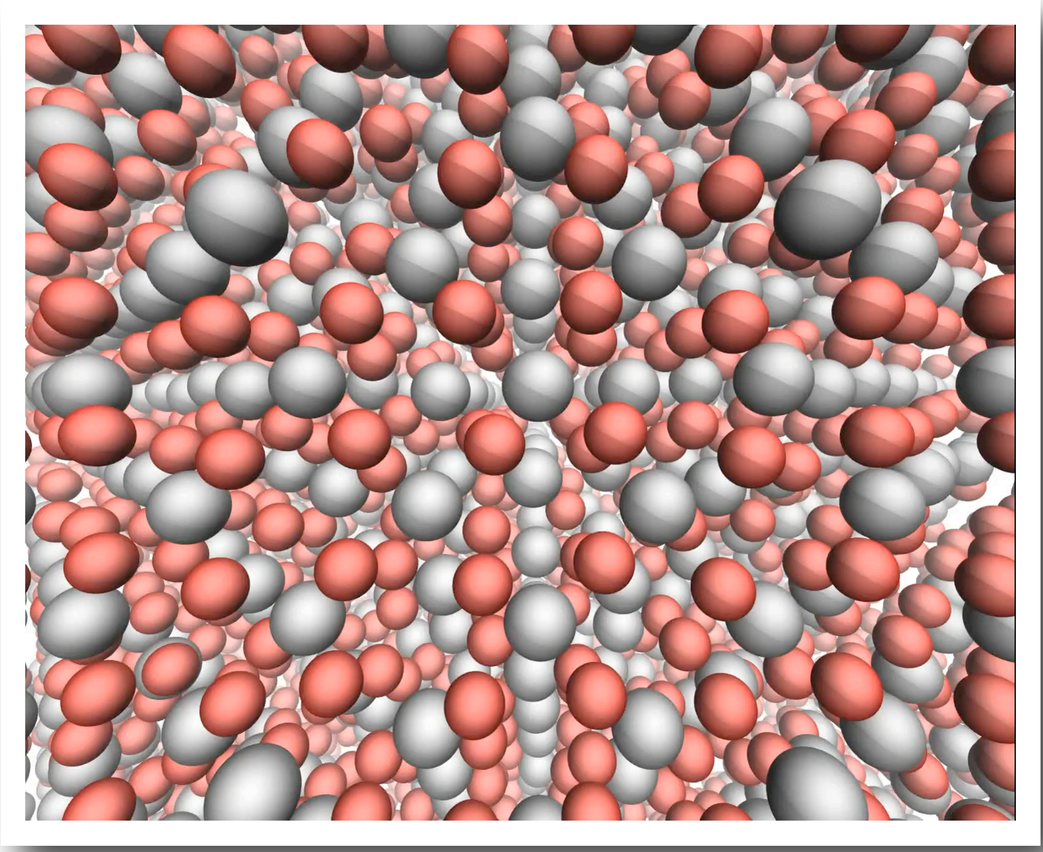
Crystalline Solids

Idealized Crystal Structure



Infinite grid of **immobile** atoms with **perfect periodicity**!

Real Materials



Everything **moves**: Perfect periodicity **broken**!

Failures of the Static Lattice Model

N. W Ashcroft and N. D. Mermin, *"Solid State Physics"* (1976).

- Inaccuracies in the **equilibrium properties** at **0K**:
  Lattice Constants, Cohesive Energies, Elastic Constants,...

- Failure to describe thermodynamic **equilibrium properties**:
  Specific Heat, Thermal Lattice Expansion, Phase Transformations, ...

- Failure to describe thermodynamic **non-equilibrium properties**:

  - ✦ **Charge Transport:** *Electrical AC/DC Conductivity, Superconductivity,...*
  - ✦ **Heat Transport:** *Thermal Conductivity, Transmission of Sound,...*
  - ✦ **Coupling of Charge & Heat Transport:** *Seebeck and Peltier Effect,...*
  - ✦ **Interaction with Radiation:** *X-Ray, Infrared, Neutron, ...*

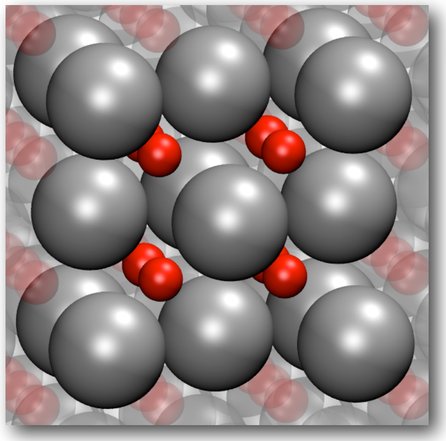
Thermodynamic Equilibrium in a Nutshell

A classical system with *N* **atoms**, a **Volume** *V* and a **Temperature** *T* is described by its **canonical partition function** *Z(T,V,N)* viz. its Helmholtz Free Energy *F(T,V,N)*.

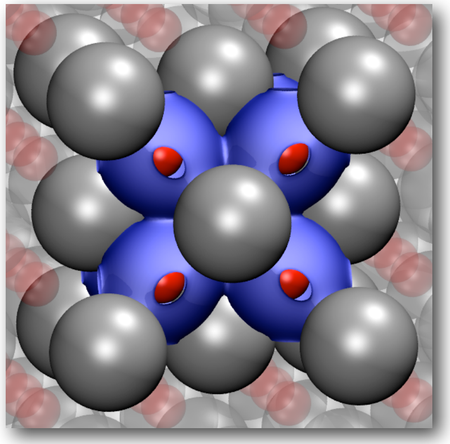
$$
\begin{aligned}
F(T,V,N) &= -k_B \ln\left(Z(T,V,N)\right) \\
&= -k_B \ln\left(\frac{1}{N!\hbar^{3N}} \int \exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right) \{d^3\mathbf{x}_i\}\{d^3\mathbf{p}_i\}\right)
\end{aligned}
$$

Calculating the energy of **all possible configurations** $\{x_i\}$ is numerically **unfeasible** even for very small systems.

Molecular Dynamics



Electronic Structure Theory Code



Input:
Geometry, Species

Output:
total **energy** & **forces**

Update geometry

Iterative Approach: Explore the Dynamics of the Atoms!

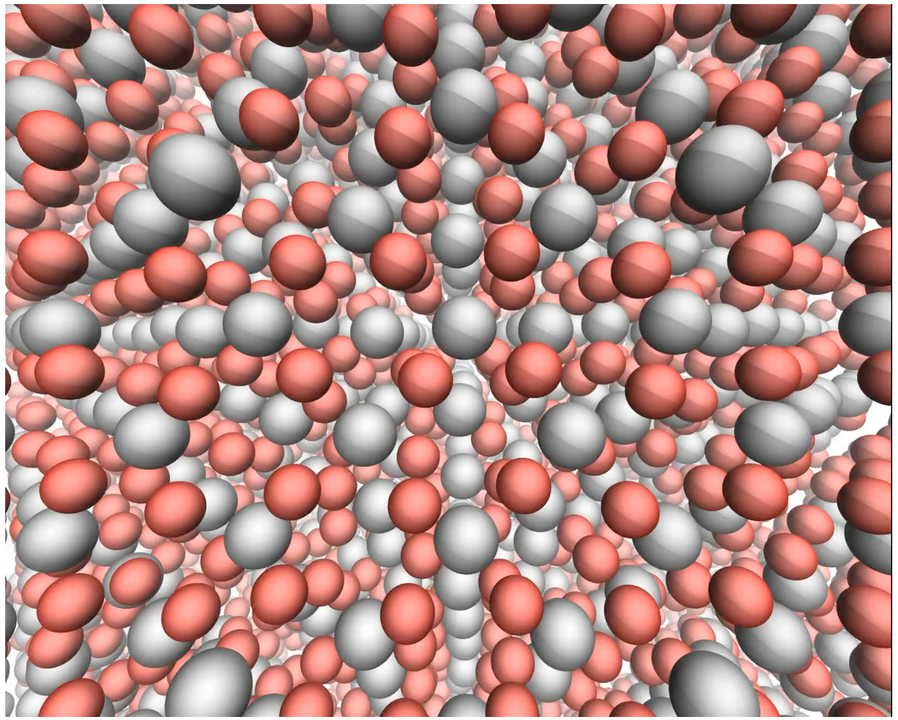
MOLECULAR DYNAMICS

Numerical Integration
of the **equations of motion**

L. Verlet, *Phys. Rev.* **159**, 98 (1967).

$$M_I \ddot{\mathbf{R}}_I(t) = \mathbf{F}_I(\mathbf{R}_1(t), \cdots, \mathbf{R}_N(t))$$

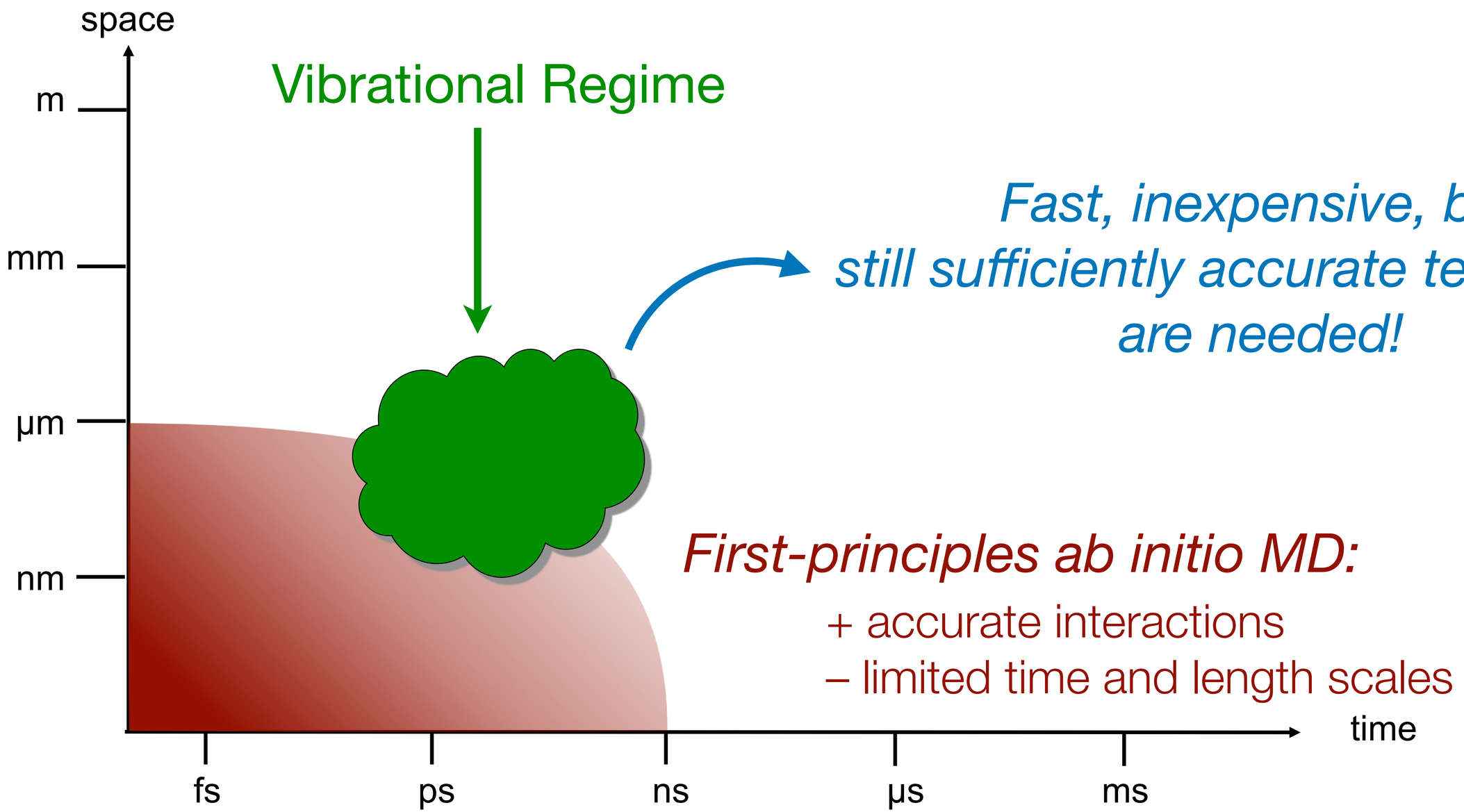
Initial conditions have to be specified!



The **Verlet Algorithm** conserves the number of particles **N**, the volume **V**, and the energy **E**.

⇒ Micro-canonical Ensemble

Time and Length Scales

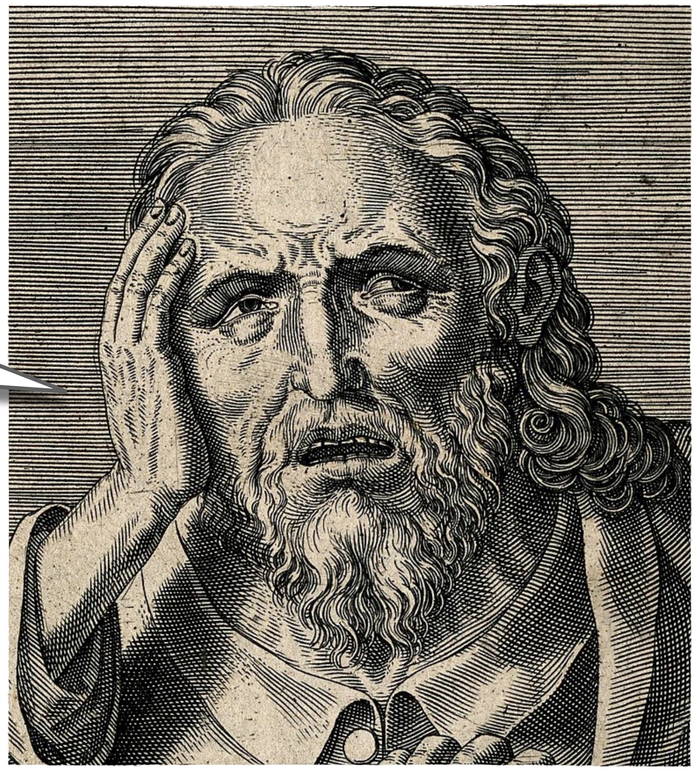


Take-Home Messages

- **Everything moves!** Nuclei and atoms are never at rest.

Panta rhei,

παντα ῥεῖ!



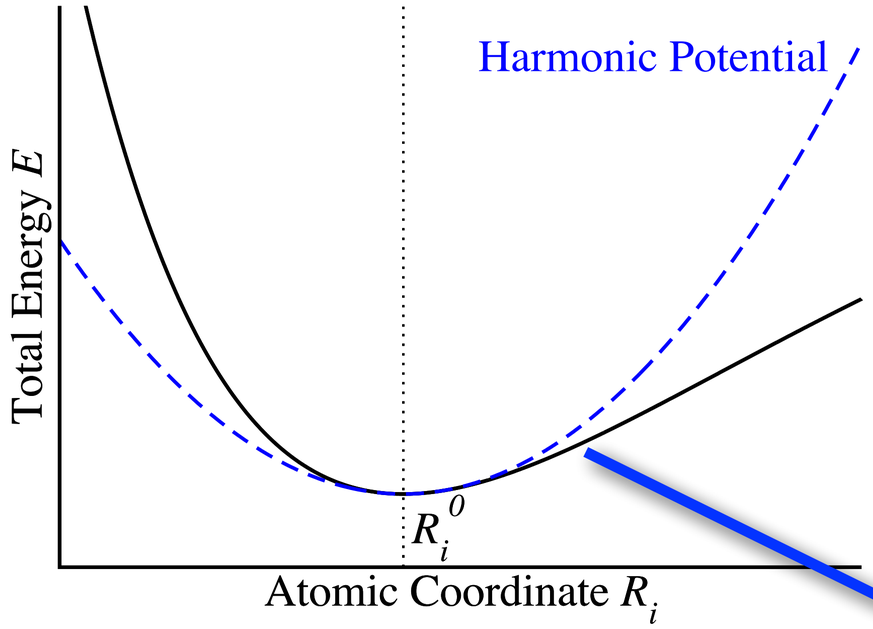
Heraclitus of Ephesus (500 BCE)

The Harmonic Approximation

"Physics is that subset of human experience,
which can be reduced to coupled harmonic oscillators."

Michael Peskin

The Harmonic Approximation



The total energy ***E*** is a ***3N-dimensional surface:***

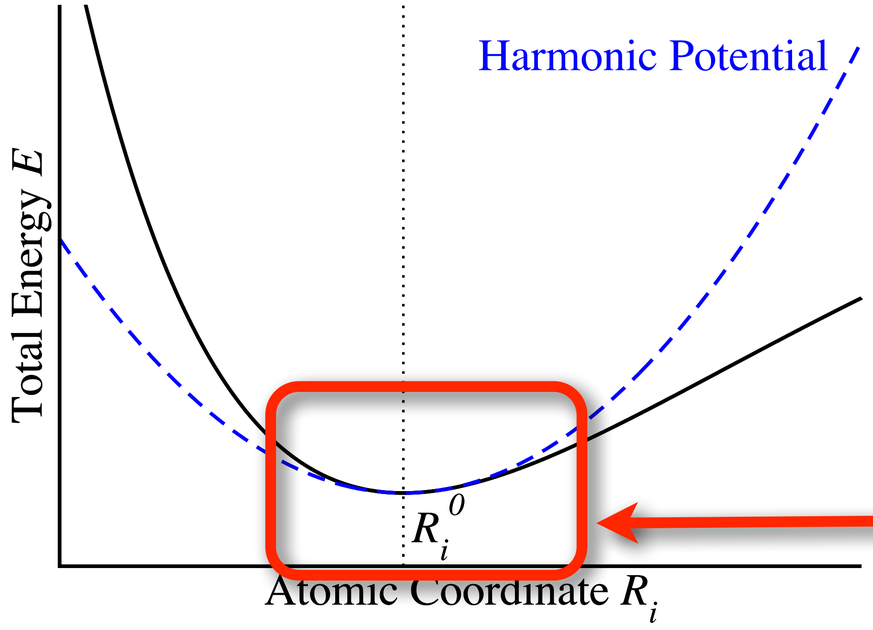
$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

Approximate by Taylor Expansion around the Static Equilibrium

$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \sum_i \frac{\partial E}{\partial \mathbf{R}_i}\bigg|_{\mathbf{R}_0} \Delta\mathbf{R}_i + \frac{1}{2}\sum_{i,j} \frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\bigg|_{\mathbf{R}_0} \Delta\mathbf{R}_i \Delta\mathbf{R}_j$$

Hessian Φ_{ij}

The Harmonic Approximation



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$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

WARNING:
Harmonic Approximation
is only valid
for **small** displacements!

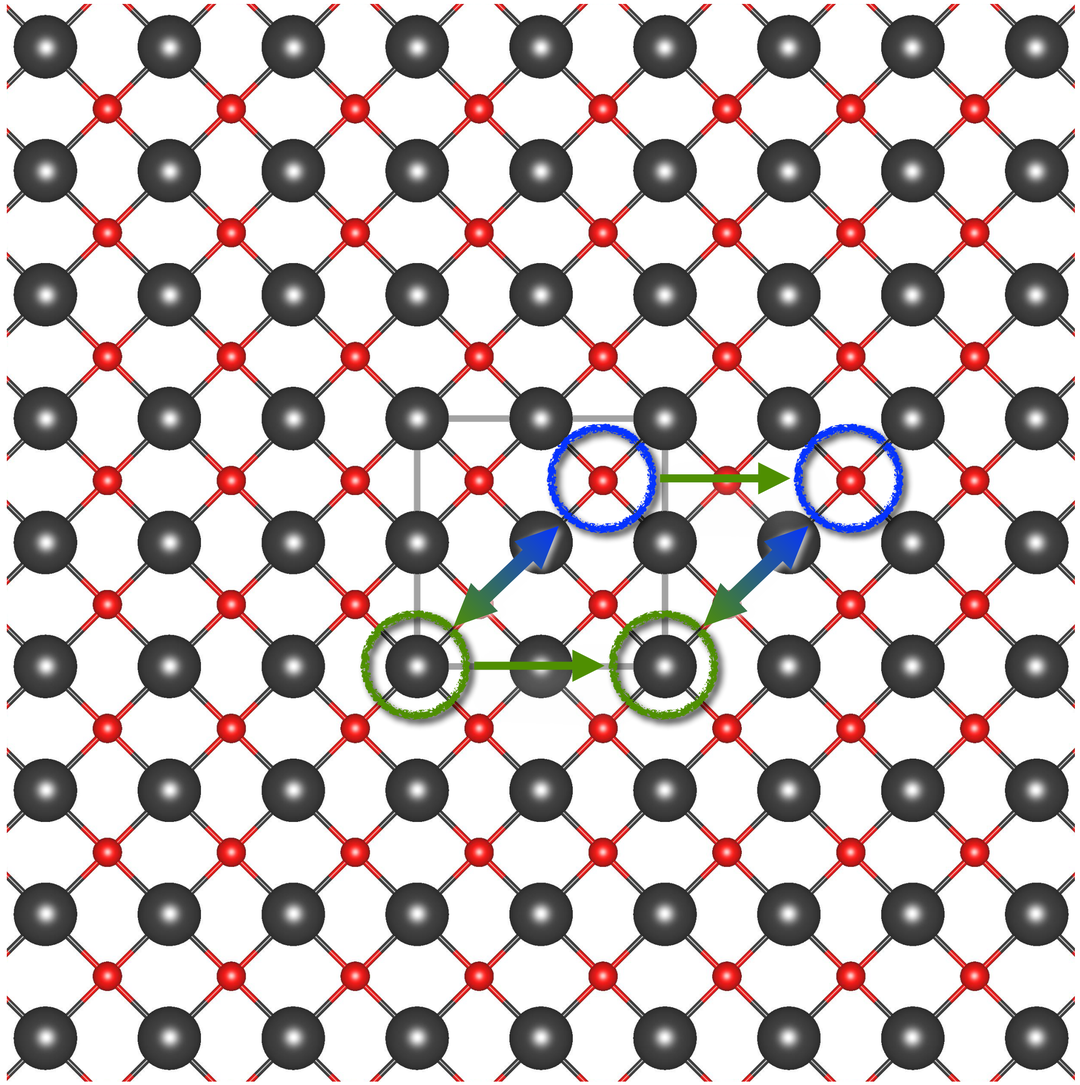
$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \cancel{\sum_i \left.\frac{\partial E}{\partial \mathbf{R}_i}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i} + \frac{1}{2}\sum_{i,j} \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i \Delta\mathbf{R}_j$$

The Harmonic Force Constants

Hessian: $$\Phi_{IJ}^{\alpha\beta} = \frac{\partial^2 E}{\partial \mathbf{R}_I^\alpha \partial \mathbf{R}_J^\beta}\bigg|_{\mathbf{R}_0} = -\frac{\partial \mathbf{F}_I^\alpha}{\partial \mathbf{R}_J^\beta}\bigg|_{\mathbf{R}_0}$$

*"How much does **Force** on **atom I** change when moving **atom J**?"*

The Harmonic Force Constants



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Nota bene: The Hessian is **pair-wise** translationally invariant.

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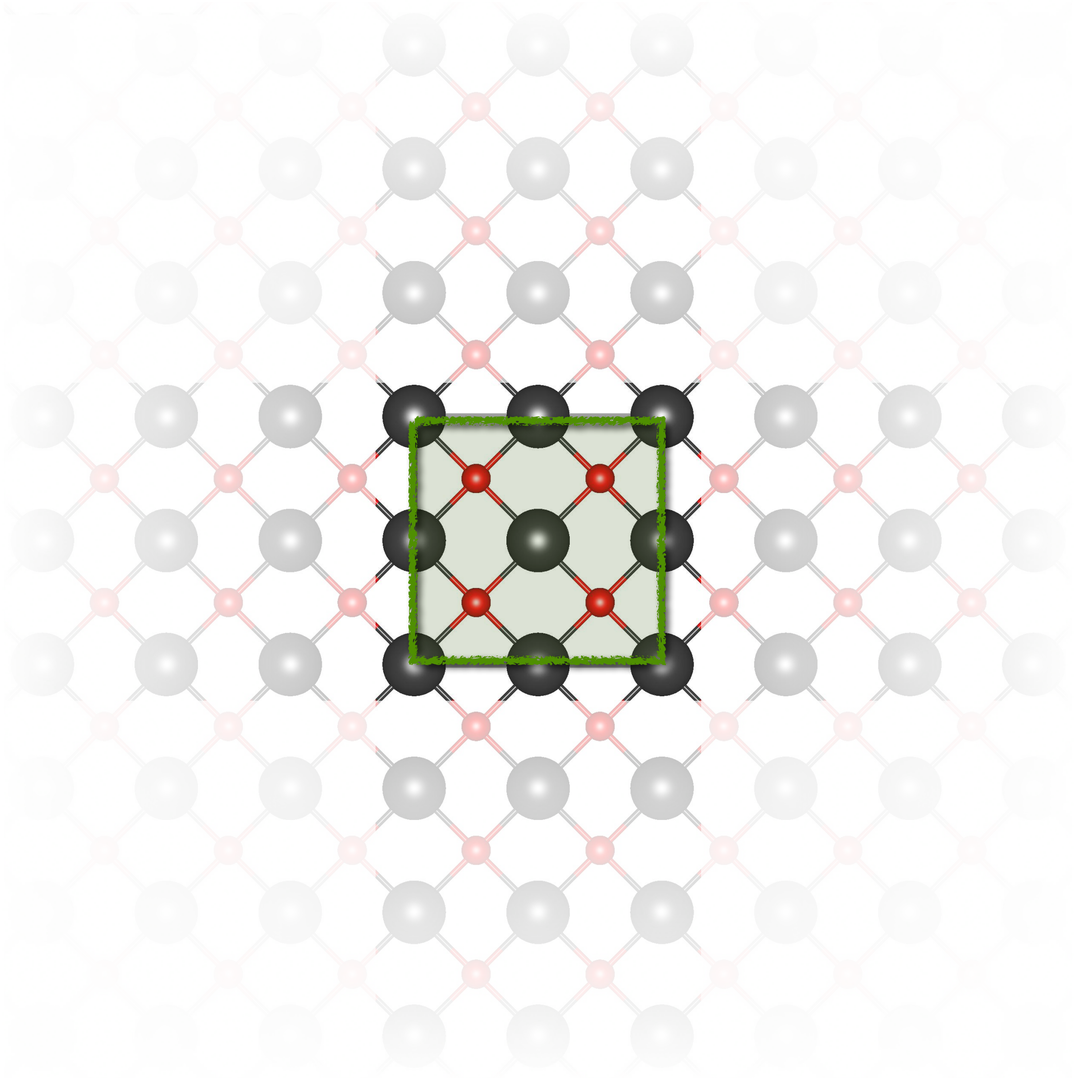

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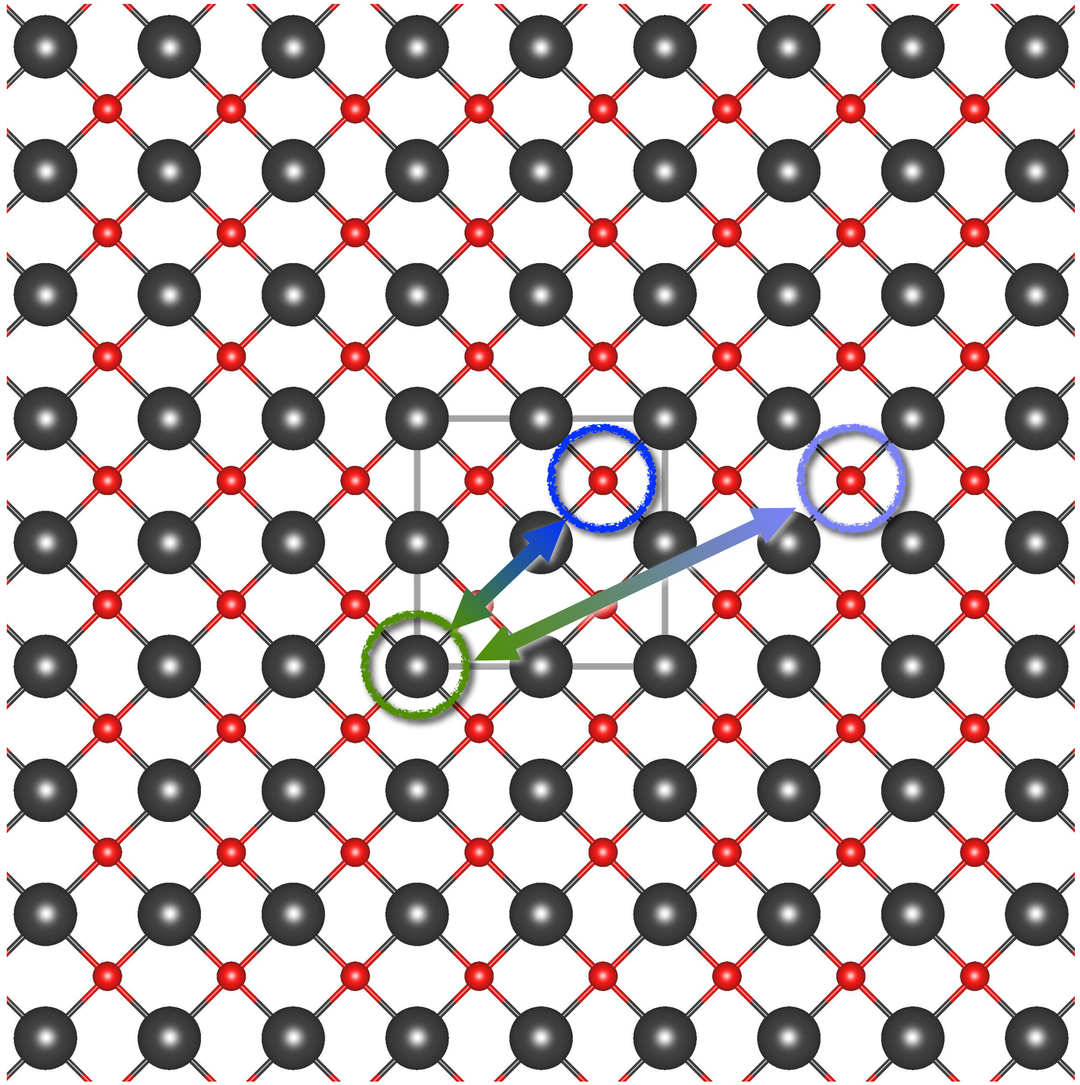
$\Longrightarrow$ **One** index can be restricted to the **primitive unit cell**.

The Harmonic Force Constants



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Different **periodic images** of **atom J** results in different force constants.

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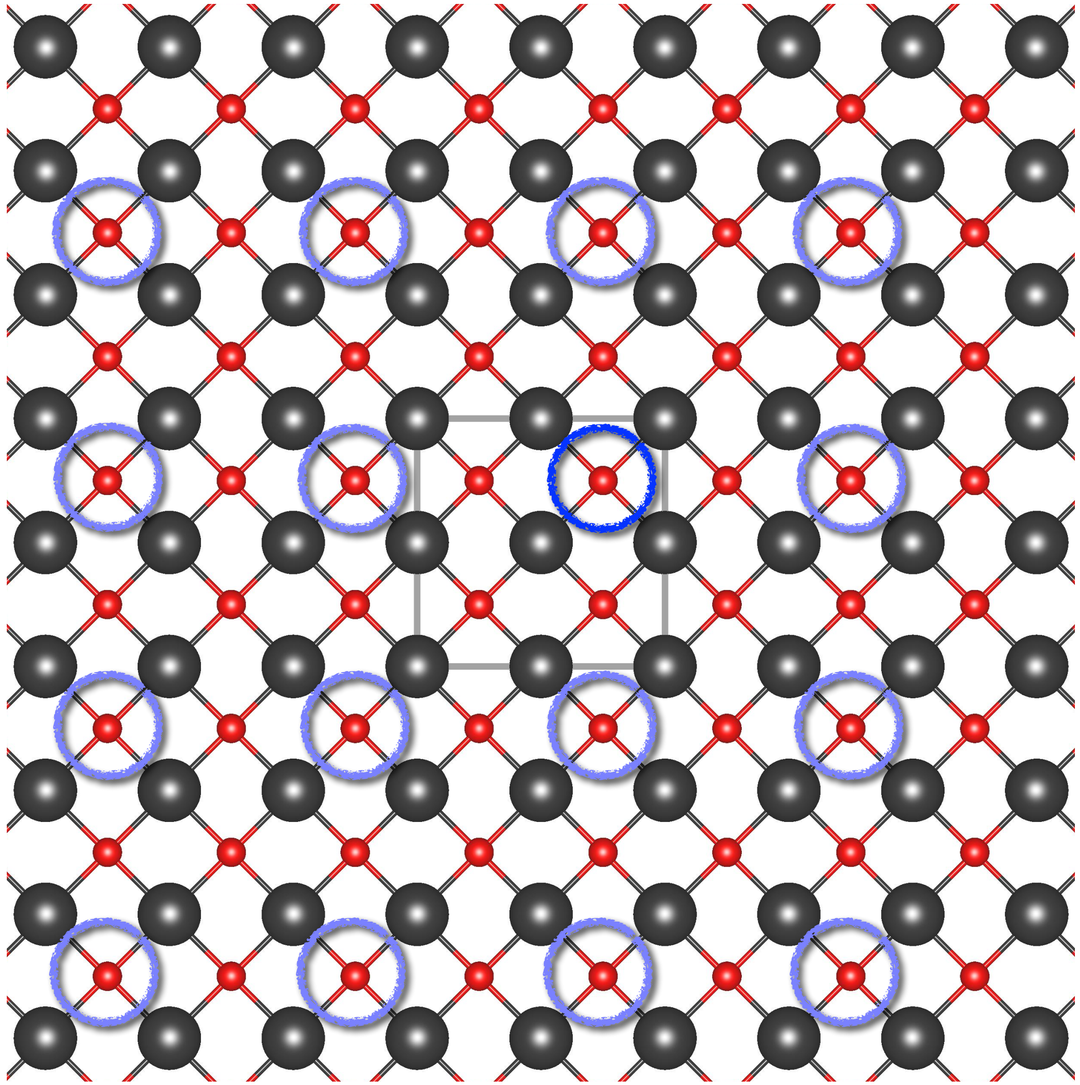

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Different **periodic images** of **atom J** results in different force constants.

$\Longrightarrow$ The second index runs over the **whole, infinite** crystal.

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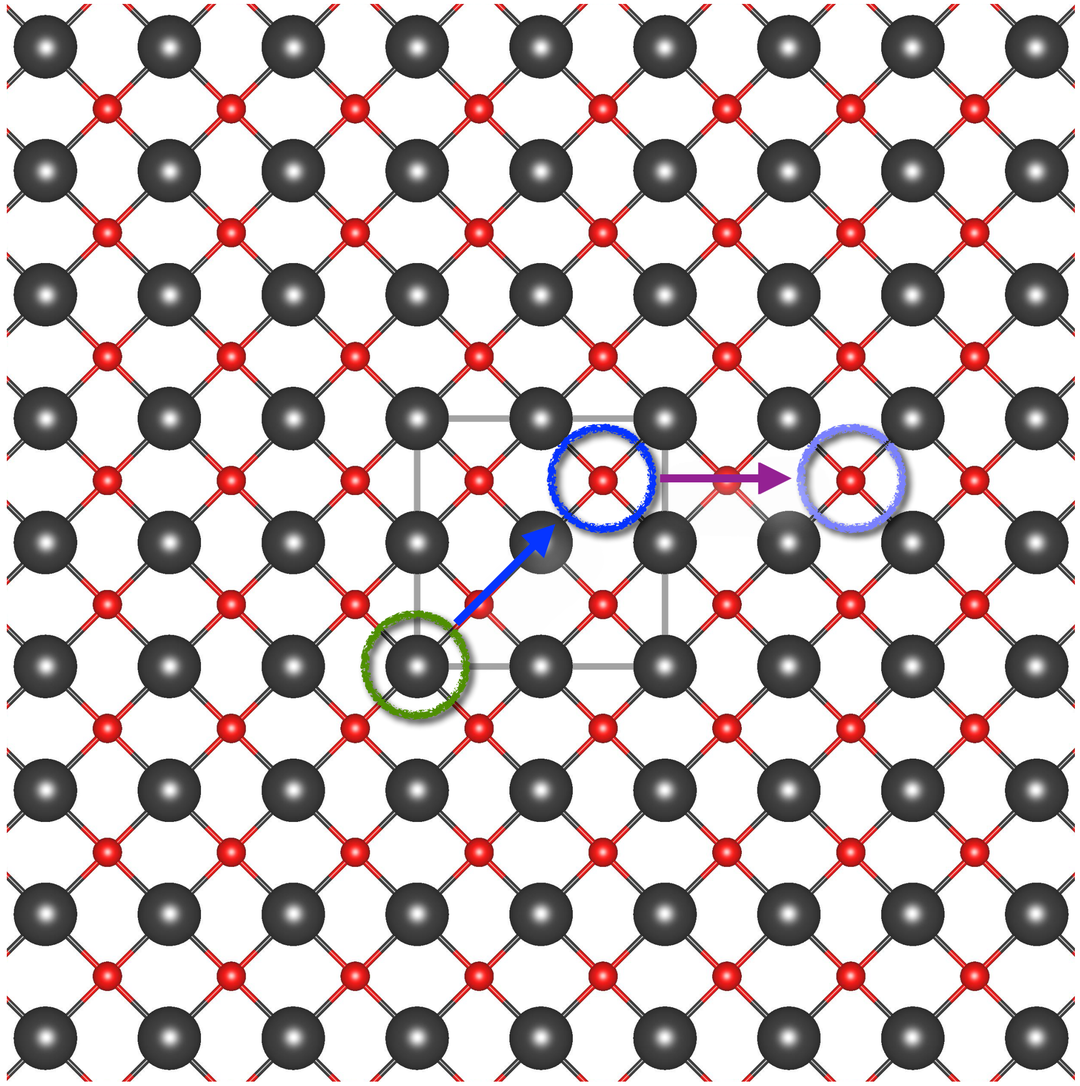

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$$\Phi_{IJ}^{\alpha\beta} \to \Phi_{I,Jlmn}^{\alpha\beta} = \left.\frac{\partial^2 E}{\partial \mathbf{R}_I^\alpha \partial \mathbf{R}_{J,lmn}^\beta}\right|_{\mathbf{R}_0} = \left.\frac{\partial \mathbf{F}_I^\alpha}{\partial \mathbf{R}_{J,lmn}^\beta}\right|_{\mathbf{R}_0}$$

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The Harmonic Force Constants

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$$\mathbf{R}_{J,lmn} = \mathbf{R}_J + l\,\mathbf{L}_x + m\,\mathbf{L}_y + n\,\mathbf{L}_z \qquad l,m,n \in \mathbb{Z}$$

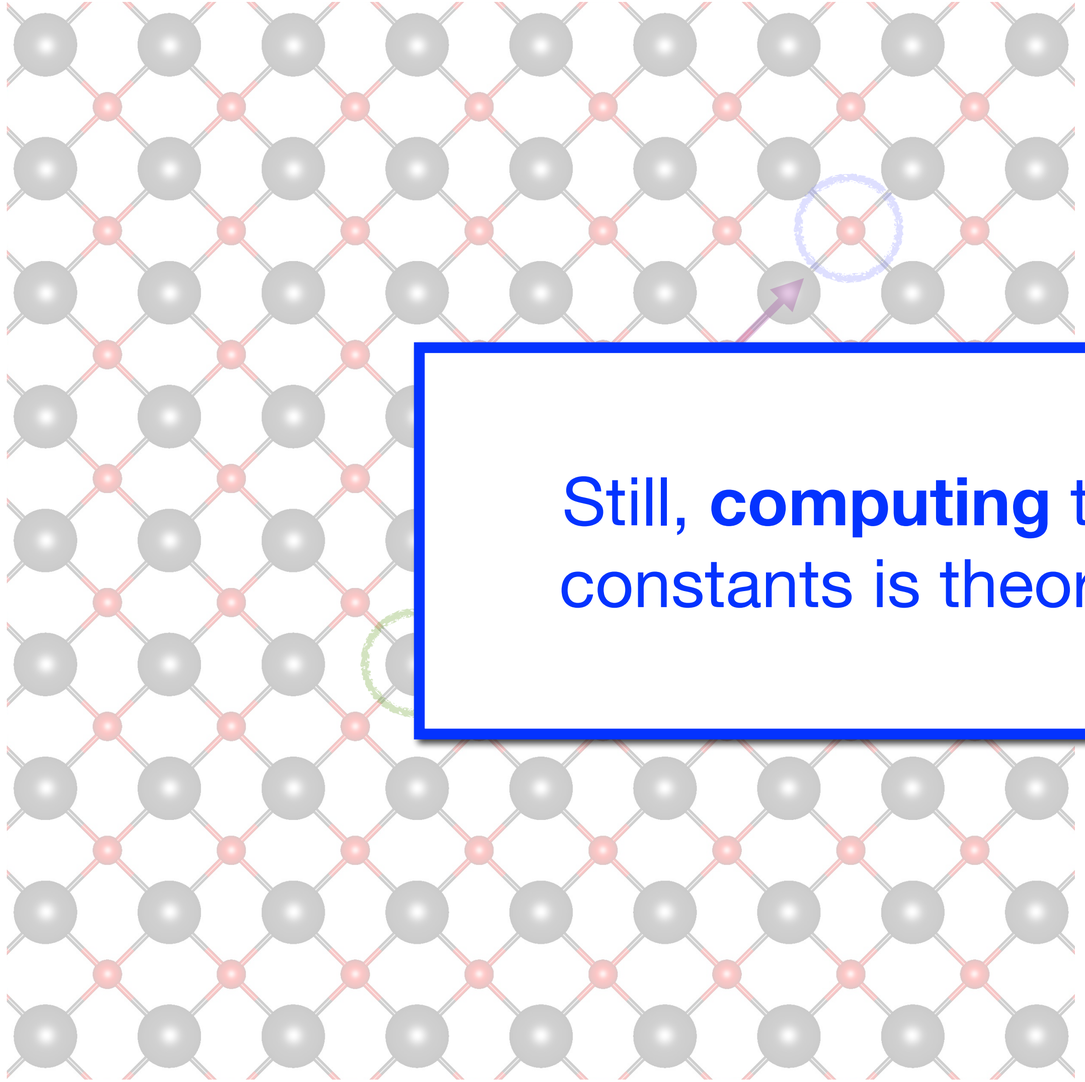
Nota bene:

Interactions in crystals **decay** rapidly with distance.

$$\Phi_{IJ}^{\alpha\beta} \rightarrow 0 \quad \text{for} \quad |\mathbf{R}_{J,lmn} - \mathbf{R}_I| \rightarrow \infty$$

The interactions in the **infinite crystal** can be described by a **finite number** of force constants.

The Harmonic Force Constants



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$$\mathbf{R}_{J,lmn} = \mathbf{R}_J + l\,\mathbf{L}_x + m\,\mathbf{L}_y + n\,\mathbf{L}_z \qquad l,m,n \in \mathbb{Z}$$

Still, **computing** these harmonic force constants is theoretically **challenging**!

ne:

ystals **decay**

istance.

$$\Phi_{IJ} \to 0 \quad \text{for} \quad |\mathbf{R}_{J,lmn} - \mathbf{R}_I| \to \infty$$

The interactions in the **infinite crystal** can be described by a **finite number** of force constants.

Hellman-Feynman Theorem

Born-Oppenheimer Approximation:
Ground State Electrons determine the **Potential Energy**

Potential-Energy Surface: $U(\mathbf{R}) = \langle \Psi_{\mathbf{R}}(\mathbf{r}) | \, \mathbb{H}_{\mathbf{R}} \, | \Psi_{\mathbf{R}}(\mathbf{r}) \rangle$

Forces

$$\mathbf{F}_i = -\frac{\partial U(\mathbf{R})}{\partial \mathbf{R}_i}$$

$$= -\langle \Psi_{\mathbf{R}}(\mathbf{r}) | \, \frac{\partial \mathbb{H}_{\mathbf{R}}}{} \, | \Psi_{\mathbf{R}}(\mathbf{r}) \rangle - \cancel{\langle \frac{\partial \Psi_{\mathbf{R}}(\mathbf{r})}{} | \, \mathbb{H}_{\mathbf{R}} \, | \Psi_{\mathbf{R}}(\mathbf{r}) \rangle - \langle \Psi_{\mathbf{R}}(\mathbf{r}) | \, \mathbb{H}_{\mathbf{R}} \, | \frac{\partial \Psi_{\mathbf{R}}(\mathbf{r})}{} \rangle}$$

Forces are an expectation value of the **wave function** and do ***not*** depend on ***changes*** in the *wave function* itself.

Higher Order Derivatives

$$\mathbf{\Phi}_{ij} = -\frac{\partial \mathbf{F}_i}{\partial \mathbf{R}_j}$$

Hessian

$$= \langle \Psi_{\mathbf{R}}(\mathbf{r}) | \frac{\partial^2 \mathbb{H}_{\mathbf{R}}}{\partial \mathbf{R}_i \partial \mathbf{R}_j} | \Psi_{\mathbf{R}}(\mathbf{r}) \rangle - \langle \Psi_{\mathbf{R}}(\mathbf{r}) | \frac{\partial \mathbb{H}_{\mathbf{R}}}{\partial \mathbf{R}_i} | \partial \Psi_{\mathbf{R}}(\mathbf{r}) / \partial \mathbf{R}_j \rangle - \langle \partial \Psi_{\mathbf{R}}(\mathbf{r}) / \partial \mathbf{R}_j | \frac{\partial \mathbb{H}_{\mathbf{R}}}{\partial \mathbf{R}_i} | \Psi_{\mathbf{R}}(\mathbf{r}) \rangle$$

Hessian **depends** explicitly on the **response** of the *wave function* to a **nuclear displacement**.

⇒ *Adiabatic Electron-Phonon Coupling*

***2n+1* Theorem:**

$(2n+1)^{\text{th}}$ derivative of the **energy** requires the n^{th} derivative of the **wave function / electron density**.

X. Gonze and J.-P. Vigneron, *Phys. Rev. B* **39, 13120** (1989).

Computing Harmonic Force Constants

Finite Differences
(aka Frozen Phonons)

K. Kunc, and R. M. Martin, *Phys. Rev. Lett.* **48**, 406 (1982).
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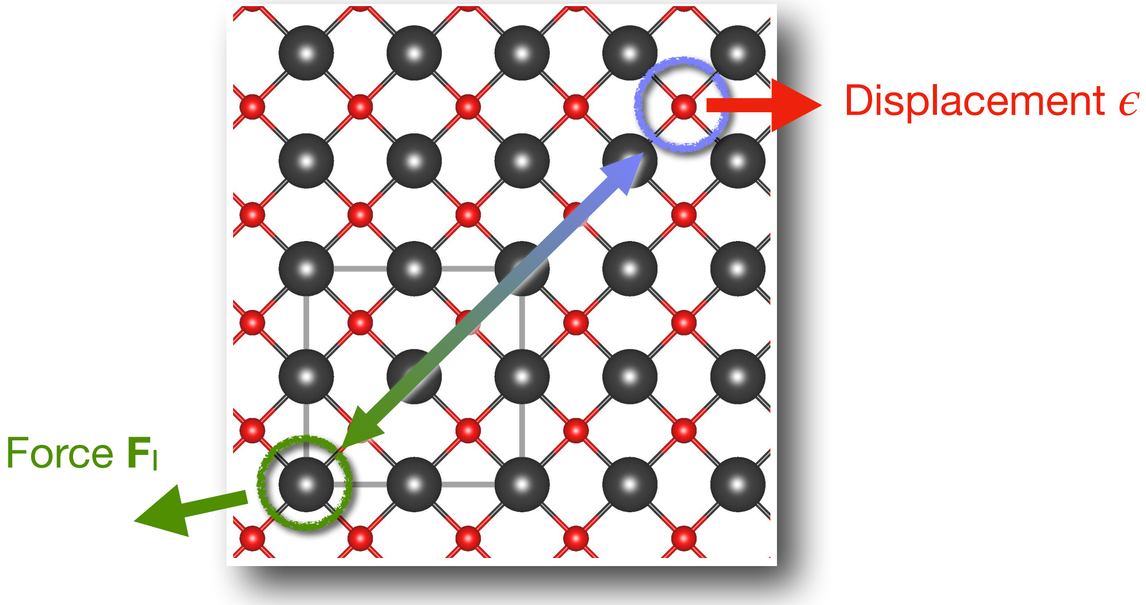
$$\Phi^{\alpha\beta}_{I,Jlmn} = -\left.\frac{\partial \mathbf{F}^{\alpha}_{I}}{\partial \mathbf{R}^{\beta}_{J,lmn}}\right|_{\mathbf{R}_0} \approx -\lim_{\epsilon\to 0}\frac{\mathbf{F}^{\alpha}_{I}\left[\mathbf{R}^{\beta}_{J,lmn}+\epsilon\right]}{\epsilon}$$



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Advantages:

- works with **all** electronic-structure methods
- trivially **parallel**

Disadvantages:

- requires **explicit** supercells
- **numerical noise** affects low-symmetry systems

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Density-Functional Perturbation Theory

S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987)
S. Baroni, *et al., Rev. Mod. Phys.* **73**, 515 (2001).

2n+1 Theorem:

$$\mathbf{\Phi}_{I,Jlmn} = \langle\Psi|\,\partial_I\partial_{Jlmn}\mathbb{H}\,|\Psi\rangle - \langle\Psi|\,\partial_I\mathbb{H}\,|\partial_{Jlmn}\Psi\rangle - \langle\partial_{Jlmn}\Psi|\,\partial_I\mathbb{H}\,|\Psi\rangle$$

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Starting Point:
Kohn-Sham Equations

$$\hat{h}_{\mathrm{KS}}\psi_i = \left[\hat{t} + \hat{v}_{\mathrm{ext}}(r) + \hat{v}_{\mathrm{H}} + \hat{v}_{\mathrm{xc}}\right]\psi_i = \epsilon_i\psi_i$$

First-order expansion of all relevant quantities with respect to a perturbation λ

$$\begin{aligned}
\hat{h}_{\mathrm{KS}}(\lambda) &= \hat{h}^{(0)}_{\mathrm{KS}} + \overbrace{\frac{d\hat{h}_{\mathrm{KS}}}{d\lambda}}^{\hat{h}^{(1)}_{\mathrm{KS}}}\Delta\lambda + \cdots \\
\psi_i(\lambda) &= \psi_i^{(0)} + \psi_i^{(1)}\Delta\lambda + \cdots \\
\varepsilon_i(\lambda) &= \varepsilon_i^{(0)} + \varepsilon_i^{(1)}\Delta\lambda + \cdots
\end{aligned}$$

Solve: *Sternheimer Equation*

$$\hat{h}_{\mathrm{KS}}(\lambda)\,\psi_i(\lambda) = \varepsilon_i(\lambda)\psi_i(\lambda) \Rightarrow \left(\hat{h}^{(0)}_{\mathrm{KS}} - \varepsilon_i^{(0)}\right)\psi_i^{(1)} = -\left(\hat{h}^{(1)}_{\mathrm{KS}} - \epsilon_i^{(1)}\right)\psi_i^{(0)} + o(\lambda^2)$$

R.M. Sternheimer, *Phys. Rev.* **96** 951 (1954).

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R.M. Sternheimer, *Phys. Rev.* **96** 951 (1954).

Route A: *Density-functional Perturbation Theory* $\quad \psi_i^{(1)} = \sum_l C_{il}\psi_l^{(0)}$

Route B: *Coupled-Perturbed Self-Consistent Field* $\quad \psi_i^{(1)} = \sum_l C_{il}\varphi_l$

Additional Self-Concistency Cycle
required **per perturbation**!

Density-Functional Perturbation Theory

S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987) &
S. Baroni, *et al., Rev. Mod. Phys.* **73**, 515 (2001).

Solve: *Sternheimer Equation*

$$\hat{h}_{\mathrm{KS}}(\lambda)\,\psi_i(\lambda) = \varepsilon_i(\lambda)\psi_i(\lambda) \Rightarrow \left(\hat{h}^{(0)}_{\mathrm{KS}} - \varepsilon^{(0)}_i\right)\psi^{(1)}_i = -\left(\hat{h}^{(1)}_{\mathrm{KS}} - \epsilon^{(1)}_i\right)\psi^{(0)}_i + o(\lambda^2)$$

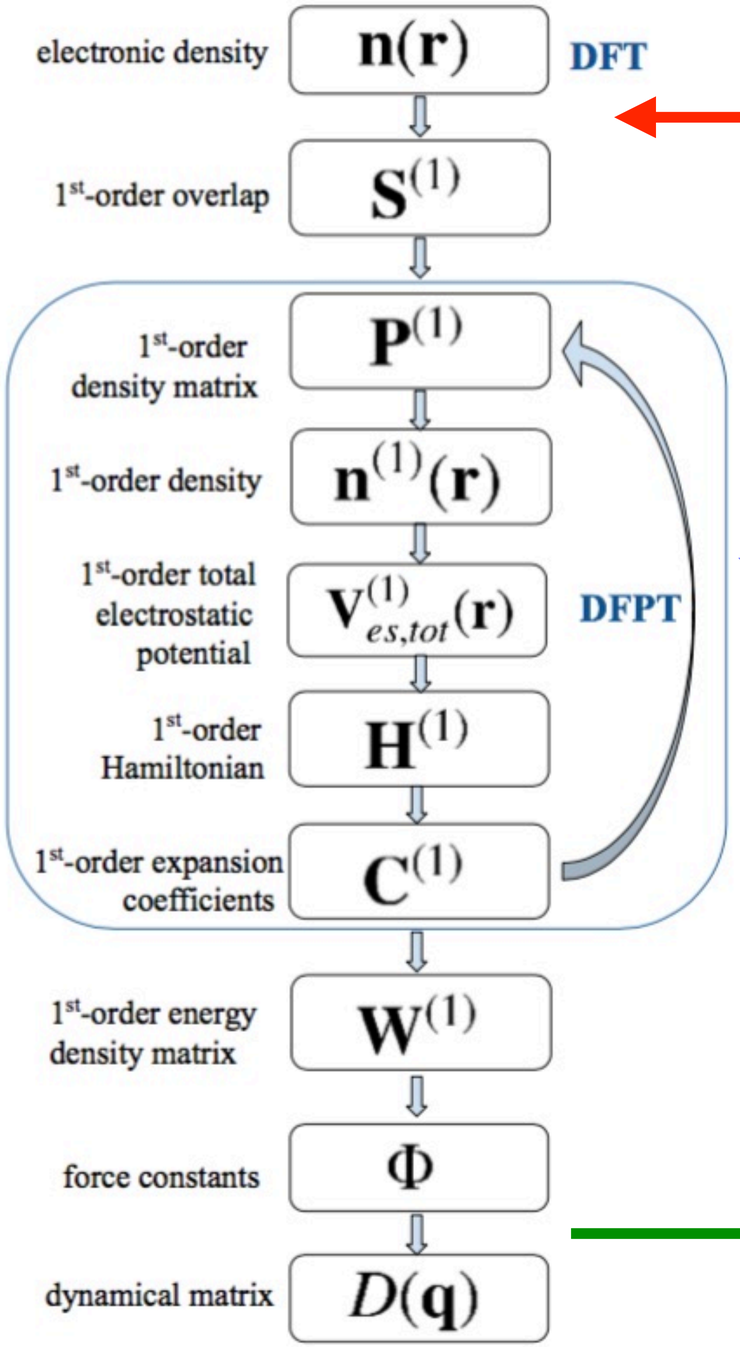
Normalization Conditions:

$$\left\langle \psi^{(0)}_i \middle| \psi^{(0)}_i \right\rangle = 1 \qquad \left\langle \psi^{(1)}_i \middle| \psi^{(0)}_i \right\rangle + \left\langle \psi^{(0)}_i \middle| \psi^{(1)}_i \right\rangle = 0$$

Phase Freedom: The phase of the perturbation can be freely chosen.

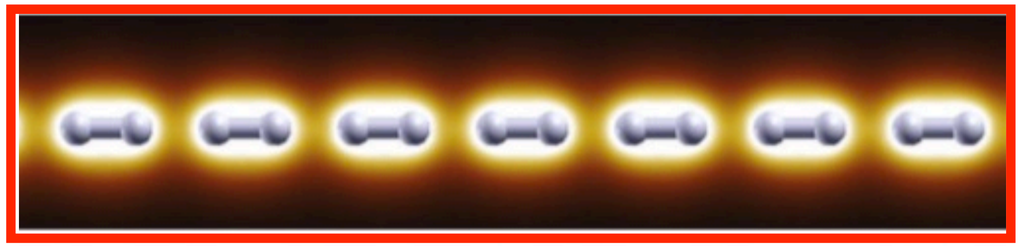
⇒ Extended Perturbations $\lambda(\mathbf{q})$ can be treated

in the unit cell!



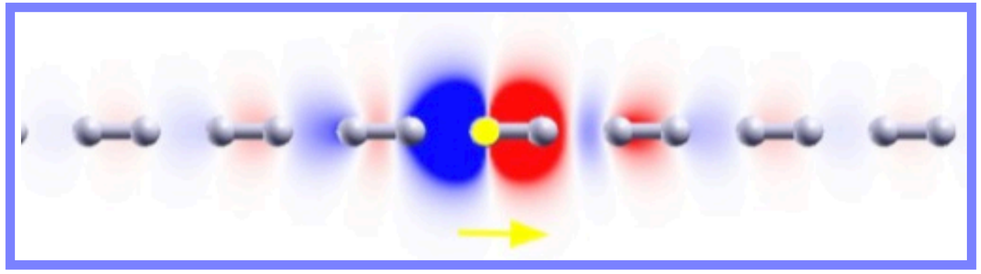
Density Functional Theory:

*density n(**r**)*



Density Functional Perturbation Theory:

density response $dn(\mathbf{r})/d\mathbf{R}_I$

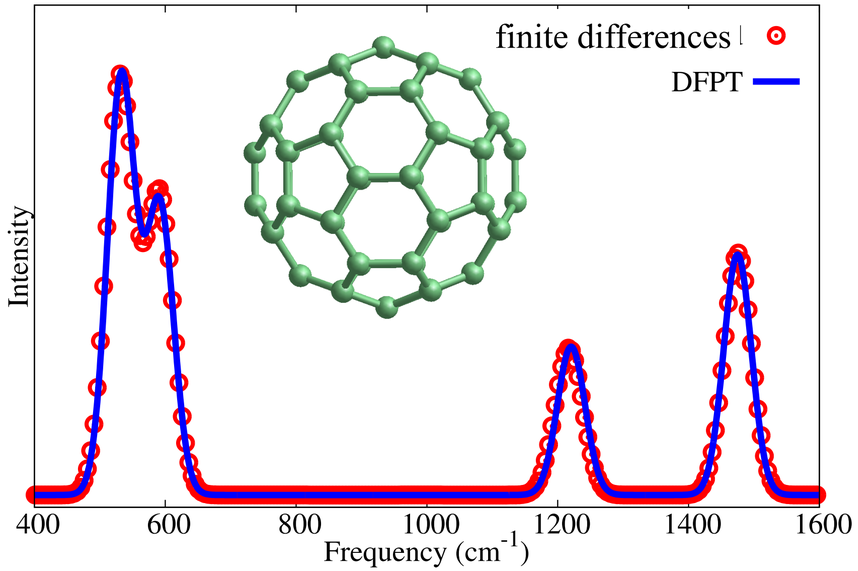


All phonon properties!

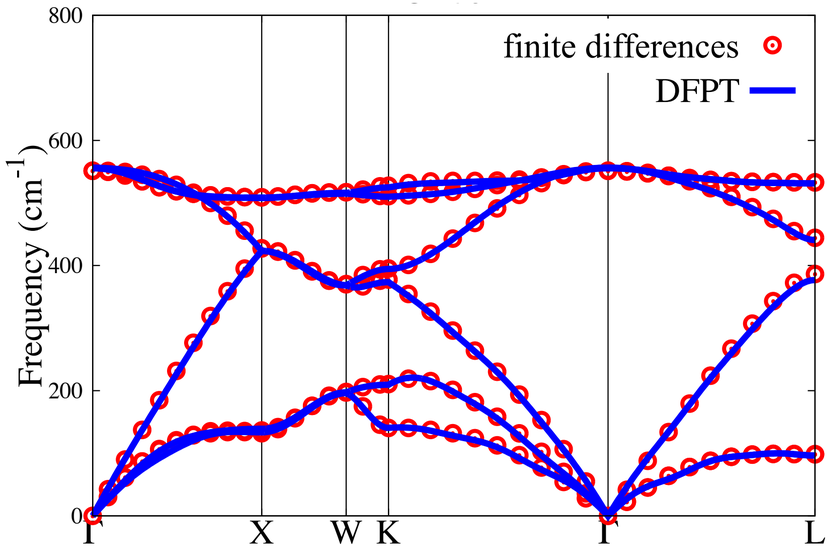
DF-Perturbation Theory in *FHI-aims*

H. Shang, C. Carbogno, P. Rinke, and M. Scheffler, Comp. Phys. Comm. ***215****, 26 (2017).*

Finite Systems: C_{60}

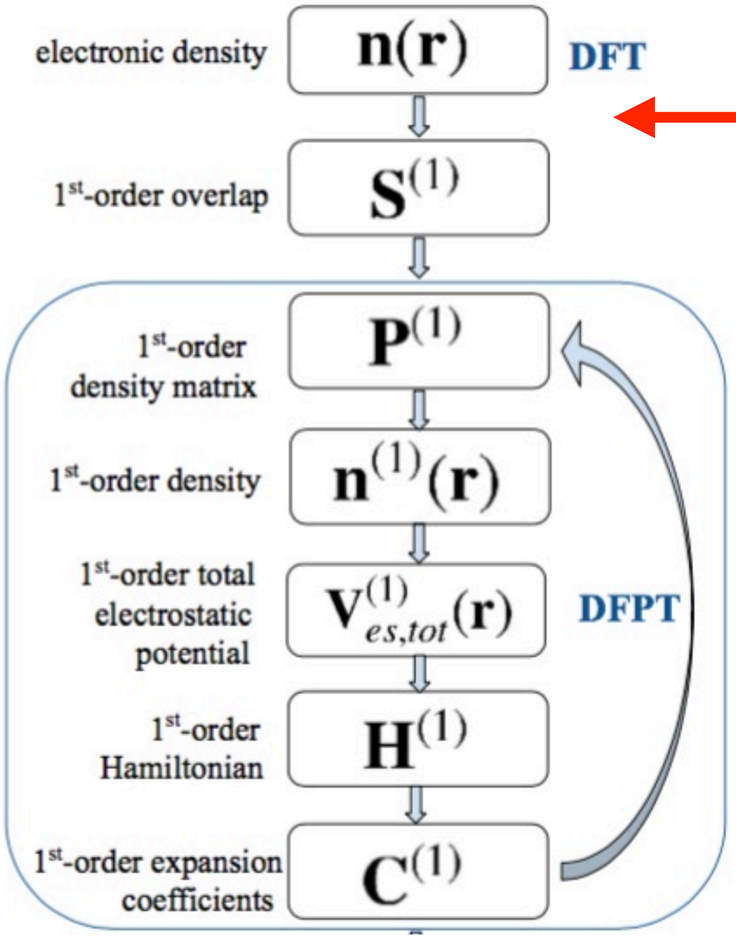


Periodic Systems: Silicon



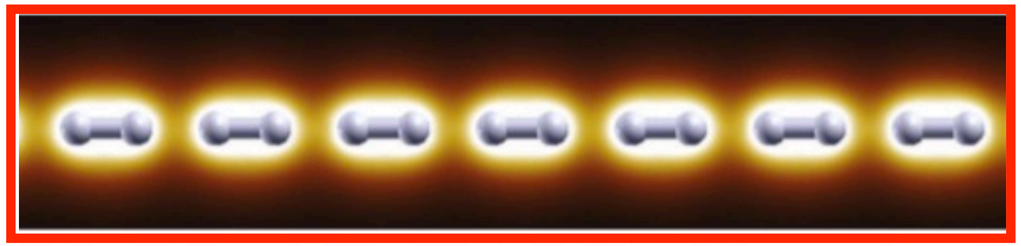
Validation:

Comparison **DFPT** and **finite differences** for vibrational properties



Density Functional Theory:

density $n(\mathbf{r})$



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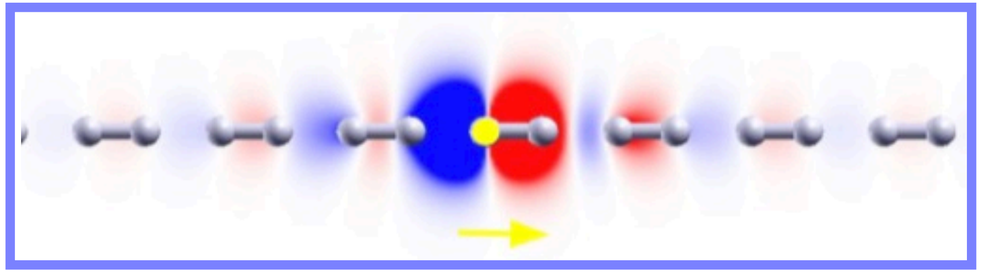
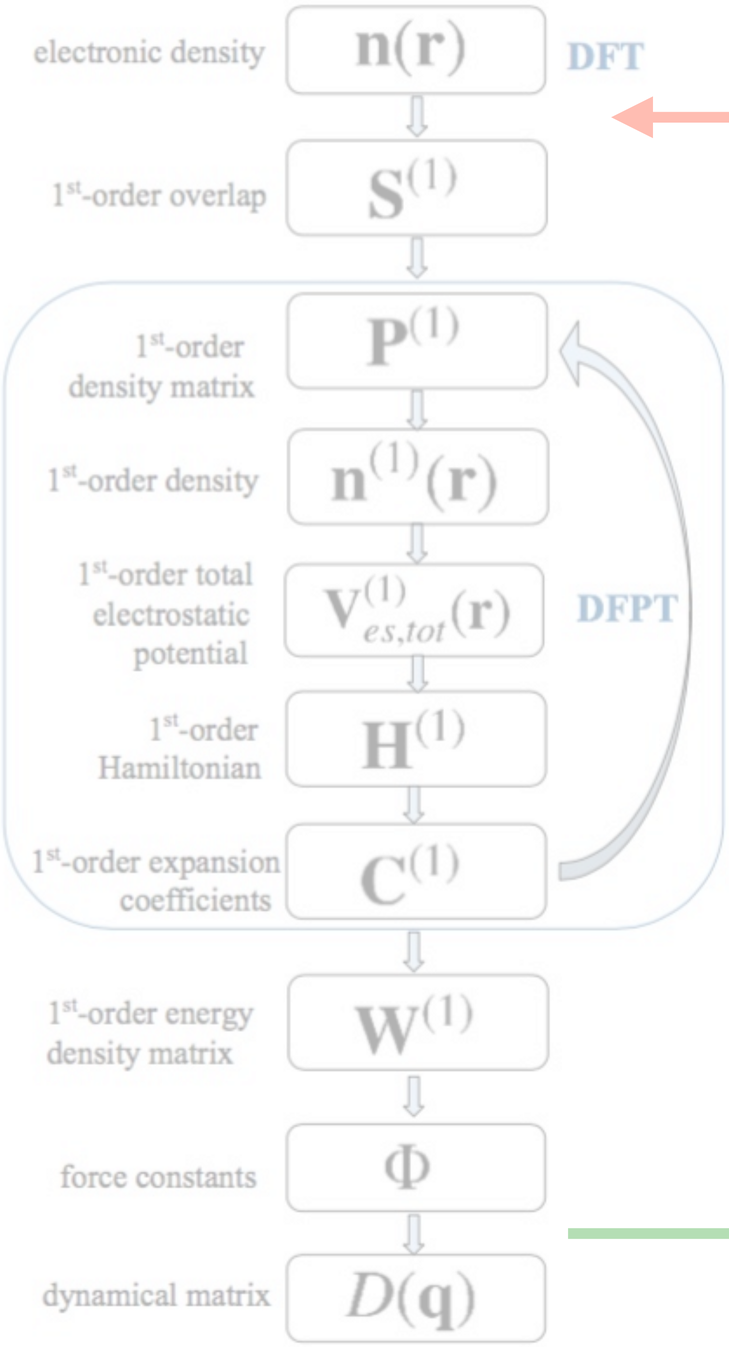


Electron-Phonon Coupling

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \left\langle \Psi^{(0)}_{m\mathbf{k}+\mathbf{q}} \middle| \underbrace{\Delta_{\mathbf{q}\nu} v^{\mathrm{KS}}}_{\hat{h}^{(1)}_{\mathrm{KS}}(\nu,\mathbf{q})} \middle| \Psi^{(0)}_{n\mathbf{k}} \right\rangle_{\mathrm{uc}}$$



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density $n(\mathbf{r})$

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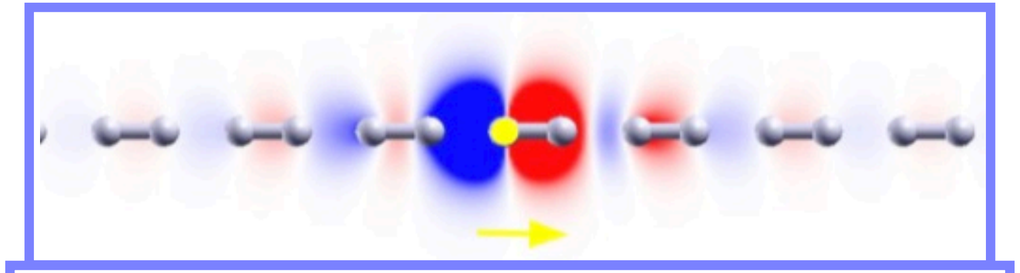


Density response is localized in real space.

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

electronic density $\mathbf{n(r)}$ DFT

1st-order overlap $\mathbf{S}^{(1)}$

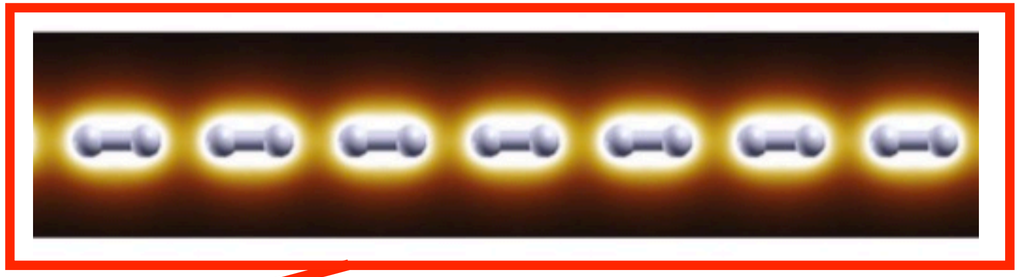
Using techniques developed for describing **delocalized properties** to describe a **localized response** is **not efficient**!

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

force constants Φ

dynamical matrix $D(\mathbf{q})$

Density Functional Theory:
density $n(\mathbf{r})$



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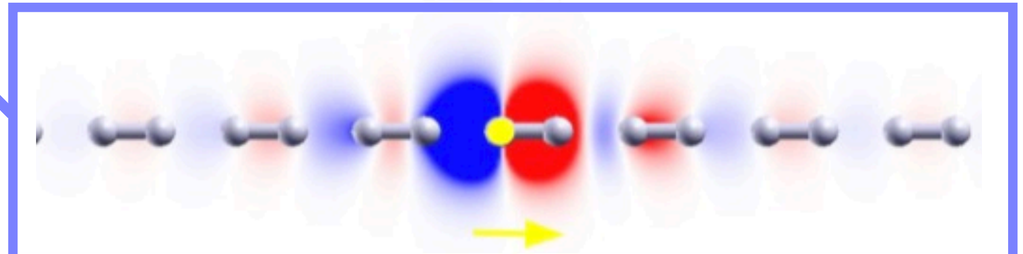

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Accelerating DFPT

e.g.: F. Giustino, M. Cohen, and S. Louie, *Phys. Rev. B* **76** 165108 (2007).
EPW Software: Ponce, *et al.*, *Comp. Phys. Comm.* **209**, 116 (2016).

Response computed in **reciprocal-space** on a finite **q-grid.**

Truncated Fourier-Transform to **real-space**.

Localization enables **real-space interpolation**
(e.g. *Wannier:* Vanderbilt, Marzari, Giustino, etc.)

Truncated Fourier-Transform back to **reciprocal-space**.

Computing Harmonic Force Constants

Finite Differences (aka Frozen Phonons)

K. Kunc, and R. M. Martin, *Phys. Rev. Lett.* **48**, 406 (1982).
K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997).

$$\Phi^{\alpha\beta}_{I,Jlmn} = -\left.\frac{\partial \mathbf{F}^{\alpha}_{I}}{\partial \mathbf{R}^{\beta}_{J,lmn}}\right|_{\mathbf{R}_0} \approx -\lim_{\epsilon\to 0}\frac{\mathbf{F}^{\alpha}_{I}\left[\mathbf{R}^{\beta}_{J,lmn}+\epsilon\right]}{\epsilon}$$

Advantages:

- works with **all** electronic-structure methods
- trivially **parallel**

Disadvantages:

- requires **explicit** supercells
- **numerical noise** affects low-symmetry systems

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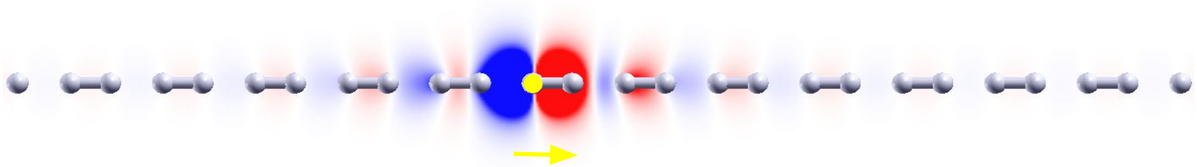
2n+1 Theorem:

$$\mathbf{\Phi}_{I,Jlmn} = \langle\Psi|\,\partial_I\partial_{Jlmn}\mathbb{H}\,|\Psi\rangle - \langle\Psi|\,\partial_I\mathbb{H}\,|\partial_{Jlmn}\Psi\rangle - \langle\partial_{Jlmn}\Psi|\,\partial_I\mathbb{H}\,|\Psi\rangle$$

Explicit response from *Sternheimer Equation*:

$$(\epsilon_q - \epsilon_p)\,\langle\psi_q\,|\,\partial\psi_p\rangle = -\left(\left\langle\psi_q\left|\partial\hat{h}_{\mathrm{KS}}\right|\psi_p\right\rangle - \partial\epsilon_p\delta_{qp}\right)$$



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Advantages:

- works within **primitive** unit cells
- full access to the **electronic** perturbation

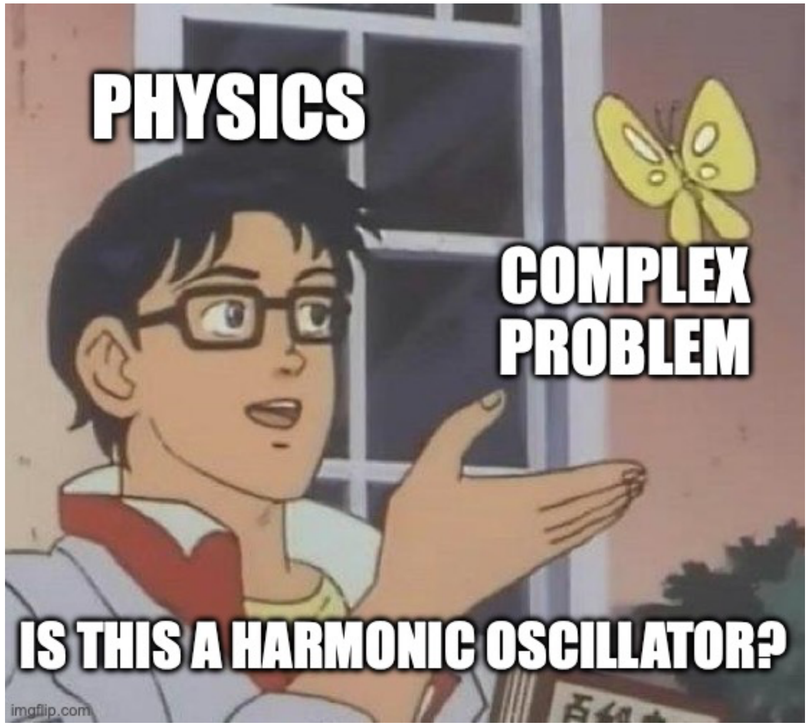
Disadvantages:

- requires **exchange-correlation** derivatives
- **costly** in extended, low-symmetry systems

Take-Home Messages

- **Everything moves!** Nuclei and atoms are never at rest.

- The potential-energy surface on which the nuclei move can be ***approximated*** using a ***harmonic potential***.
  This requires calculating *2nd order derivatives at equilibrium*.



The Harmonic Equations of Motion

Energy:

$$E^{\text{harm}} = \frac{1}{2}\sum_{I,J}\sum_{abc,lmn}\Phi_{Iabc,Jlmn}\Delta\mathbf{R}_{Iabc}\Delta\mathbf{R}_{Jlmn}$$

Forces:

$$\mathbf{F}_{Iabc} = -\sum_{Jlmn}\Phi_{Iabc,Jlmn}\Delta\mathbf{R}_{Jlmn}$$

Equation of Motion:

$$M_I\ddot{\mathbf{R}}_{Iabc} = -\sum_{Jlmn}\Phi_{Iabc,Jlmn}\Delta\mathbf{R}_{Jlmn}$$

$$\Delta\mathbf{R}_{Jlmn} = \frac{1}{\sqrt{M_J}}\mathbf{U}_J\exp(i\mathbf{q}\mathbf{L}_{lmn}) \quad \text{with} \quad \mathbf{L}_{lmn} = l\,\mathbf{L}_x + m\,\mathbf{L}_y + n\,\mathbf{L}_z$$

$$\sqrt{M_I}\ddot{\mathbf{U}}_I\exp(i\mathbf{q}\mathbf{L}_{abc}) = -\sum_{Jlmn}\frac{\Phi_{Iabc,Jlmn}}{\sqrt{M_J}}\mathbf{U}_J\exp(i\mathbf{q}\mathbf{L}_{lmn})$$

$$\ddot{\mathbf{U}}_I = -\sum_{Jlmn}\frac{\Phi_{Iabc,Jlmn}}{\sqrt{M_IM_J}}\exp(i\mathbf{q}(\mathbf{L}_{lmn}-\mathbf{L}_{abc}))\,\mathbf{U}_J$$

$$\ddot{\mathbf{U}}_I = -\sum_{Jlmn}\frac{\Phi_{I000,Jlmn}}{\sqrt{M_IM_J}}\exp(i\mathbf{q}\mathbf{L}_{lmn})\,\mathbf{U}_J$$

$$\ddot{\mathbf{U}}_I = -\sum_{J}D_{I,J}(\mathbf{q})\,\mathbf{U}_J$$

Dynamic Matrix: $\Rightarrow D_{I,J}(\mathbf{q}) = \sum_{lmn}\frac{\Phi_{I000,Jlmn}}{\sqrt{M_IM_J}}\exp(i\mathbf{q}\mathbf{L}_{lmn})$

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with $\mathbf{L}_{lmn} = l\,\mathbf{L}_x + m\,\mathbf{L}_y + n\,\mathbf{L}_z$

Infinite number of degrees of freedom!

$$\sqrt{M_I}\ddot{\mathbf{U}}_I\exp(i\mathbf{q}\mathbf{L}_{abc}) = -\sum_{Jlmn}\frac{\Phi_{Iabc,Jlmn}}{\sqrt{M_J}}\mathbf{U}_J\exp(i\mathbf{q}\mathbf{L}_{lmn})$$

$$= -\sum_{Jlmn}\frac{\Phi_{Iabc,Jlmn}}{\sqrt{M_IM_J}}\exp(i\mathbf{q}(\mathbf{L}_{lmn}-\mathbf{L}_{abc}))\,\mathbf{U}_J$$

$$= -\sum_{Jlmn}\frac{\Phi_{I000,Jlmn}}{\sqrt{M_IM_J}}\exp(i\mathbf{q}\mathbf{L}_{lmn})\,\mathbf{U}_J$$

However, we have to address all **q***-points in the 1st Brillouin zone.*

$$\ddot{\mathbf{U}}_I = -\sum_J D_{I,J}(\mathbf{q})\,\mathbf{U}_J$$

Finite number of degrees of freedom!

Dynamic Matrix: $\Rightarrow D_{I,J}(\mathbf{q}) = \sum_{lmn}\frac{\Phi_{I000,Jlmn}}{\sqrt{M_IM_J}}\exp(i\mathbf{q}\mathbf{L}_{lmn})$

The Harmonic Equations of Motion

3 N_p solutions $\{\omega_s^2(\mathbf{q}), \tilde{\mathbf{U}}_s(\mathbf{q})\}$

Complex Amplitudes fully determined by initial conditions!

$$\Delta\mathbf{R}_{Jlmn}(t) = \frac{1}{(2\pi)^3}\sum_s \int_{\mathrm{BZ}} \frac{A_s(\mathbf{q})}{\sqrt{M_J}} \exp(i\mathbf{q}\mathbf{L}_{lmn}) \exp[i\omega_s(\mathbf{q})t] \cdot \tilde{\mathbf{U}}_{s,J}(\mathbf{q})$$

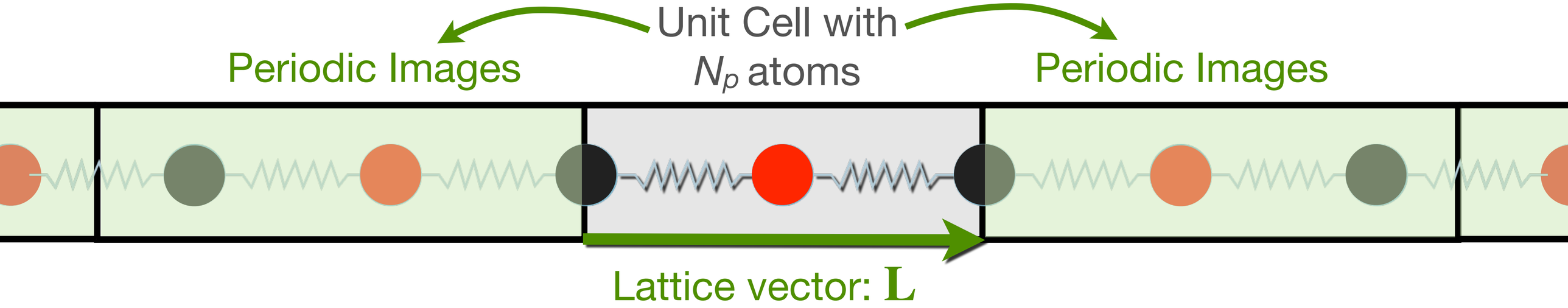
Eigenvalue problem:

$$\omega^2(\mathbf{q})\ \tilde{\mathbf{U}}_I(\mathbf{q}) \quad = \quad \sum_J D_{I,J}(\mathbf{q})\ \tilde{\mathbf{U}}_J(\mathbf{q}) \Longrightarrow \quad \omega^2(\mathbf{q})\ \tilde{\mathbf{U}}(\mathbf{q}) = \mathbf{D}(\mathbf{q})\ \tilde{\mathbf{U}}_J(\mathbf{q})$$

$$\mathbf{U}_J \quad = \quad \exp[i\omega(\mathbf{q})t] \cdot \tilde{\mathbf{U}}_J(\mathbf{q})$$

$$\ddot{\mathbf{U}}_I \quad = \quad -\sum_J D_{I,J}(\mathbf{q})\ \mathbf{U}_J$$

One Simple Example



Real Space:

Hessian $\Phi_{I,Jlmn}$

with ∞ entries

Fourier Transform

$$D_{I,J}(\mathbf{q}) = \sum_{lmn} \frac{\Phi_{I000,Jlmn}}{\sqrt{M_I M_J}} \exp(i\mathbf{q}\mathbf{L}_{lmn})$$

Reciprocal Space:

Dynamical Matrix $D_{IJ}(\mathbf{q})$

with $I,J \leq N_p$

Vibrations in a Crystal 101

K. Parlinski, Z. Q. Li, and Y. Kawazoe, *Phys. Rev. Lett.* **78**, 4063 (1997).

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Hessian $\Phi_{I,Jlmn}$ with ∞ entries

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Reciprocal Space:

Dynamical Matrix $D_{IJ}(\mathbf{q})$ with $I,J \leq N_p$

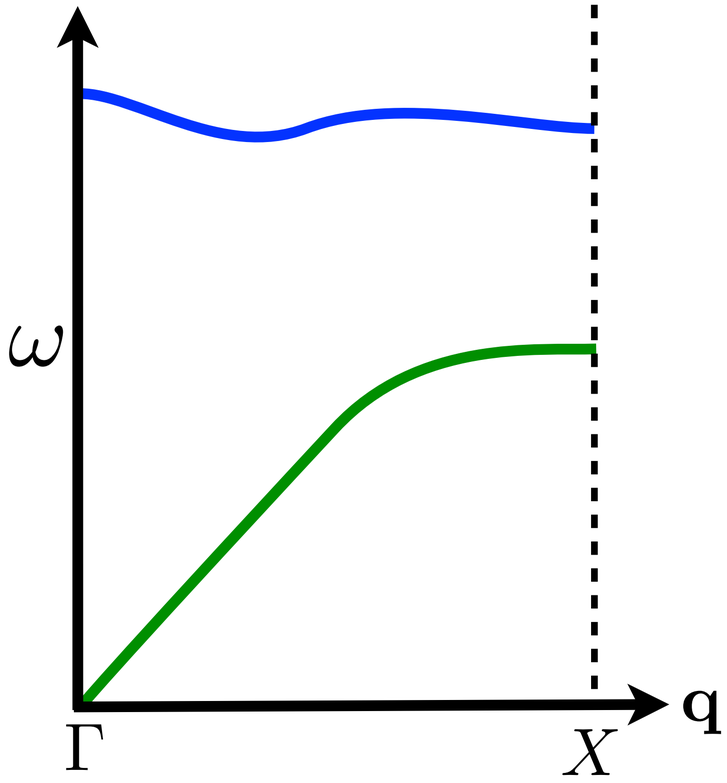
Fourier Transform can be truncated since $\Phi_{I,Jlmn} = 0$ for large $\mathbf{L}_{lmn}$

Hessian $\Phi_{I,Jlmn}$ with **finite** number of non-zero entries

Dynamical Matrix $D_{IJ}(\mathbf{q})$ known for the **whole** *reciprocal space*

Vibrations in a Crystal 101

see, e.g., N. W Ashcroft and N. D. Mermin, *"Solid State Physics"* (1976).



Dynamical matrix:

$$D_{I,J}(\mathbf{q}) = \sum_{lmn} \frac{\Phi_{I000,Jlmn}}{\sqrt{M_I M_J}} \exp(i\mathbf{q}\mathbf{L}_{lmn})$$

Eigenvalue problem:

$$\mathbf{D}(\mathbf{q})\ \tilde{\mathbf{U}}_J(\mathbf{q}) = \omega^2(\mathbf{q})\tilde{\mathbf{U}}(\mathbf{q})$$

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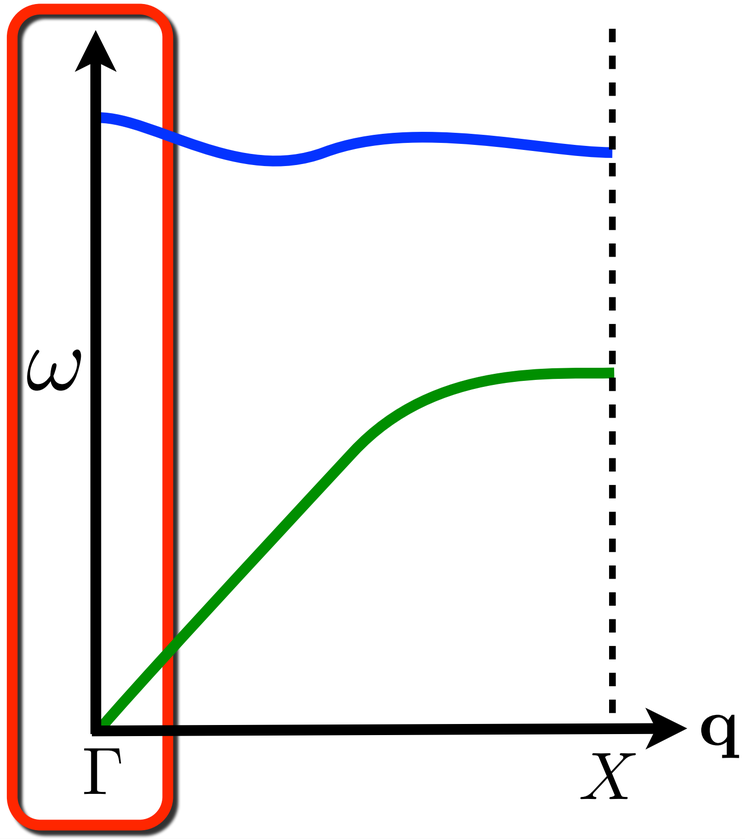


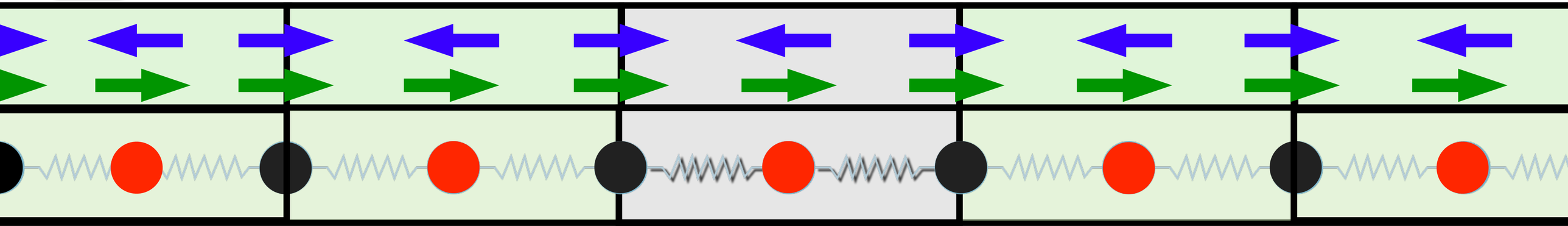
Dynamical matrix:

$$D_{I,J}(\mathbf{\Gamma}) = \sum_{lmn} \frac{\Phi_{I000,Jlmn}}{\sqrt{M_I M_J}} \exp(i\mathbf{q}\mathbf{L}_{lmn})$$

=1

Eigenvalue problem:

$$\mathbf{D}(\mathbf{\Gamma})\ \tilde{\mathbf{U}}_J(\mathbf{\Gamma}) = \omega^2(\mathbf{\Gamma})\tilde{\mathbf{U}}(\mathbf{\Gamma})$$



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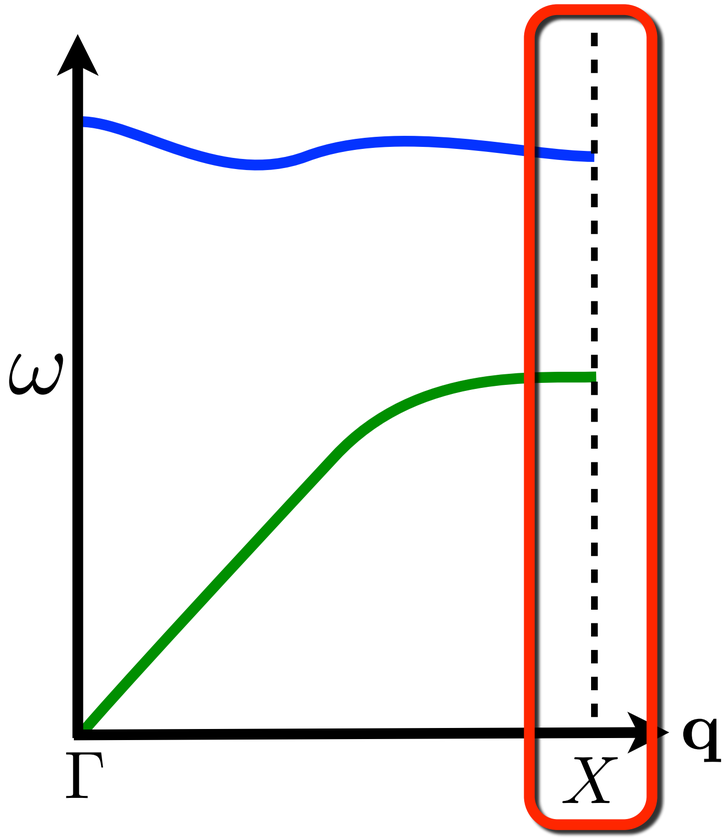

Dynamical matrix:

alternating ± 1

$$D_{I,J}(X) = \sum_{lmn} \frac{\Phi_{I000,Jlmn}}{\sqrt{M_I M_J}} \exp(i\mathbf{q}\mathbf{L}_{lmn})$$

Eigenvalue problem:

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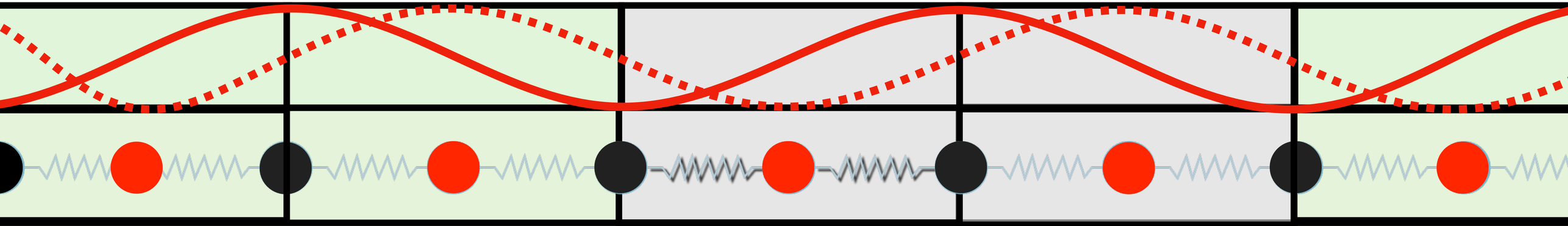

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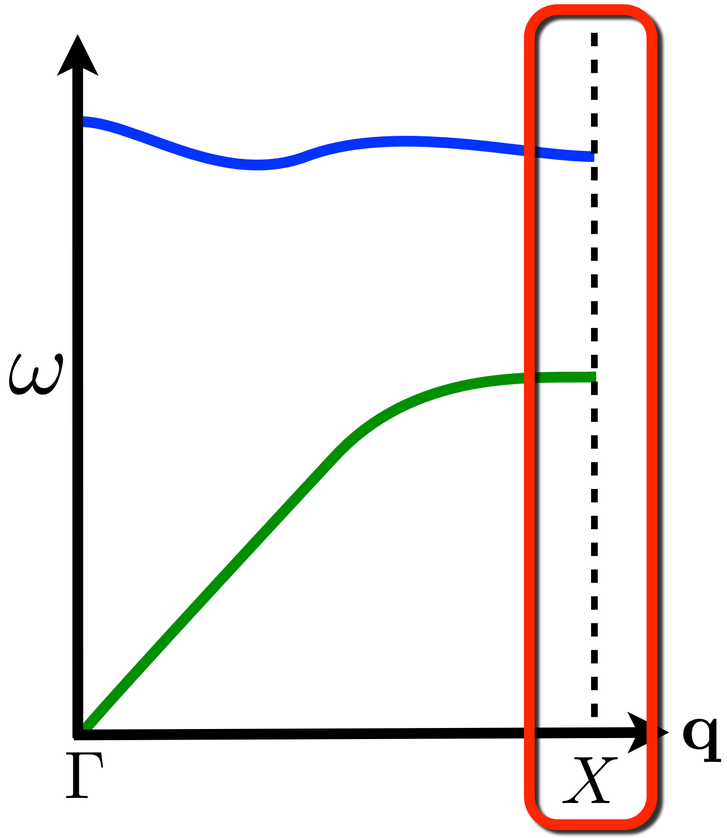

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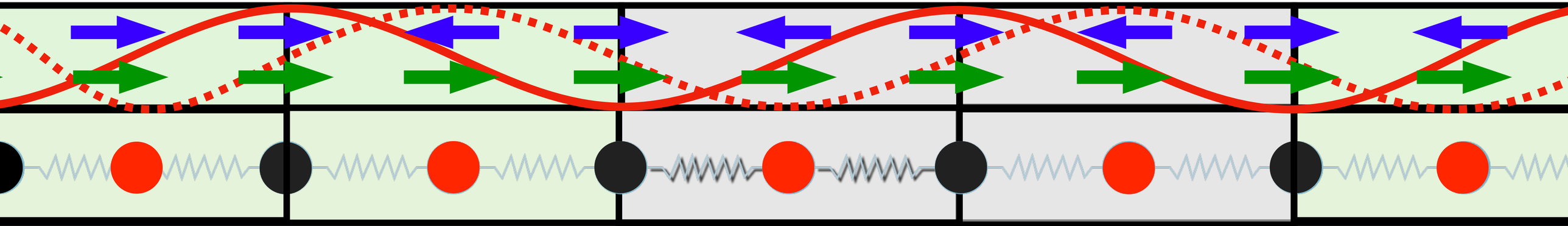

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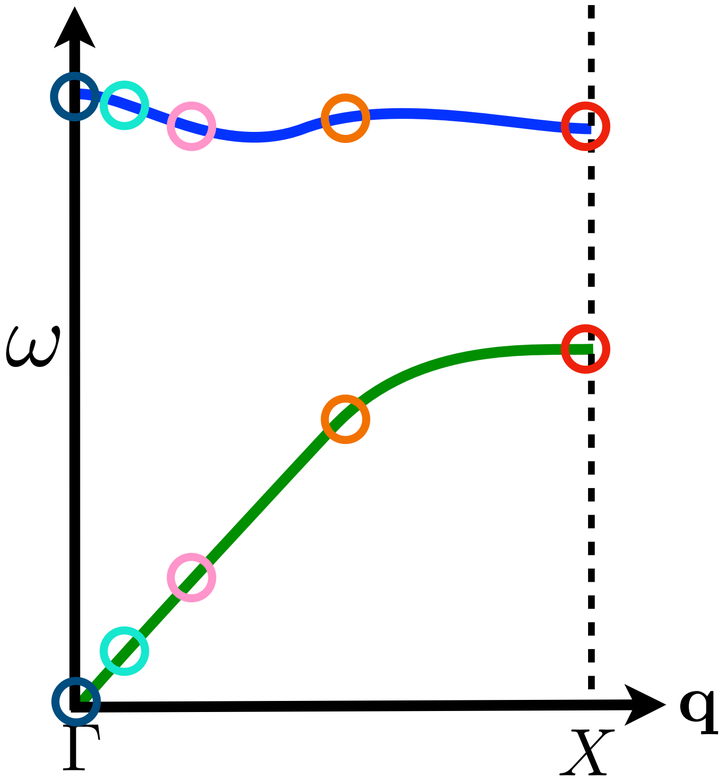

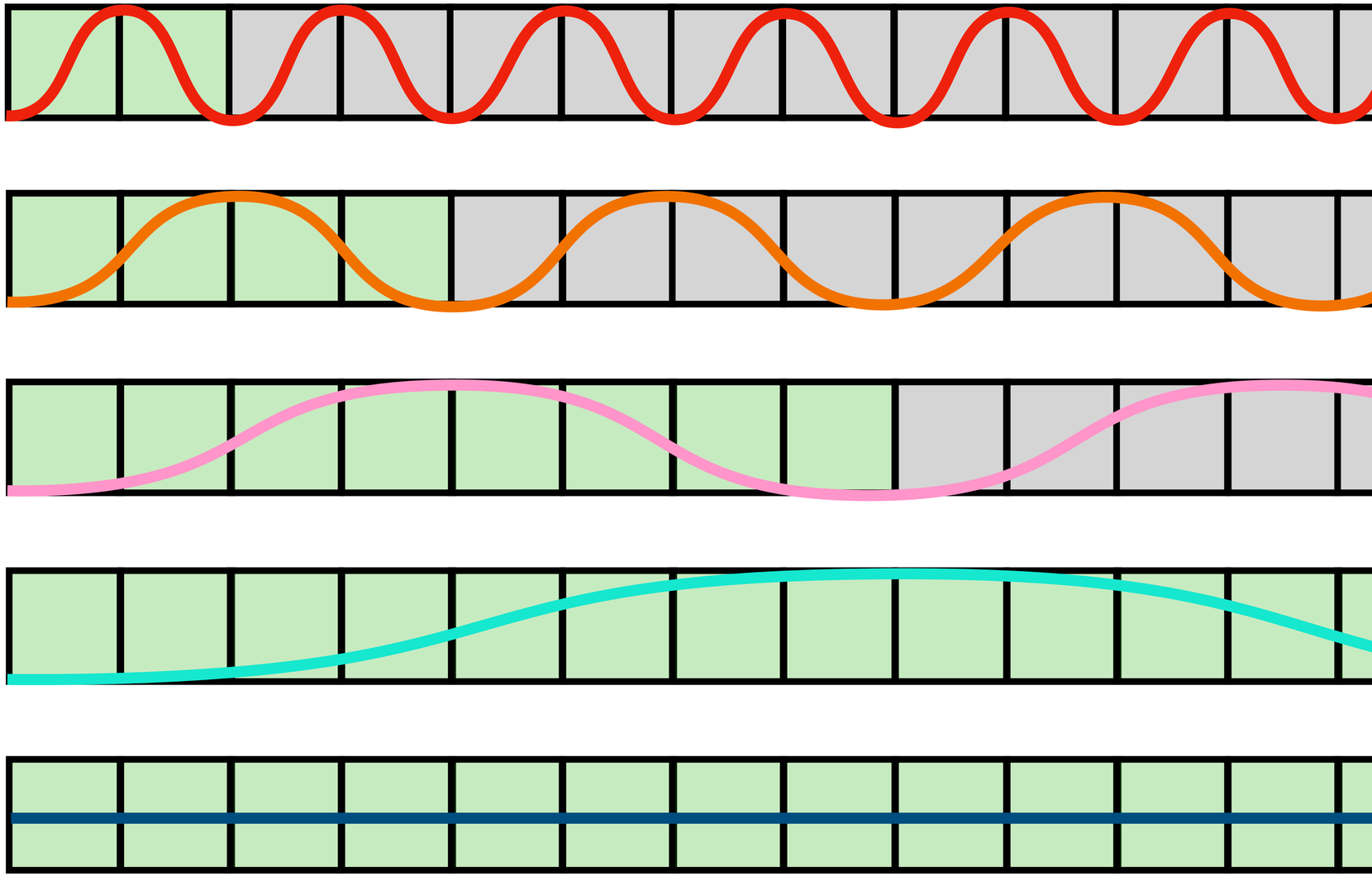

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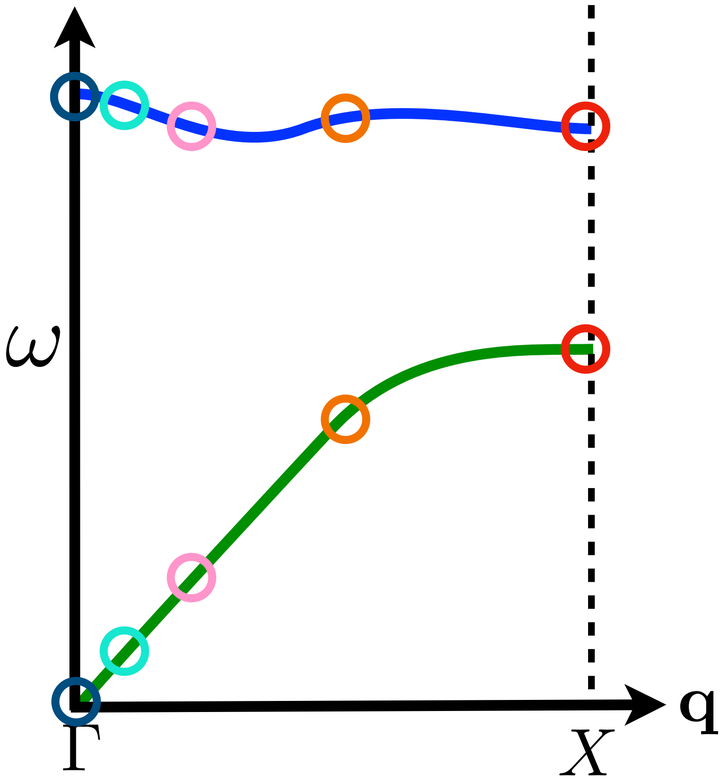

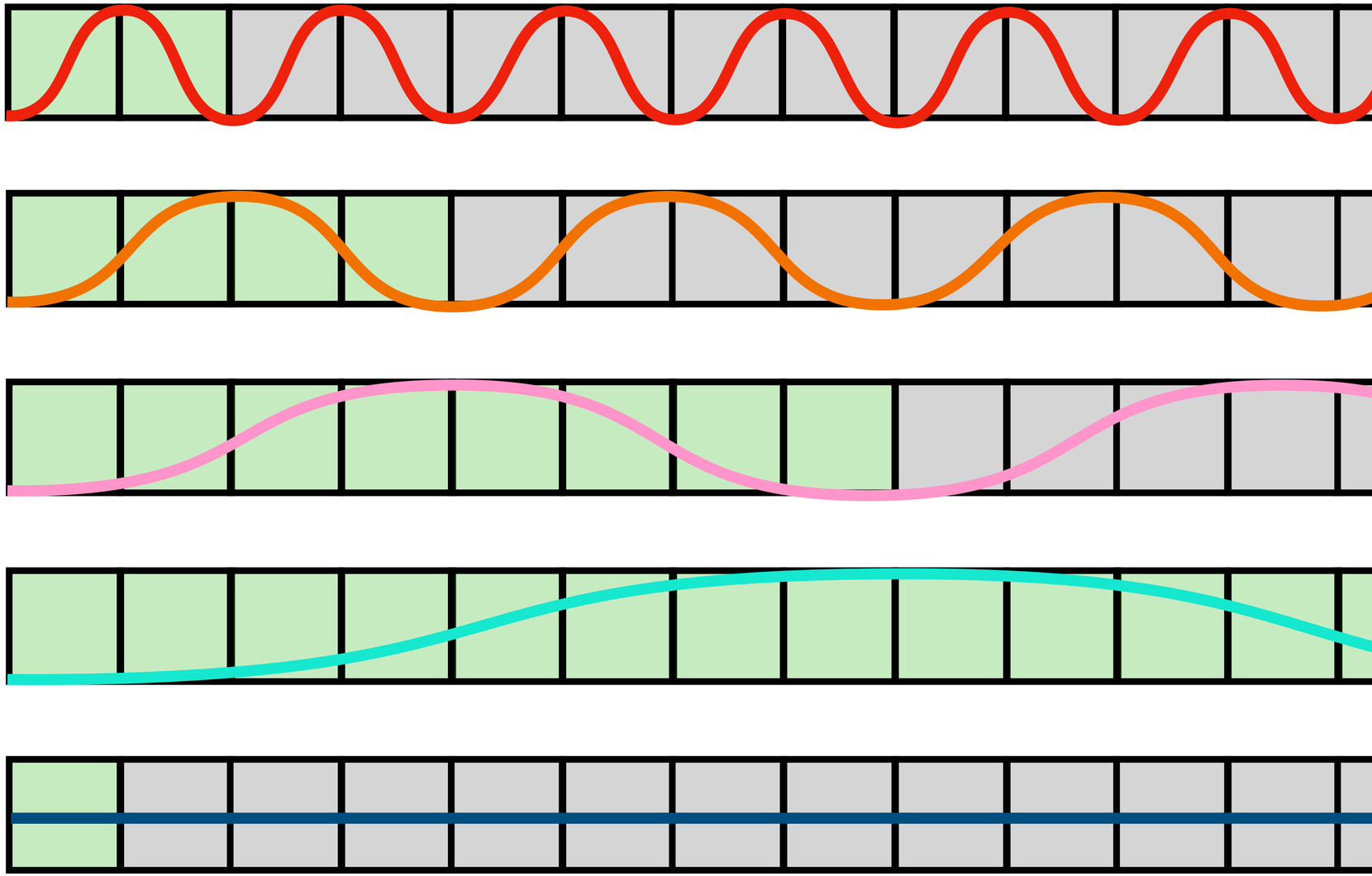

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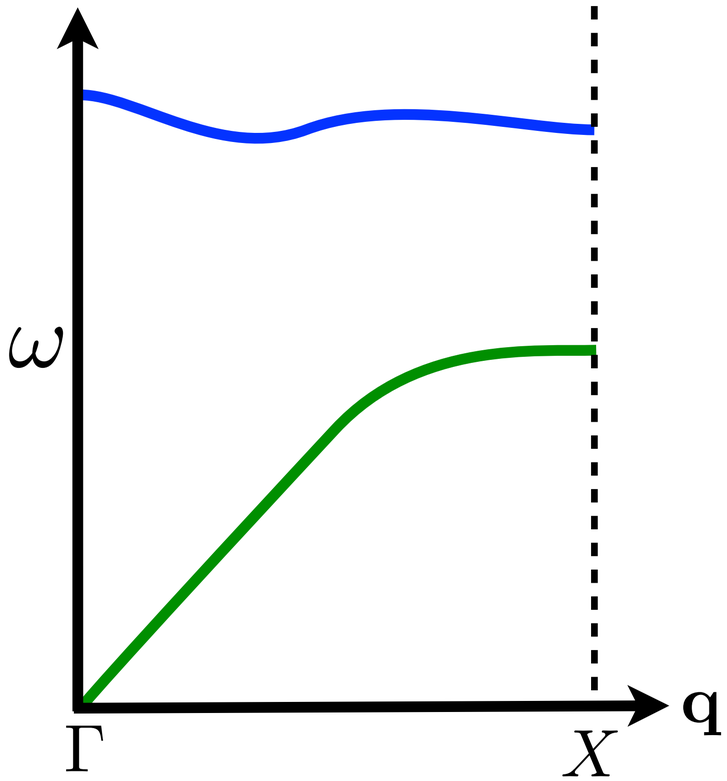


For N_p atoms in the unit cell there are:

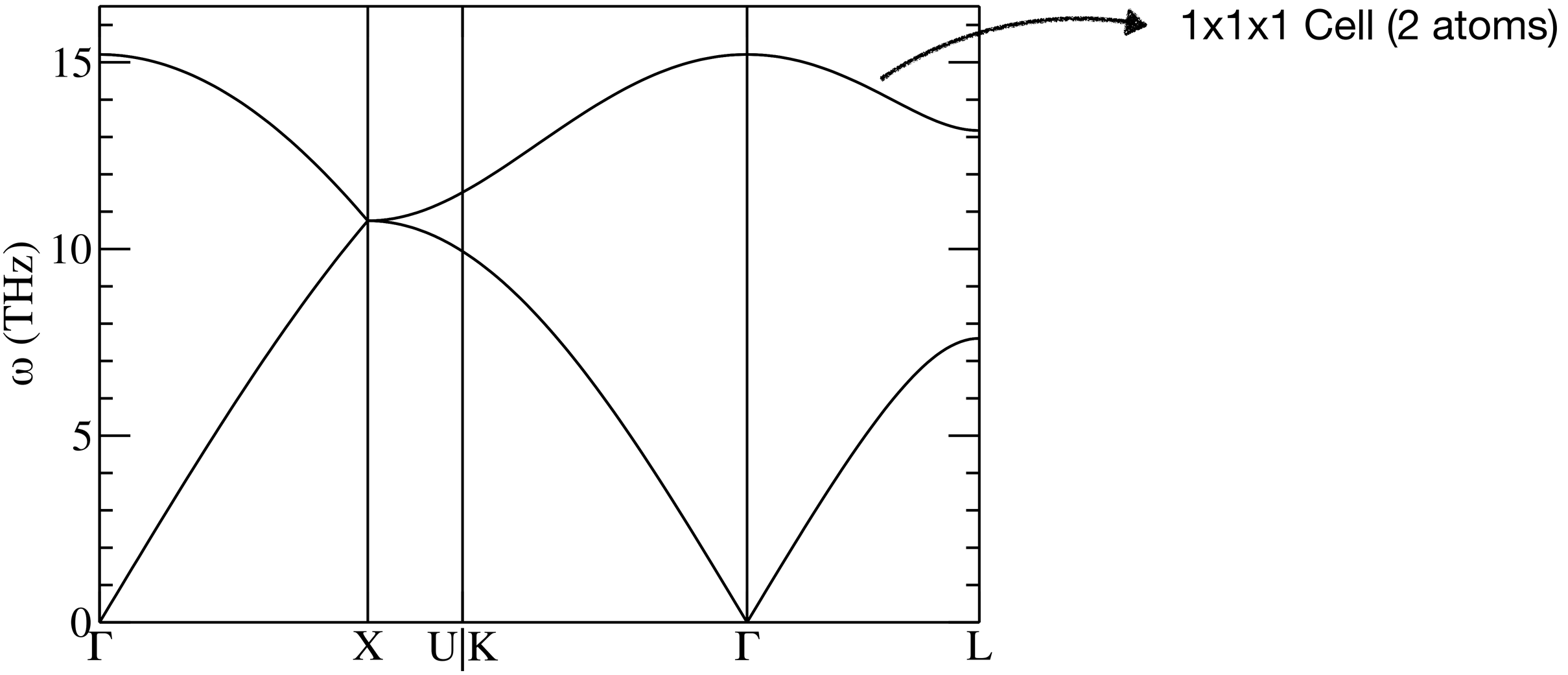
3 Acoustic modes:

- Atoms in unit cell **in-phase**
- Acoustic modes **vanish** at Γ
- **Strong** (typically linear) **dispersion** close to Γ

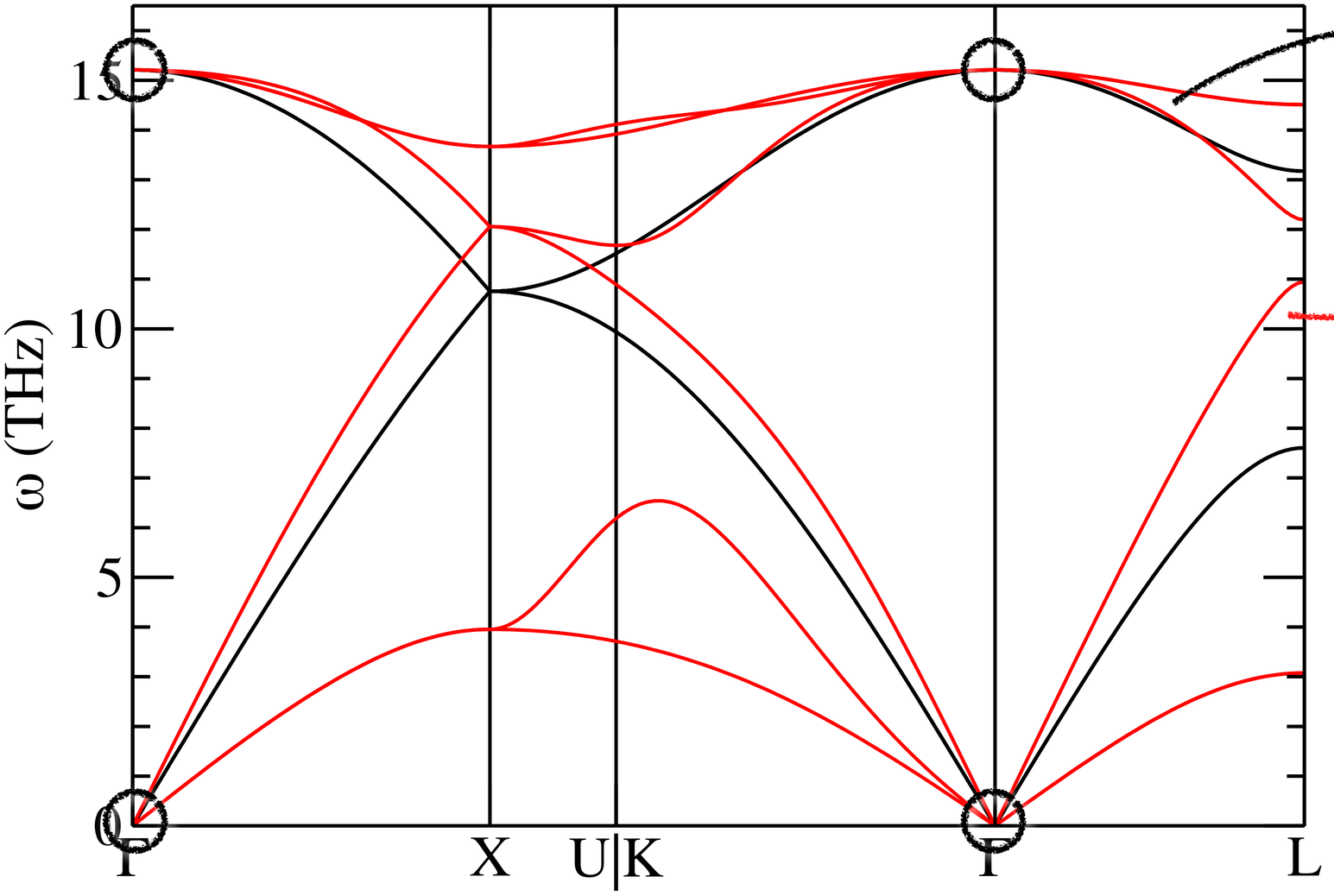
$(3N_p - 3)$ Optical modes:

- Atoms in unit cell **out-of-phase**
- $\omega > 0$ at Γ (and everywhere else)
- **Weak** dispersion

A Real Example: Diamond Si

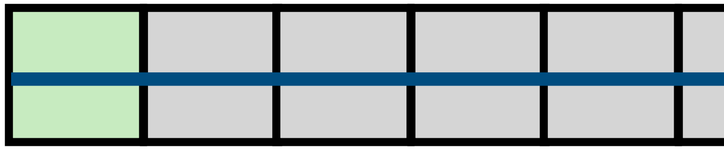


A Real Example: Diamond Si



1x1x1 Cell (2 atoms)

2x2x2 Cell (16 atoms)



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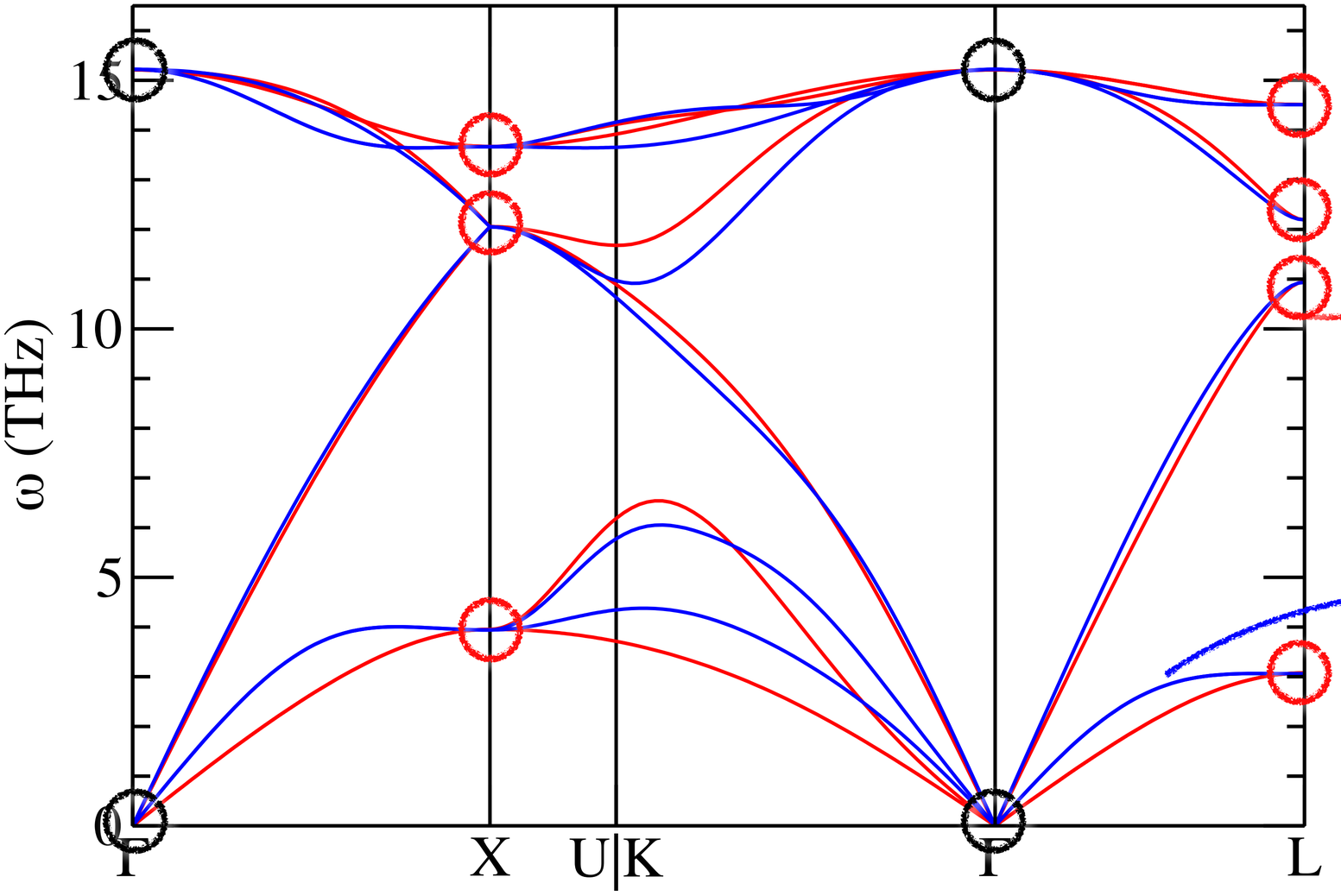
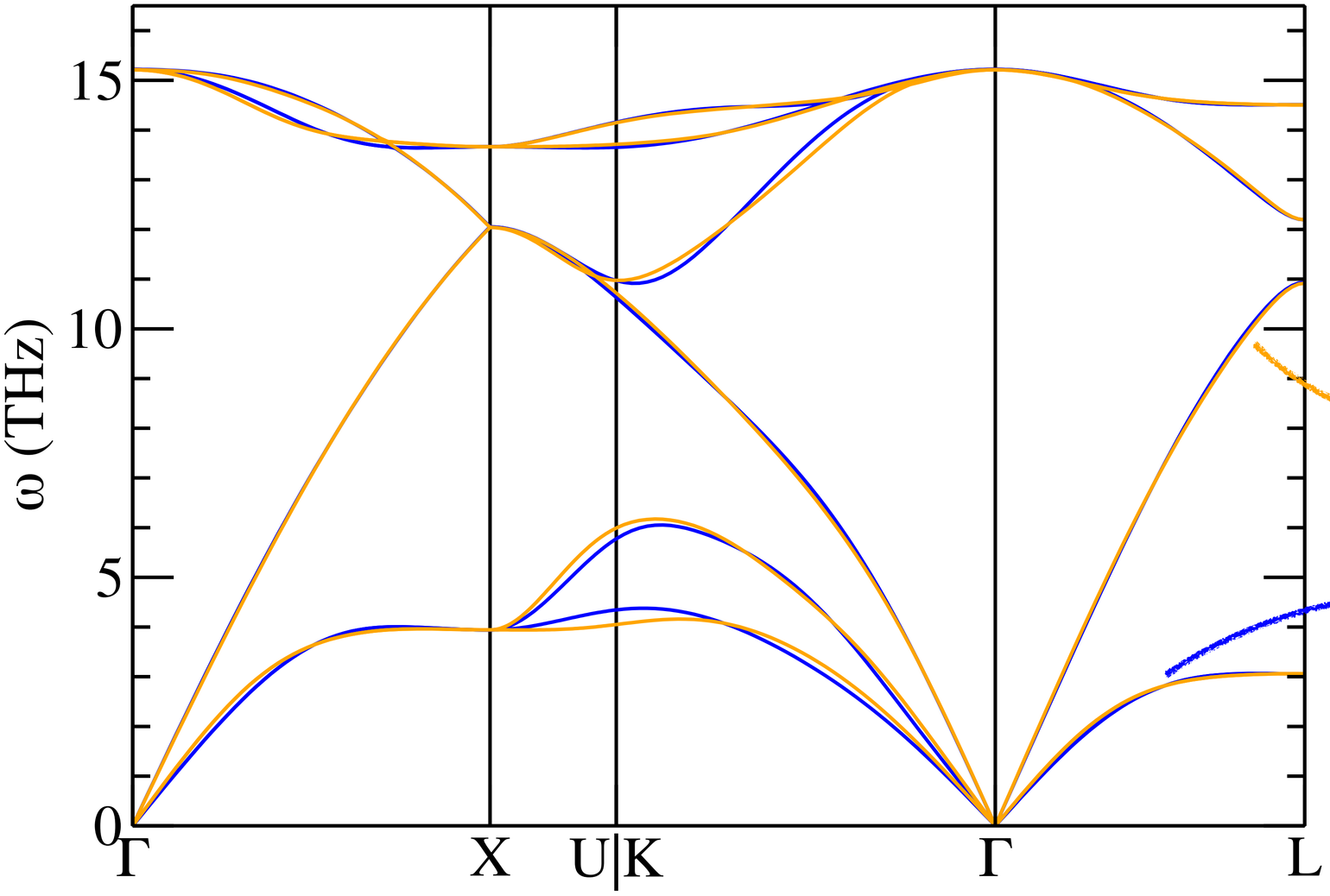


2x2x2 Cell (16 atoms)

4x4x4 Cell (128 atoms)

A Real Example: Diamond Si



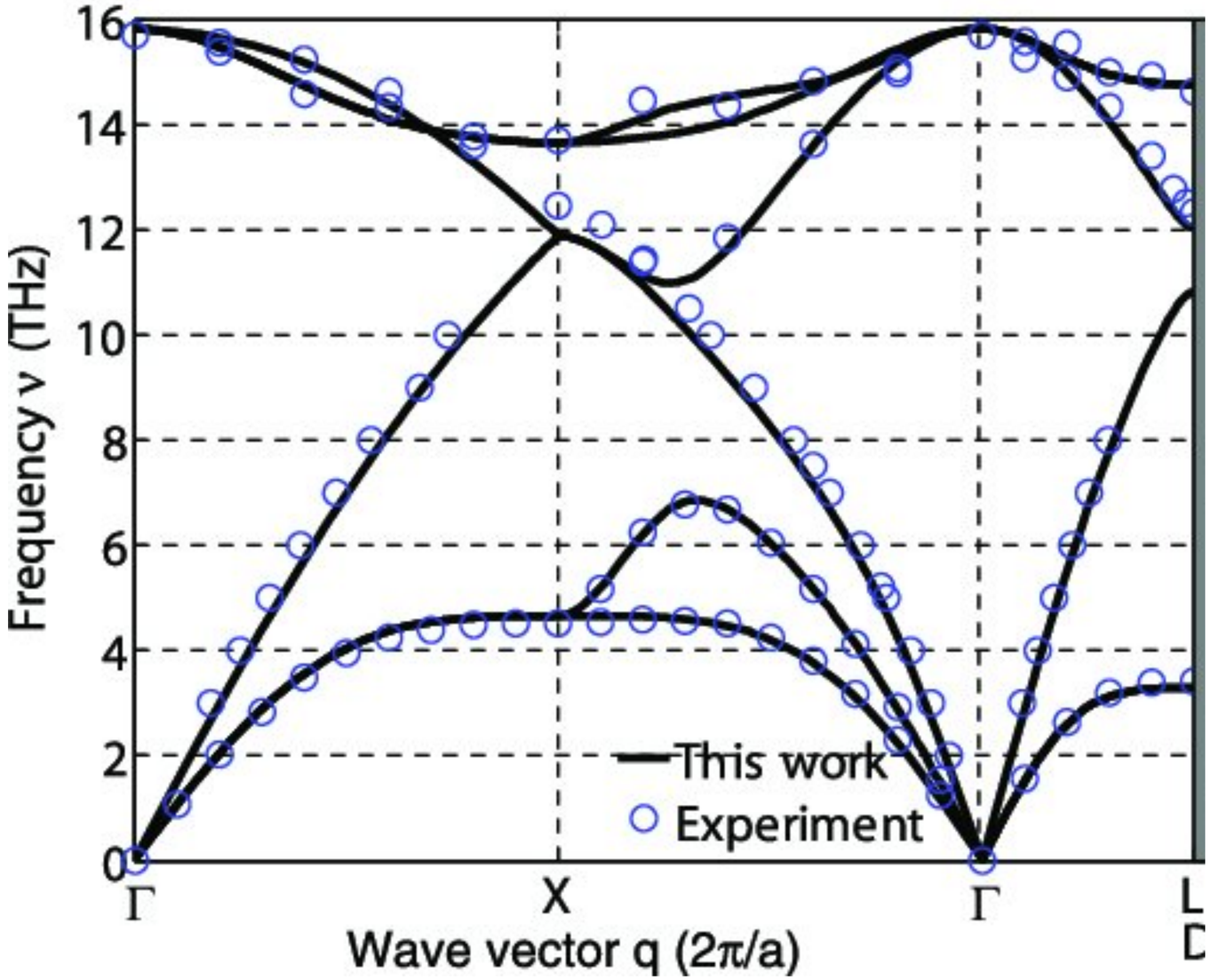
Convergence achieved!

N.B. 1 THz ≈ 4 meV

6x6x6 Cell (432 atoms)

4x4x4 Cell (128 atoms)

A Real Example: Diamond Si

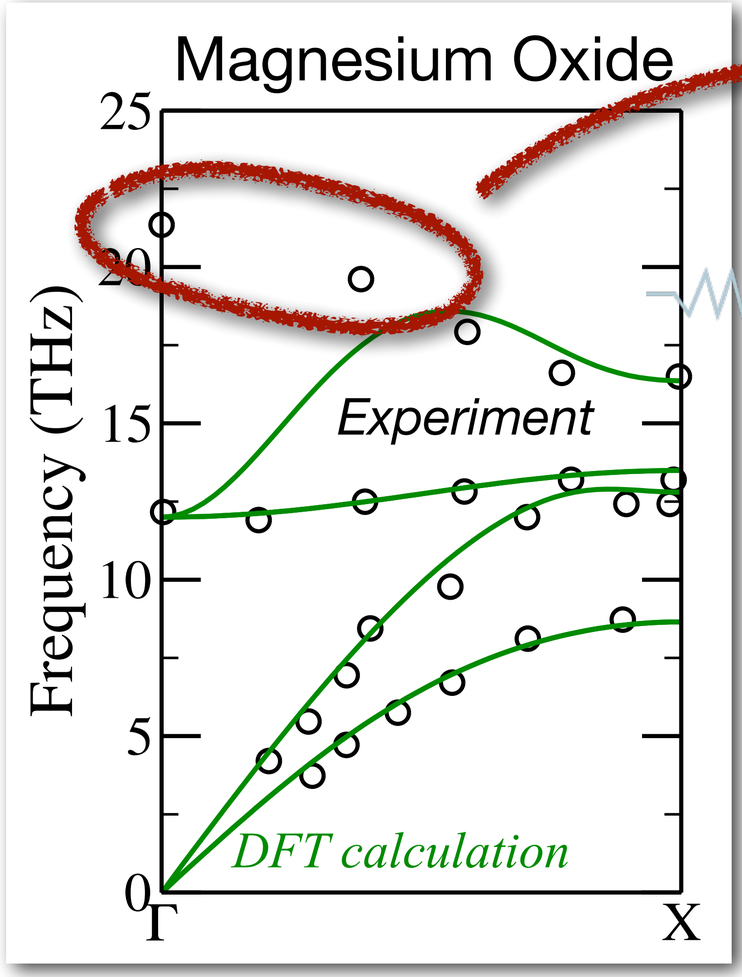


Comparison to experiment

Audrey Valentin *et al.*,
J. Phys.: Condens. Matter **20** 145213 (2008)

Polar Crystals

P. Giannozzi, S. Degironcoli, P. Pavone, and S. Baroni, *Phys. Rev. B* **43**, 7231 (1991).
X. Gonze, and C. Lee, *Phys. Rev. B* **55**, 10355 (1997).



Experiment: M. J. L. Sangster, G. Peckham, and D. H. Saunderson, J. Phys. C **3**, 1026 (1970).

What is wrong here?

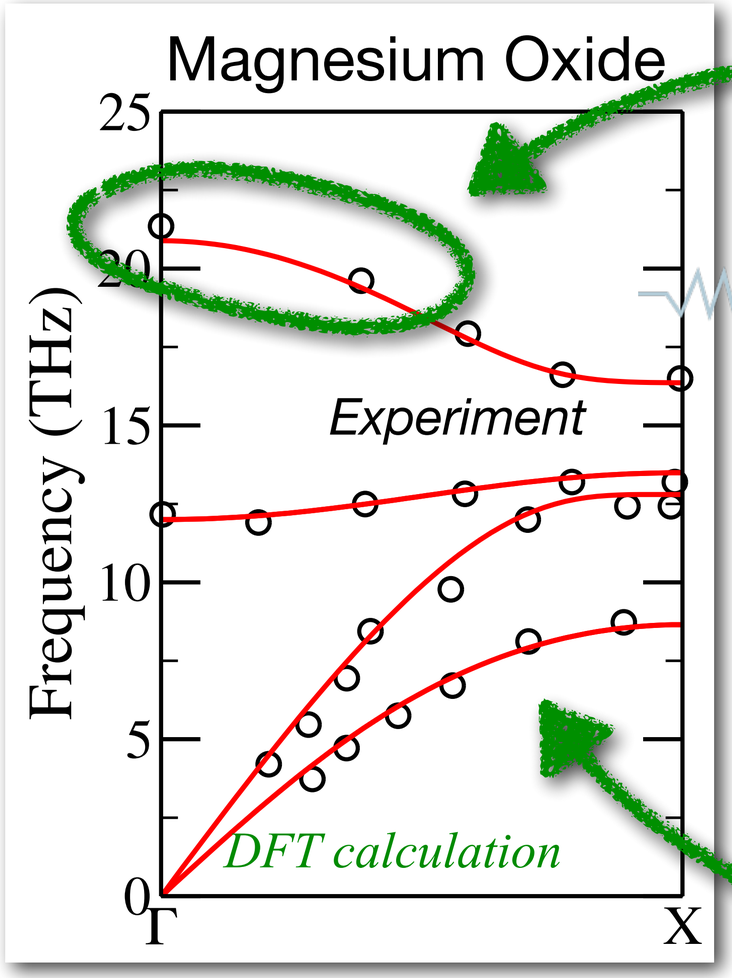
When *charged* atoms are *displaced*,
a **weak, long-ranged** dipole field is induced.

In the **short-range** ($q \gg 0$) this interaction is clouded by all other forces.

In the **long-range** ($q \approx 0$)
this interaction becomes **significant**.

Polar Crystals

P. Giannozzi, S. Degironcoli, P. Pavone, and S. Baroni, *Phys. Rev. B* **43**, 7231 (1991).
X. Gonze, and C. Lee, *Phys. Rev. B* **55**, 10355 (1997).



Experiment: M. J. L. Sangster, G. Peckham, and D. H. Saunderson, J. Phys. C **3**, 1026 (1970).

How to account for it?

★Calculate *Born Effective Charges* $\mathbf{Z}_i^*$, i.e., the **derivative** of the **polarisation**.

★Calculate dielectric constant ε_∞, i.e, how the electric field is screened.

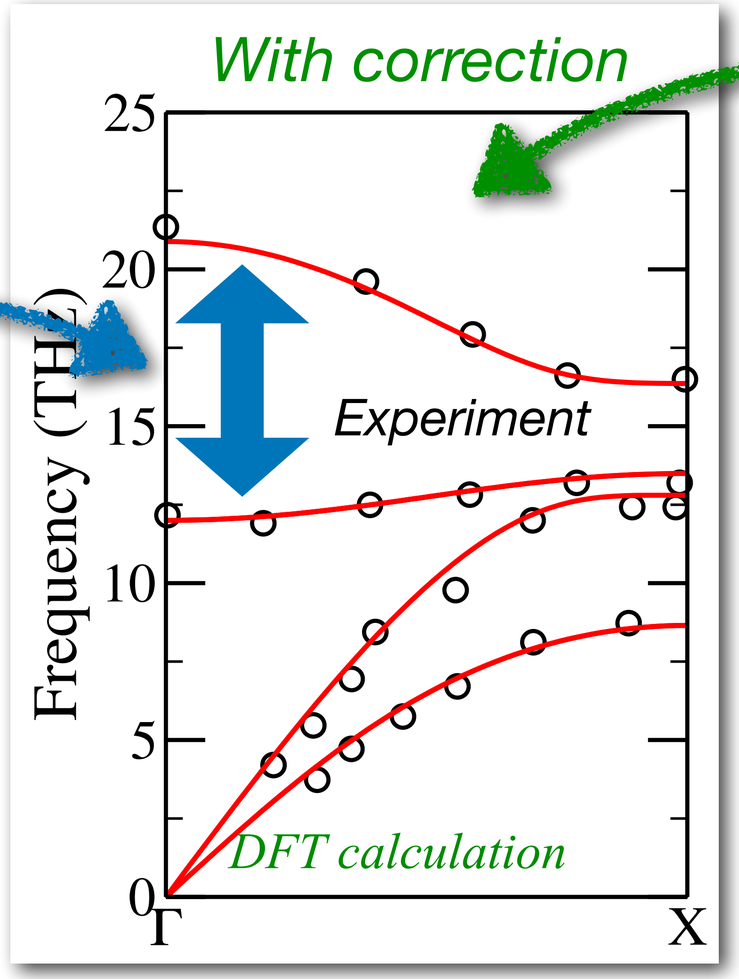
★Add the **additional, far-field** interaction:

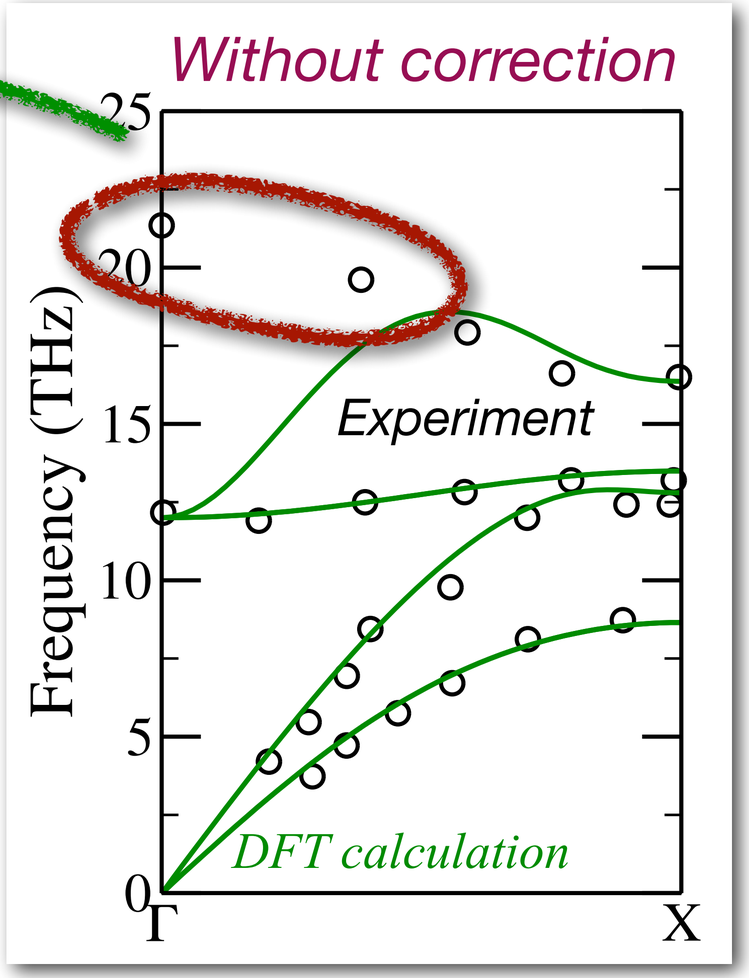
$$\mathbf{D}_{IJ}(\mathbf{q}) \rightarrow \mathbf{D}_{IJ}(\mathbf{q}) + \frac{1}{\sqrt{M_I M_J}} \frac{4\pi}{\Omega_0} \frac{[\mathbf{q}\cdot\mathbf{Z}_I^*]\,[\mathbf{q}\cdot\mathbf{Z}_J^*]}{\mathbf{q}\cdot\varepsilon^\infty\cdot\mathbf{q}}$$

Polar Crystals

P. Giannozzi, S. Degironcoli, P. Pavone, and S. Baroni, *Phys. Rev. B* **43**, 7231 (1991).
X. Gonze, and C. Lee, *Phys. Rev. B* **55**, 10355 (1997).

LO-TO splitting





Experiment: M. J. L. Sangster, G. Peckham, and D. H. Saunderson, J. Phys. C **3**, 1026 (1970).

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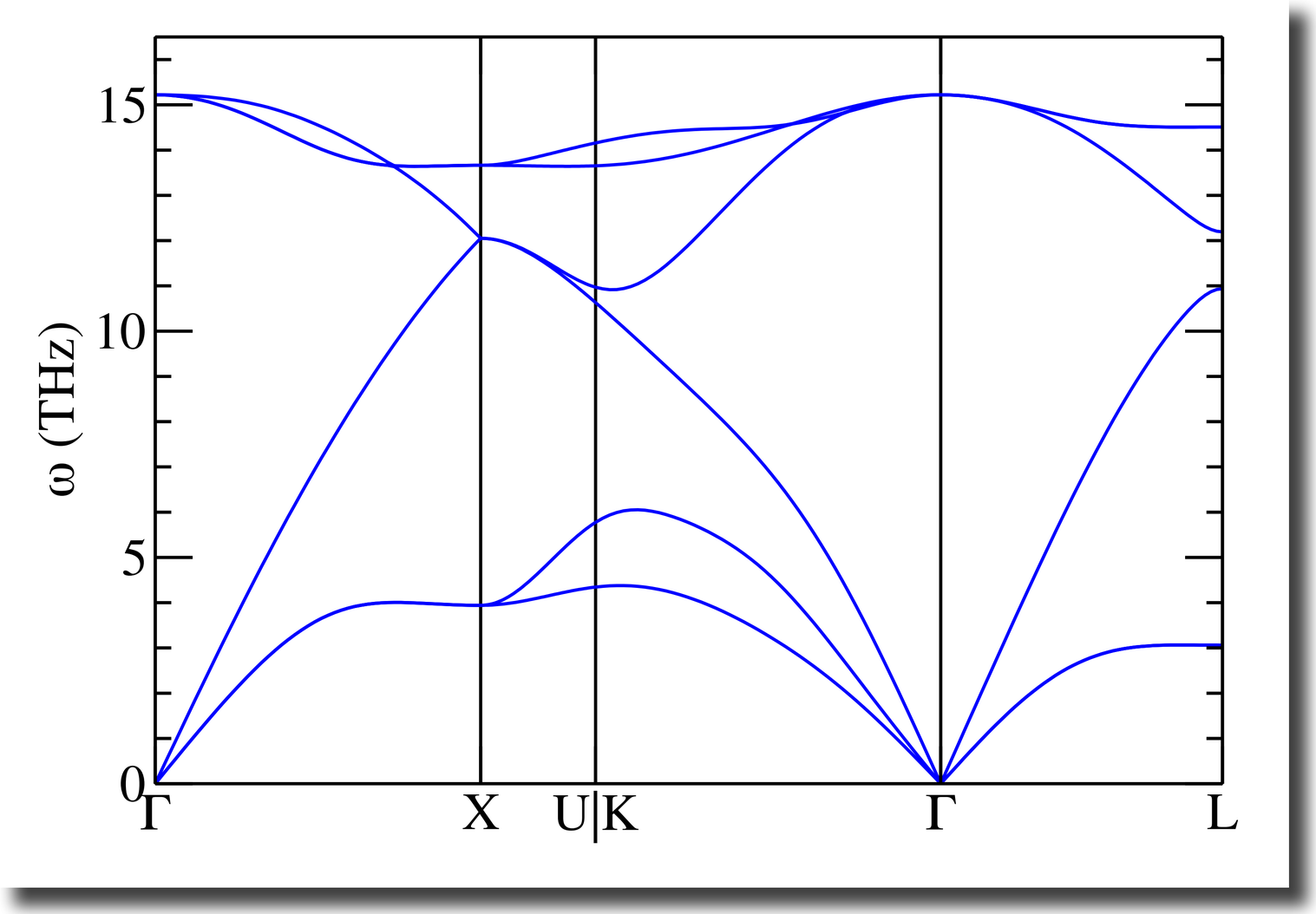
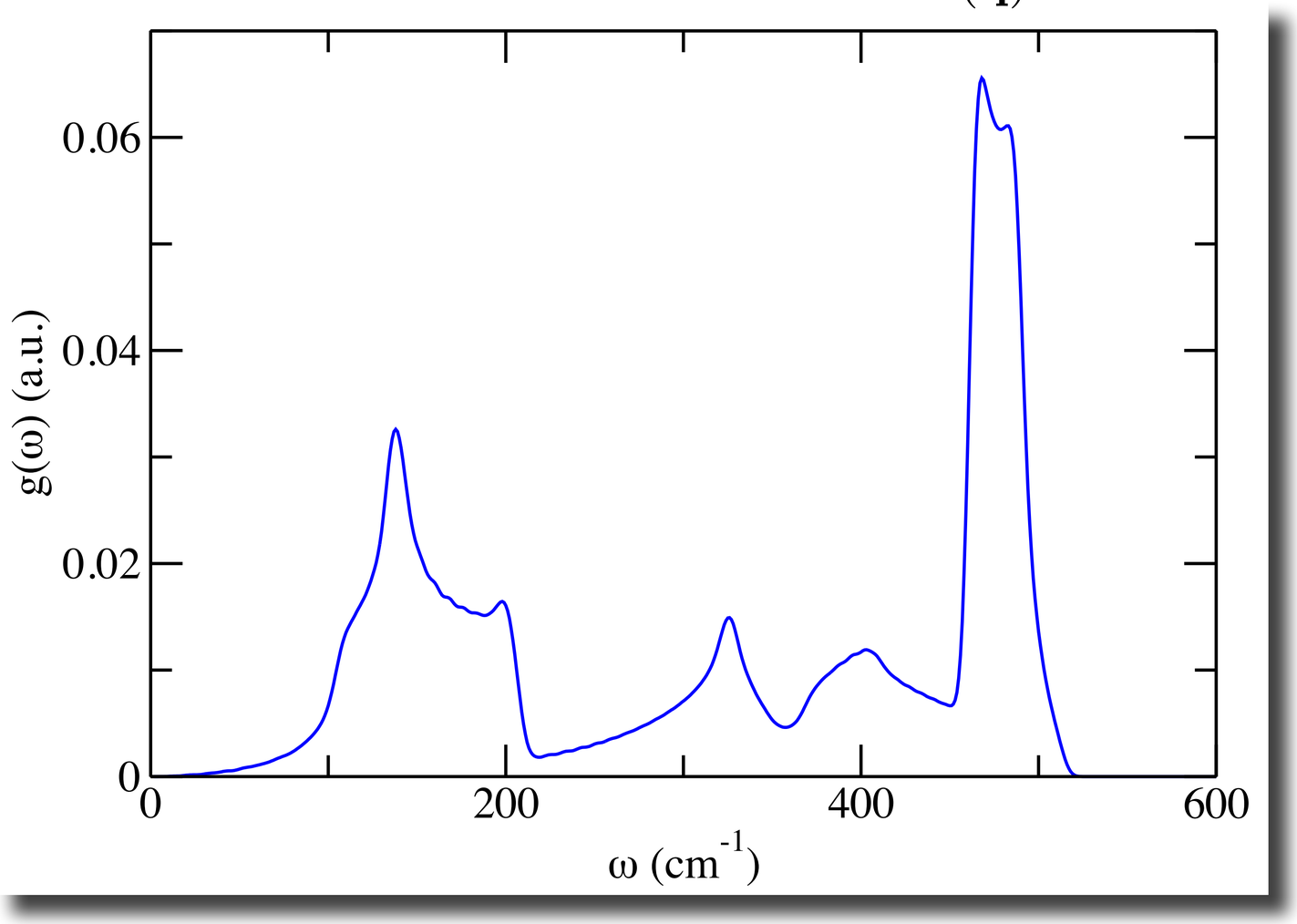
VIBRATIONAL BAND STRUCTURE



Silicon, diamond structure

VIBRATIONAL DENSITY OF STATES

$$g(\omega) = \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \delta(\omega - \omega(\mathbf{q})) = \sum_s \int_{\omega(\mathbf{q})=\omega} \frac{dS}{(2\pi)^3} \frac{1}{|\nabla \omega_s(\mathbf{q})|}$$



Take-Home Messages

- **Everything moves!** Nuclei and atoms are never at rest.
- The potential-energy surface on which the nuclei move can be ***approximated*** using a ***harmonic potential***. This requires calculating *2nd order derivatives at equilibrium*.
- With that, we obtain $3N_p$ **independent** and **q-dependent** harmonic oscillators. Their equations of motion can be solved *exactly* and *analytically*.

What about the actual thermodynamic motion?

Attention:
Quantum-Nuclear Effects

Classical Limit: Equipartition Theorem

Each mode carries $\langle E_s(\mathbf{q}, T)\rangle = k_B T$

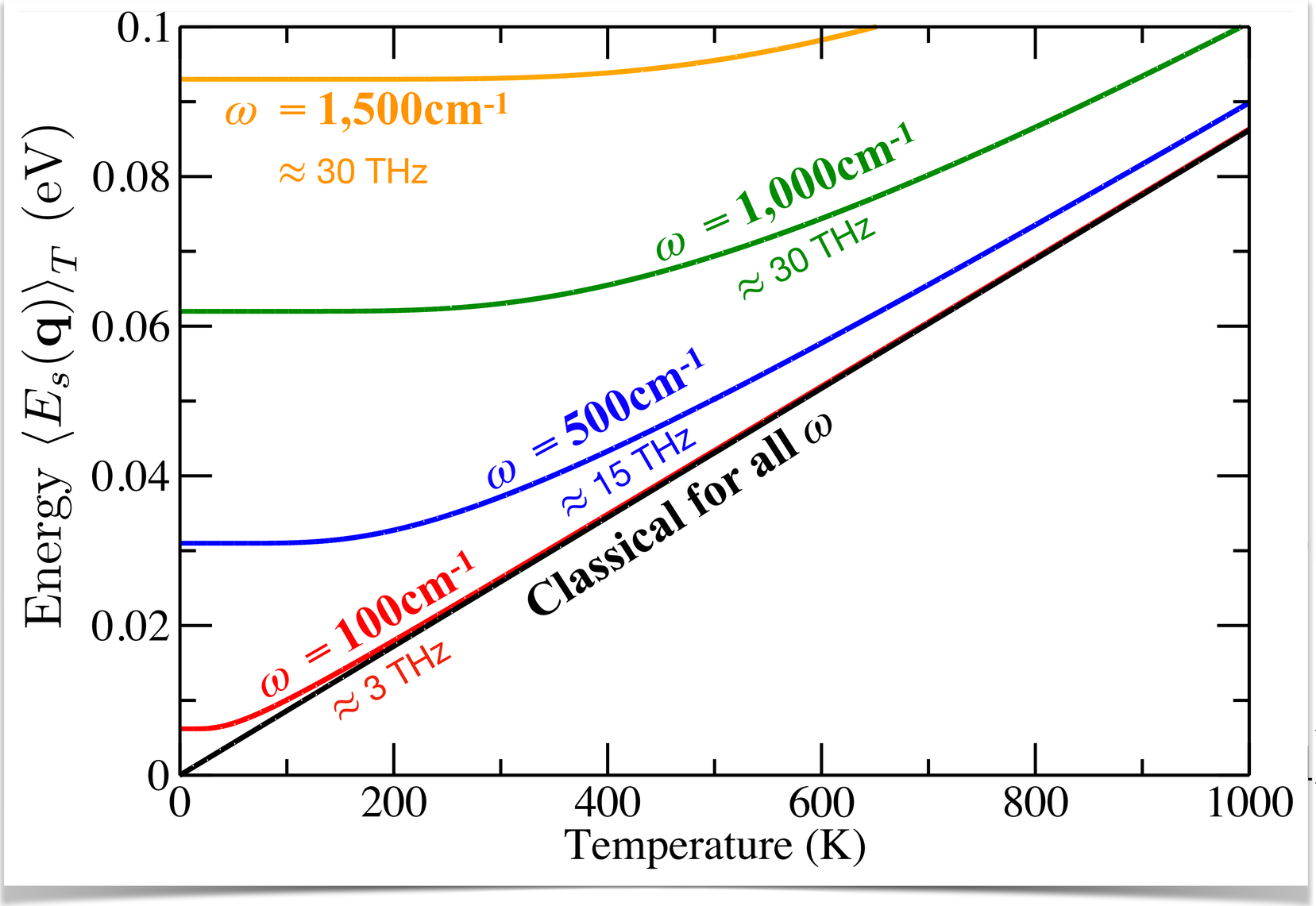
Quantum-mechanical Solution: Bose-Einstein

Each mode carries

$$\langle E_s(\mathbf{q}, T)\rangle = \hbar\omega_s(\mathbf{q}) \left(n_{\mathrm{BE}}(\omega_s(\mathbf{q}), T)) + \frac{1}{2} \right)$$

Attention:

Quantum-Nuclear Effects

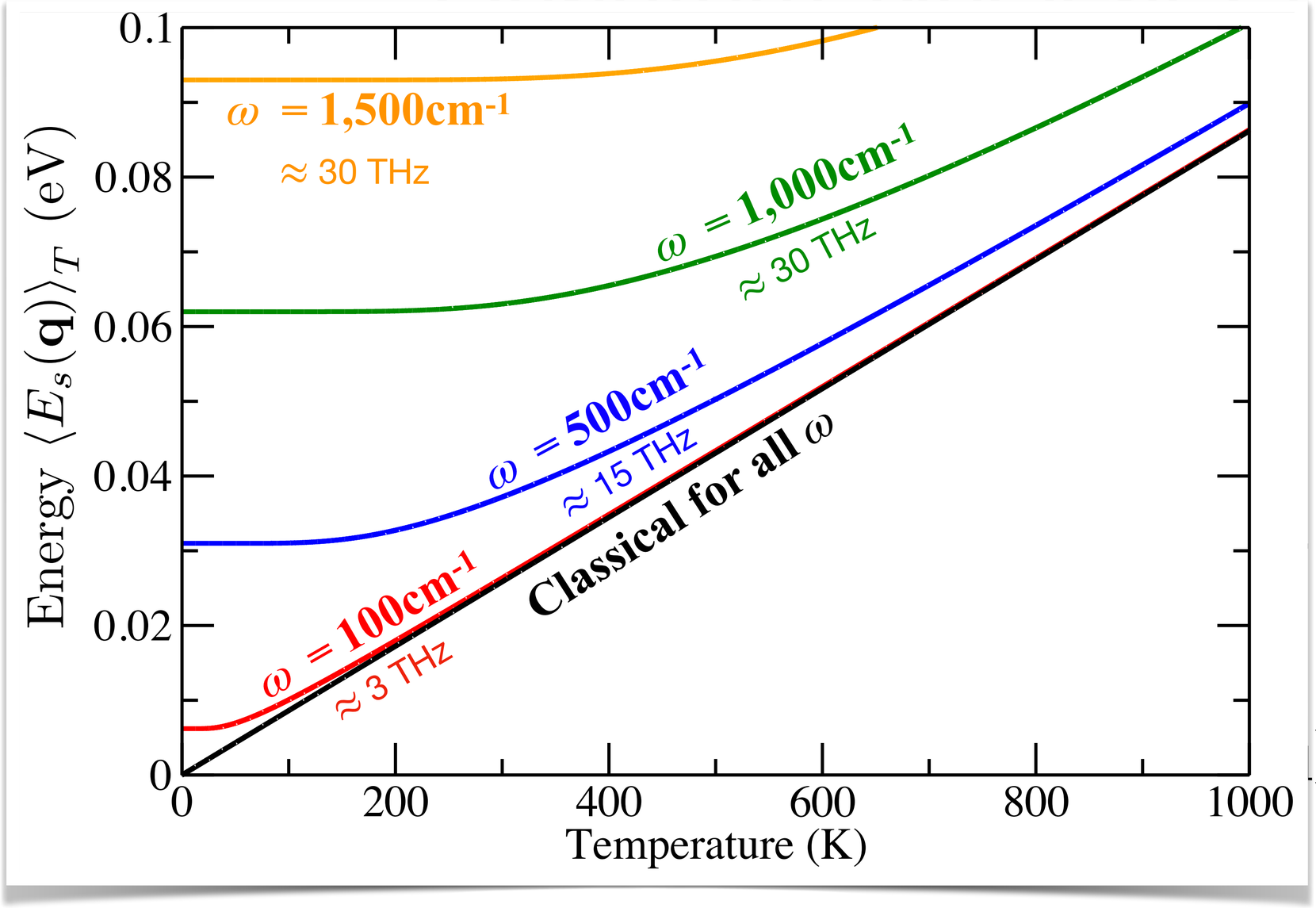


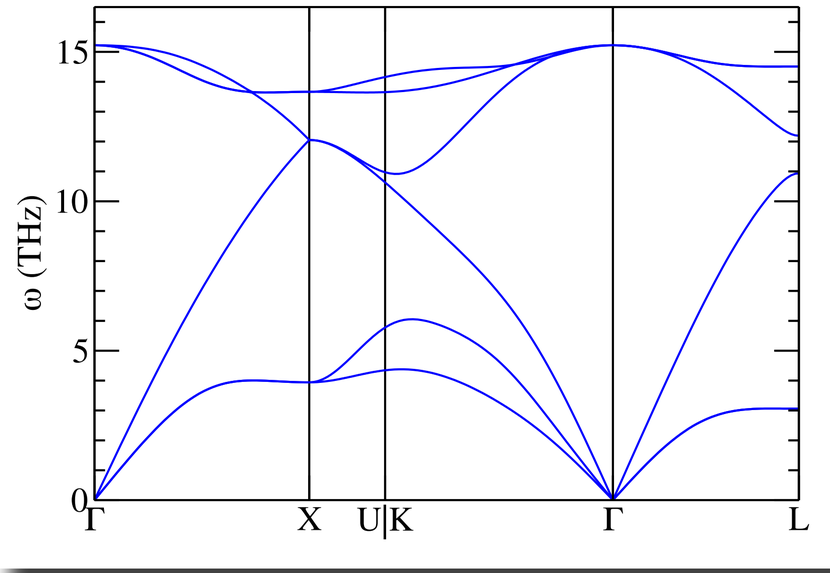
Einstein

$$\left.\right), T)) + \frac{1}{2}\Bigg)$$

Attention:

Quantum-Nuclear Effects

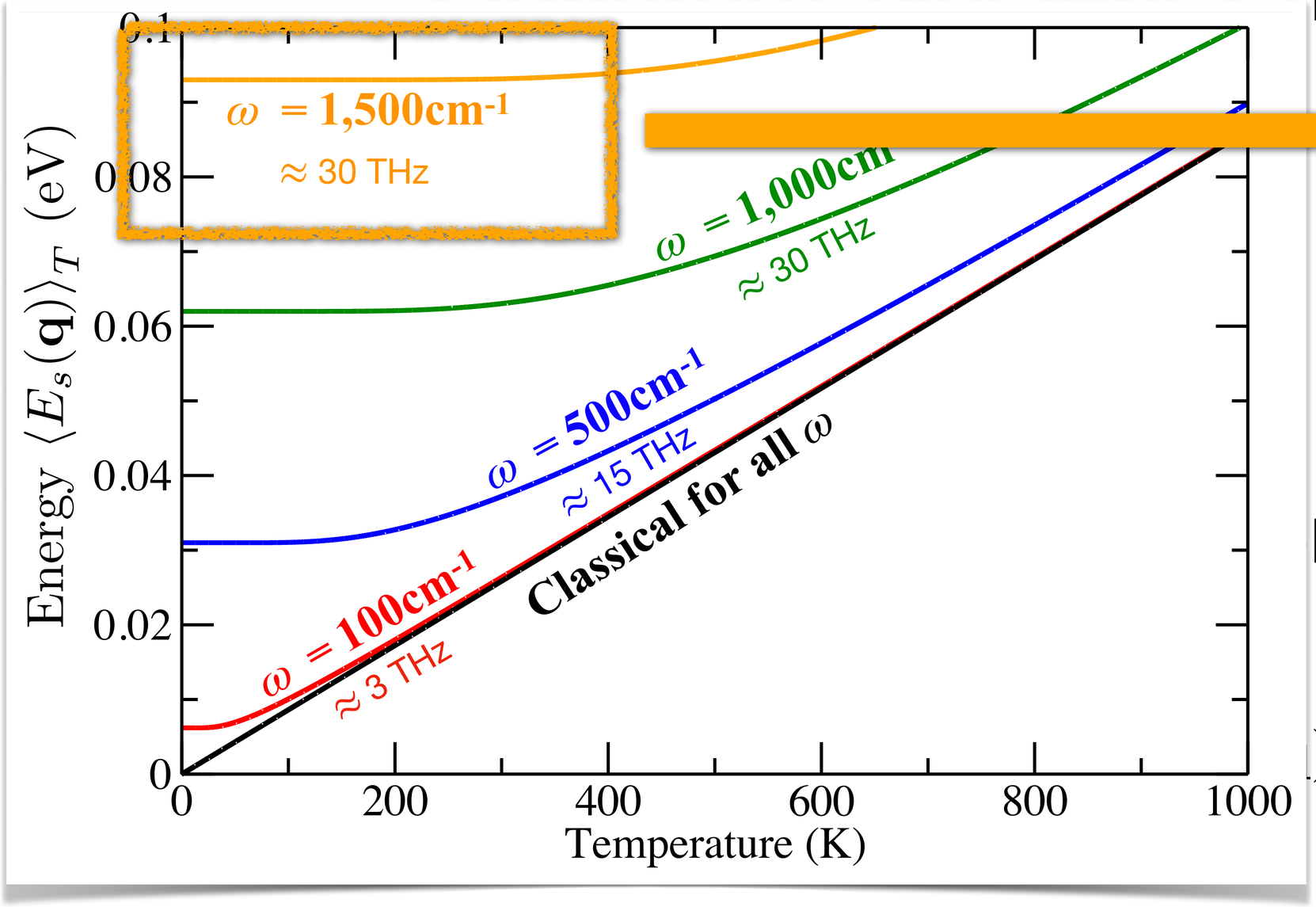




$$\left.\right), T)) + \frac{1}{2}\Bigg)$$

Attention:

Quantum-Nuclear Effects



C-H frequencies
can reach
up to
3,000 cm-1 (60 Thz)!

Einstein

$$\left.\right), T)) + \frac{1}{2}\Bigg)$$

The Harmonic Free Energy

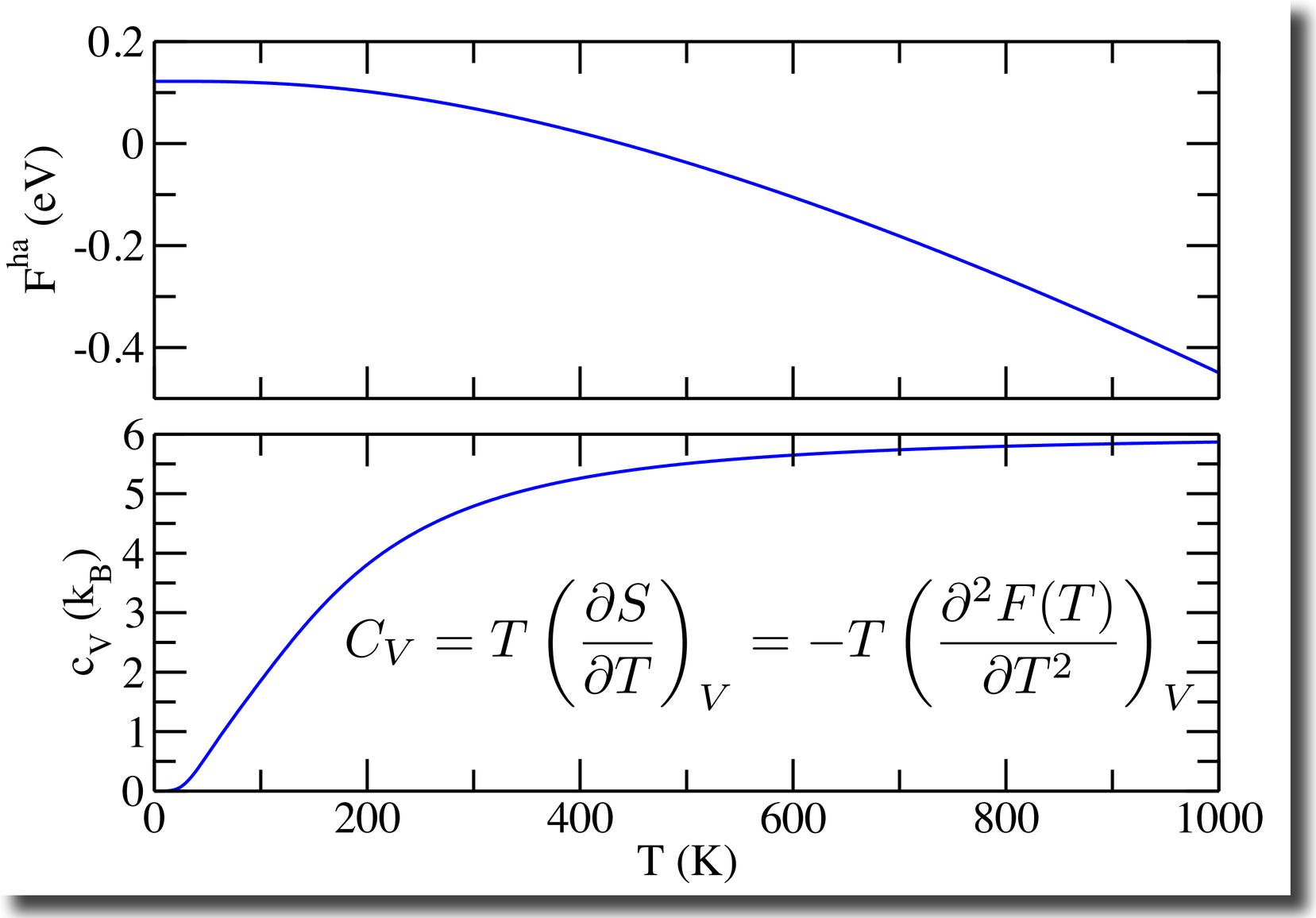
$$
\begin{aligned}
F^{ha}(T) &= E(\{\mathbf{R}_0\}) \\
&+ \int d\omega \; g(\omega) \frac{\hbar\omega}{2} \\
&+ \int d\omega \; g(\omega) \; k_B \, T \ln\left(1 - e^{\left(-\frac{\hbar\omega}{k_B \, T}\right)}\right)
\end{aligned}
$$

Static Equilibrium Energy

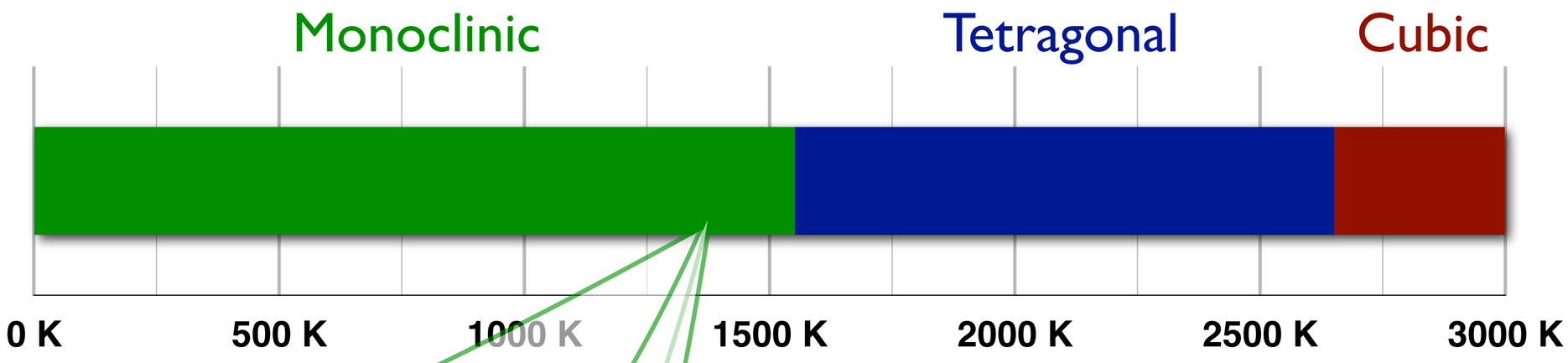
Zero-point vibration

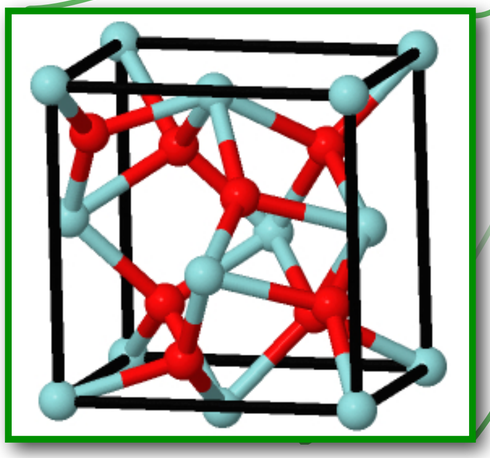
Thermally induced vibrations

The Harmonic Free Energy



AN EXAMPLE: PHASE DIAGRAM OF ZrO_2



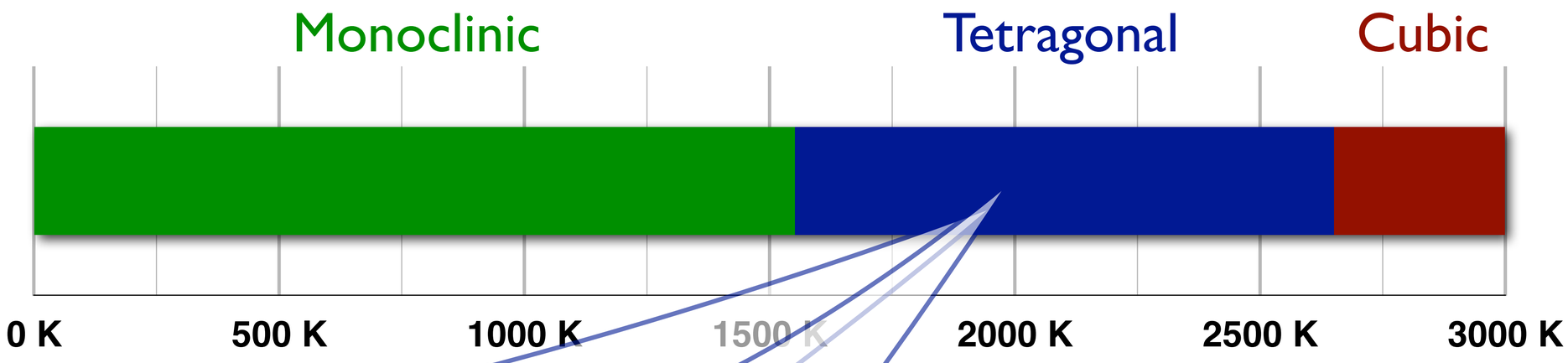


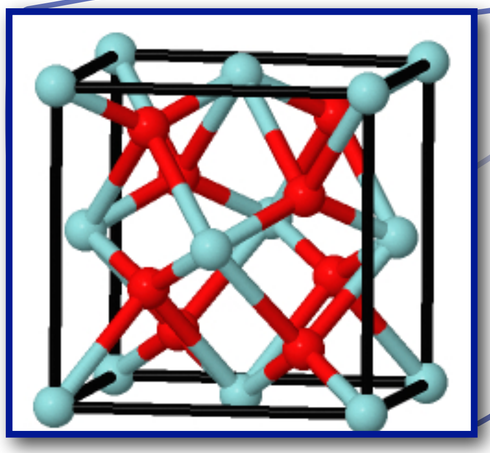
T < 1200°C

„Monoclinic“

Baddeleyite Structure

AN EXAMPLE: PHASE DIAGRAM OF ZrO_2



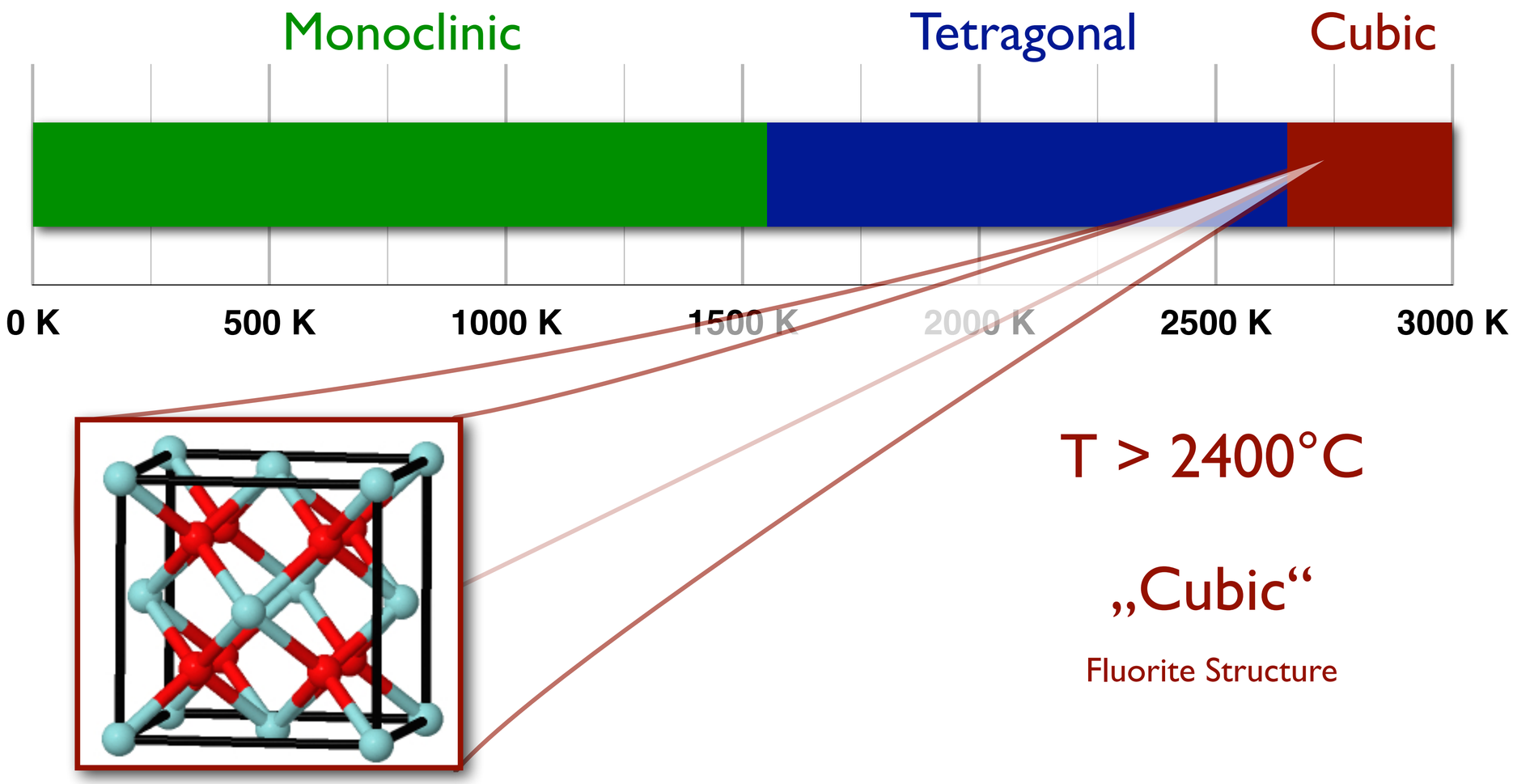


1200°C < T < 2400°C

„Tetragonal“

$P4_2/nmc$ Structure

AN EXAMPLE: PHASE DIAGRAM OF ZrO_2



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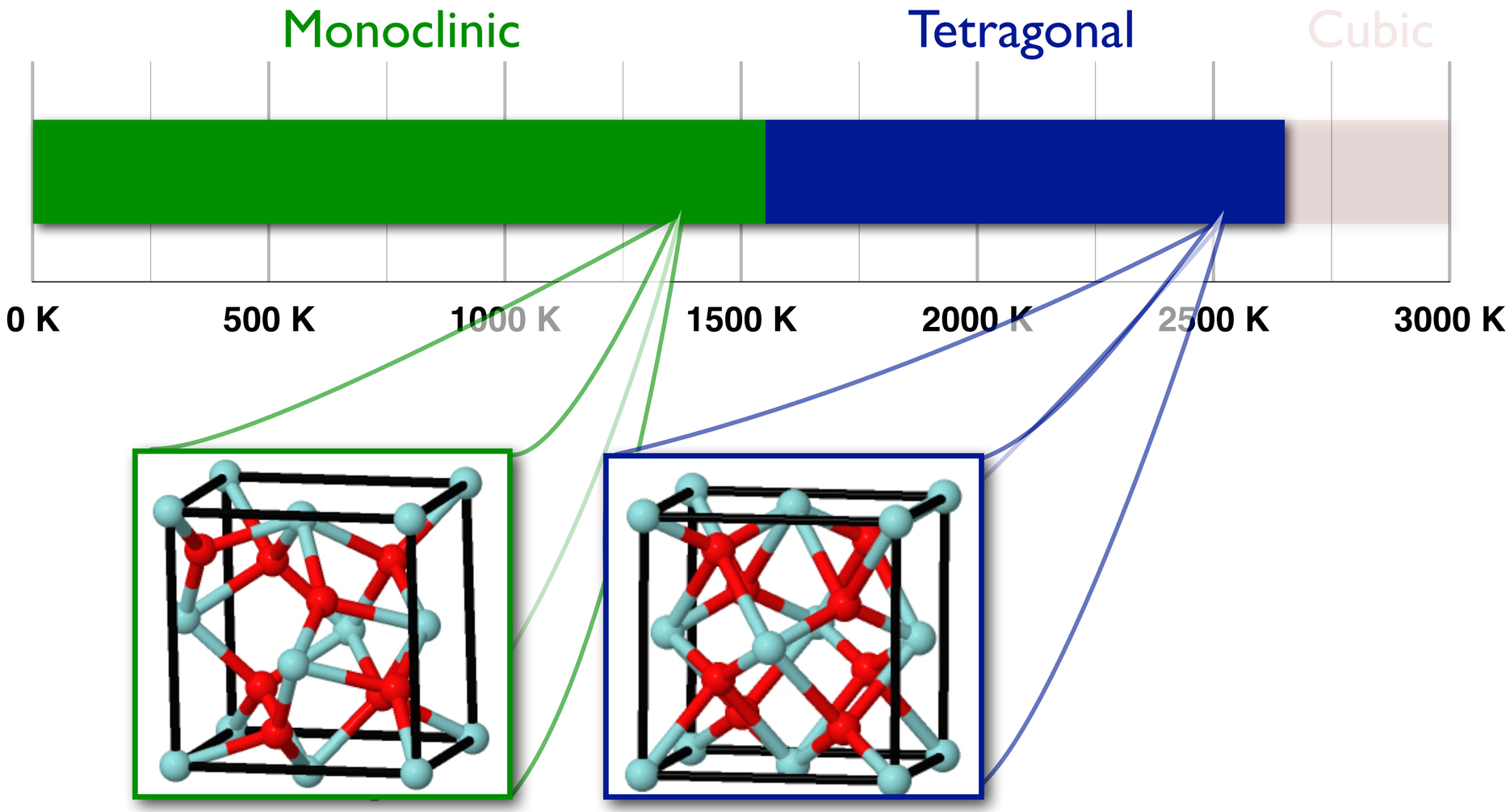
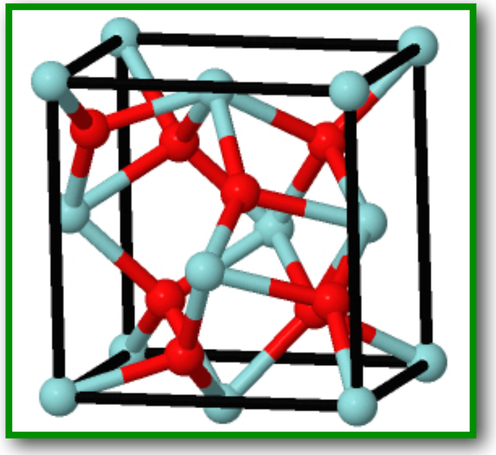
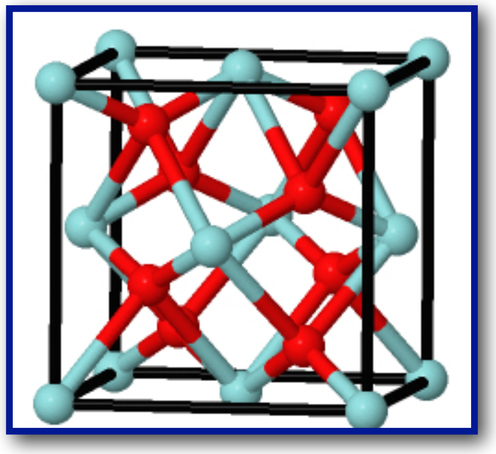
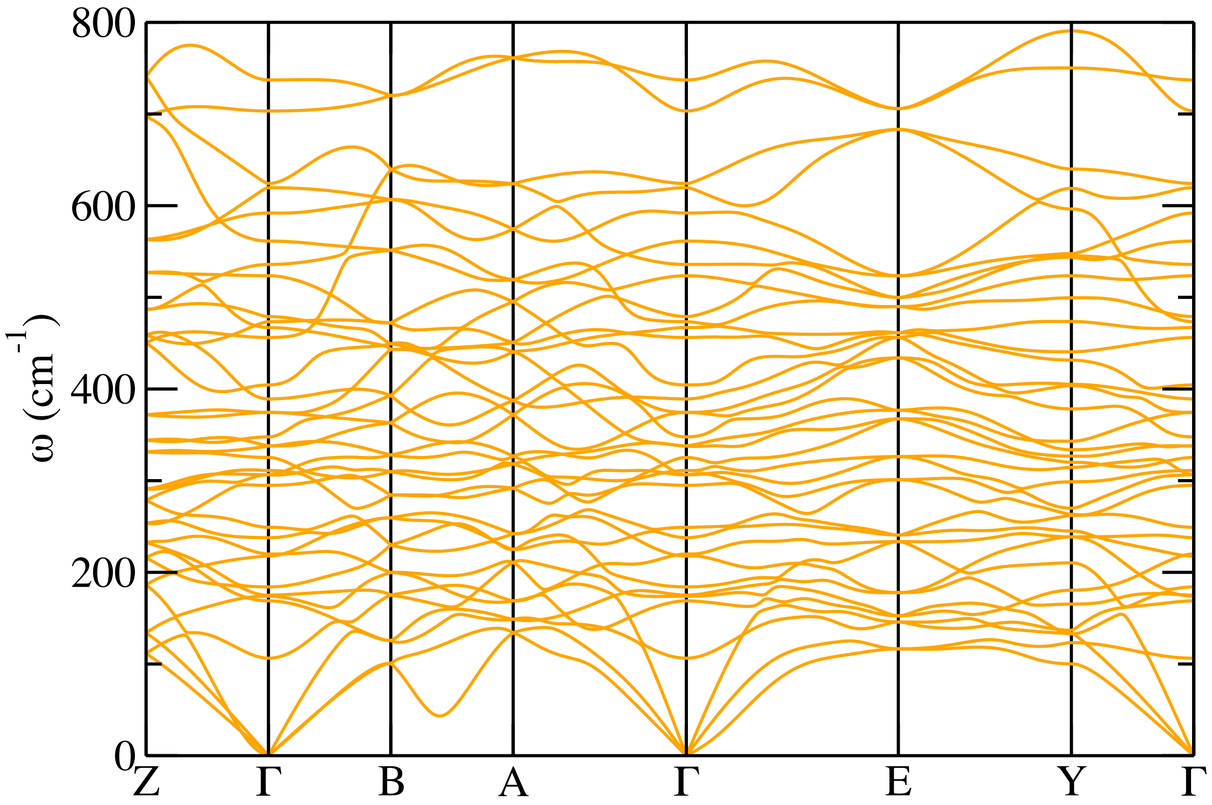
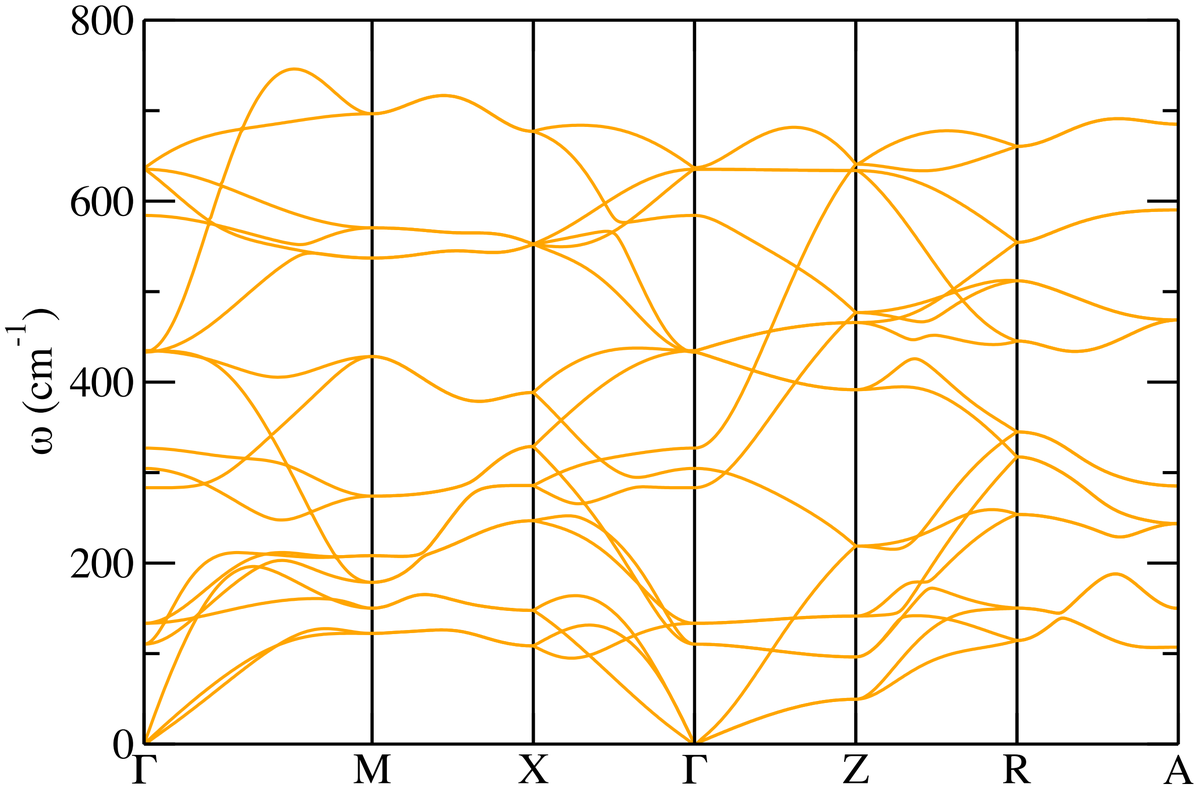




CALCULATE THE PHONONS







THE HARMONIC FREE ENERGY

$$
\begin{aligned}
F^{ha}(T) &= E_{\mathrm{DFT}}(0K) \\
&+ \int d\omega \; g(\omega) \frac{\hbar\omega}{2} \\
&+ \int d\omega \; g(\omega) \; k_B \, T \ln\left(1 - e^{\left(-\frac{\hbar\omega}{k_B \, T}\right)}\right)
\end{aligned}
$$

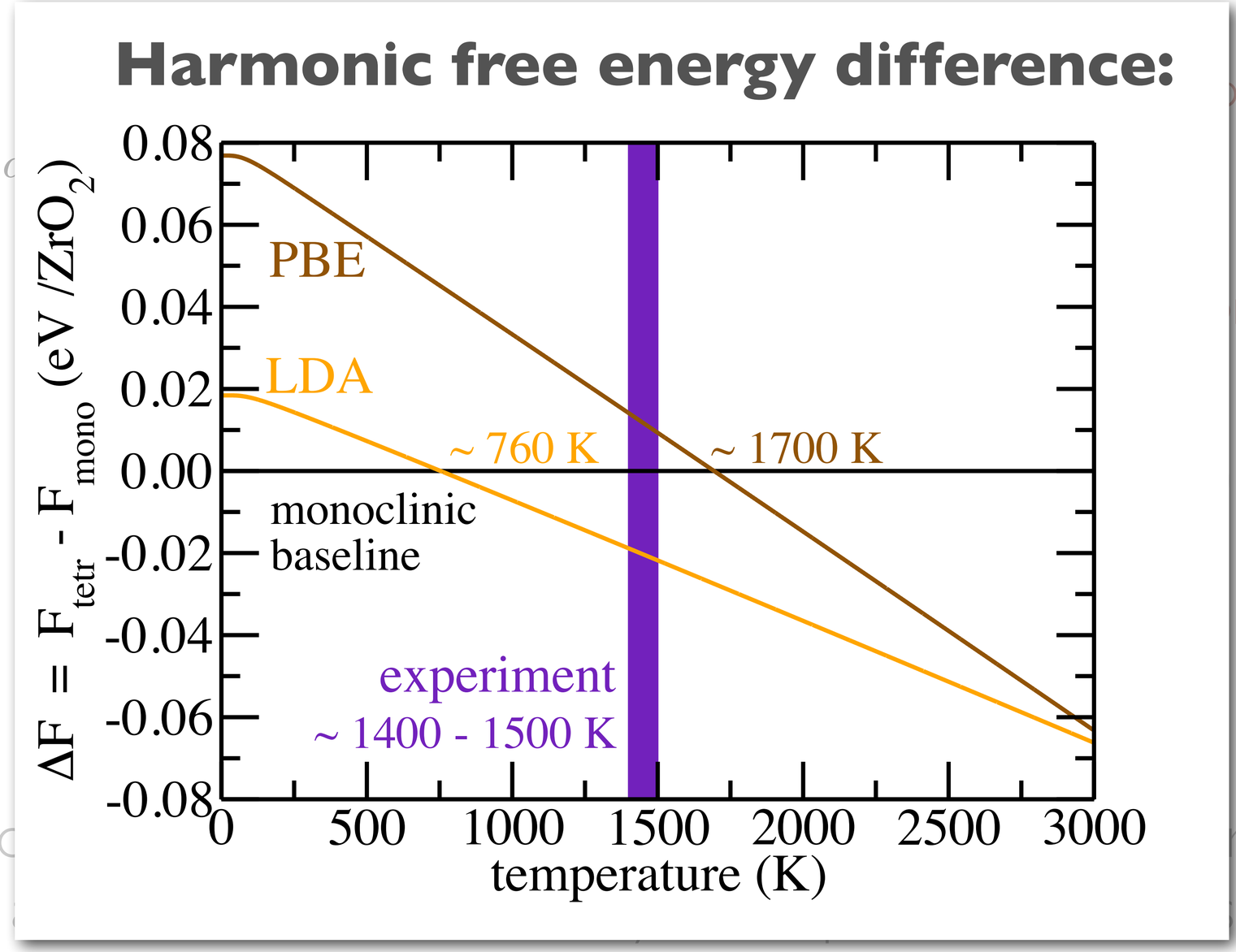
Electronic Contributions

Zero-point vibration

Thermically induced vibrations

Comparison of the **free energy** for different structures allows to assess **thermodynamic phase transitions**.

THE HARMONIC FREE ENERGY



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- The *harmonic approximation* can be used to *estimate* thermodynamics expectation values.

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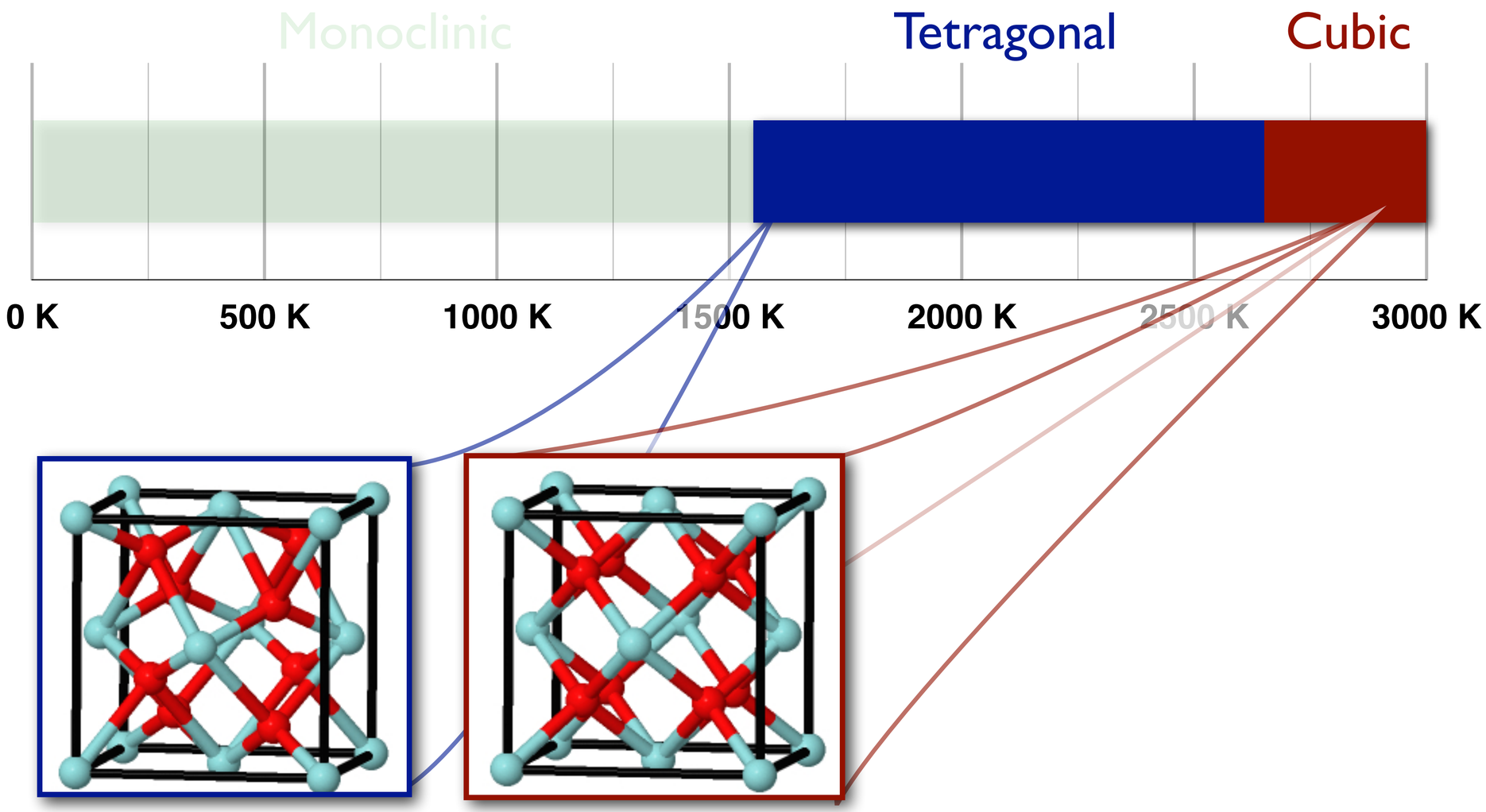
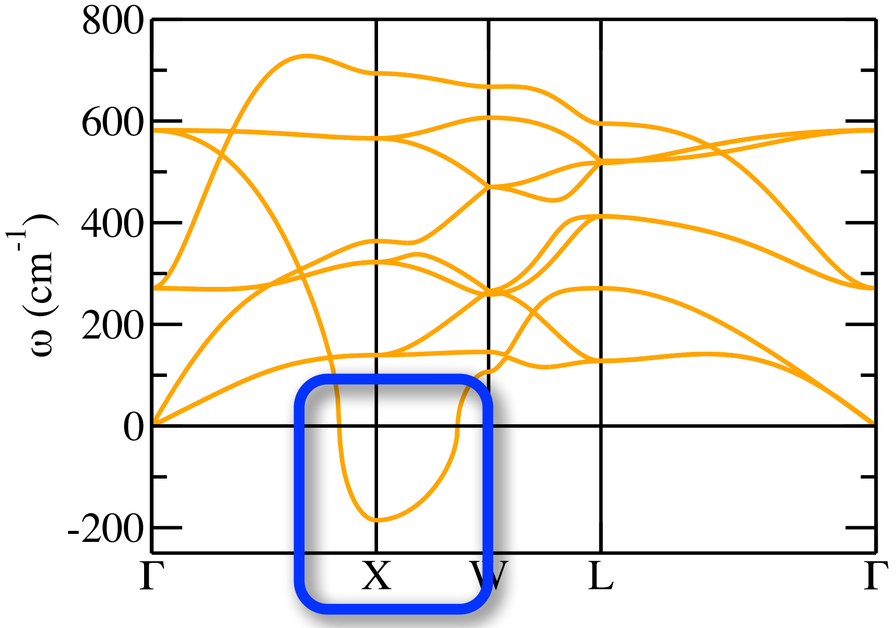
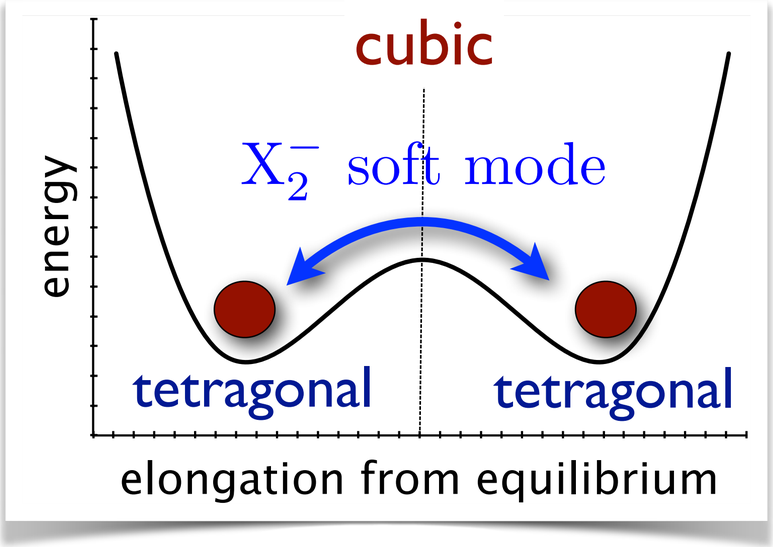
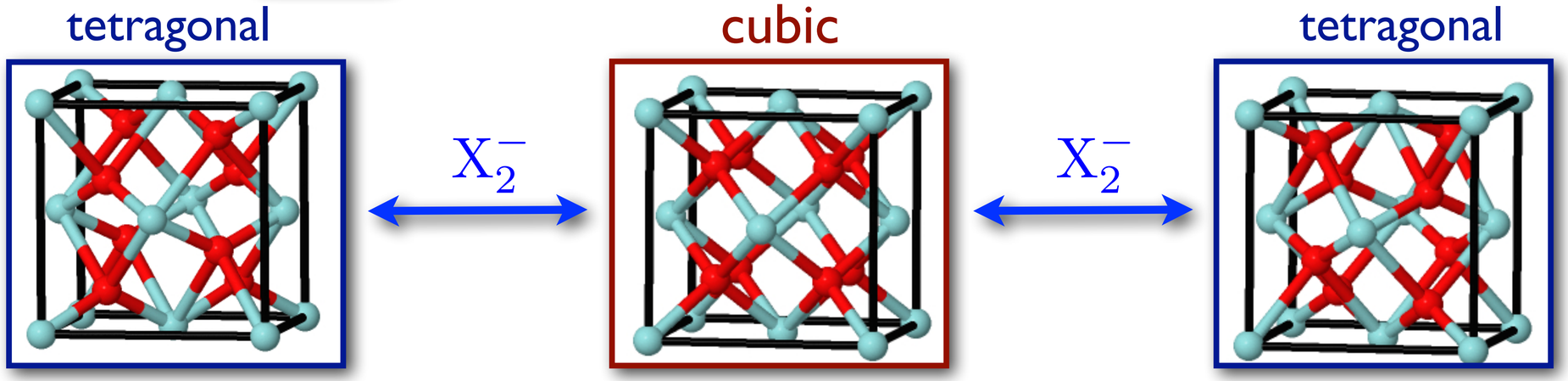


THE CUBIC ZrO_2 STRUCTURE

K. Parlinski, Z. Q. Li, and Y. Kawazoe, *Phys. Rev. Lett.* **78**, 4063 (1997).







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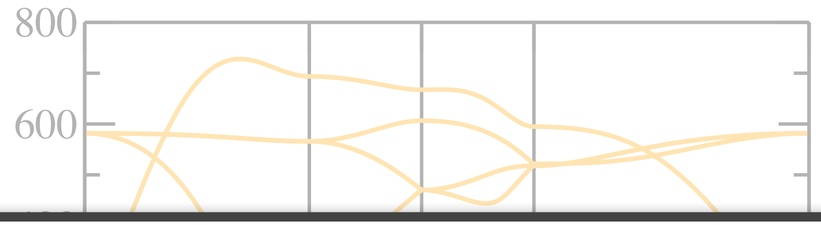
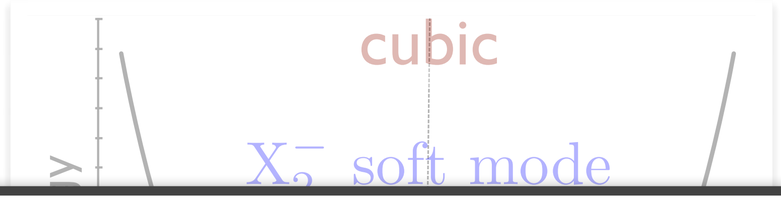
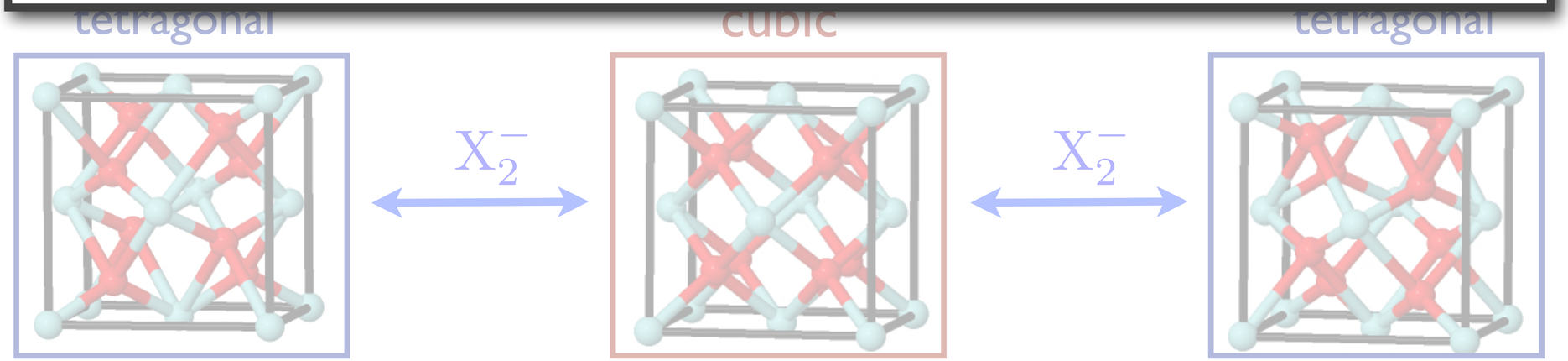
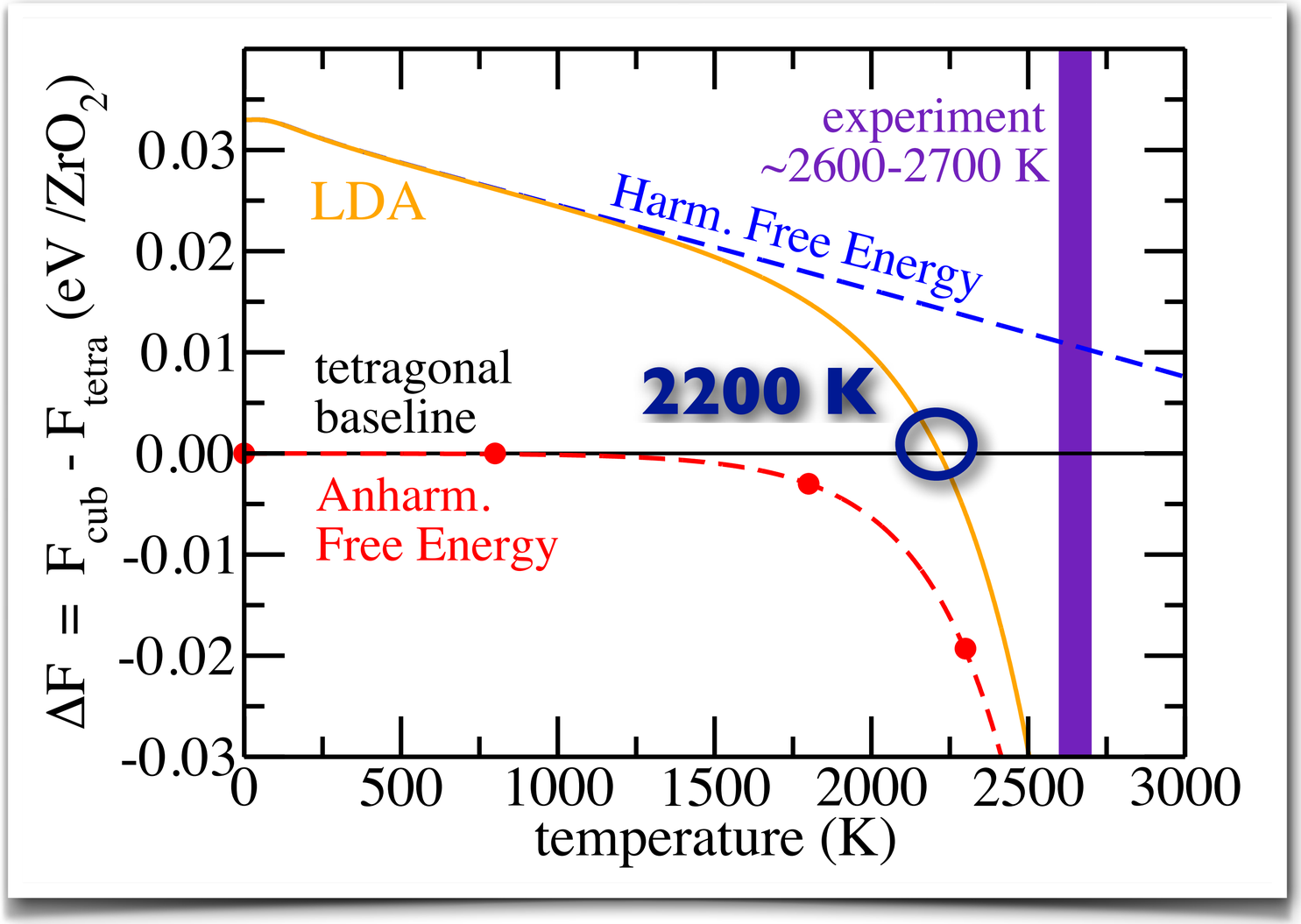




THE HARMONIC APPROXIMATION DOES NOT HOLD IN THE CASE OF SOFT MODES!



CUBIC PHASE STABILITY



Anharmonic effects dominant for T > 1500 K !

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- The *harmonic approximation* can be used to *estimate* thermodynamic expectation values.
- ***Anharmonic effects*** beyond the *harmonic approximation* are often important, too!

Karsten Reuter

Matthias Scheffler

Fritz Haber Institut of the Max Planck Society,
Berlin, Germany

Carlos G. Levi

Chris G. Van de Walle

University of California Santa Barbara,
USA

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