Advanced Phonons: Anharmonicity, Phonon-Phonon, and Electron-Phonon Coupling

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MAX-PLANCK-GESELLSCHAFT

First Steps

(1) Shut down the Docker (Type `exit` until the *Terminal* closes)!

(2) Open a new Terminal and edit `/home/triqs/.bashrc` – Uncomment the last two lines so that they read (just remove `#` in the beginning):

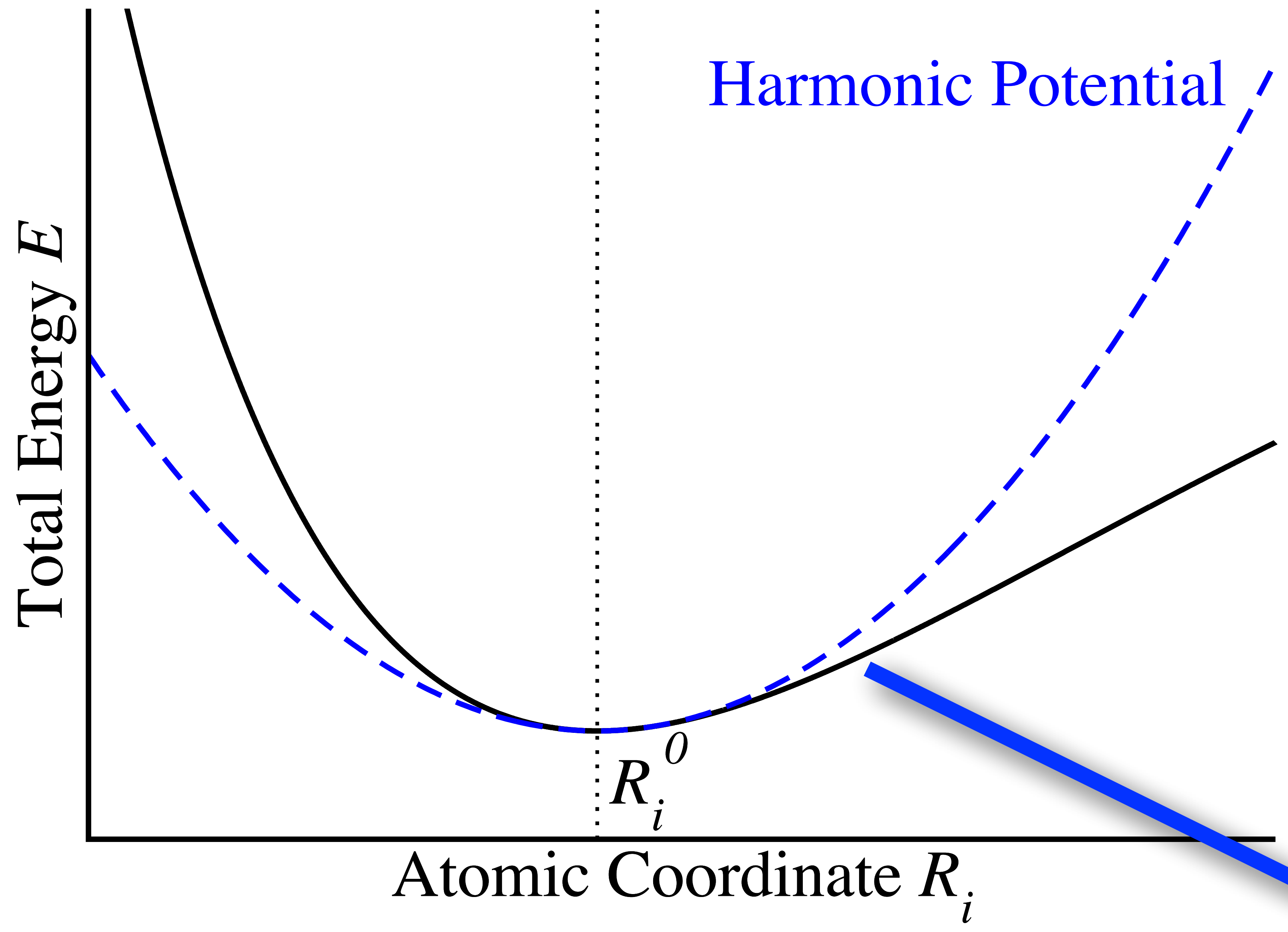
```
export PYTHONPATH=/home/triqs/FHI_local/FHI_vibes_build/:$PYTHONPATH
export PATH=/home/triqs/FHI_local/FHI_vibes_build/bin:$PATH
```

(3) Restart the docker by typing `asesma_qe` and execute `vibes`

(4) Check that you get no error, but something like:

```
❯ vibes
Usage: vibes [OPTIONS] COMMAND [ARGS]...
  vibes: lattice dynamics with python
...
```

The Harmonic Approximation



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

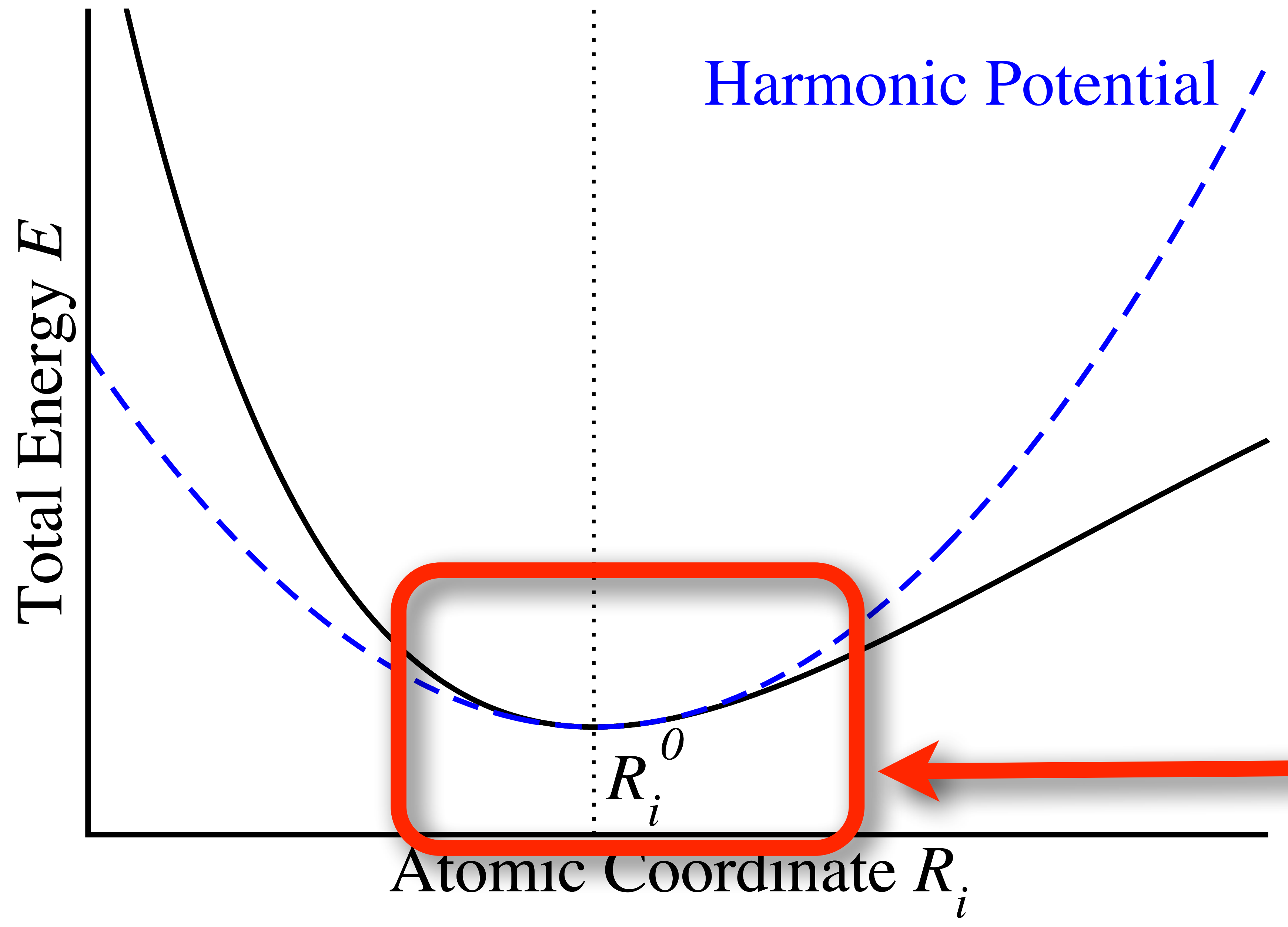
$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

Approximate by Taylor Expansion around the Static Equilibrium

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

Hessian Φ_{ij}

The Harmonic Approximation



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

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

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

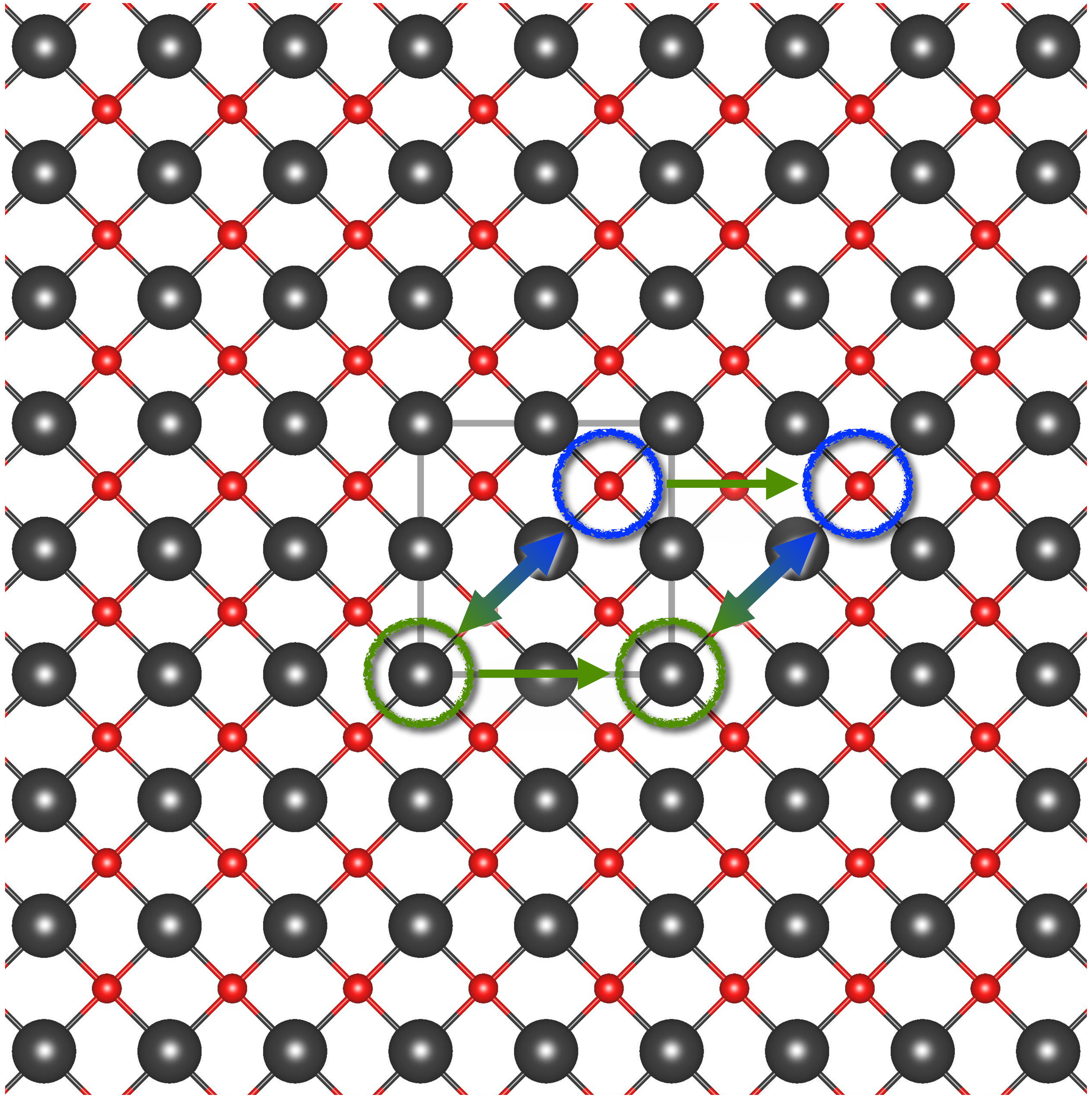
$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \sum_i \left.\frac{\partial E}{\partial \mathbf{R}_i}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i + \frac{1}{2}\sum_{i,j} \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}_0}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

The Harmonic Force Constants

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

*"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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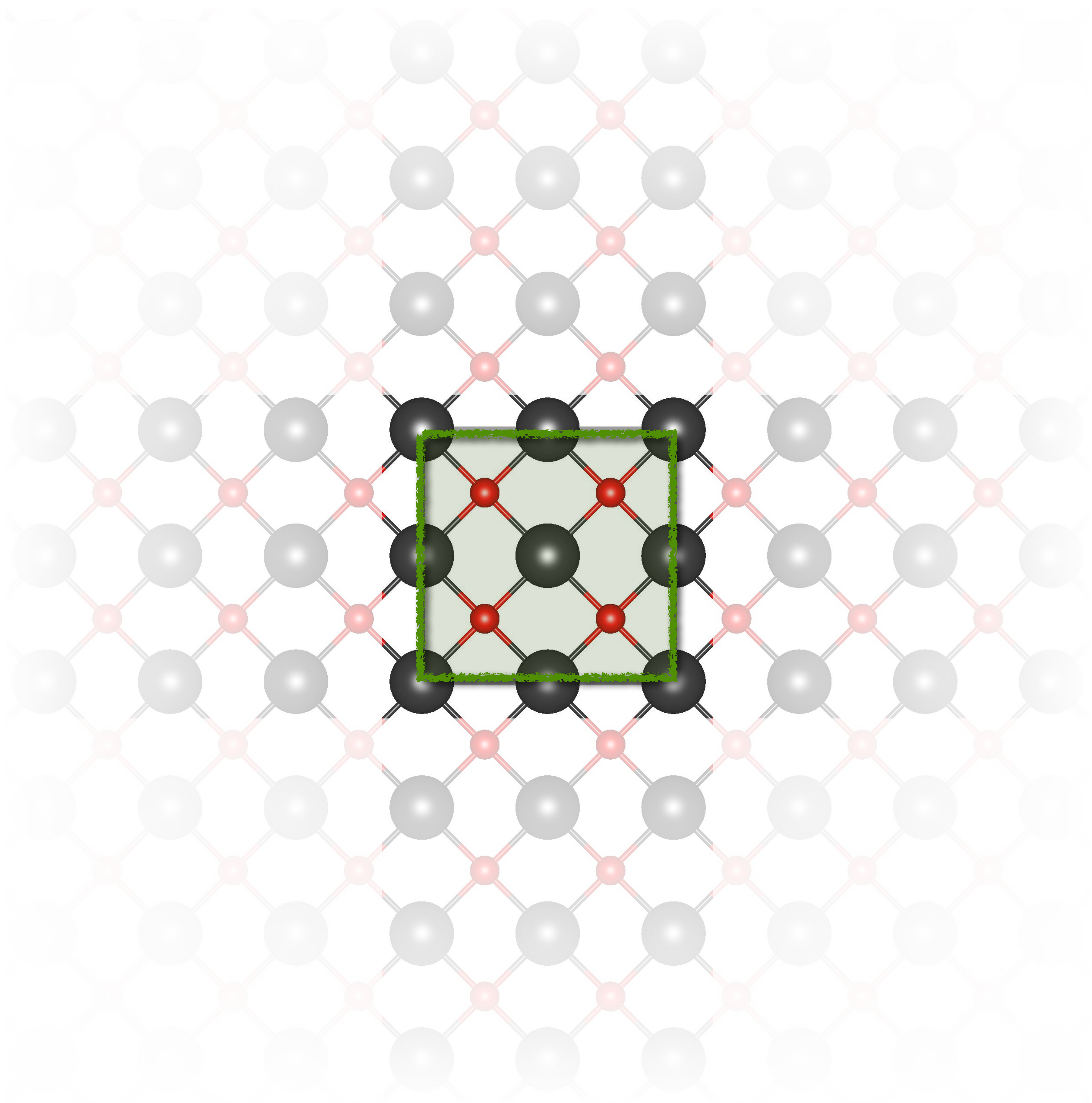

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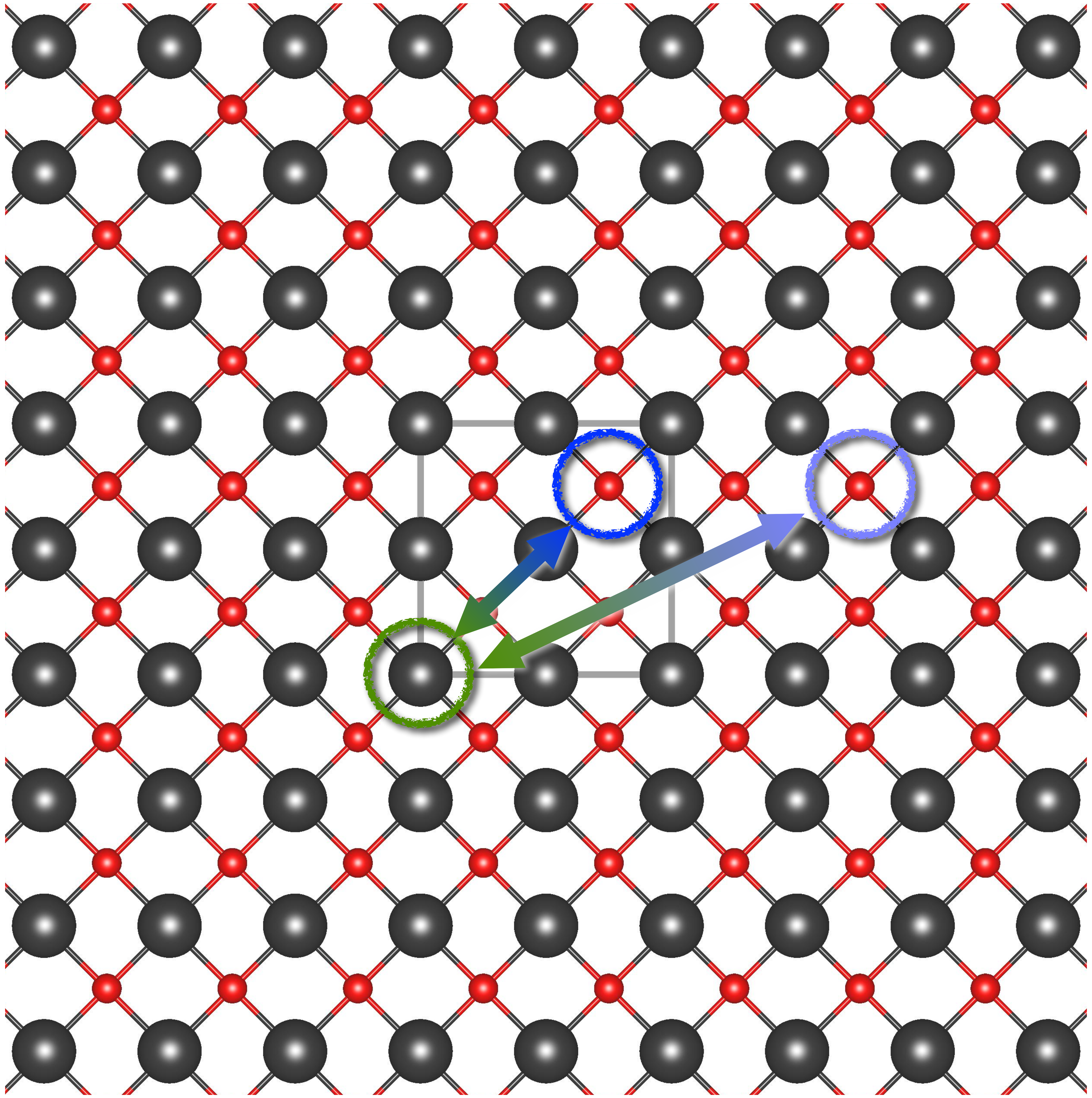
Nota bene: The Hessian is **pair-wise** translationally invariant.

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

The Harmonic Force Constants



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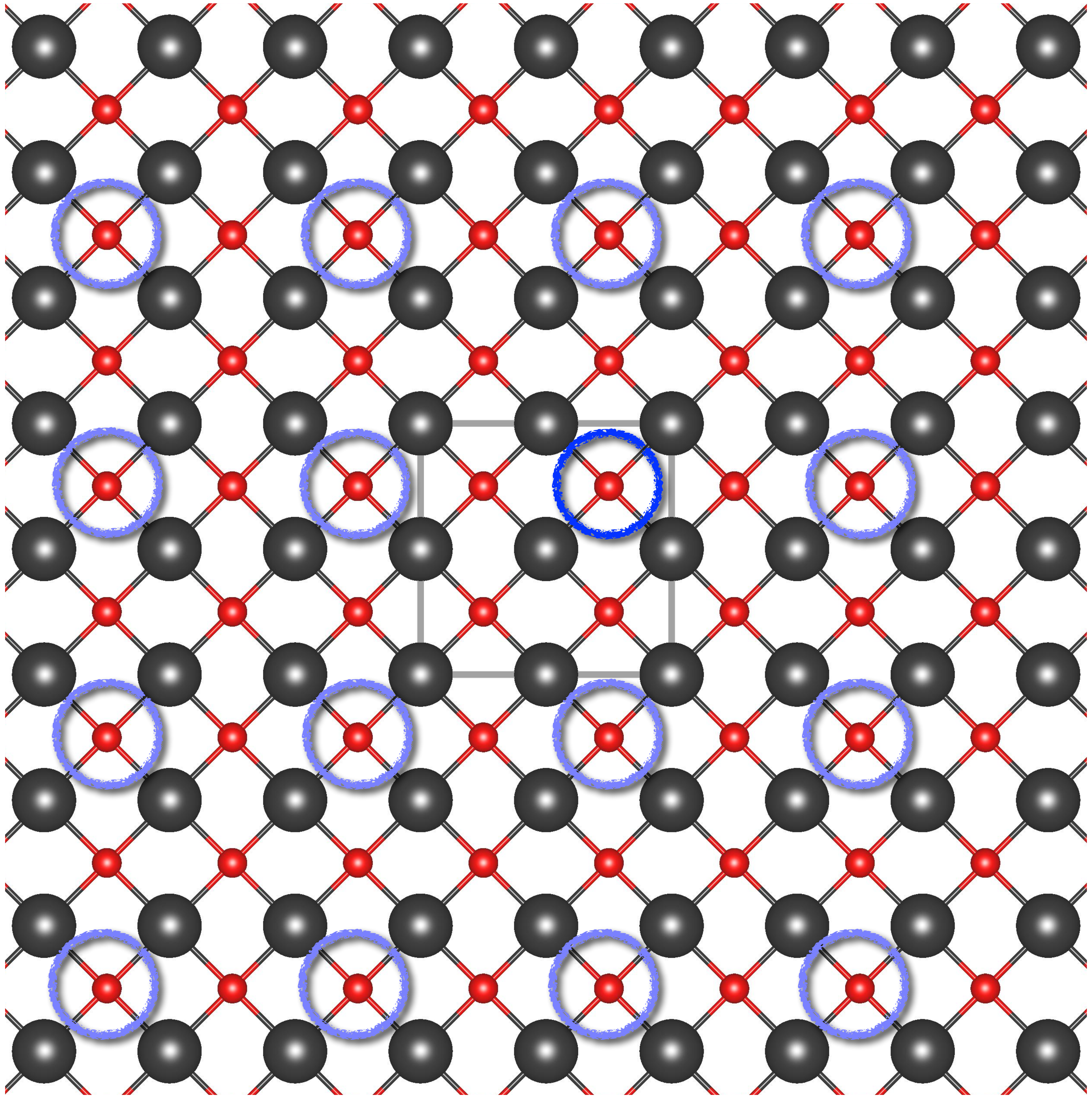
*"How much does **Force** on **atom I** change when moving **atom J**?"*

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

The Harmonic Force Constants



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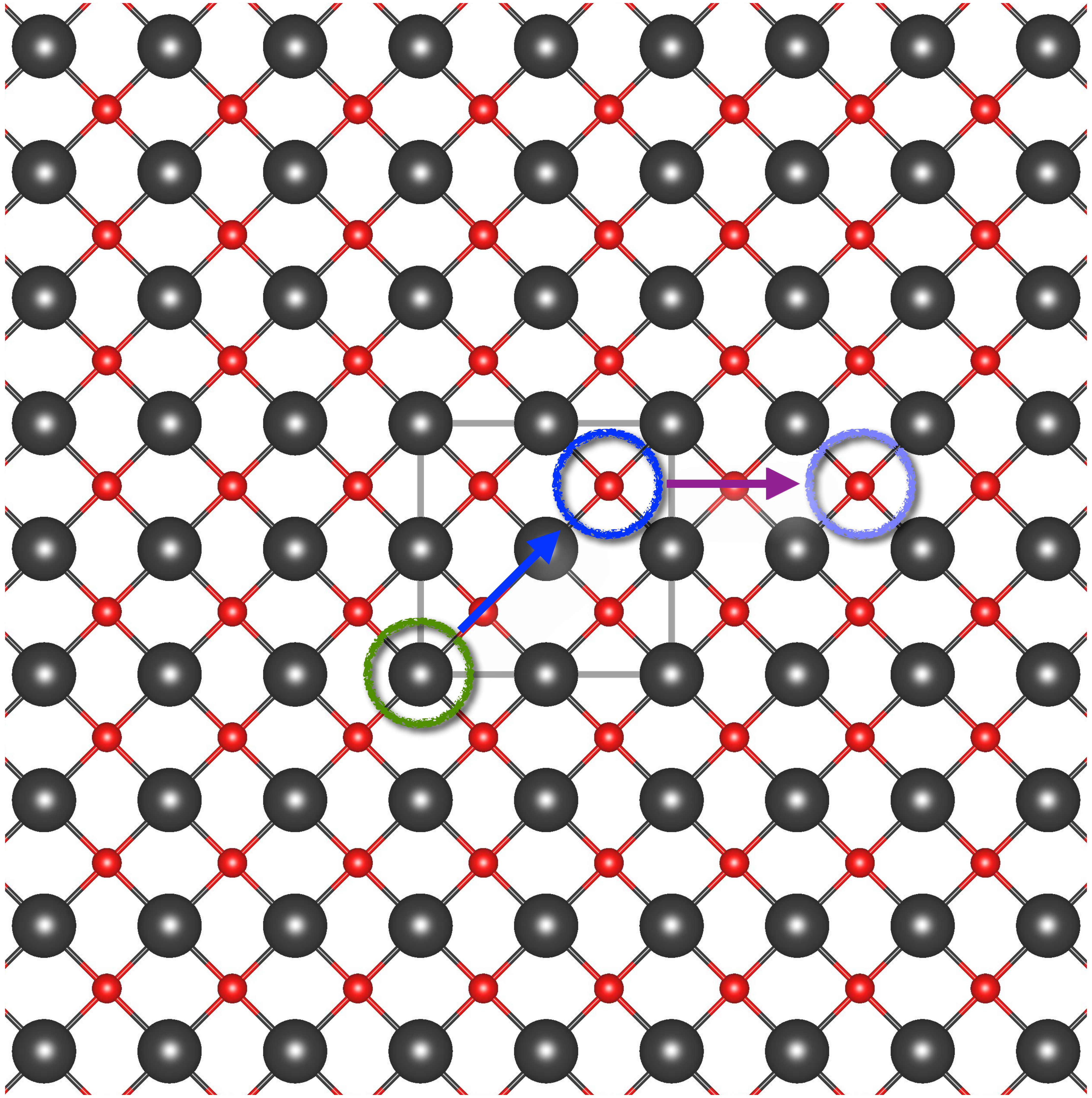
Different **periodic images** of **atom J** results in different force constants.

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

The Harmonic Force Constants



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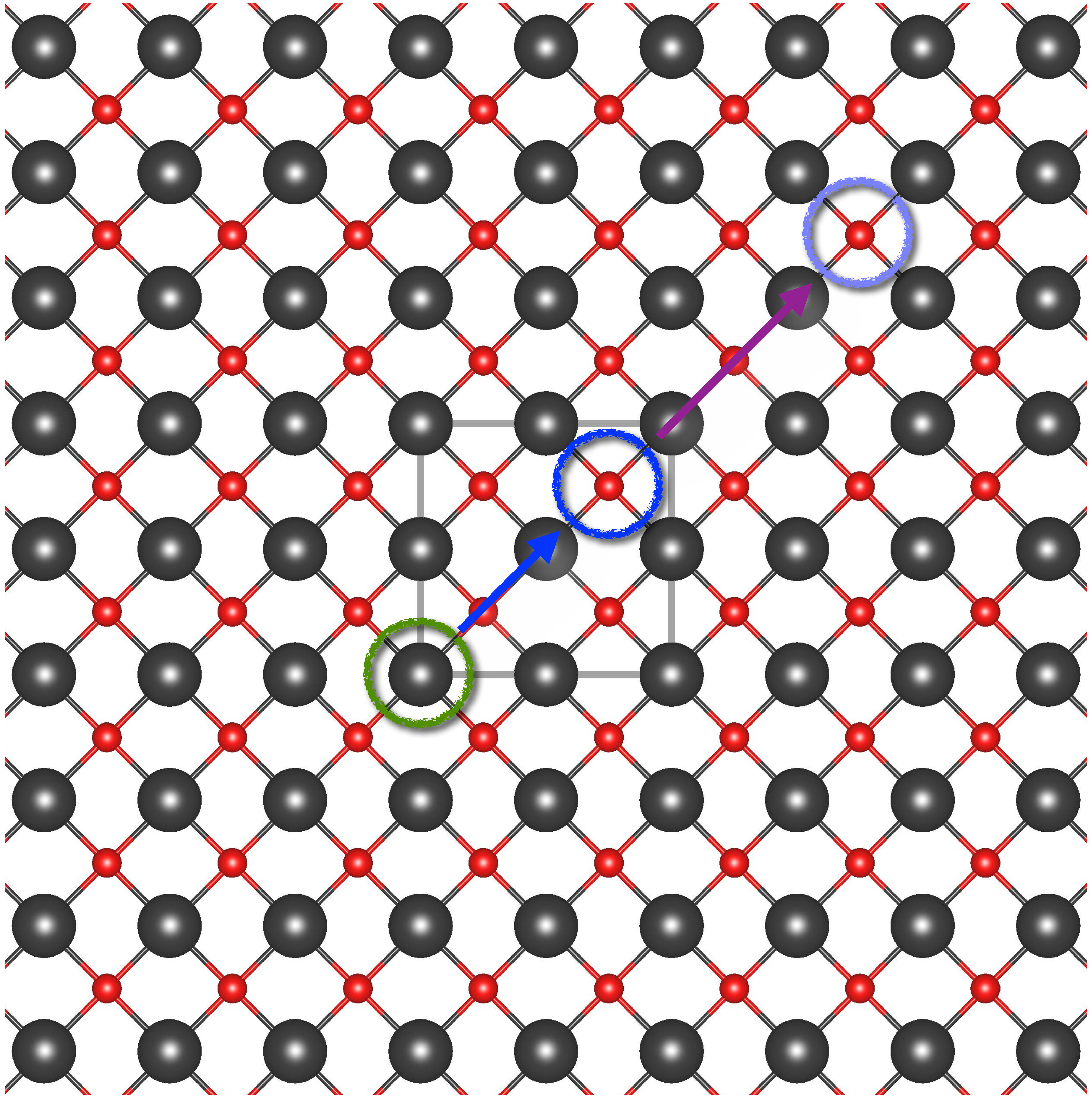
$$\Phi_{IJ}^{\alpha\beta} \rightarrow \Phi_{I,Jlmn}^{\alpha\beta} = \left.\frac{\partial^2 E}{\partial \mathbf{R}_I^\alpha \partial \mathbf{R}_{J,lmn}^\beta}\right|_{\mathbf{R}_0} = \left.\frac{\partial \mathbf{F}_I^\alpha}{\partial \mathbf{R}_{J,lmn}^\beta}\right|_{\mathbf{R}_0}$$

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

The Harmonic Force Constants



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

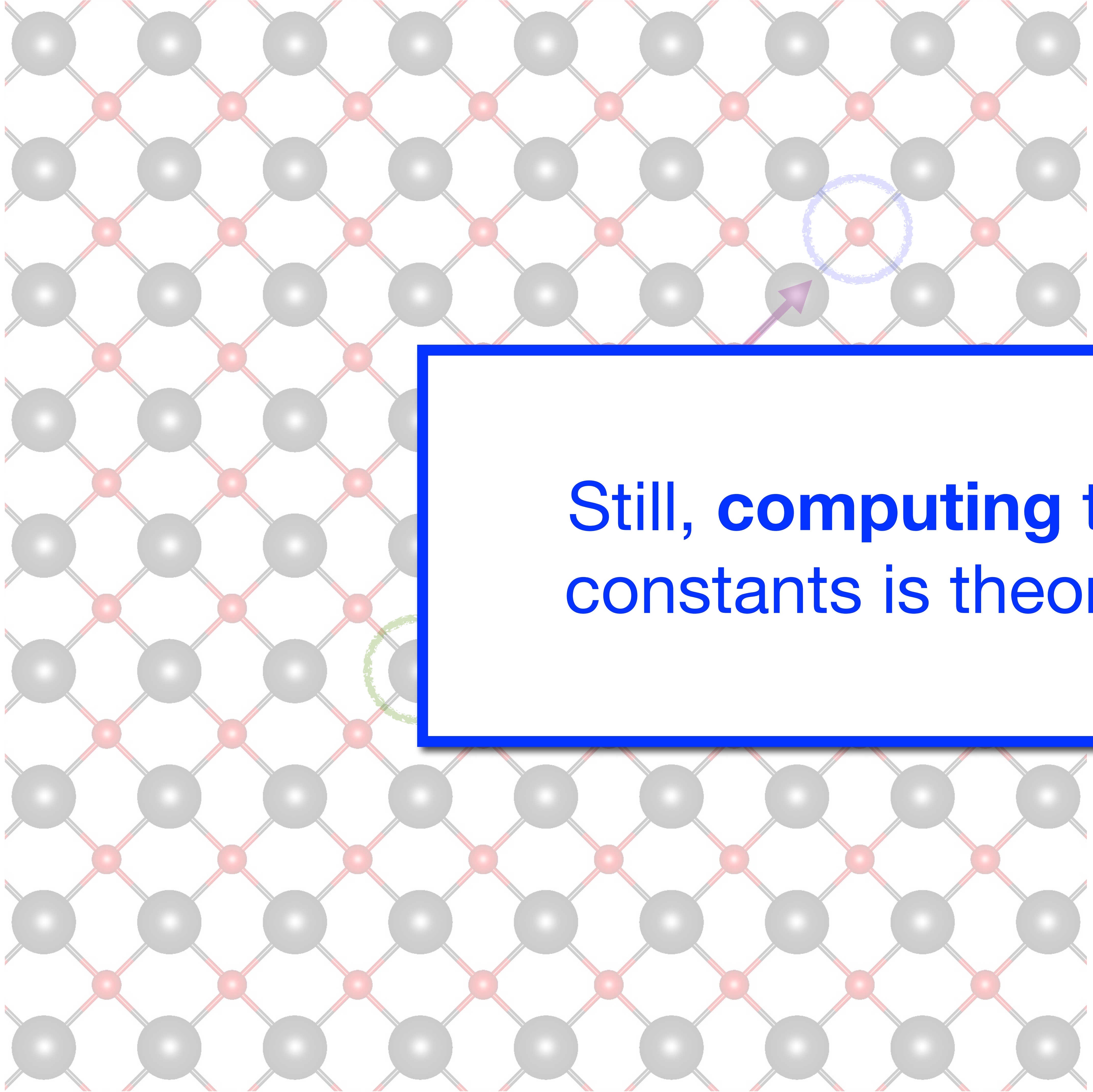
Nota bene:

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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...ne:

...stals **decay**

...istance.

$$\ldots |\mathbf{R}_{J,lmn} - \mathbf{R}_I| \rightarrow \infty$$

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

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

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

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

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

Higher Order Derivatives

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

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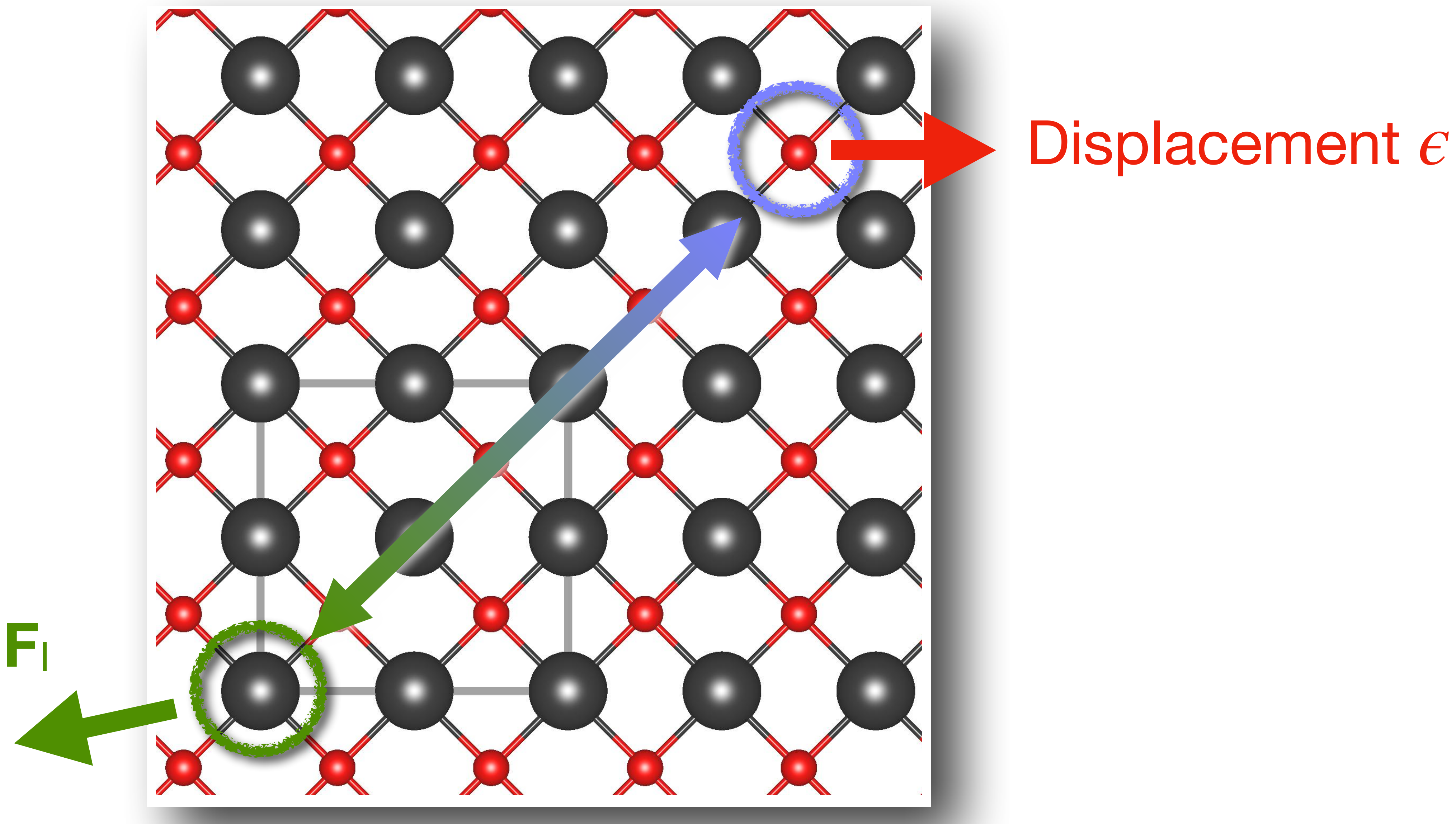
$$\Phi^{\alpha\beta}_{I,Jlmn} = -\left.\frac{\partial \mathbf{F}^{\alpha}_{I}}{\partial \mathbf{R}^{\beta}_{J,lmn}}\right|_{\mathbf{R}_0} \approx -\lim_{\epsilon\to 0}\frac{\mathbf{F}^{\alpha}_{I}\left[\mathbf{R}^{\beta}_{J,lmn}+\epsilon\right]}{\epsilon}$$



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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

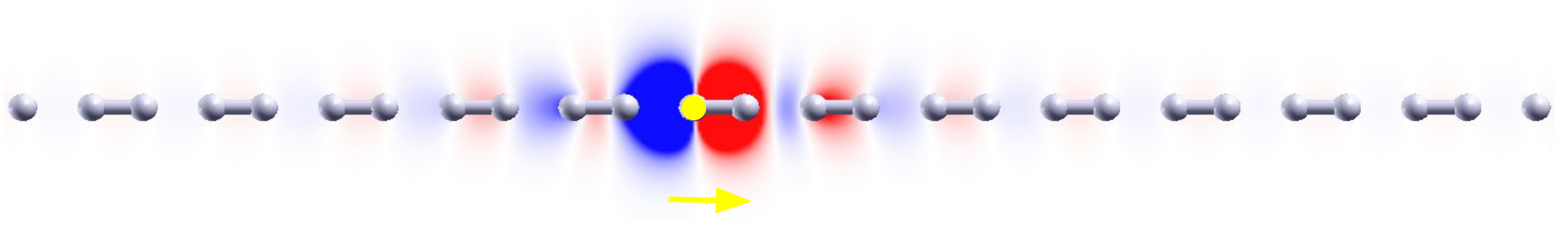
S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987)
S. Baroni, *et al., Rev. Mod. Phys.* **73**, 515 (2001).

2n+1 Theorem:

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

Explicit response from *Sternheimer Equation*:

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



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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

Computing Harmonic Force Constants

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Advanced Tutorial

⇓

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

Density-Functional Perturbation Theory

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Basic Tutorial

⇒

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

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:

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

$$\Delta\mathbf{R}_{Jlmn} = \frac{1}{\sqrt{M_J}}\mathbf{U}_J\exp(i\mathbf{q}\mathbf{L}_{lmn})$$

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

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

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

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

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

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

The Harmonic Equations of Motion

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

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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:

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

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

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

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).

Real Space:

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

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Reciprocal Space:

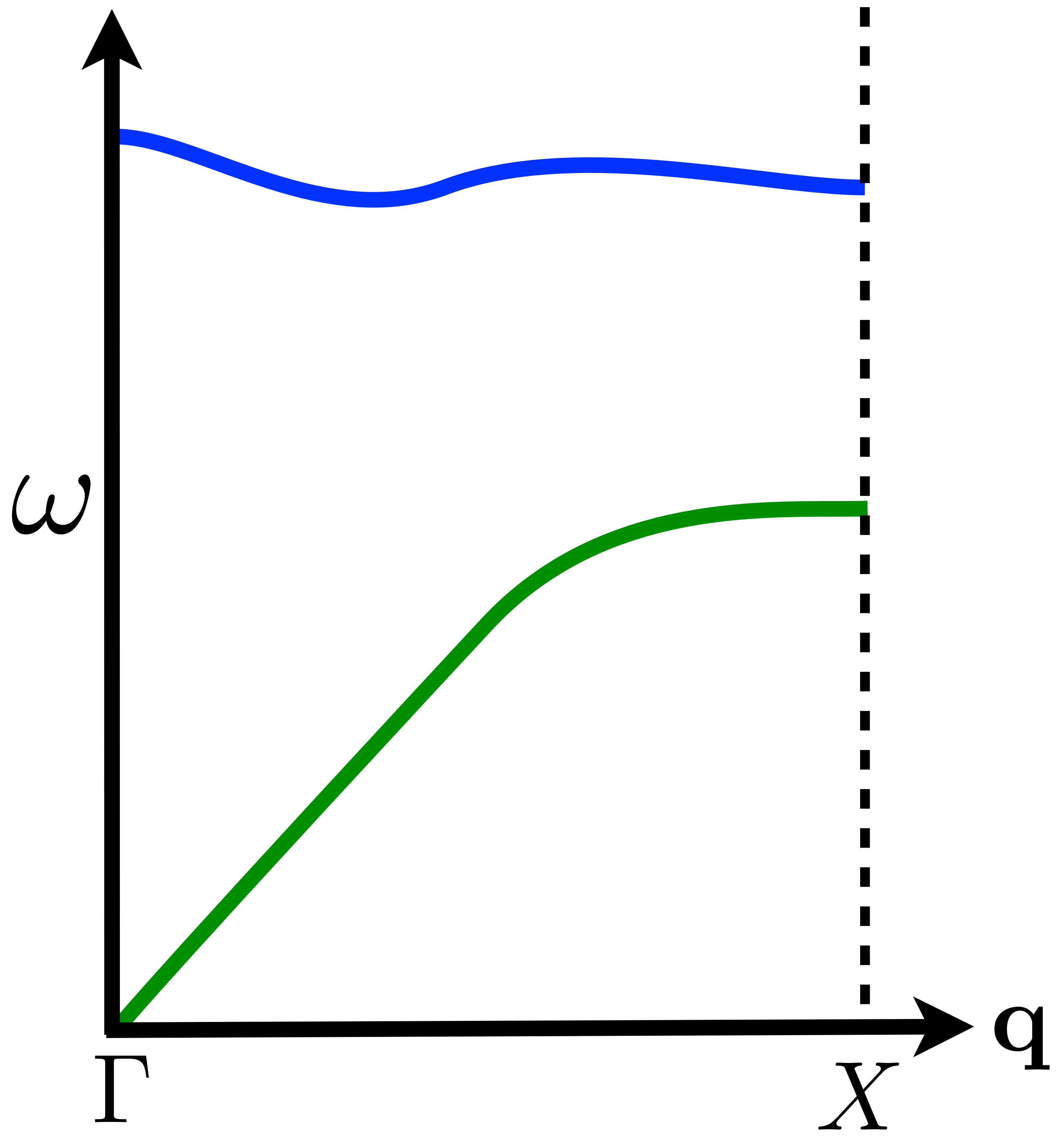
Dynamical Matrix $D_{IJ}(\mathbf{q})$ with $I,J \leq N_p$

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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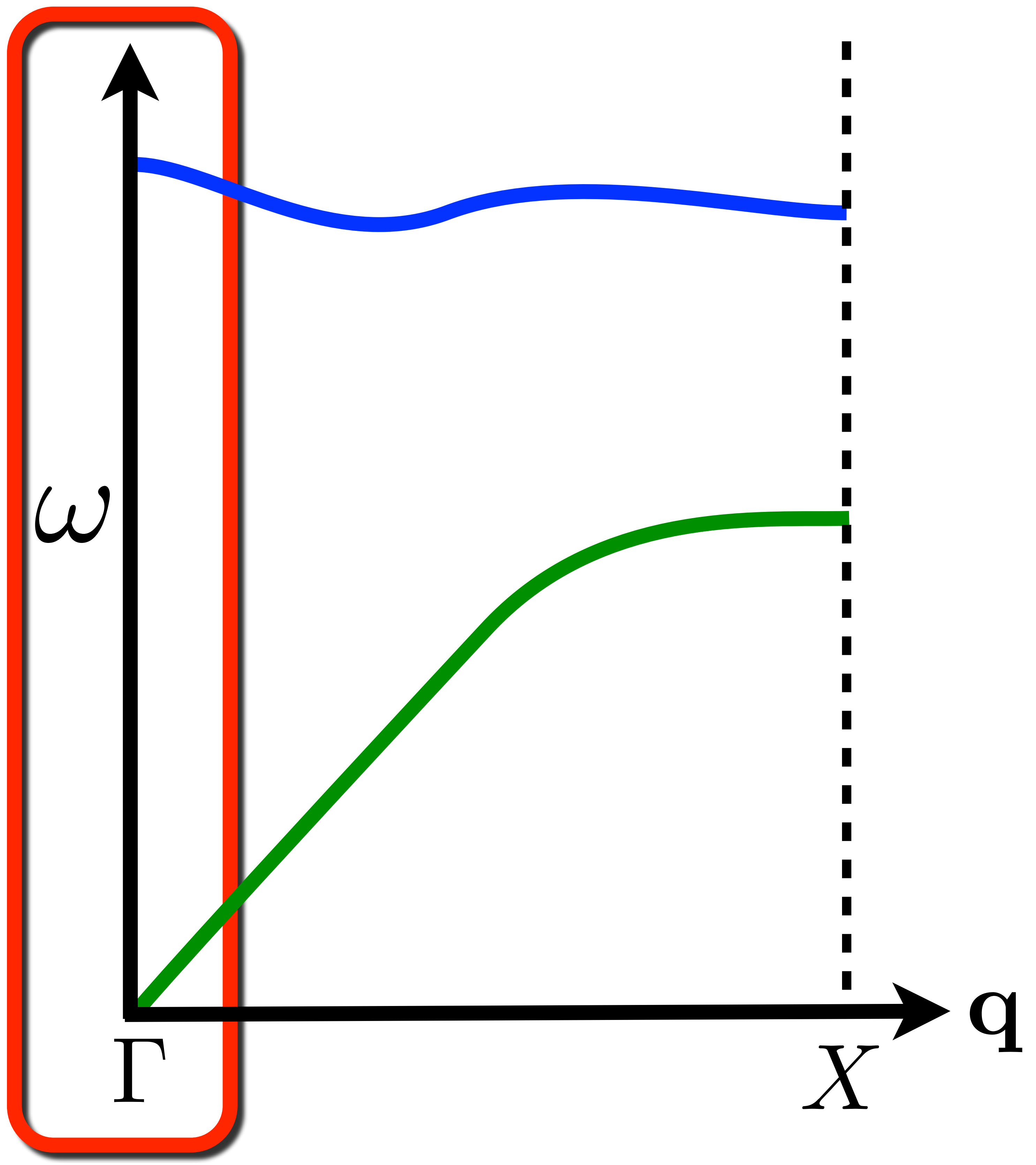


Dynamical matrix:

=1

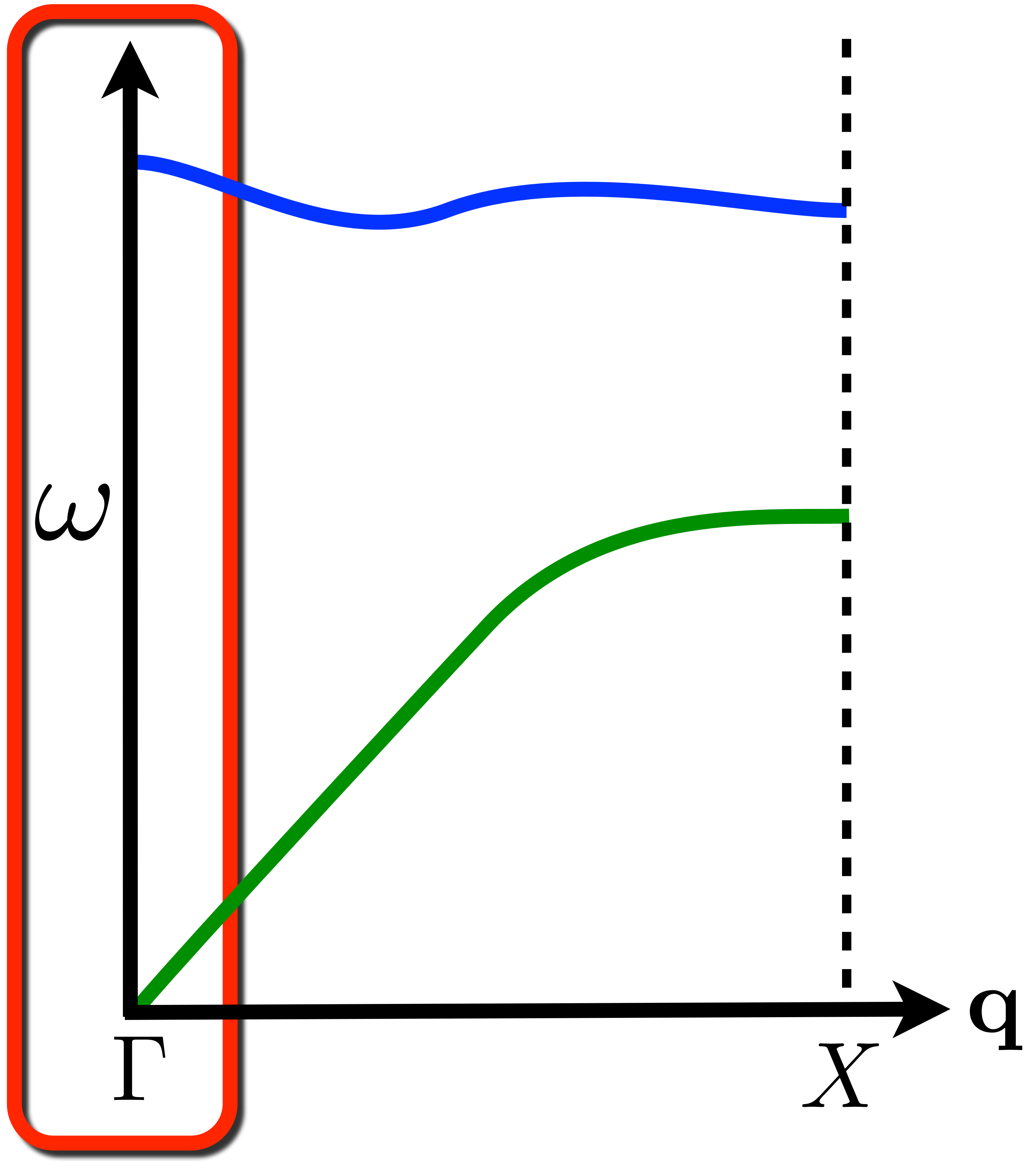
$$D_{I,J}(\mathbf{\Gamma}) = \sum_{lmn} \frac{\Phi_{I000,Jlmn}}{\sqrt{M_I M_J}} \sout{\exp(i\mathbf{q}\mathbf{L}_{lmn})}$$

Eigenvalue problem:

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

Vibrations in a Crystal 101

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



Dynamical matrix:

=1

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

Eigenvalue problem:

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

Vibrations in a Crystal 101

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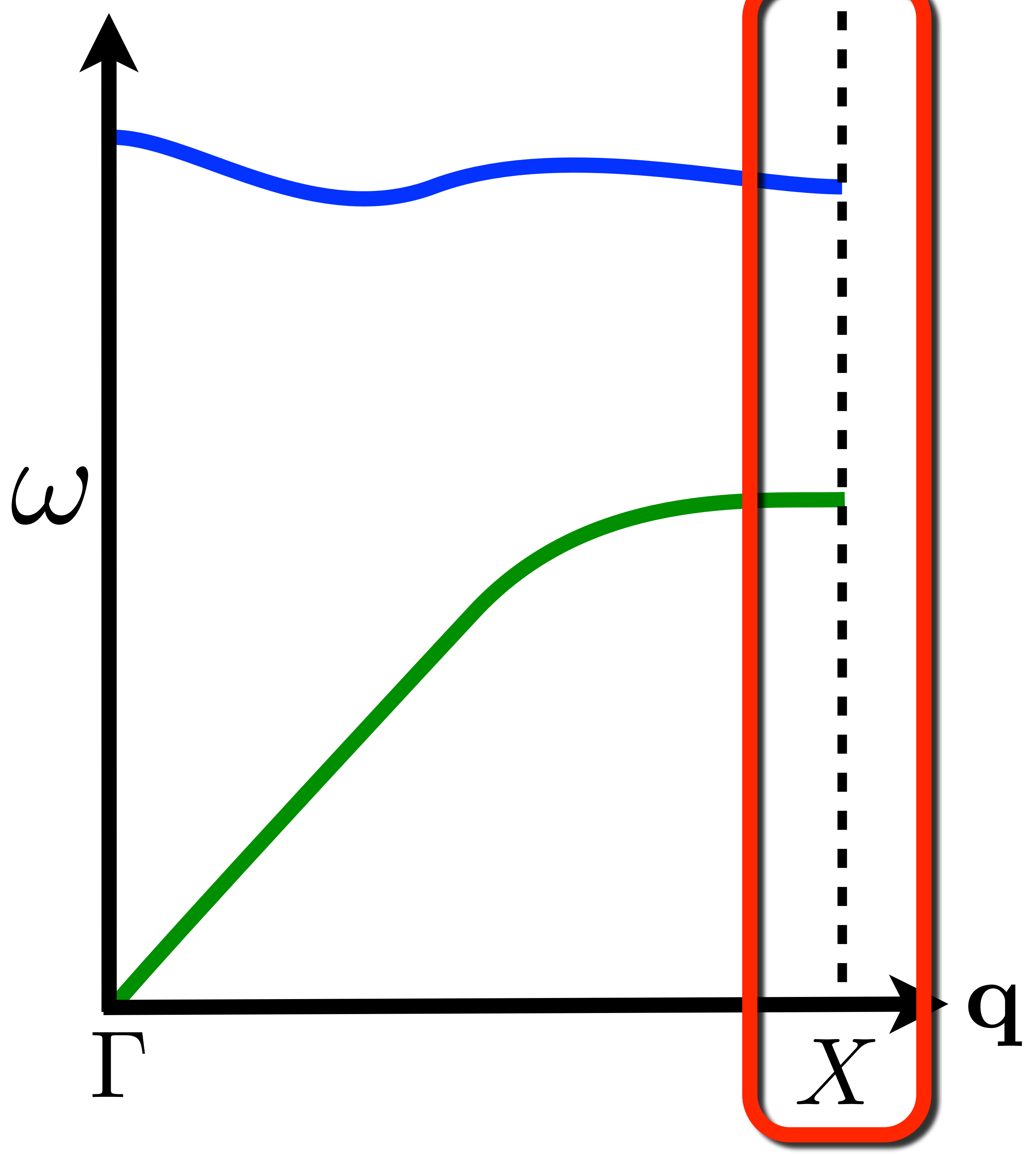


Dynamical matrix:

alternating ± 1

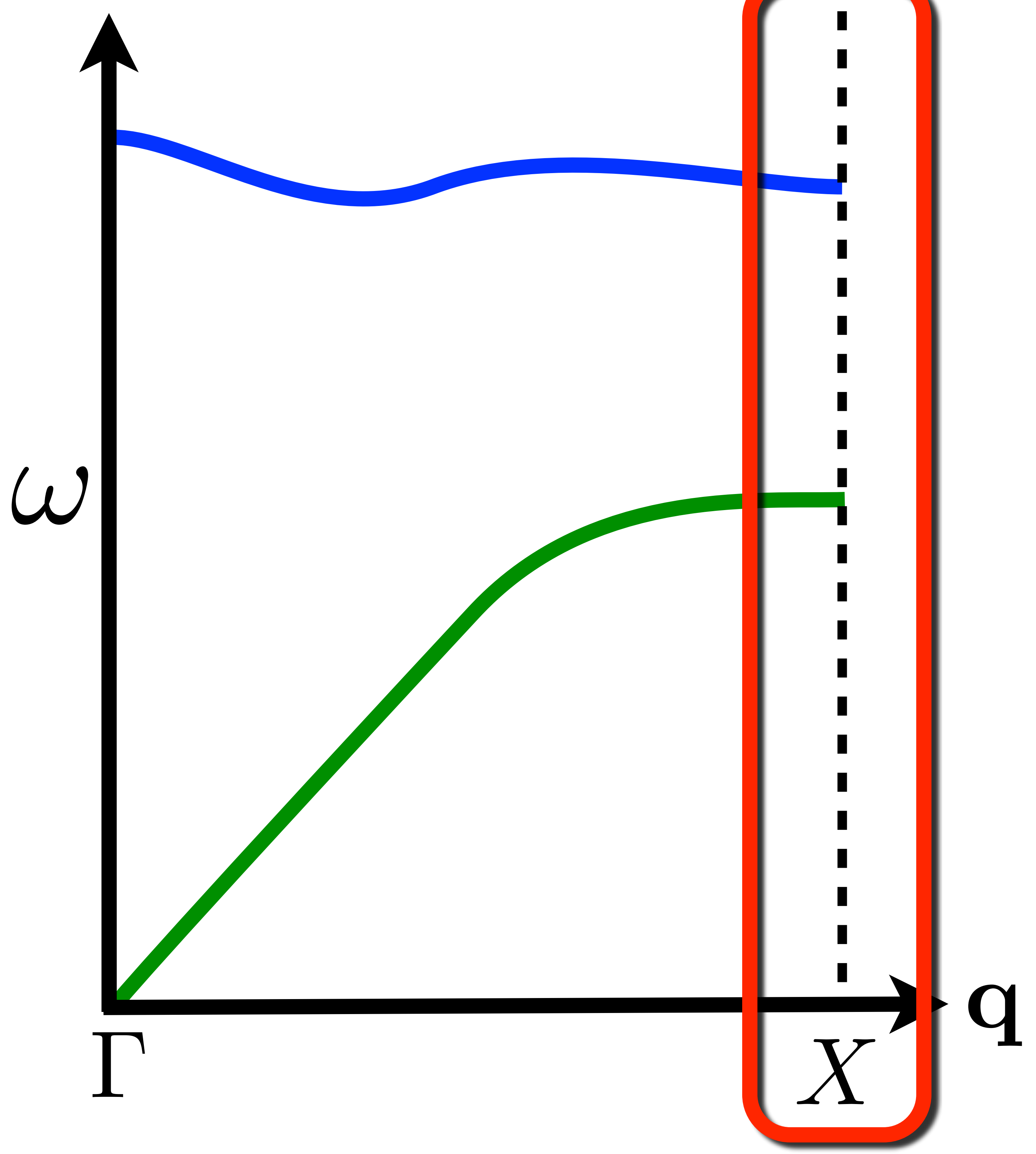
$$D_{I,J}(X) = \sum_{lmn} \frac{\Phi_{I000,Jlmn}}{\sqrt{M_I M_J}} \exp(i\mathbf{q}\mathbf{L}_{lmn})$$

Eigenvalue problem:

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

Vibrations in a Crystal 101

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



Dynamical matrix:

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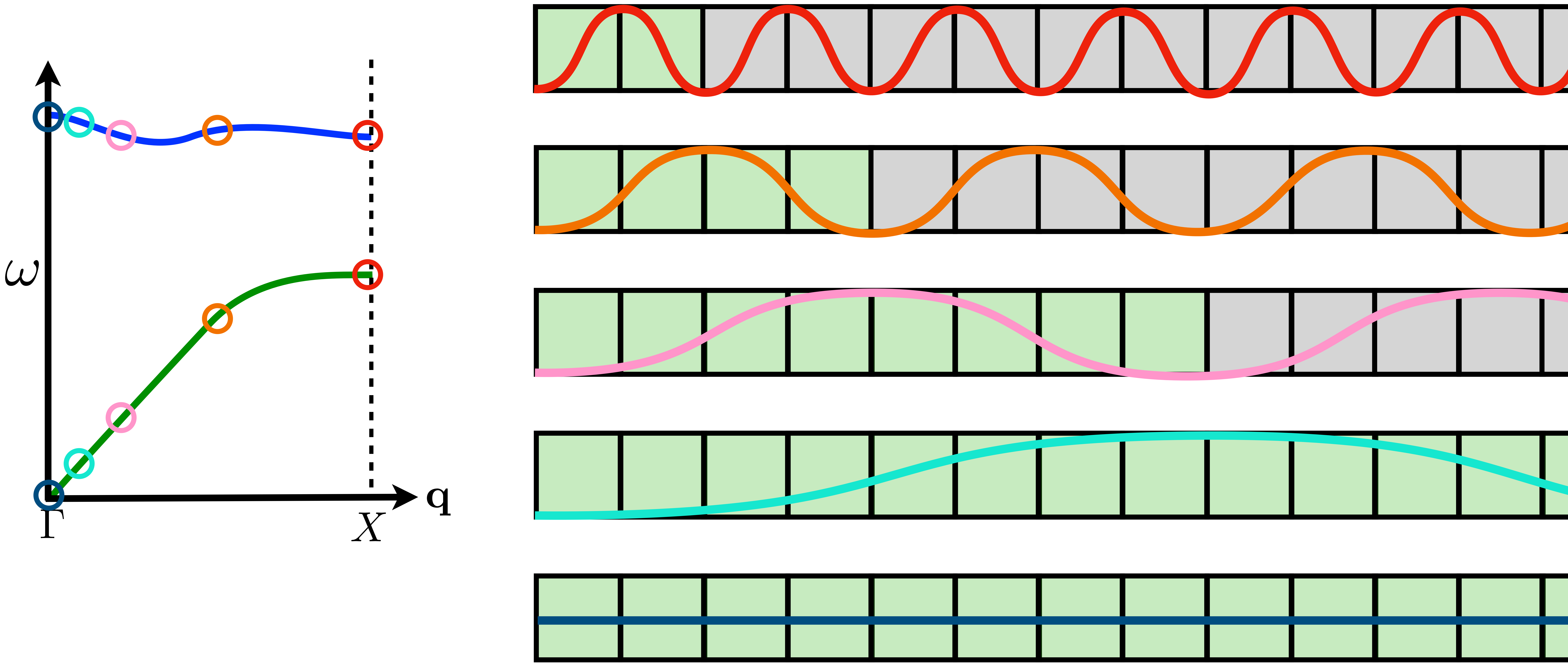

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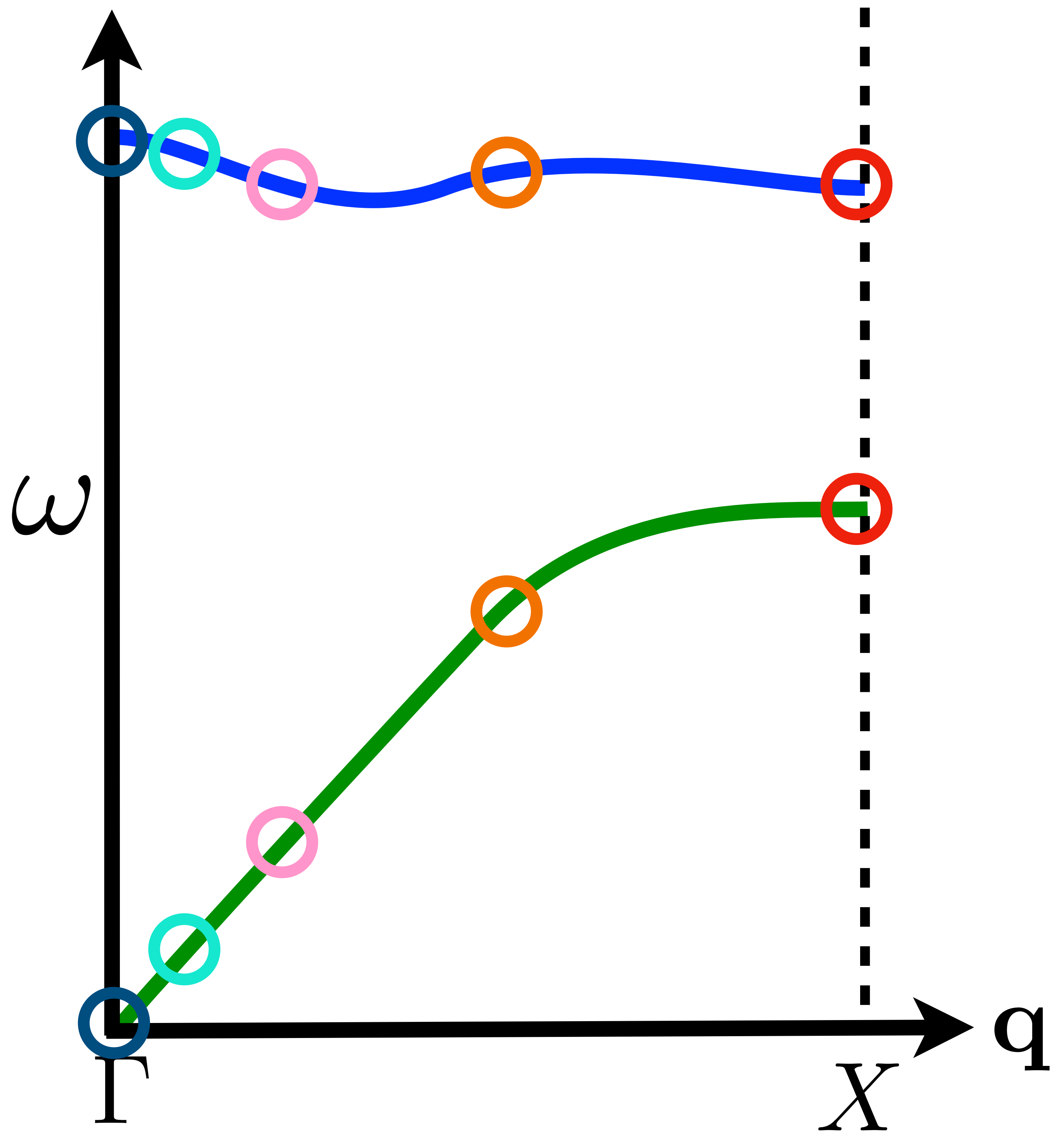

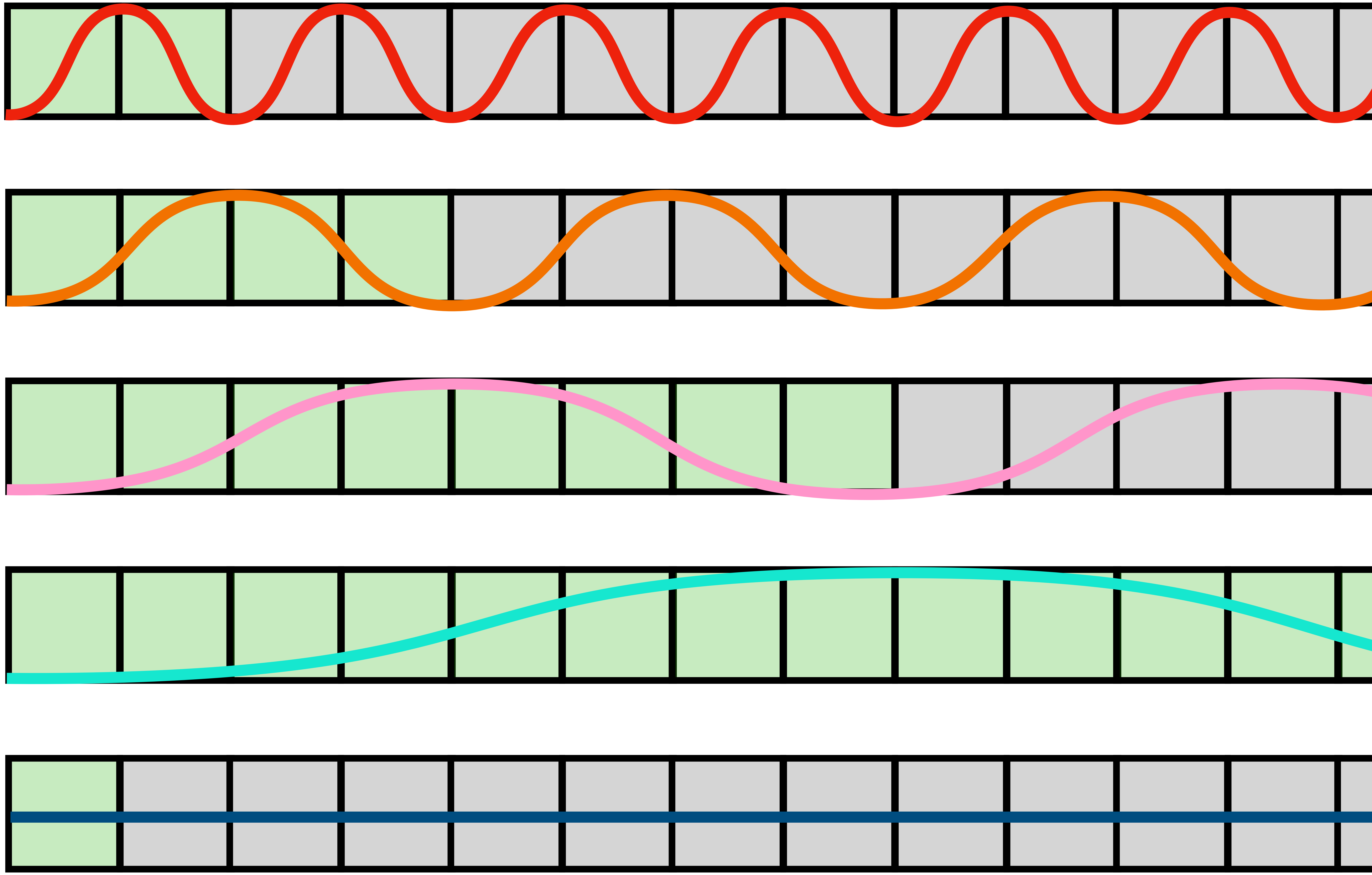

Vibrations in a Crystal 101

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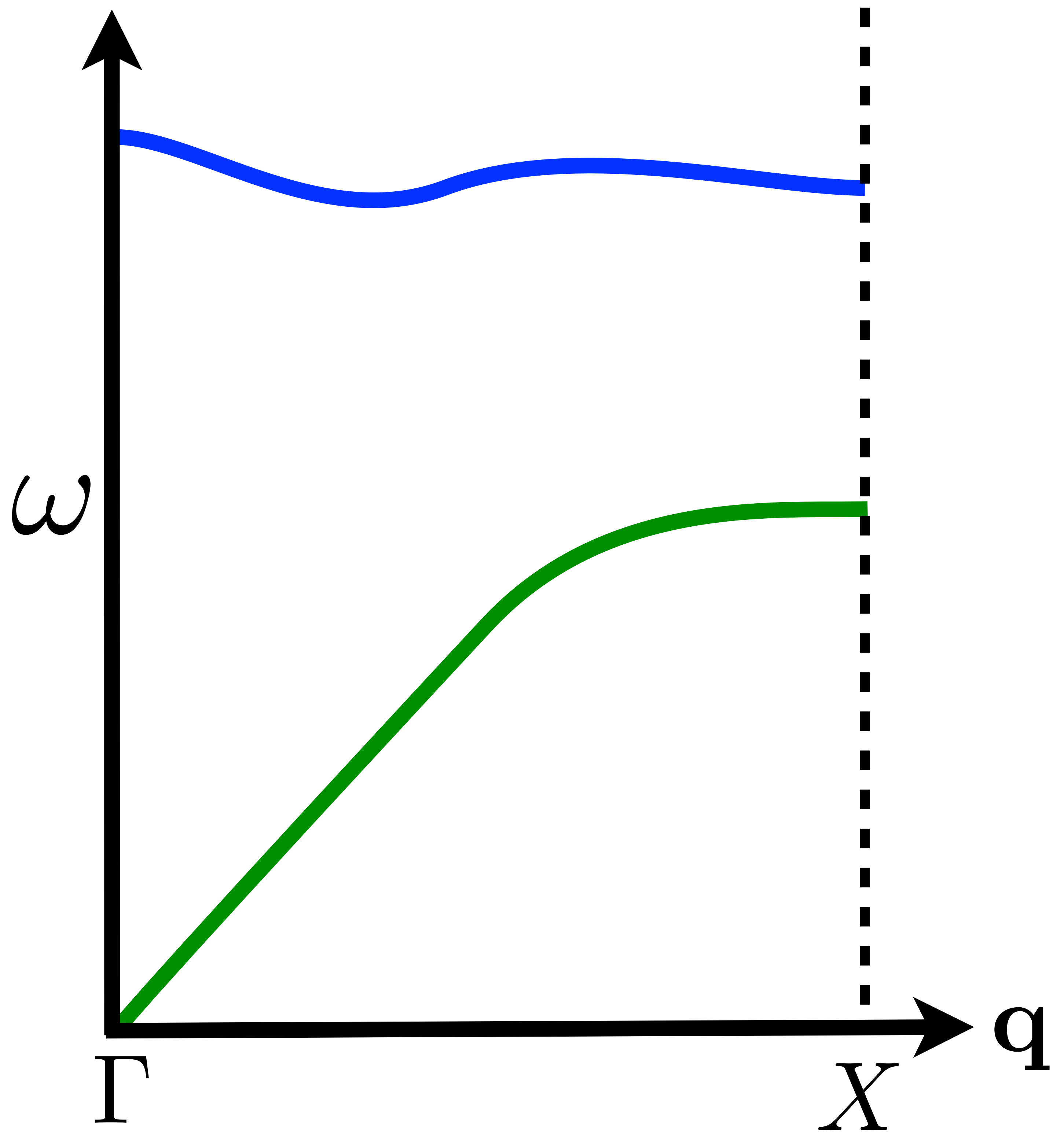


For N_p atoms in the unit cell there are:

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:

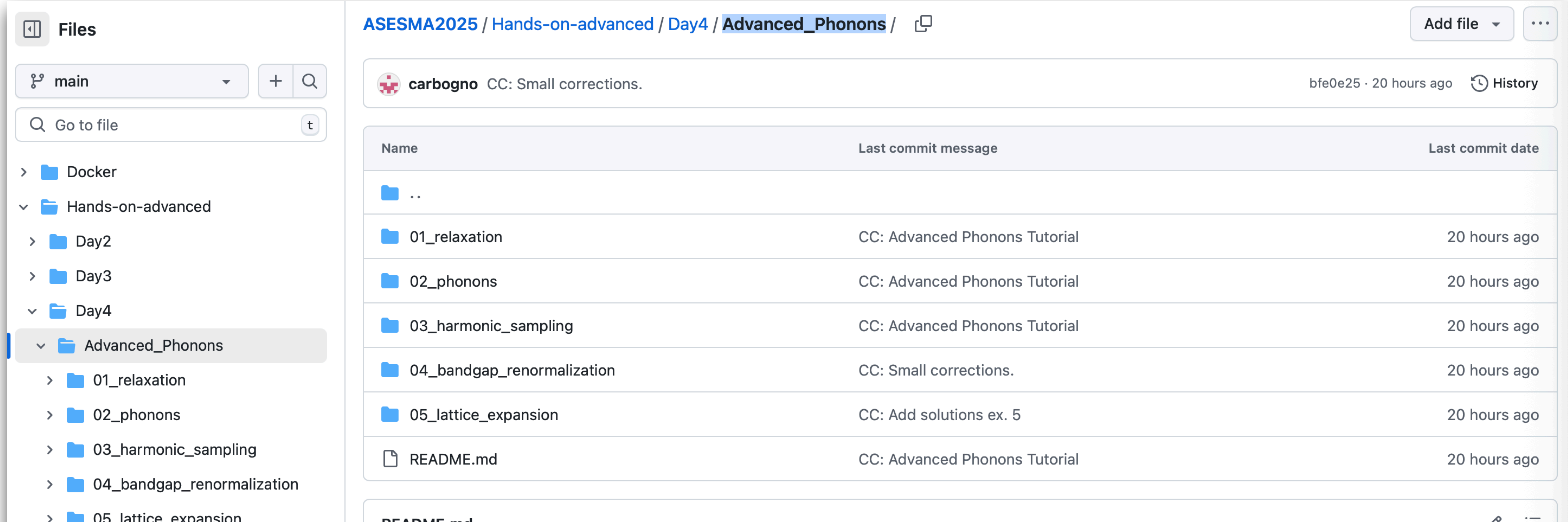
- Atoms in unit cell **out-of-phase**
- $\omega > 0$ at Γ (and everywhere else)
- **Weak** dispersion

Exercise 1 & 2

Exercise 1 & 2

Instructions can be found at:
https://github.com/asesma-org/ASESMA2025/

Go to: 📁 Hands-on-advanced —> 📁 Day 4 —> 📁 Advanced_Phonons



Exercise 1 & 2

Instructions can be found at:
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Go to: 📁 Hands-on-advanced —> 📁 Day 4 —> 📁 Advanced_Phonons

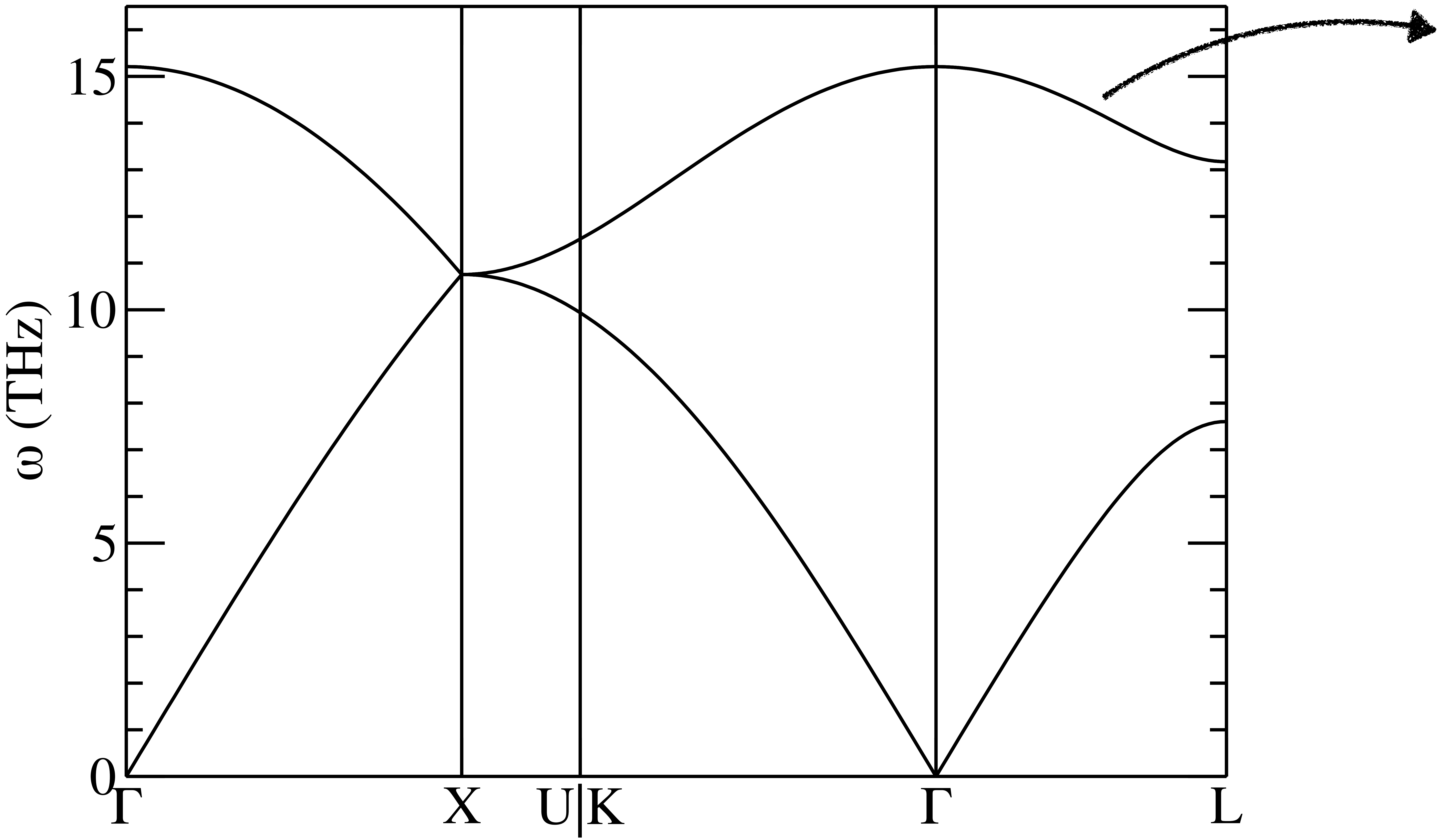
As usual, tutorial files can be found in `/home/lab4b/Desktop/ASESMA2025`

Go to: 📁 Hands-on-advanced —> 📁 Day 4 —> 📁 Advanced_Phonons

EXERCISE 1: Relaxation & *FHI-aims* settings

EXERCISE 2: Phonons with *FHI-vibes* and *phonopy*

A Real Example: Diamond Si

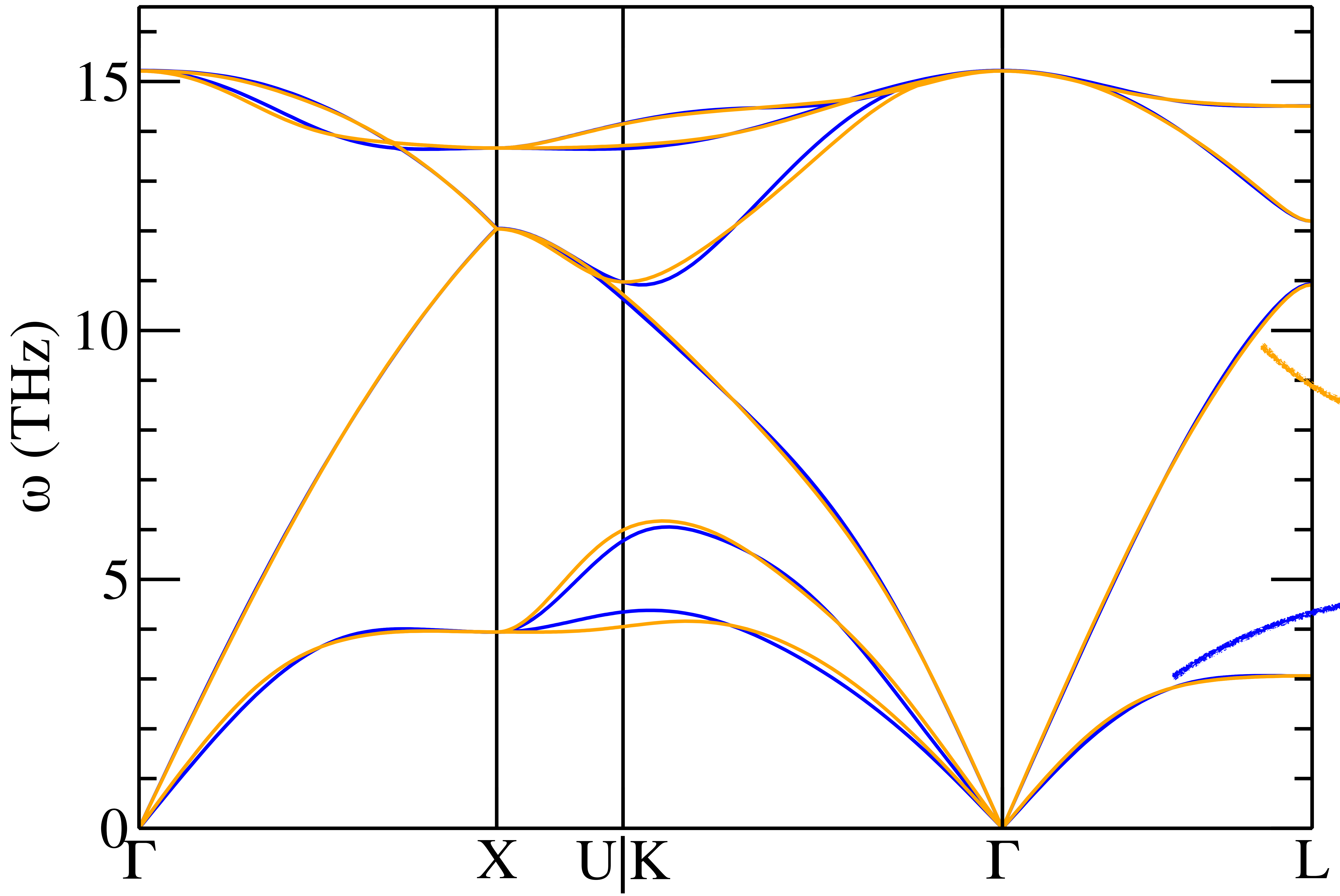


1x1x1 Cell (2 atoms)

A Real Example: Diamond Si

A Real Example: Diamond Si

A Real Example: Diamond Si



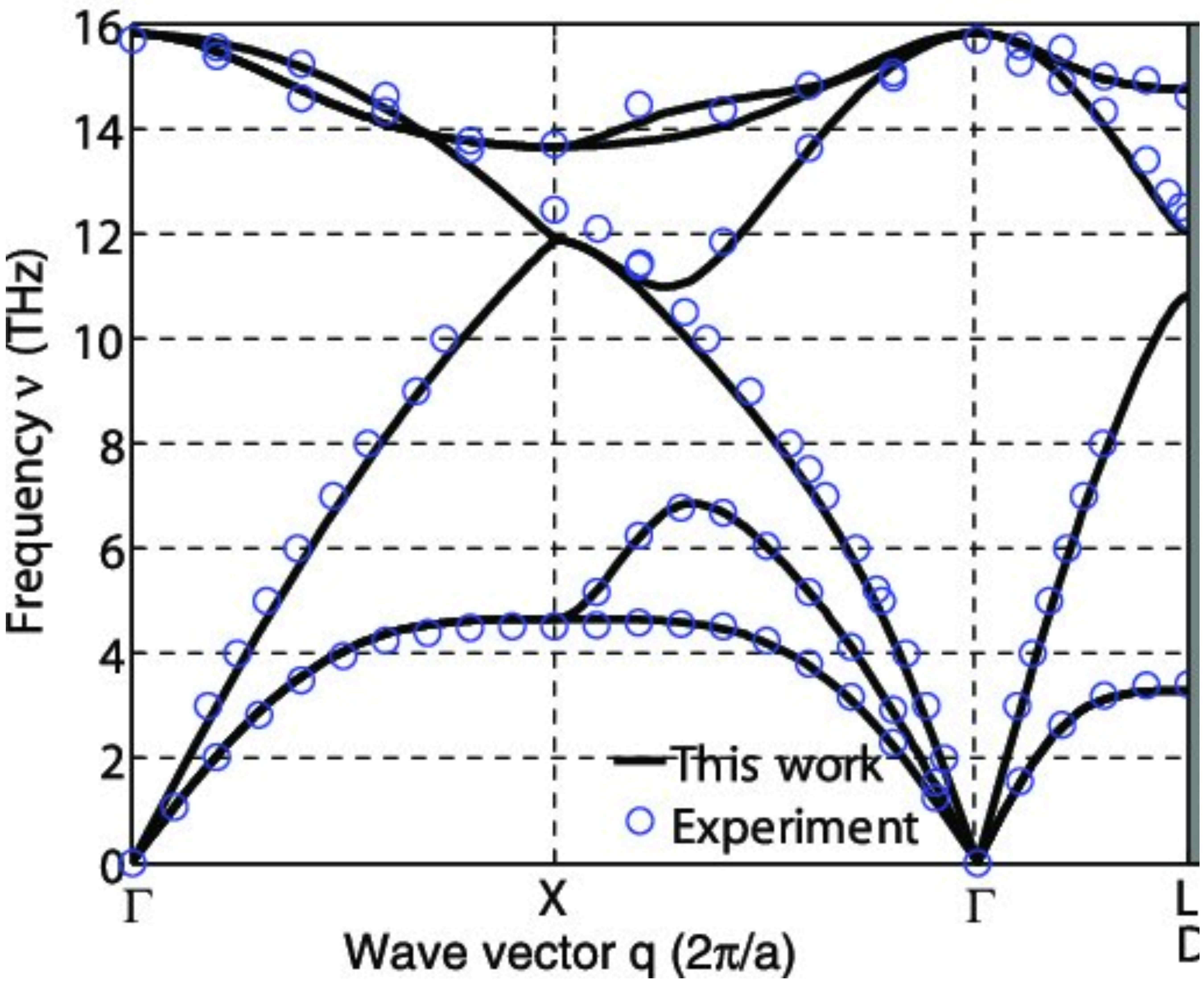
Convergence achieved!

N.B. 1 THz ≈ 4 meV

6x6x6 Cell (432 atoms)

4x4x4 Cell (128 atoms)

A Real Example: Diamond Si

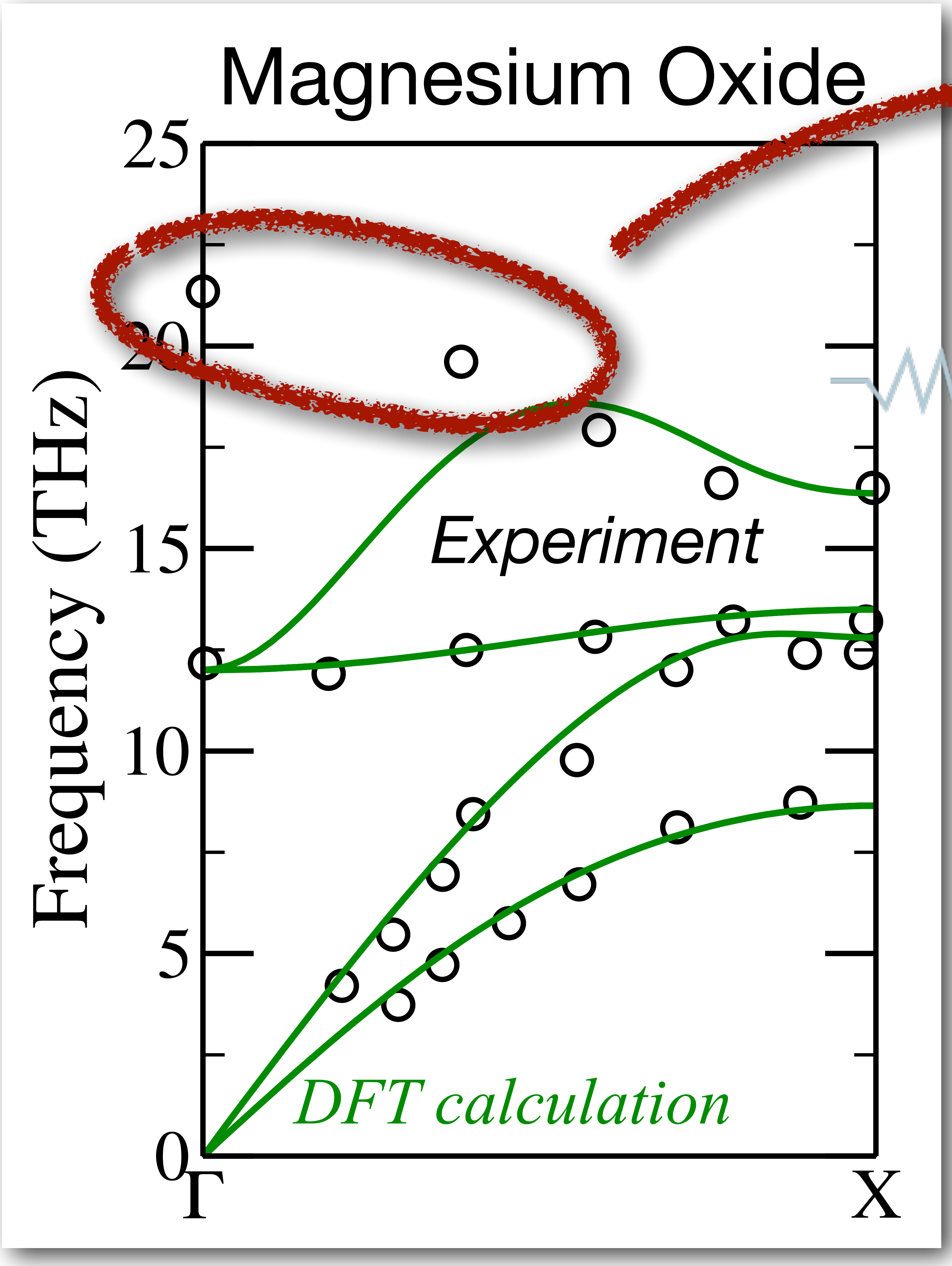


Comparison to experiment

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

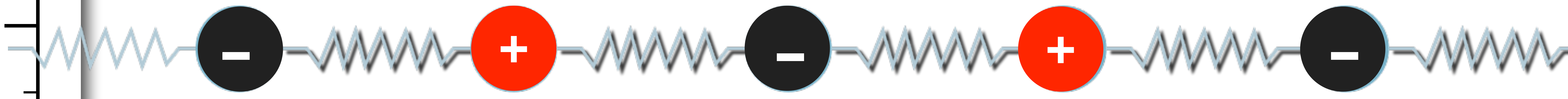
Polar Crystals

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?



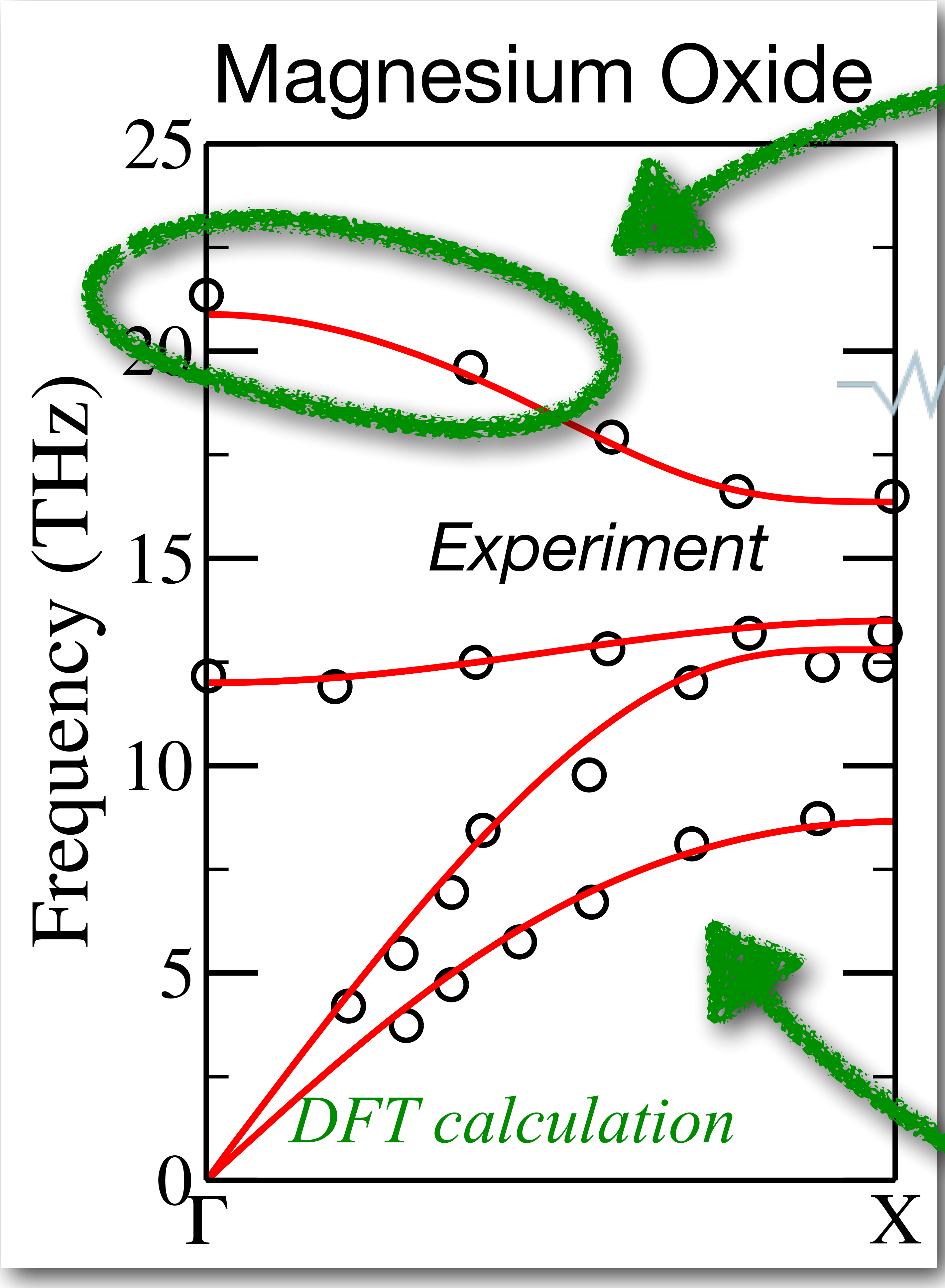
When *charged* atoms are *displaced*, a **weak, long-ranged** dipole field is induced.

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**.

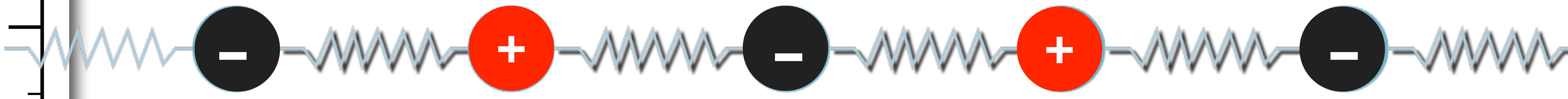
Polar Crystals

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.

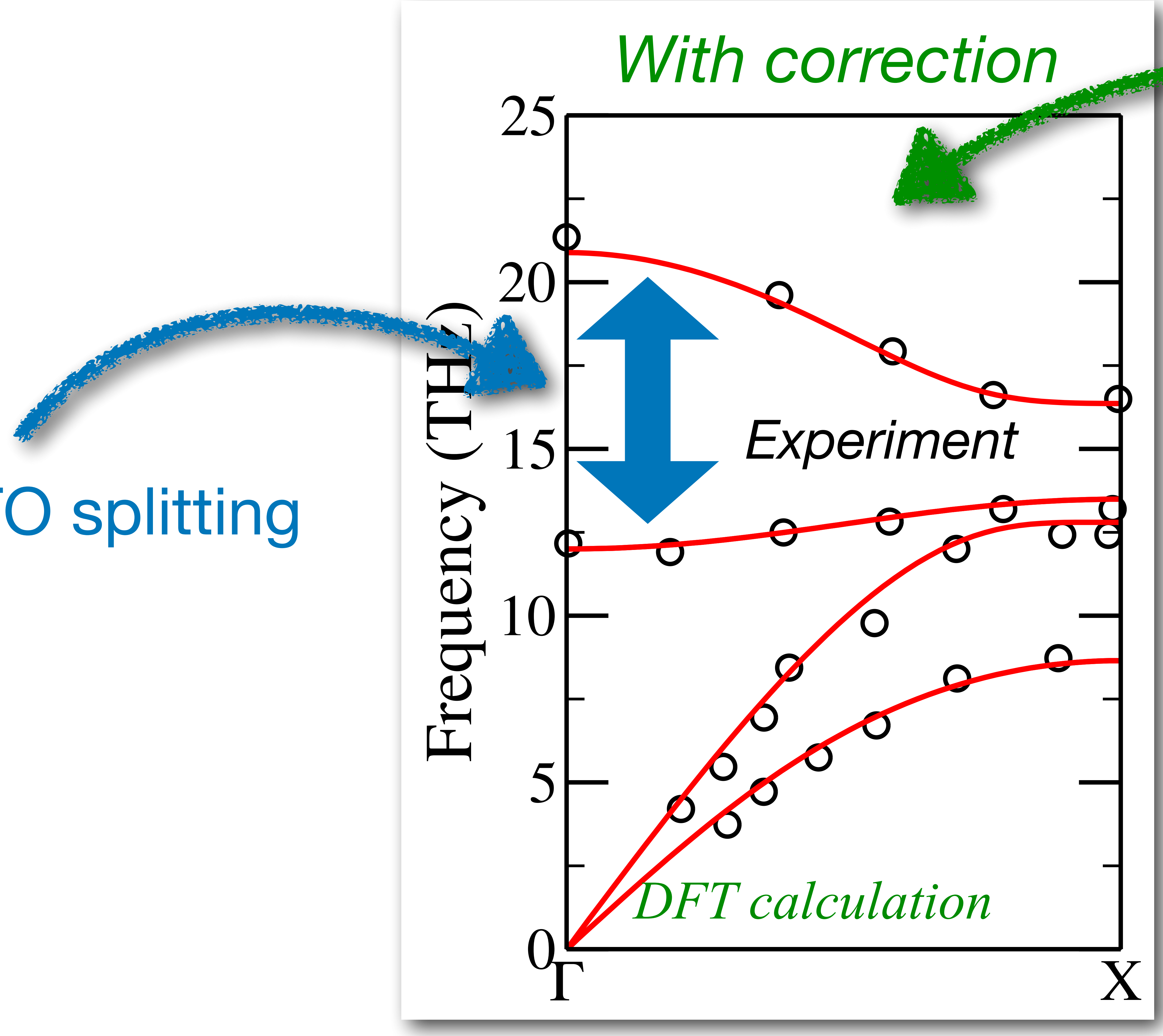
★Add the **additional, far-field** interaction:

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

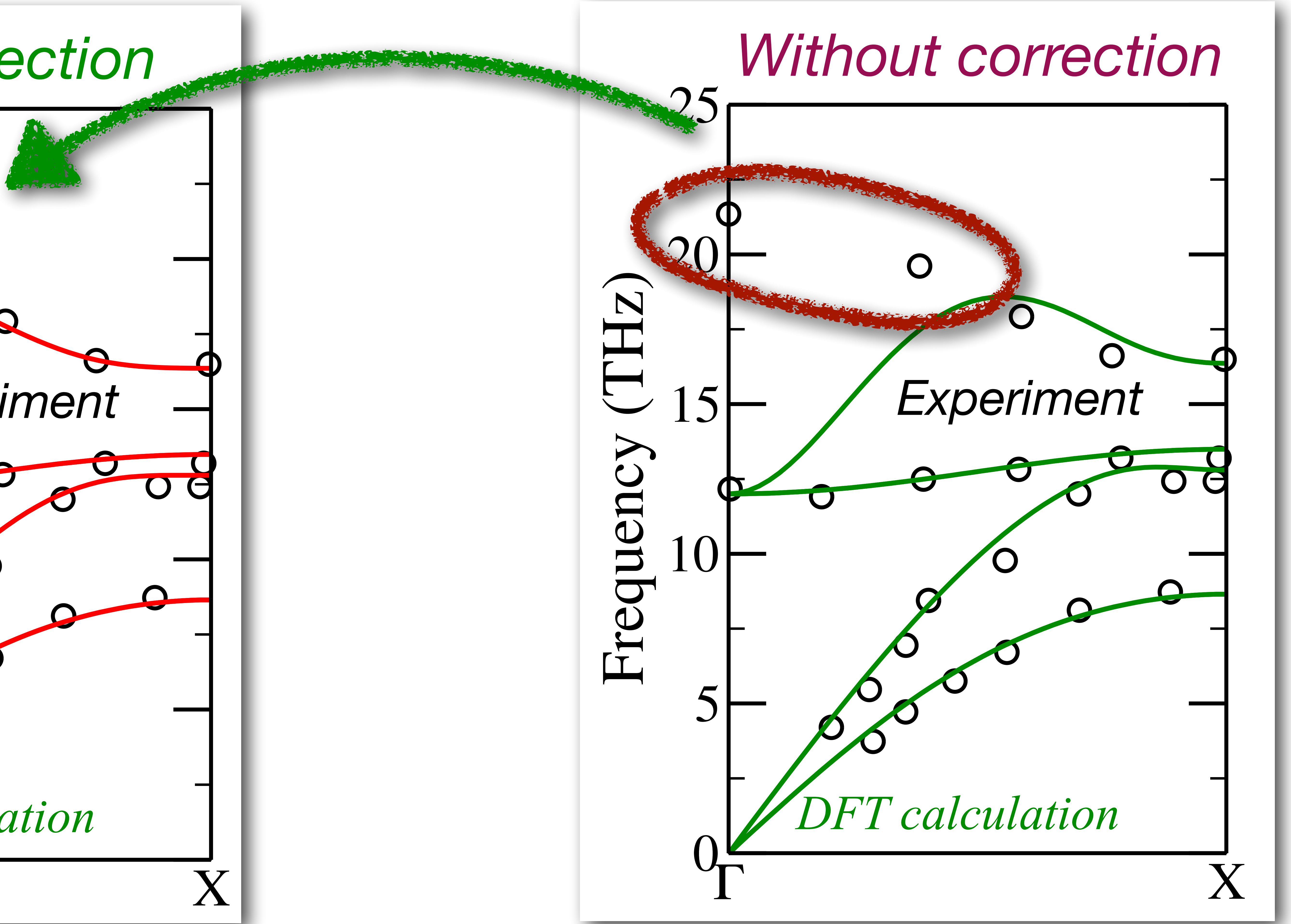
Polar Crystals

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).



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

The Harmonic Equations of Motion

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

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

Complex Amplitudes fully determined by initial conditions!

Eigenvalue problem:

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

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

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

The Harmonic Equations of Motion

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

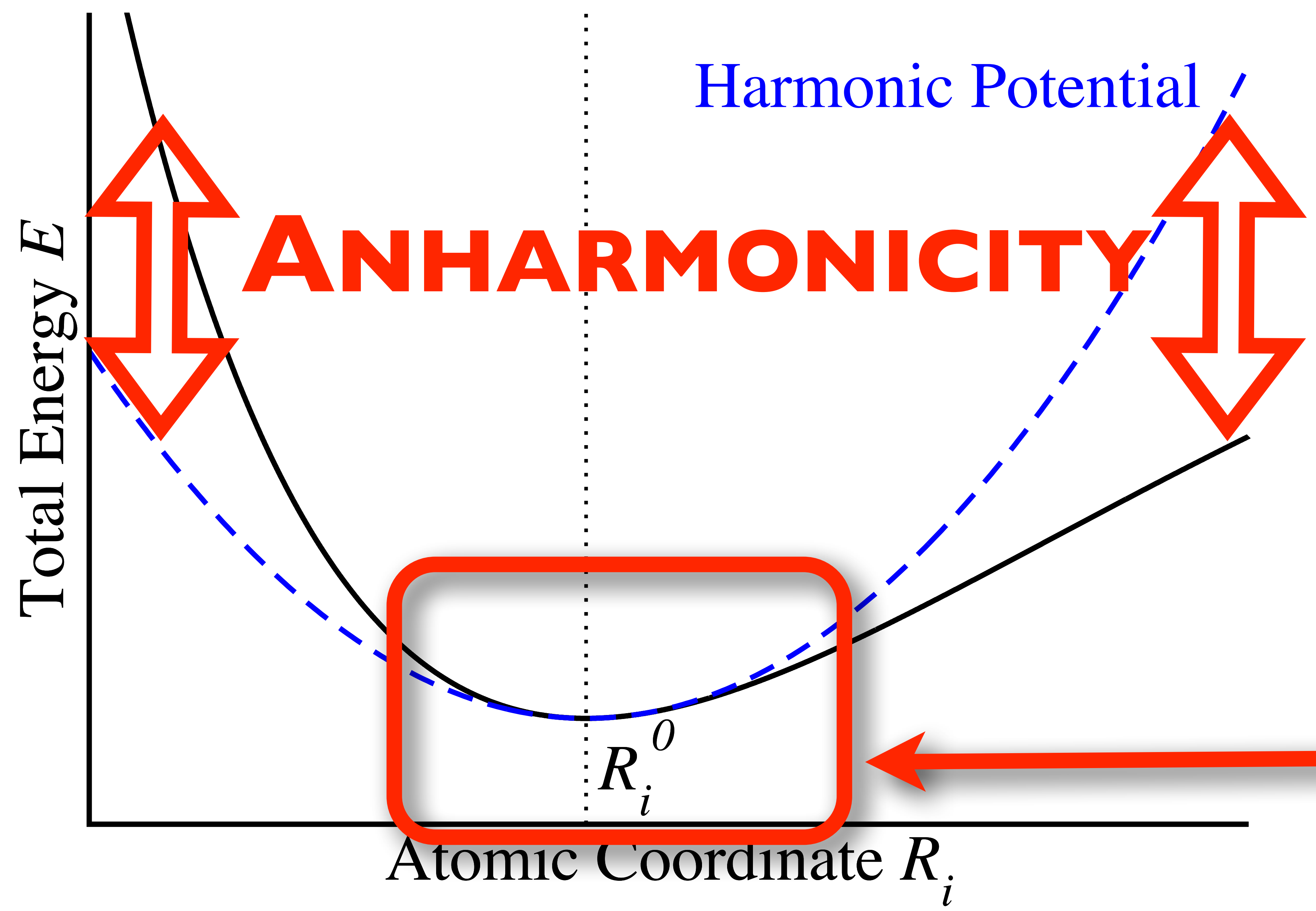
Complex Amplitudes
fully determined
by initial conditions!

When the **harmonic approximation** is **valid**,
you can immediately **sample** all
thermodynamics expectation values
analytically.

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

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

THE HARMONIC APPROXIMATION

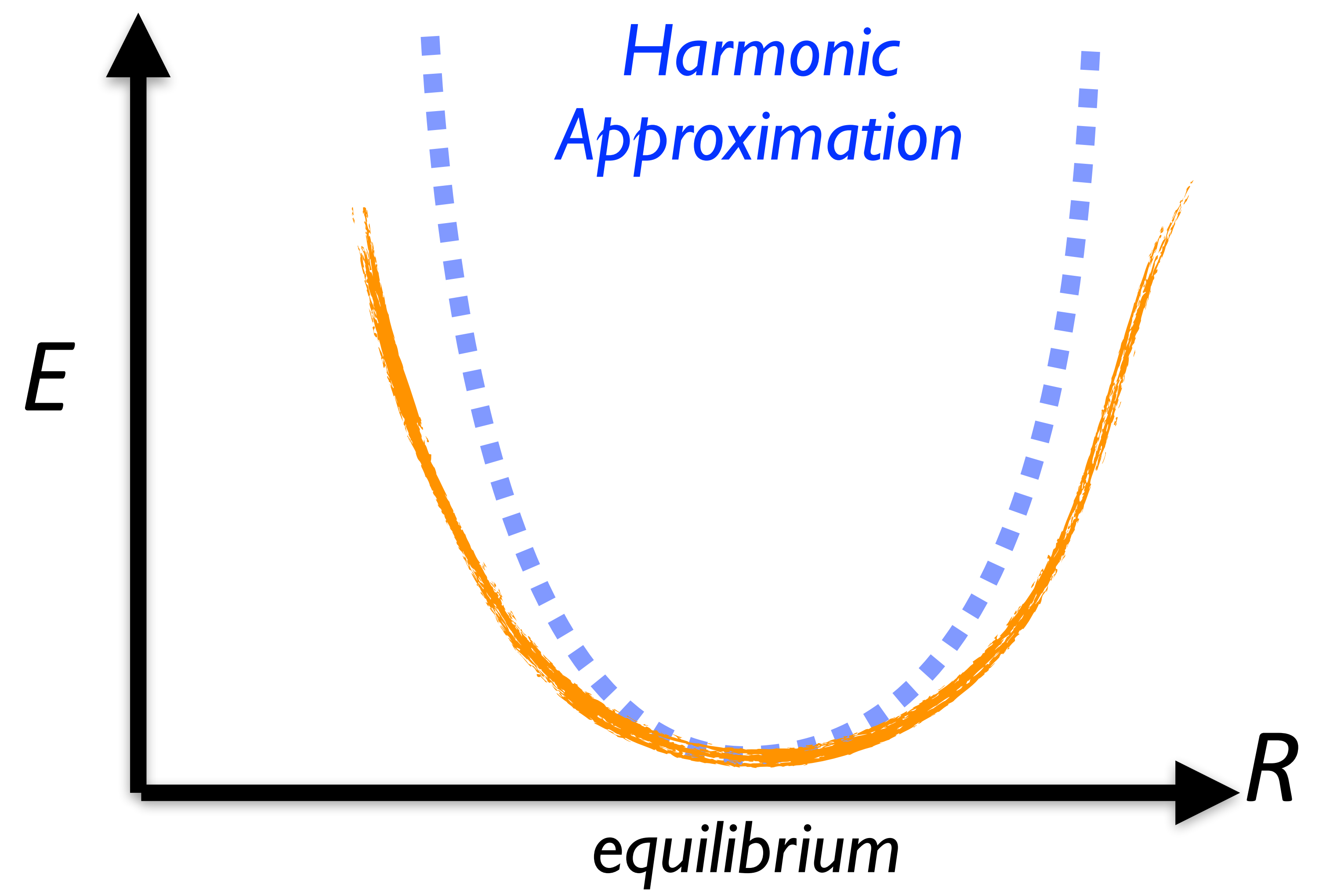


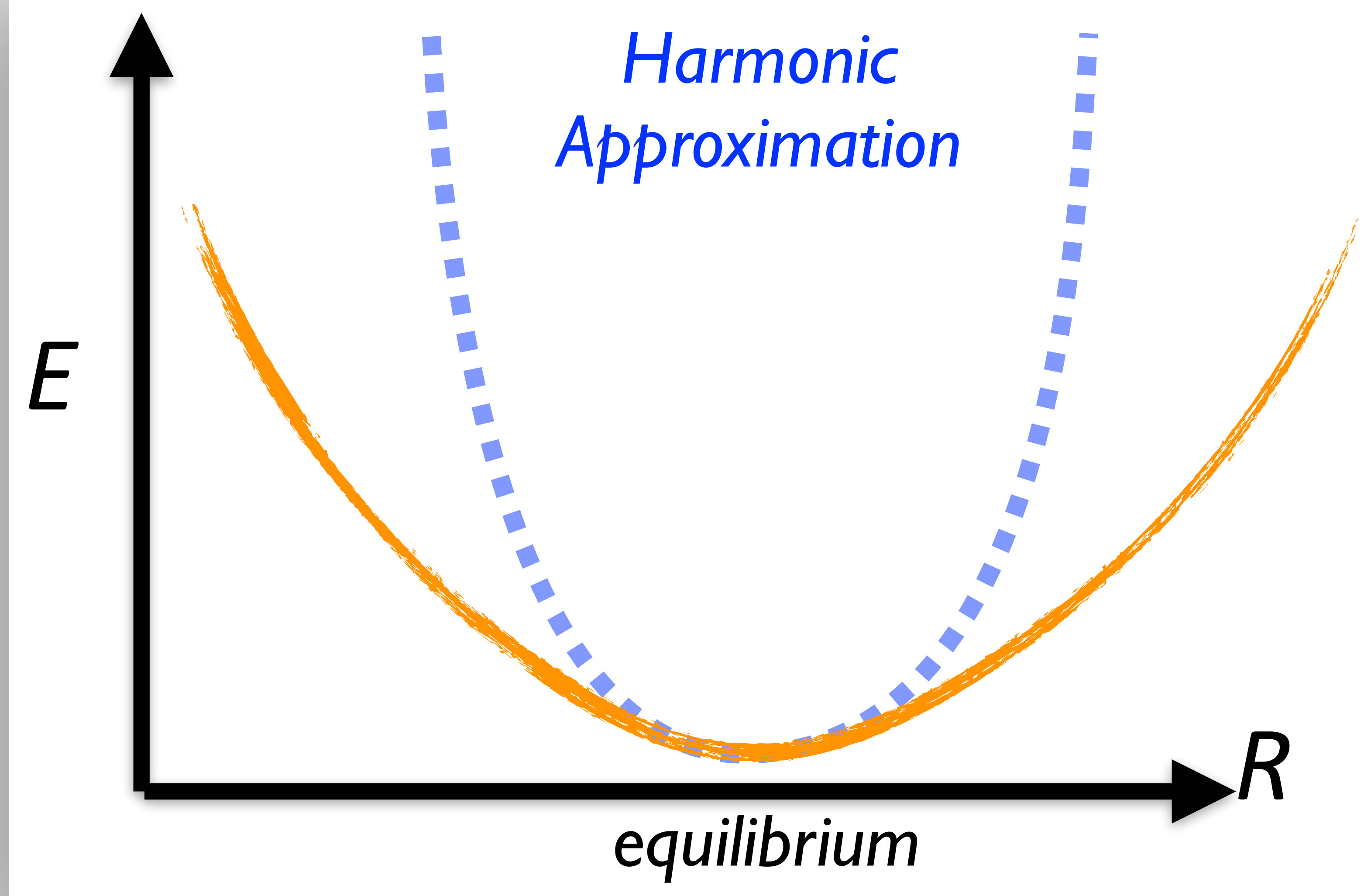
WARNING:
Harmonic Approximation is only valid for small displacements from ***R⁰***!

At elevated temperatures the harmonic approximation becomes increasingly inaccurate – and often terribly misleading!

What is Anharmonicity?

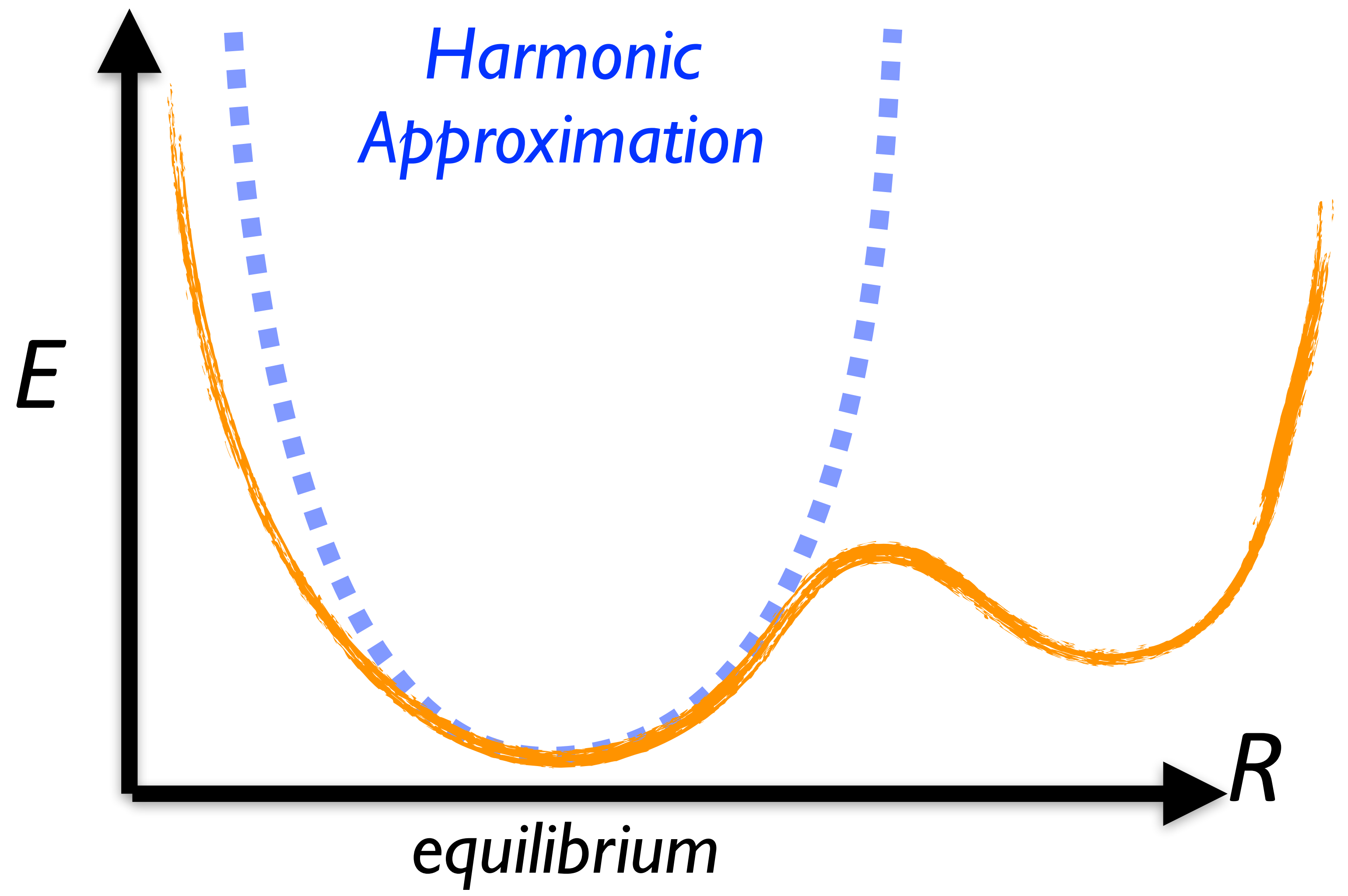
$E_{harm} \gg E_{anha}$

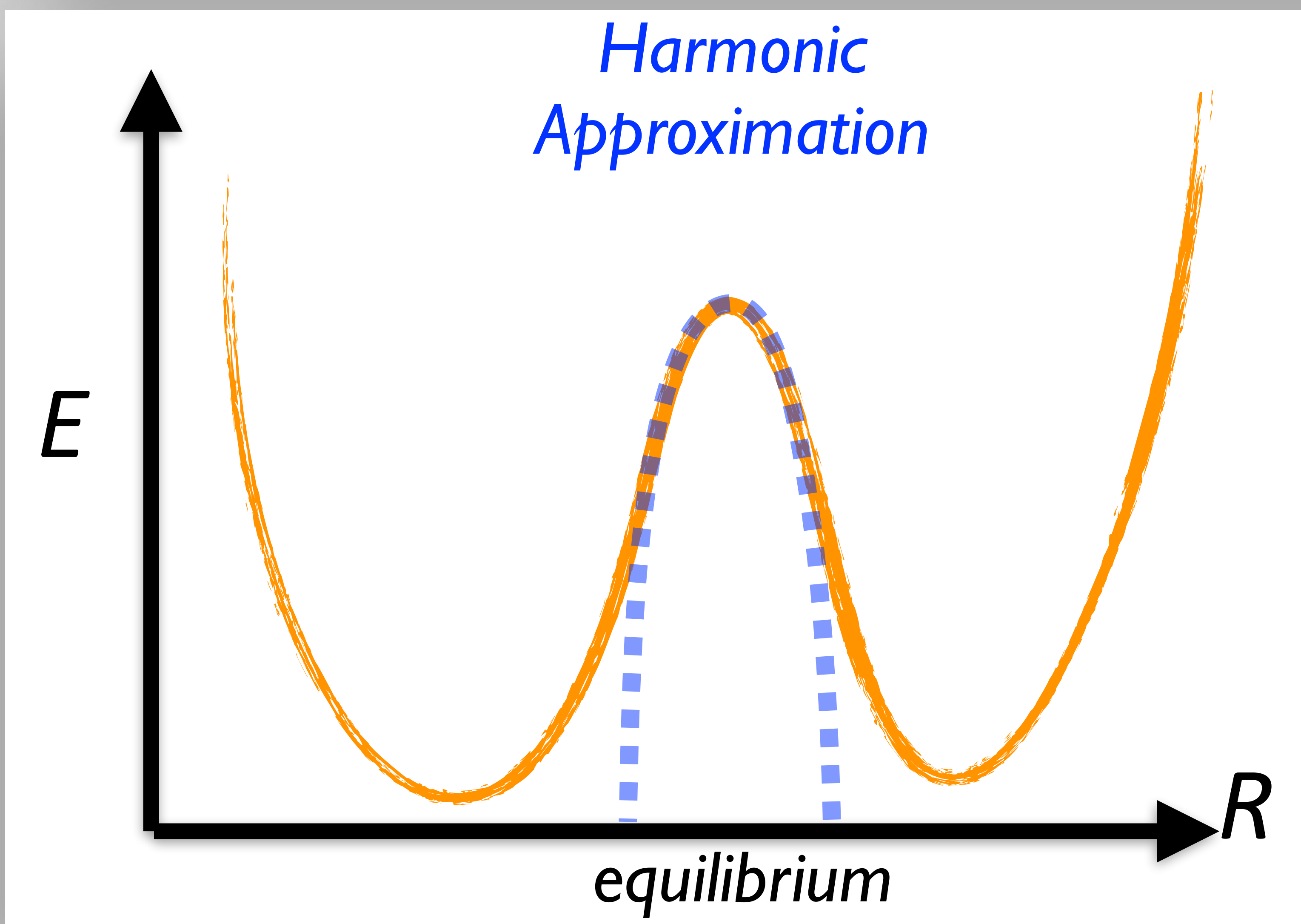




$E_{harm} \approx E_{anha}$

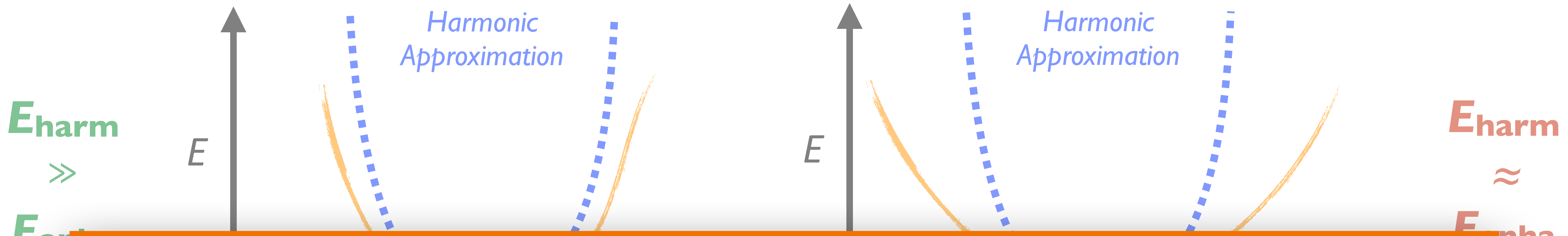
$E_{harm} \ll E_{anha}$



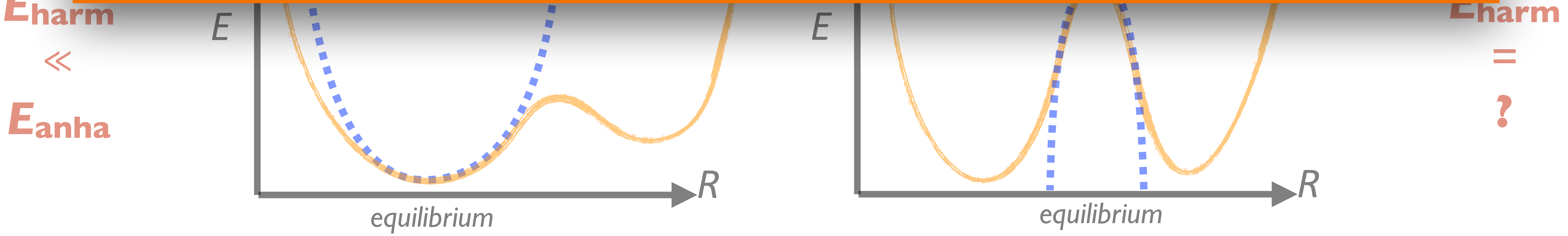


$E_{harm} = ?$

What is Anharmonicity?



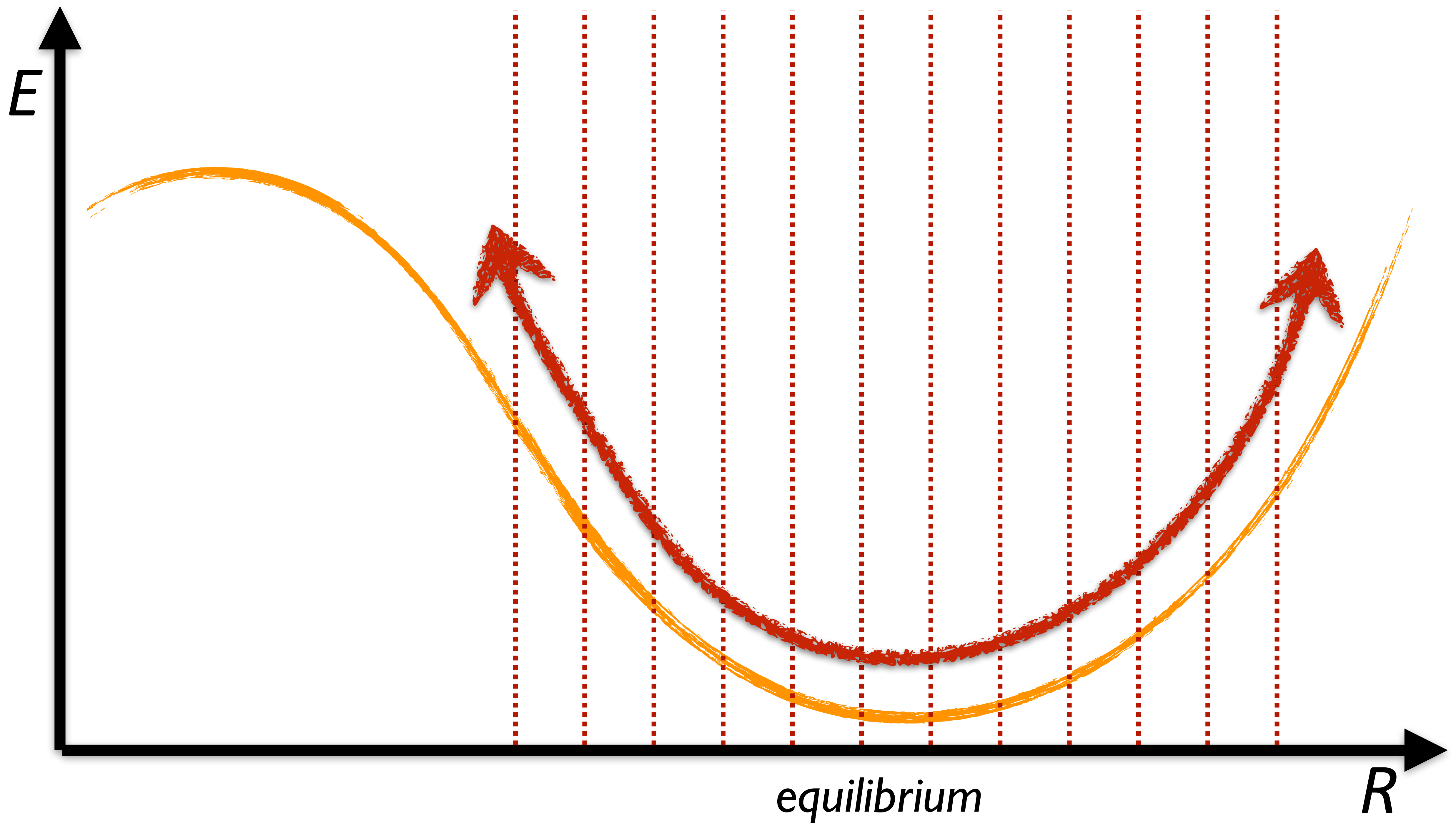
⇒ **Can we quantify anharmonicity in materials space?**



Anharmonicity Quantification

How do $\boldsymbol{E}_{\mathbf{harm}}$ and $\boldsymbol{E}_{\mathbf{anha}} = \boldsymbol{E}_{\boldsymbol{DFT}}$ compare in different materials?

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



1) Run *ab initio* MD simulations to obtain anharmonic trajectories $\boldsymbol{R}_I^{\mathrm{DFT}}(t)$.

Anharmonicity Quantification

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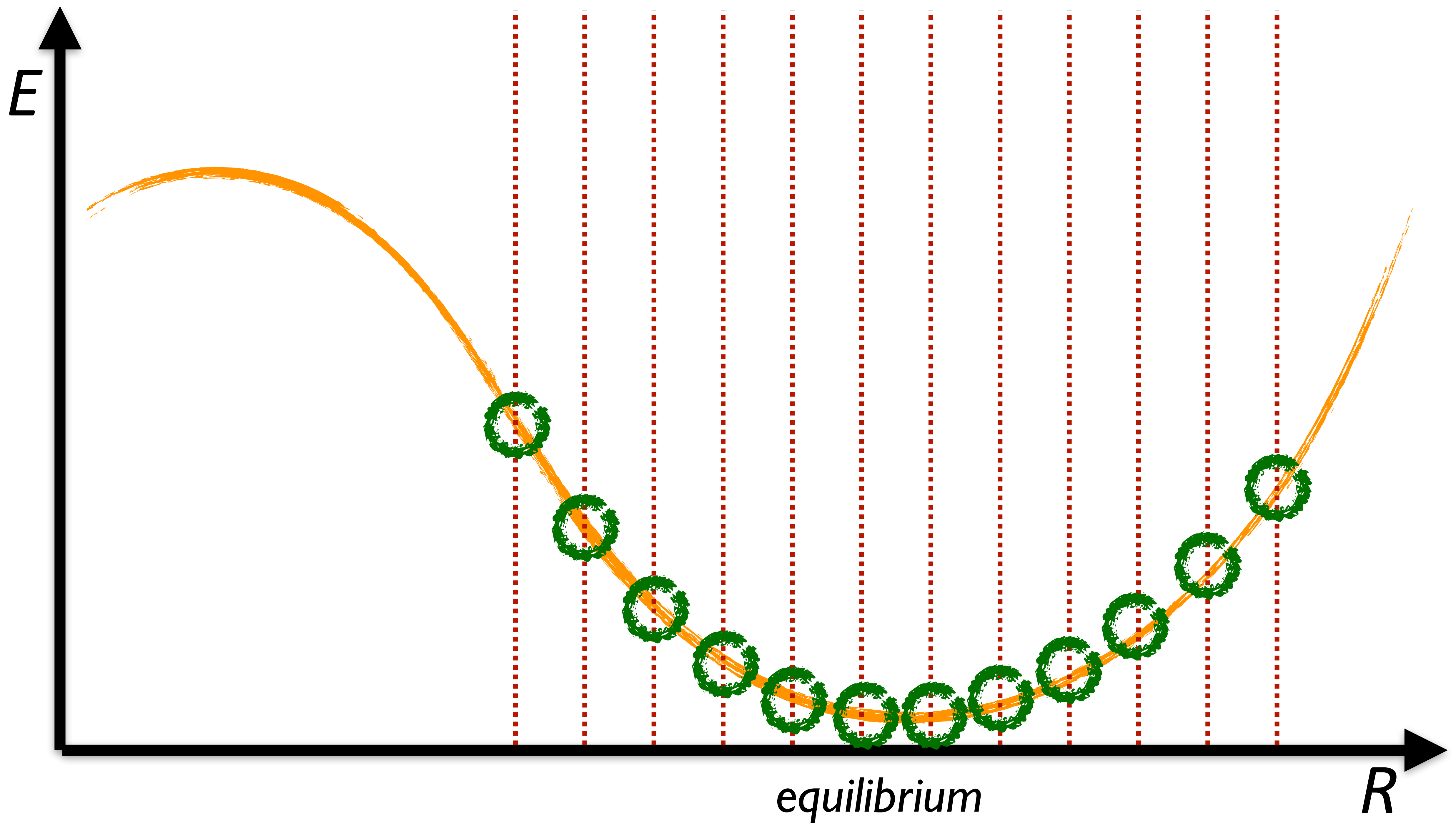

1) Run *ab initio* MD simulations to obtain anharmonic trajectories $\boldsymbol{R}_I^{\mathrm{DFT}}(\mathrm{t})$.

2) Store the potential energies $E^{\mathrm{DFT}}(\mathrm{t})$ observed along $\boldsymbol{R}_I^{\mathrm{DFT}}(\mathrm{t})$.

Anharmonicity Quantification

How do $\boldsymbol{E}_{\mathbf{harm}}$ and $\boldsymbol{E}_{\mathbf{anha}} = \boldsymbol{E}_{\boldsymbol{DFT}}$ compare in different materials?

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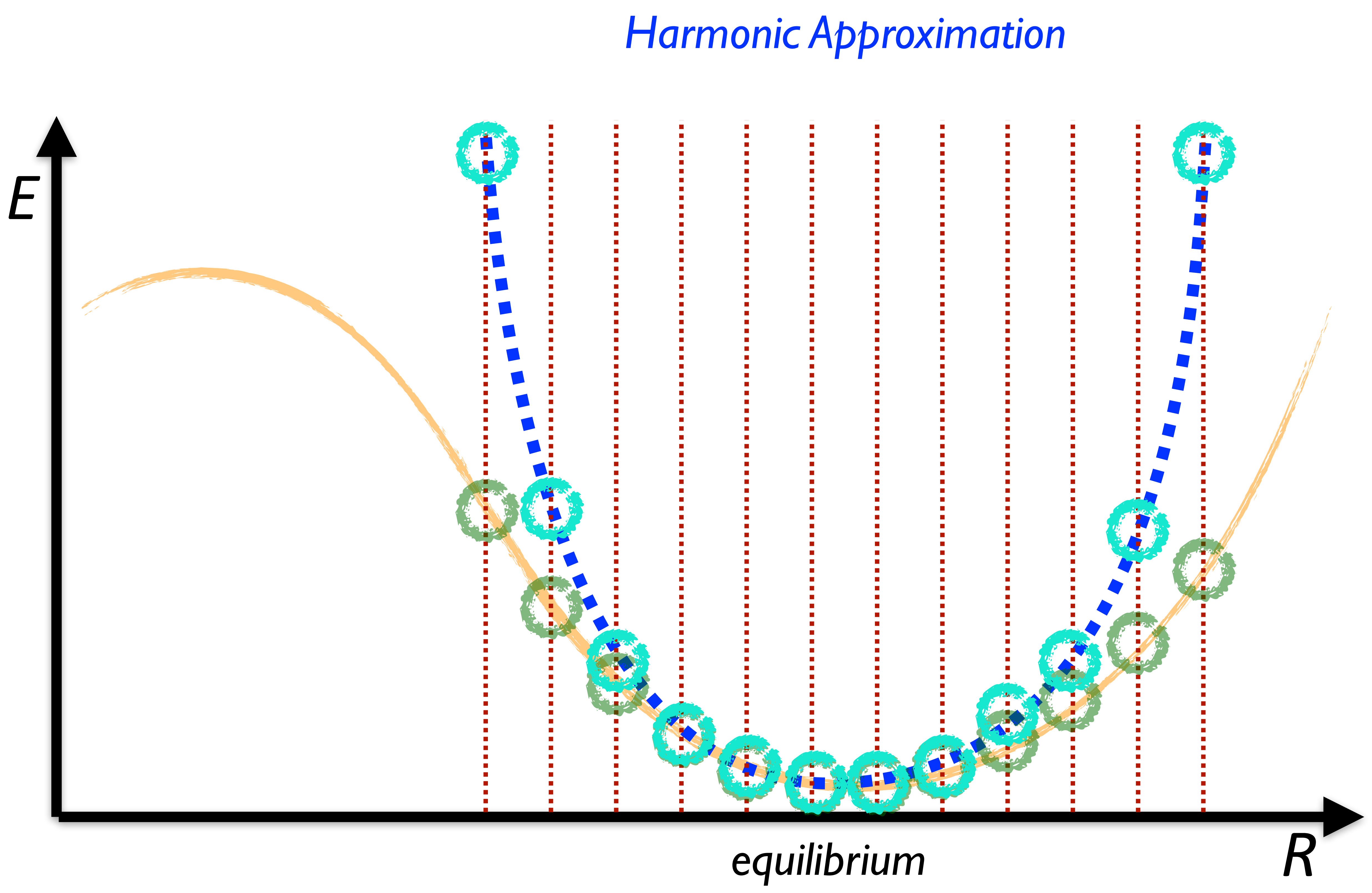

1) Run *ab initio* MD simulations to obtain anharmonic trajectories $\boldsymbol{R}_I^{DFT}(t)$.

2) Store the potential energies $E^{DFT}(t)$ observed along $\boldsymbol{R}_I^{DFT}(t)$.

3) Evaluate which potential energies $E^{harm}(t)$ the *harmonic approximation* would predict along $\boldsymbol{R}_I^{DFT}(t)$.

Anharmonicity Quantification

How do $\boldsymbol{E}_{\mathbf{harm}}$ and $\boldsymbol{E}_{\mathbf{anha}} = \boldsymbol{E}_{\boldsymbol{DFT}}$ compare in different materials?

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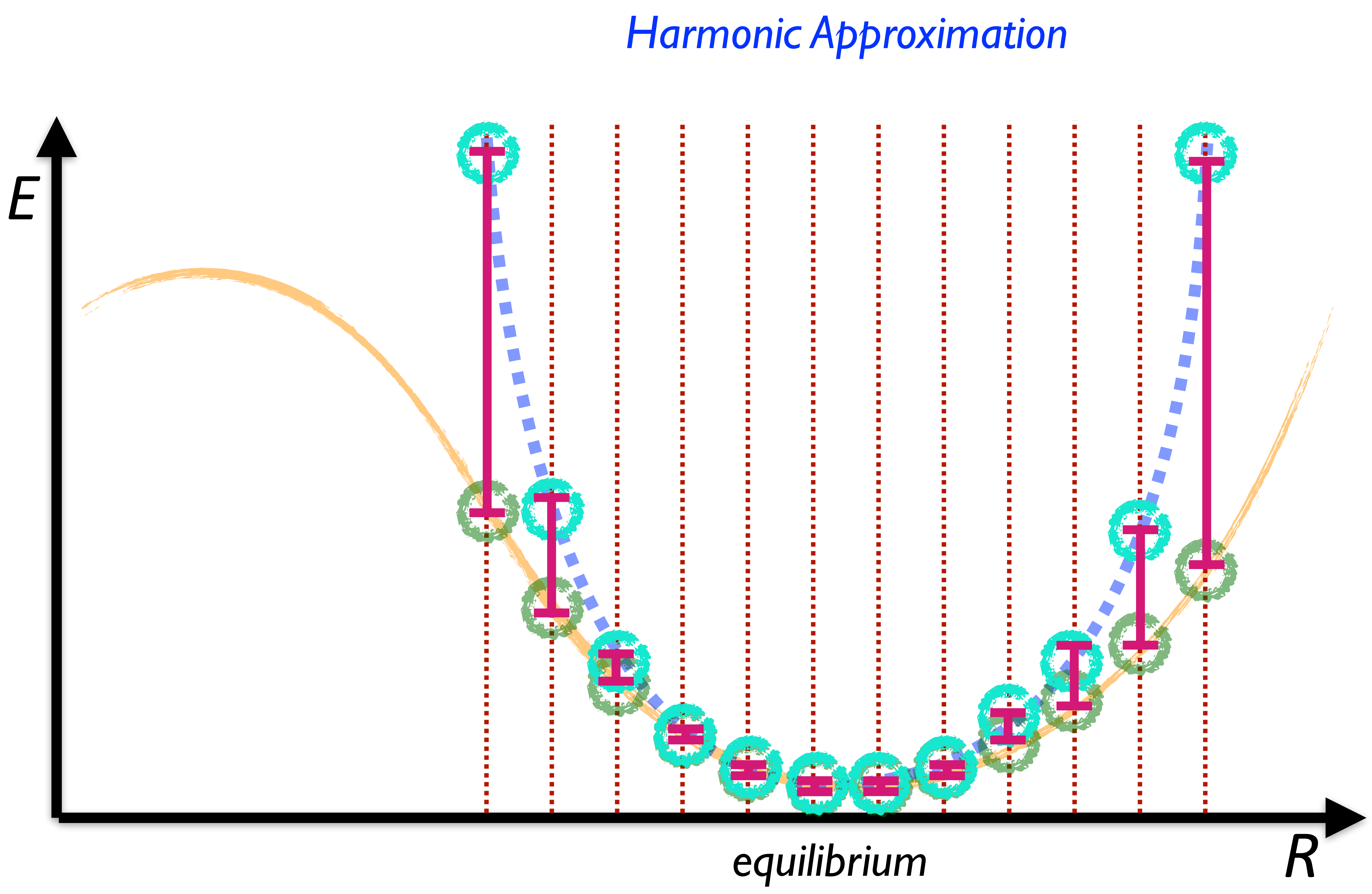


1) Run *ab initio* MD simulations to obtain anharmonic trajectories $\boldsymbol{R}_I^{\mathrm{DFT}}(\mathrm{t})$.

2) Store the potential energies $E^{\mathrm{DFT}}(\mathrm{t})$ observed along $\boldsymbol{R}_I^{\mathrm{DFT}}(\mathrm{t})$.

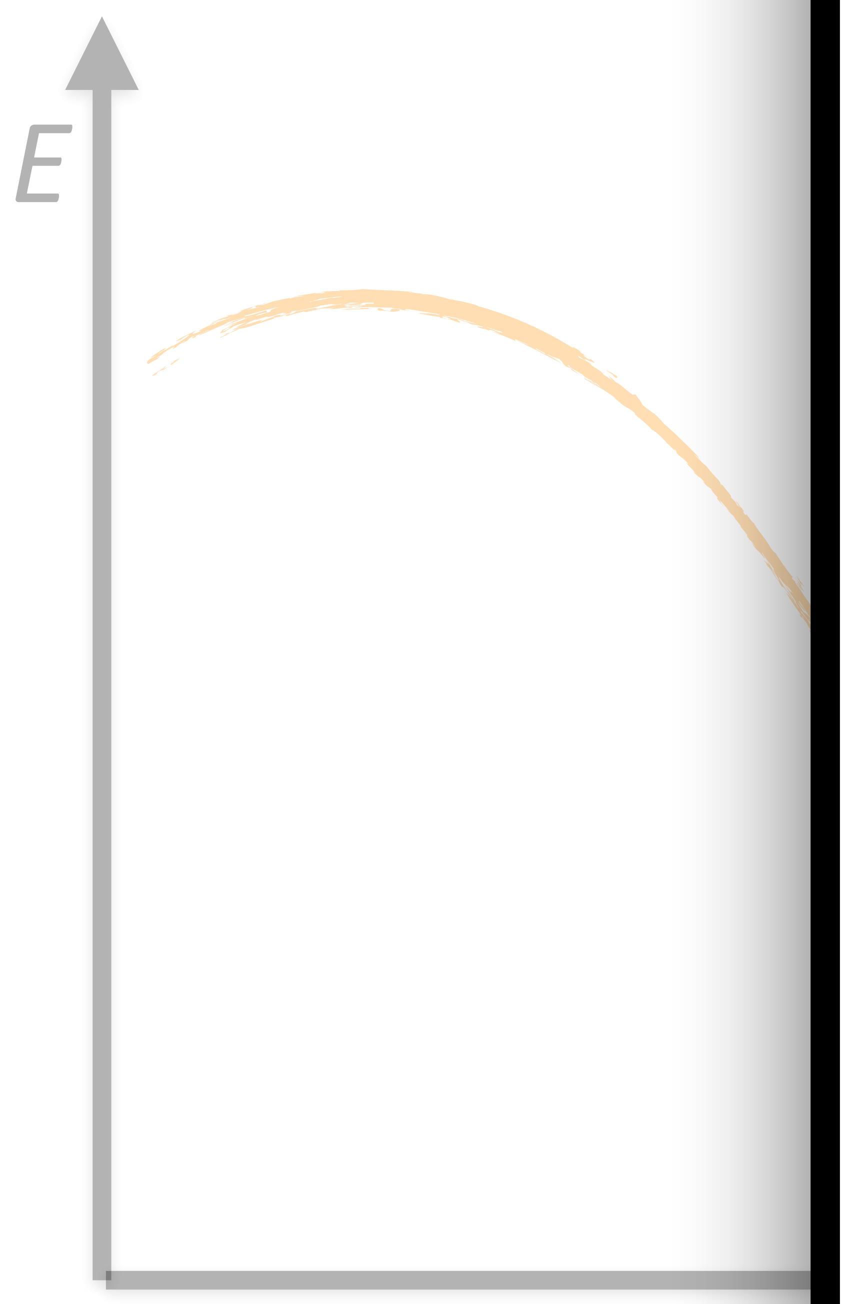
3) Evaluate which potential energies $E^{harm}(t)$ the *harmonic approximation* would predict along $\boldsymbol{R}_I^{\mathrm{DFT}}(\mathrm{t})$.

4) The difference $E^{harm}(t)$ - $E^{\mathrm{DFT}}(\mathrm{t})$ quantifies the strength of anharmonic effects.

Anharmonicity Quantification

How do $\boldsymbol{E_{harm}}$ and $\boldsymbol{E_{anha}} = \boldsymbol{E_{DFT}}$ compare in different materials?

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



In practice,
it is beneficial to work with
harmonic $\mathbf{F}_I^{harm}(t)$ and
anharmonic forces $\mathbf{F}_I^{DFT}(t)$,
since this allows for
an atom-specific resolution
of anharmonic effects.

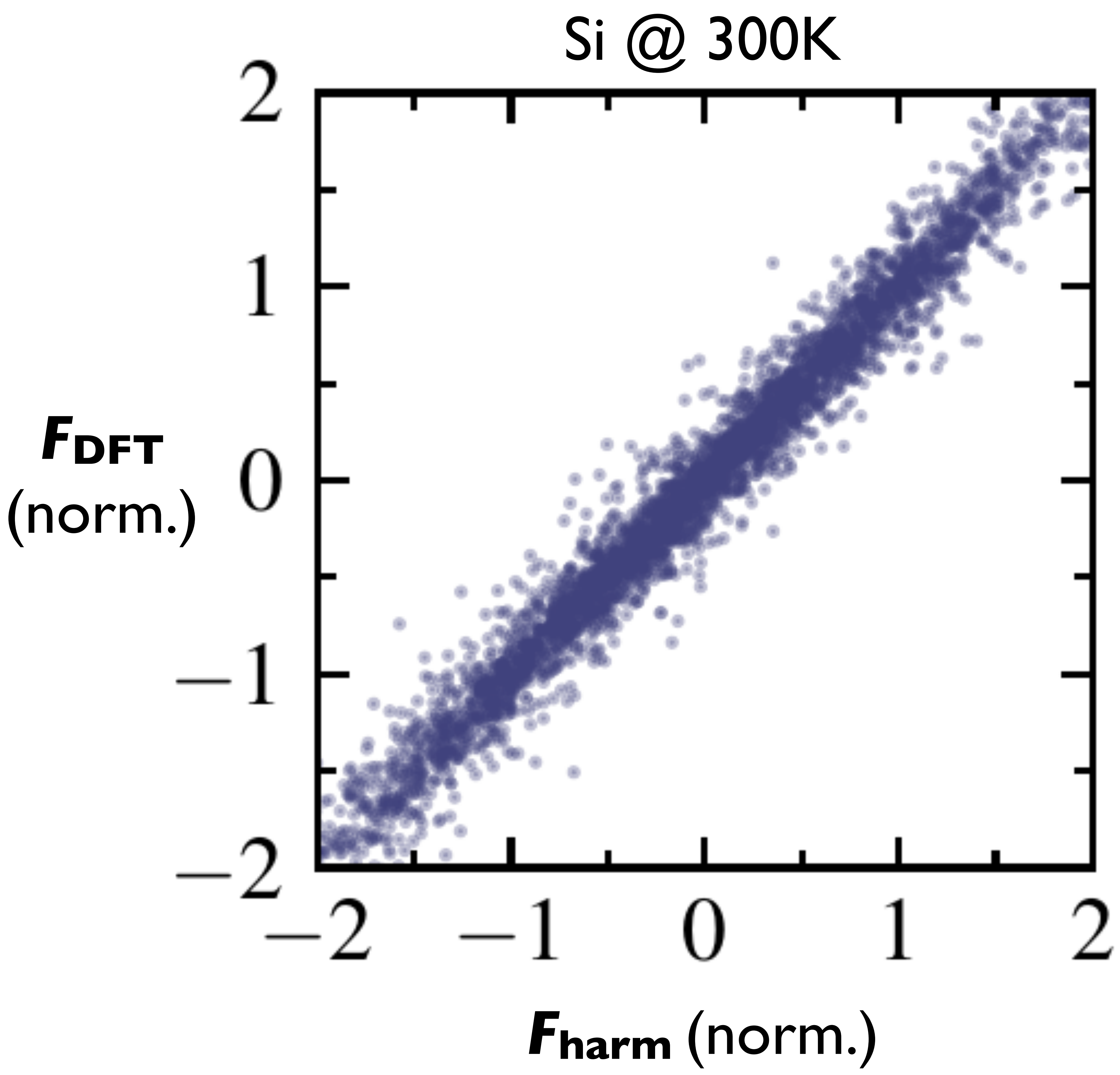
ations to obtain
es $\boldsymbol{R}_I^{DFT}(t)$.

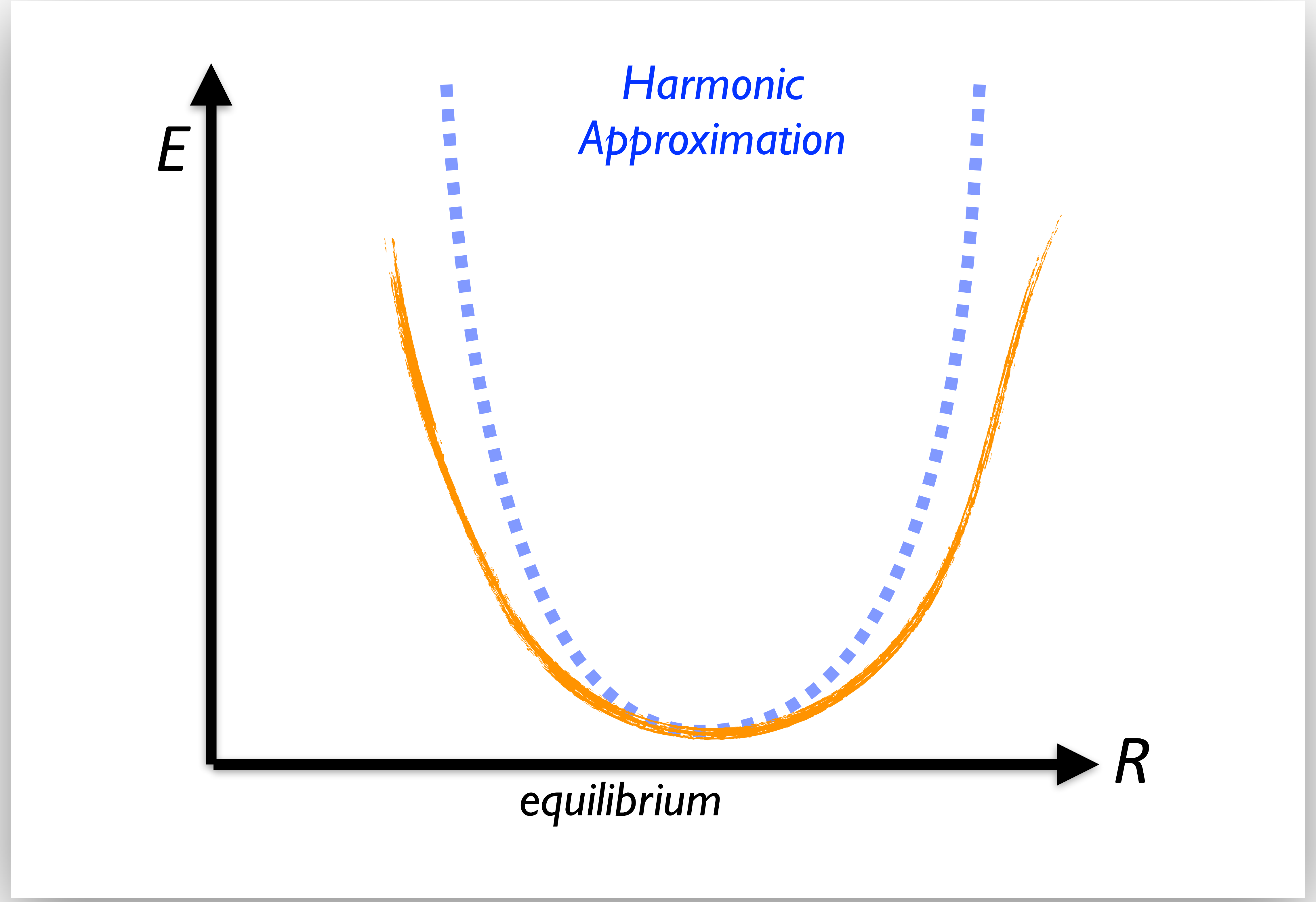
ergies $E^{DFT}(t)$
).

ial energies $E^{harm}(t)$ the
would predict along

- $E^{DFT}(t)$ quantifies the
strength of anharmonic effects.

How do E_{harm} and $E_{anha} = E_{DFT}$ compare in different materials?

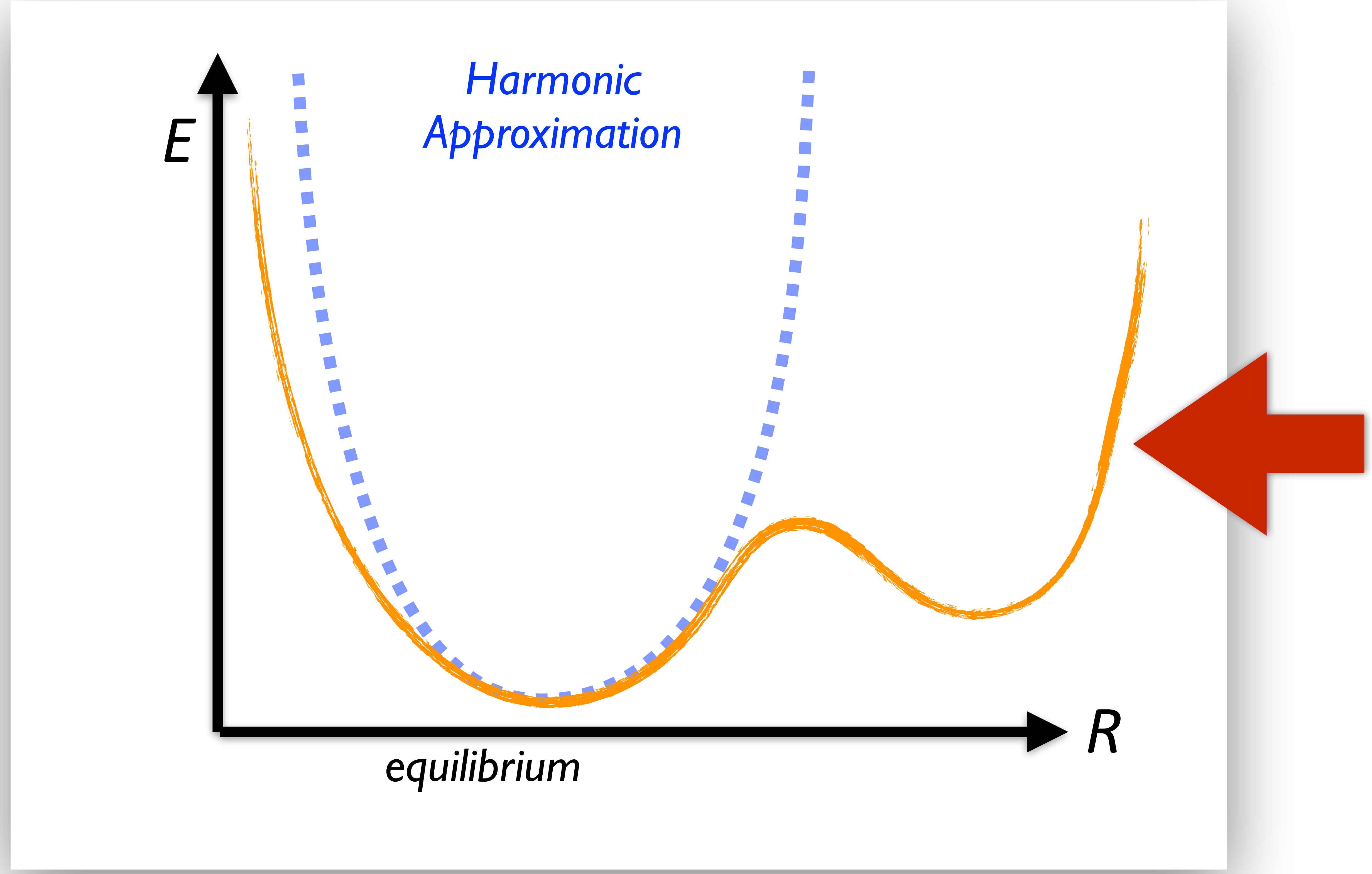


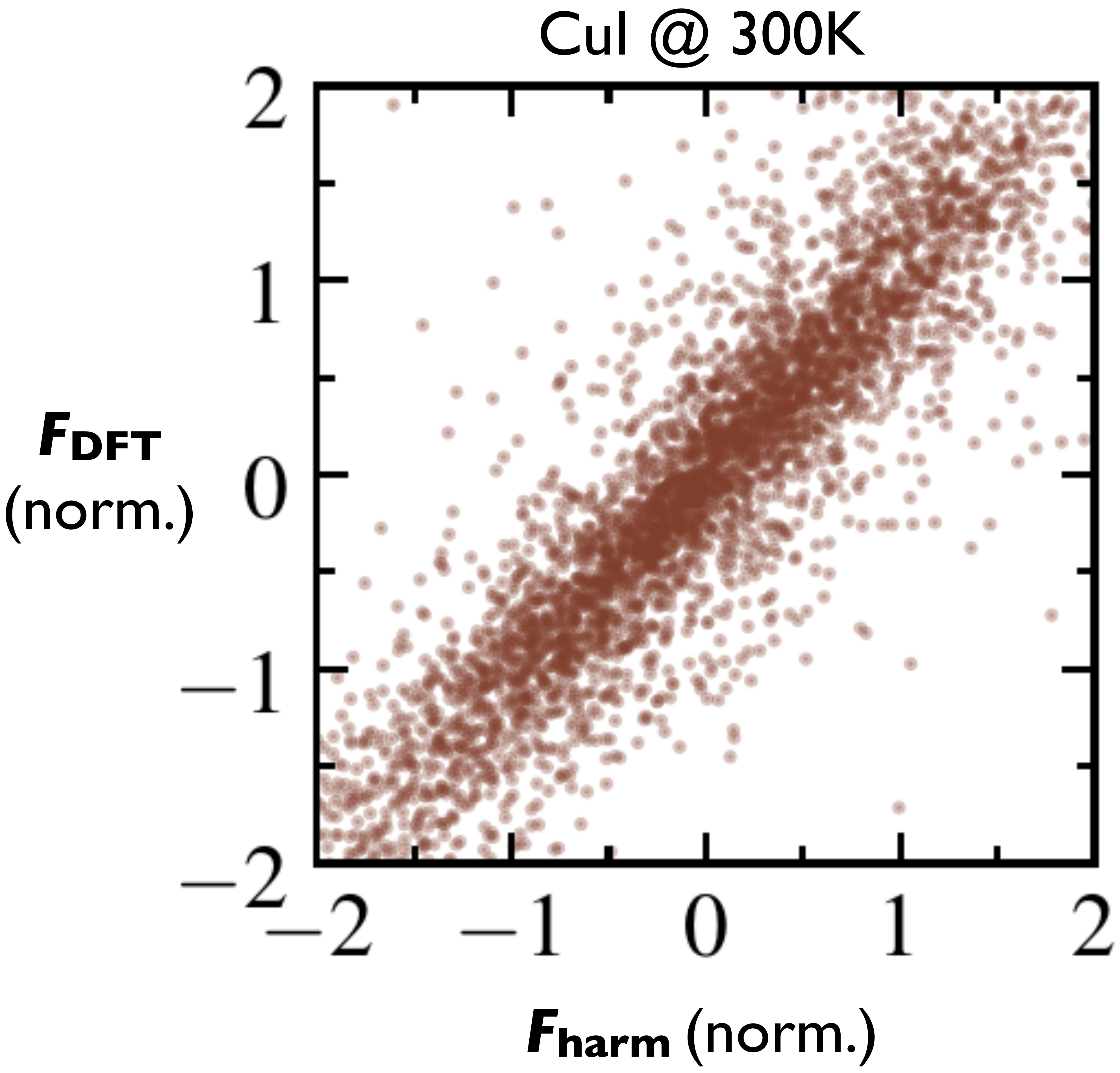


Well-behaved harmonic material!

$E_{harm} \gg E_{anha}$

How do E_{harm} and E_{anha}= E_{DFT} compare in different materials?

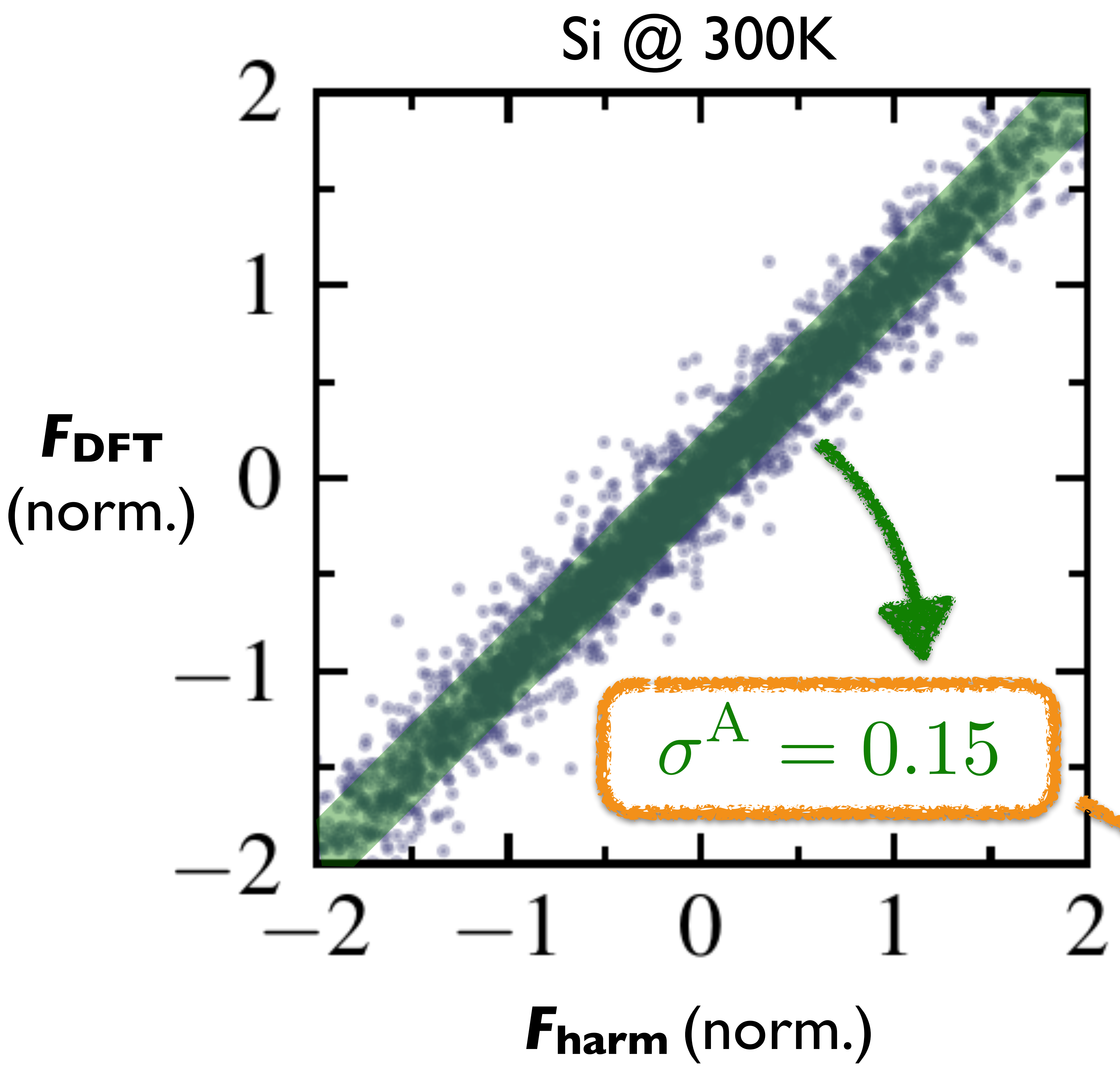


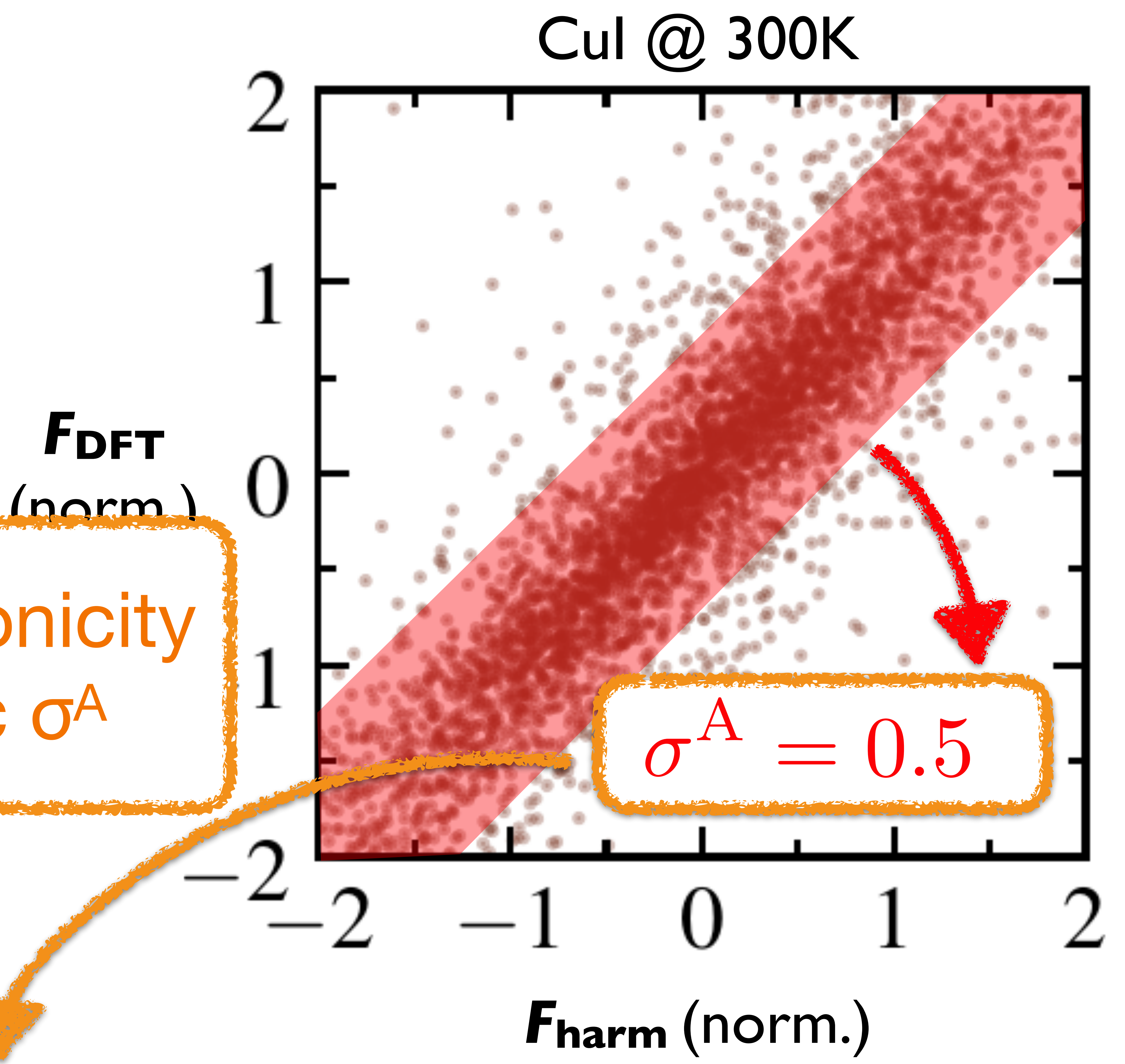


Anharmonicity dominates!

$E_{harm} \ll E_{anha}$

How do E_{harm} and $E_{anha} = E_{DFT}$ compare in different materials?





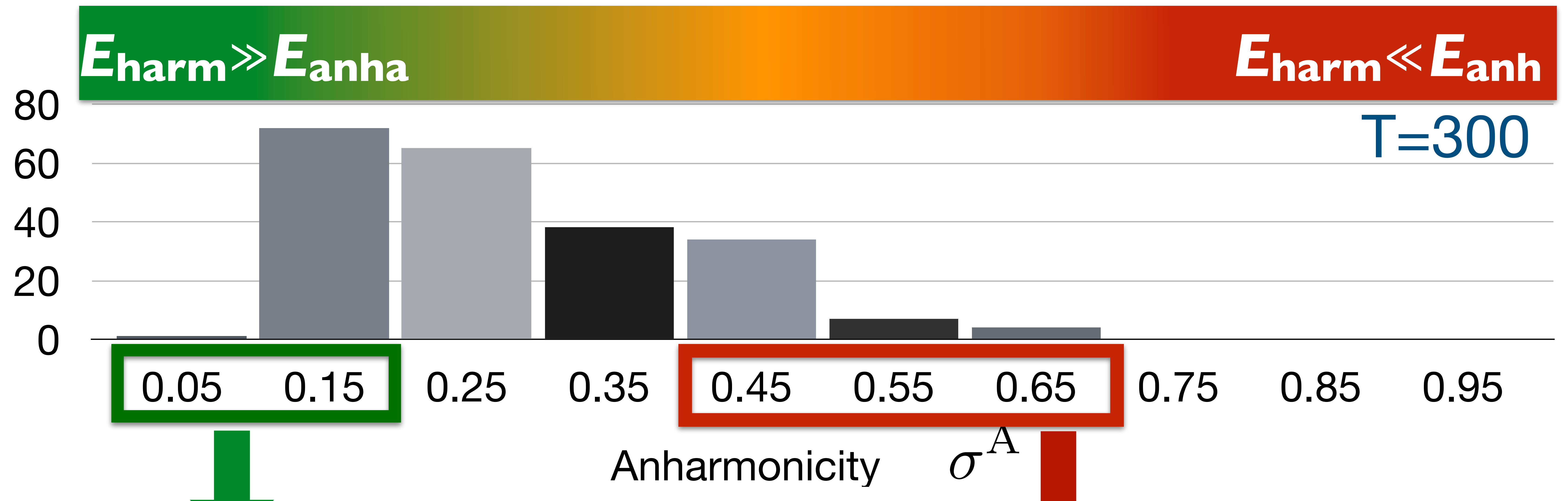
Anharmonicity Metric σ^A

How much do anharmonic effects contribute to the forces on average?

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).

Anharmonicity Quantification across Material Space

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



At **300K**, many materials indeed behave **almost perfectly harmonically**.

But even at **300K**, there are systems that exhibit a **strongly anharmonic** dynamics.

200+ Material Test Set:
- 97 Rock salt
- 67 Zincblende
- 45 Wurtzite
- 10 Perovskites

Anharmonicity Quantification across Material Space

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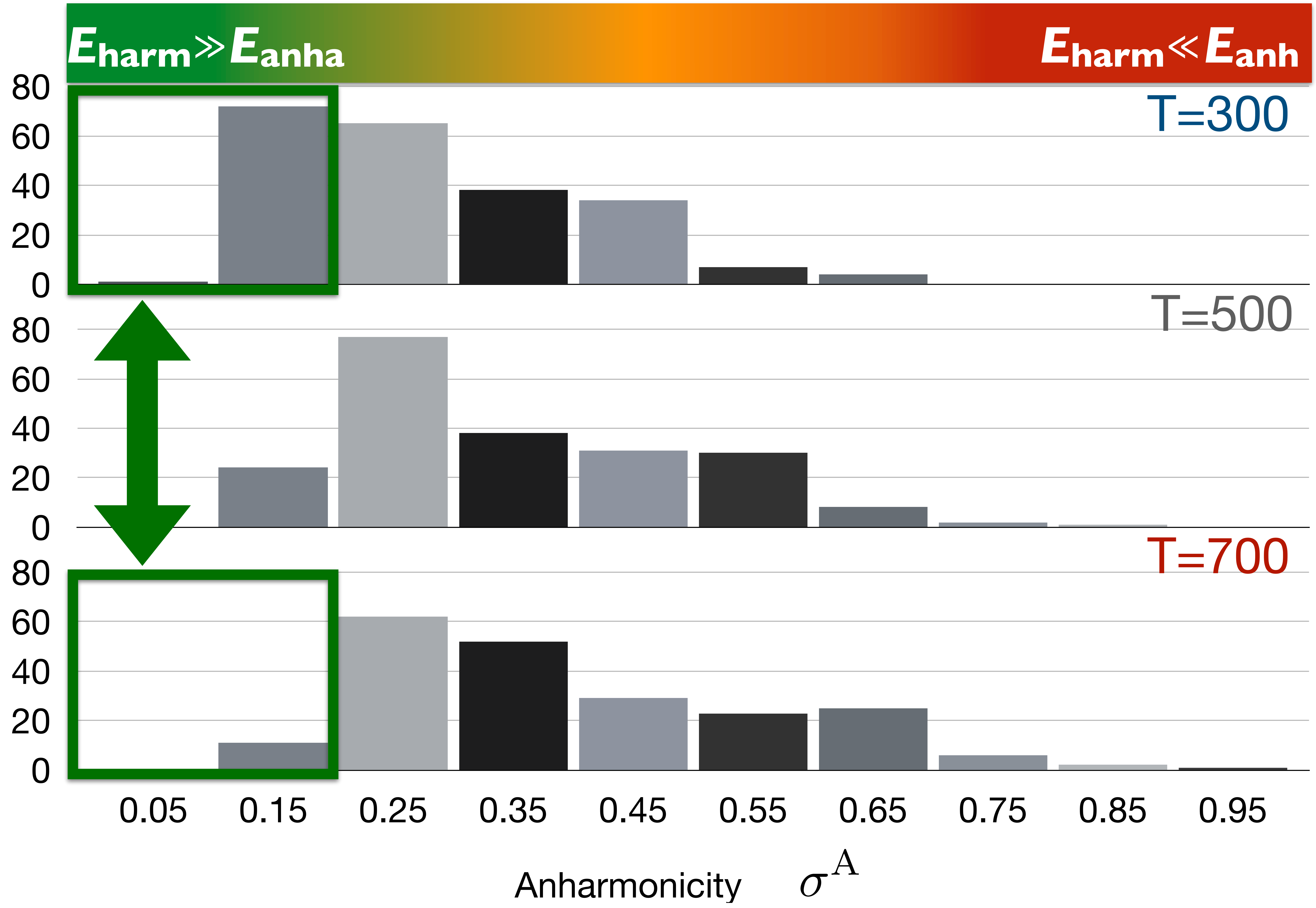


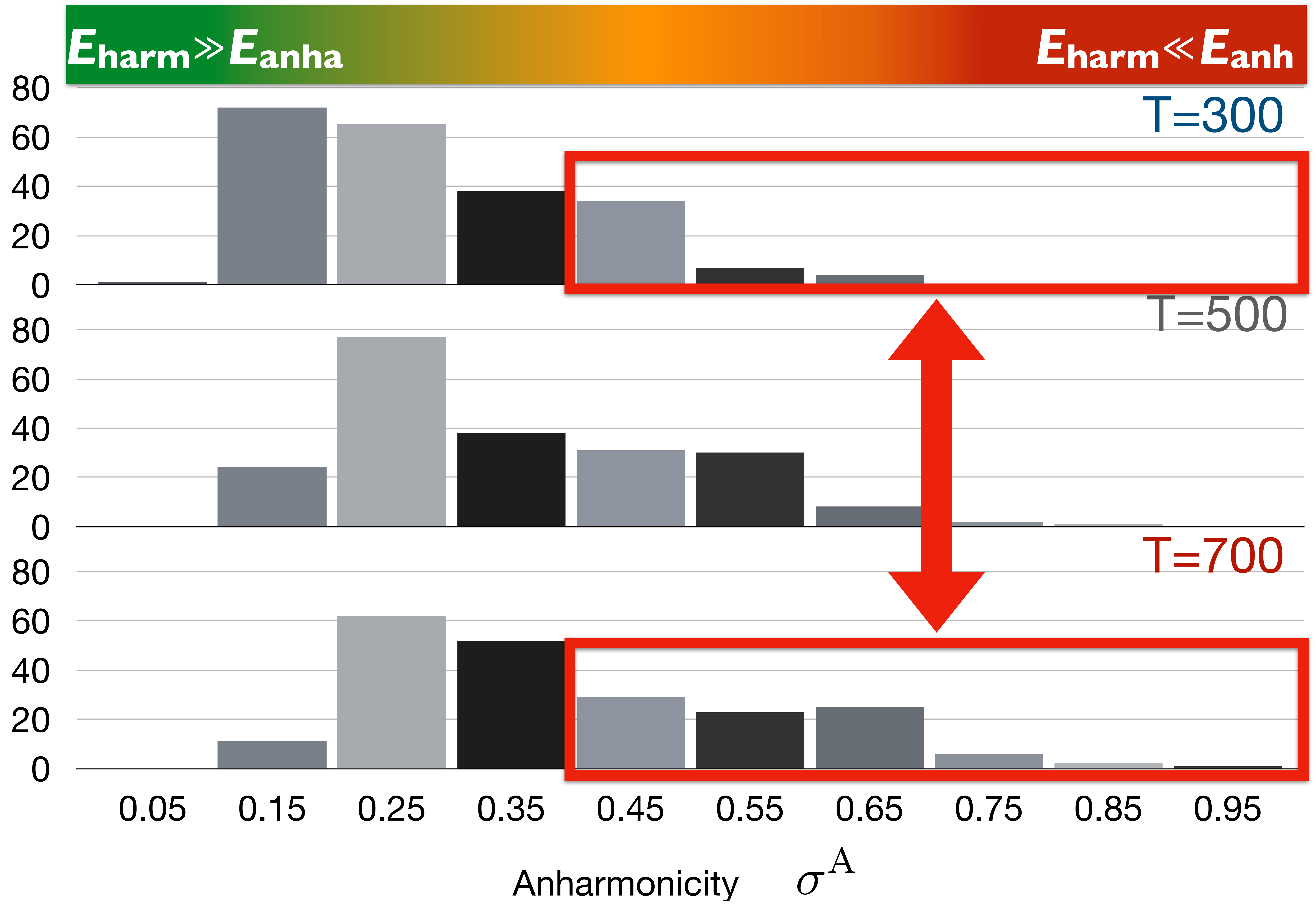
At 700K, only <35% of the materials are **almost perfectly harmonic.**

200+ Material Test Set:

- 97 Rock salt
- 67 Zincblende
- 45 Wurtzite
- 10 Perovskites

Anharmonicity Quantification across Material Space

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



At **700K**, already **>40%** of the materials exhibit **strong anharmonic effects.**

200+ Material Test Set:

- 97 Rock salt
- 67 Zincblende
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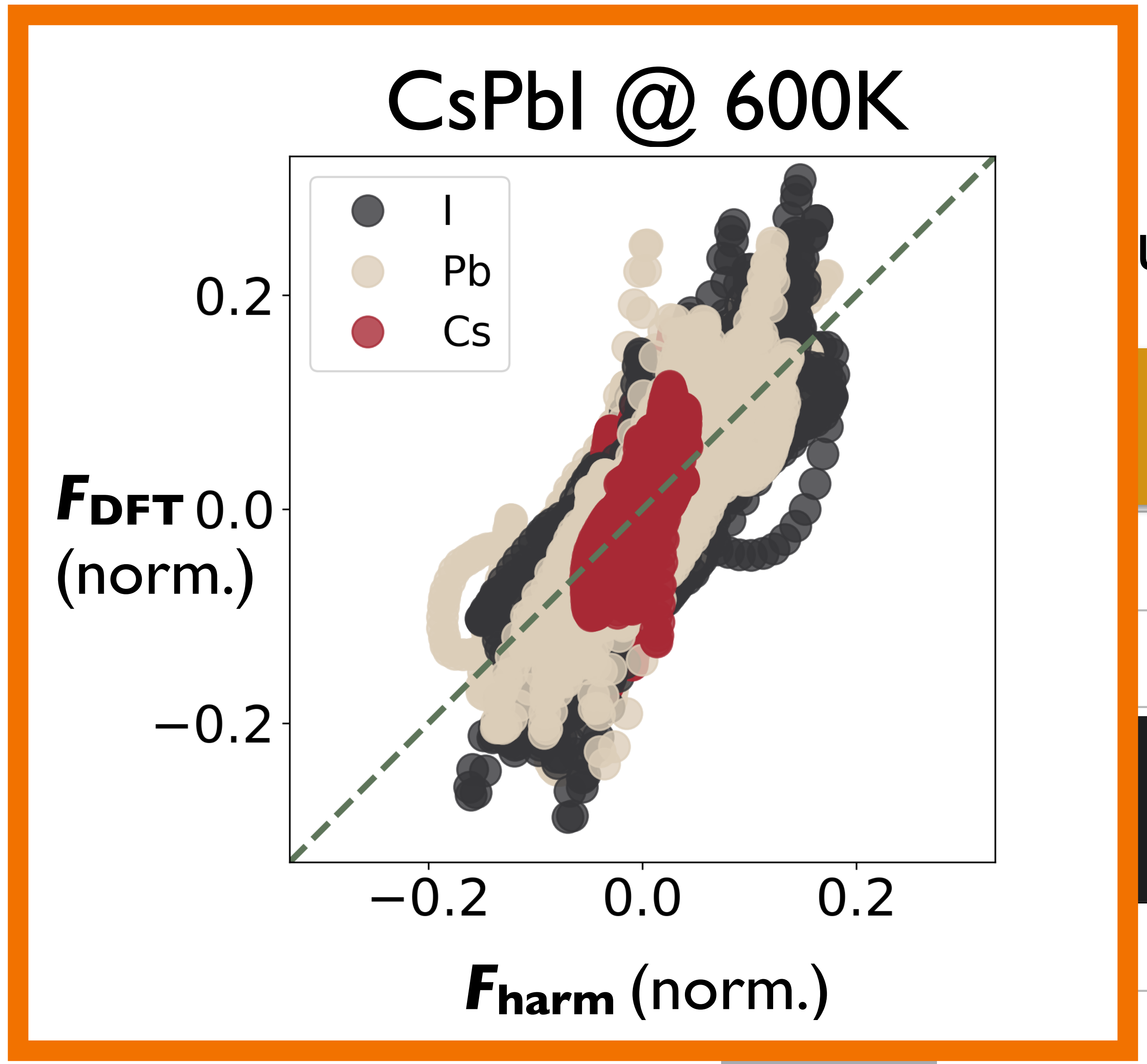
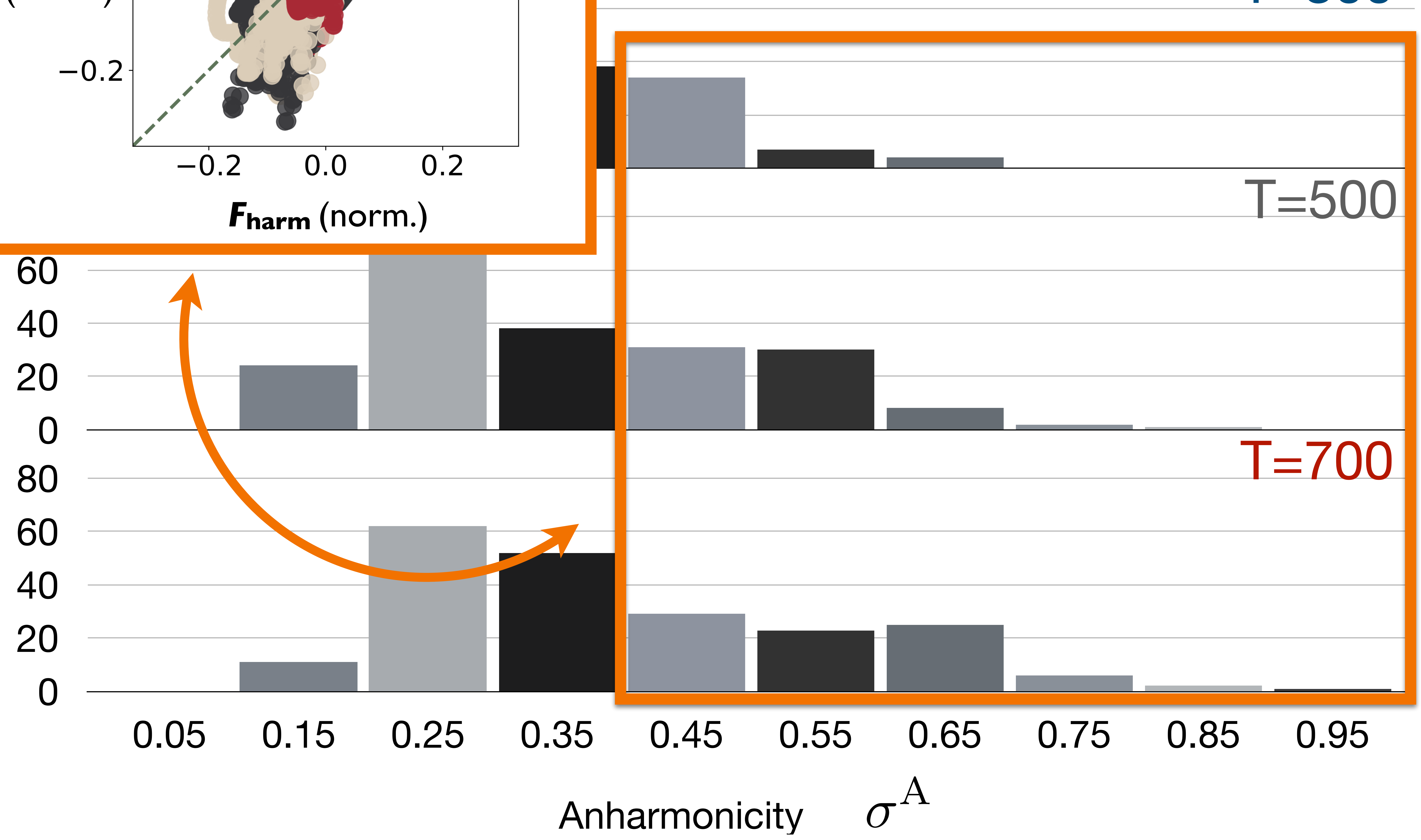
Quantification across Material Space

urcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).

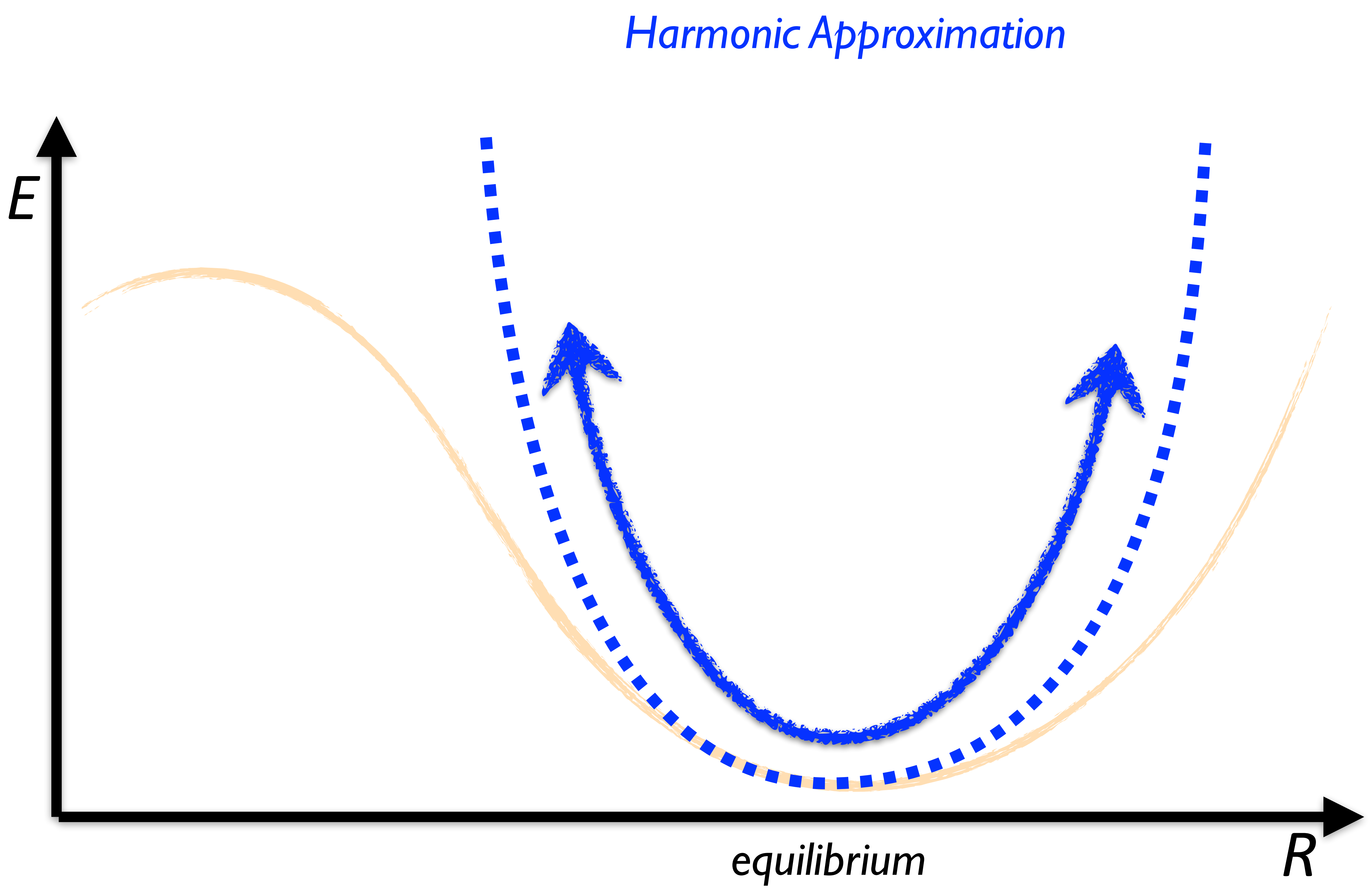




At **all** temperatures, **complex materials** exhibit **stronger anharmonic effects.**

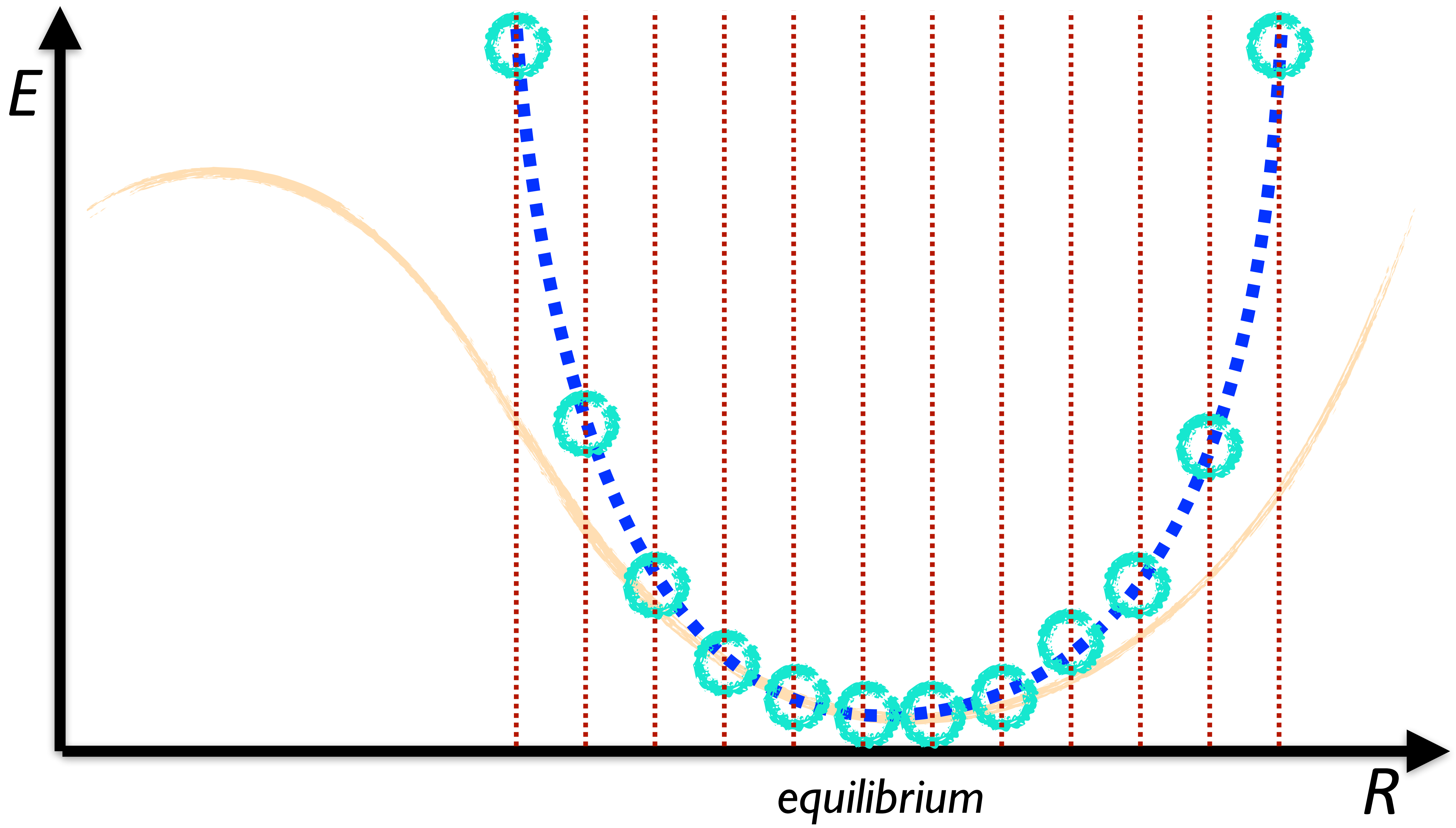
200+ Material Test Set:
- 97 Rock salt
- 67 Zincblende
- 45 Wurtzite
- 10 Perovskites

Exercise 3: *Estimate Anharmonicity*



1) Approximately sample the *real* dynamics using the harmonic approximation.

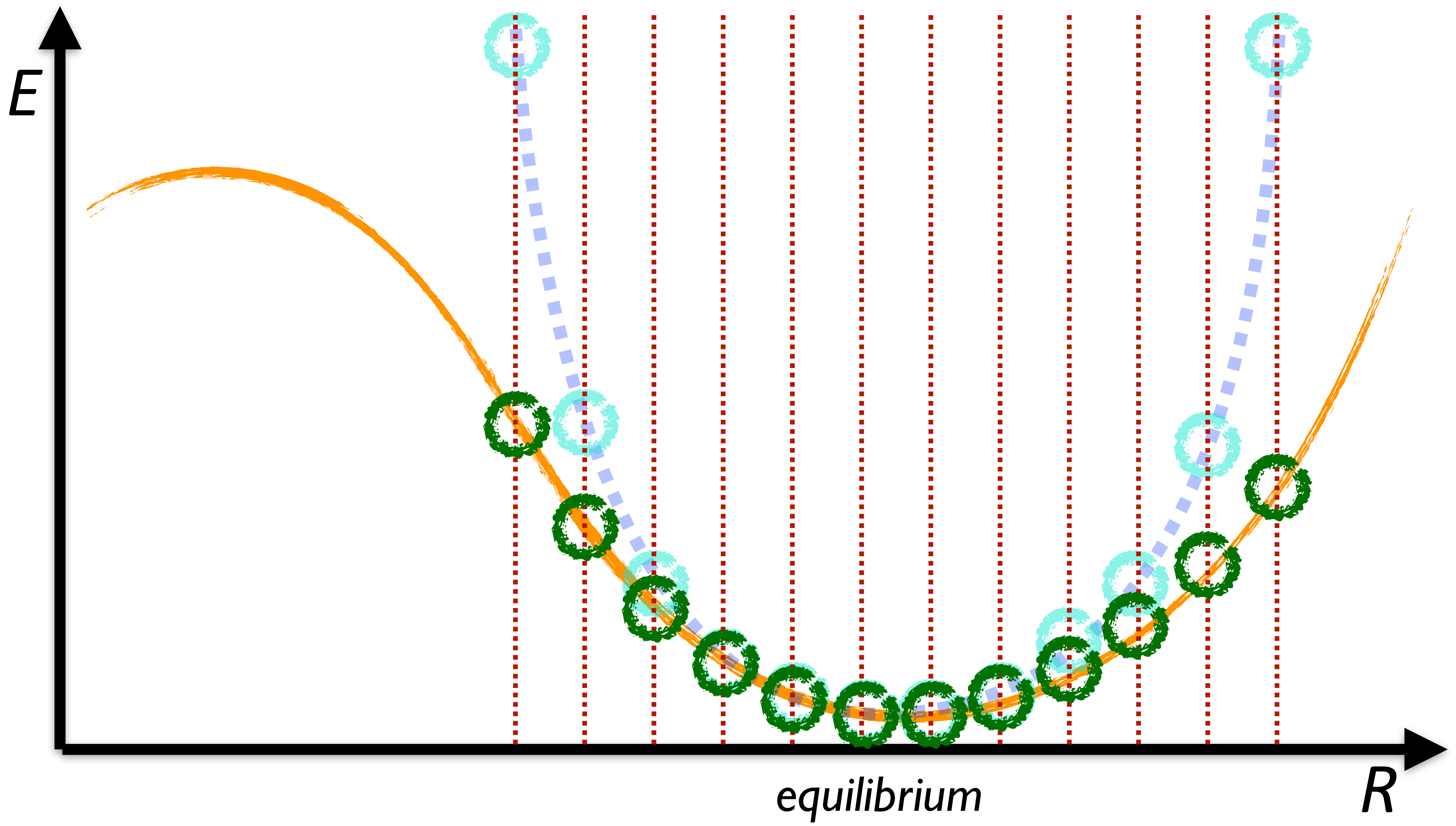
Exercise 3: *Estimate Anharmonicity*



1) Approximately sample the *real* dynamics using the harmonic approximation.

2) Store the potential energies $E^{harm}(t)$ observed along $\boldsymbol{R}_I^{harm}(t)$.

Exercise 3: *Estimate Anharmonicity*

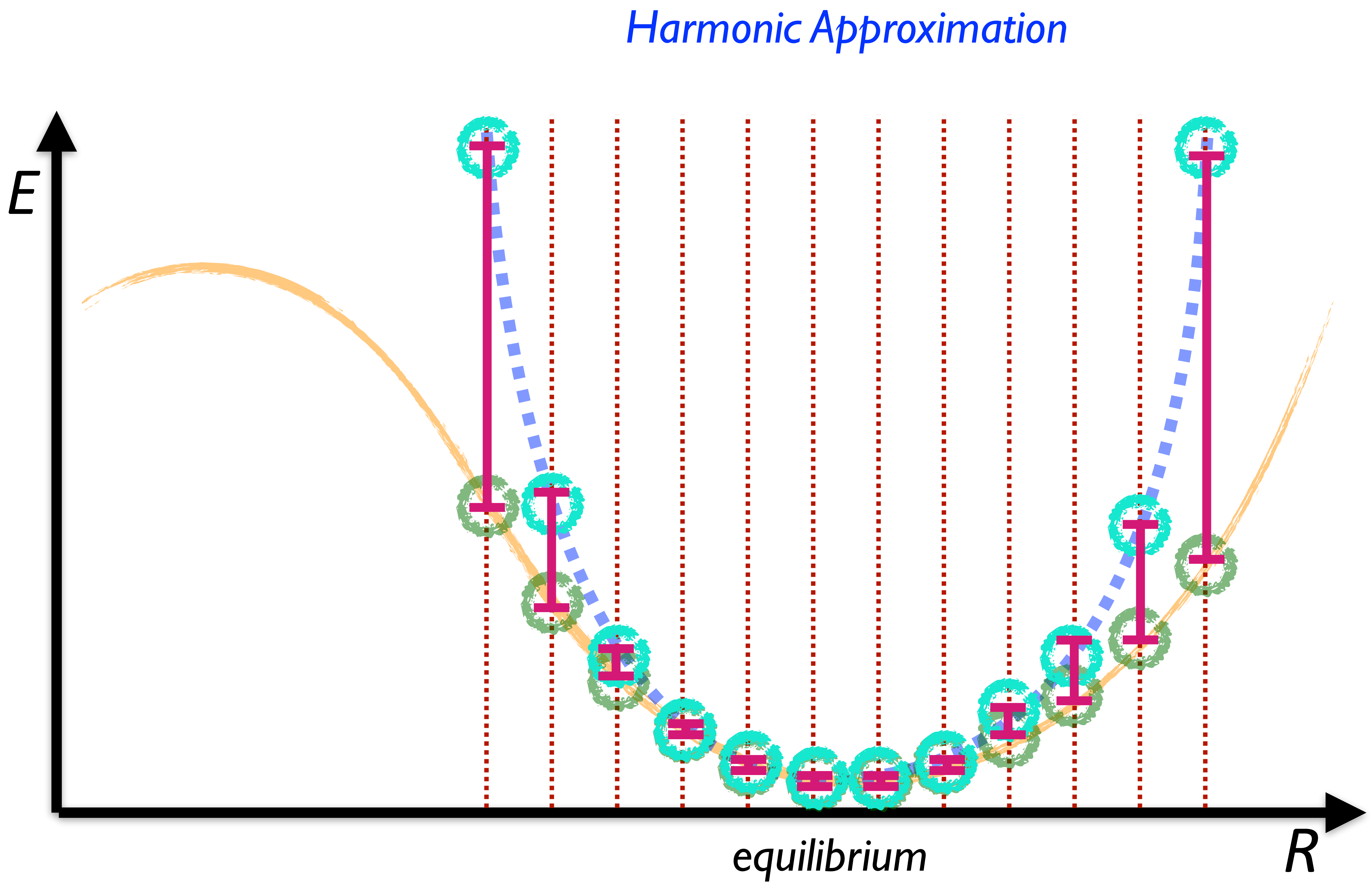


1) Approximately sample the *real* dynamics using the harmonic approximation.

2) Store the potential energies $E^{harm}(t)$ observed along $\boldsymbol{R}_I^{\mathrm{harm}}(t)$.

3) Compute the potential energies $E^{\mathrm{DFT}}(t)$ for these samples.

Exercise 3: *Estimate Anharmonicity*



1) Approximately sample the *real* dynamics using the harmonic approximation.

2) Store the potential energies $E^{harm}(t)$ observed along $\mathbf{R}_I^{harm}(t)$.

3) Compute the potential energies $E^{DFT}(t)$ for these samples.

4) The difference $E^{harm}(t)$ - $E^{DFT}(t)$ quantifies the strength of anharmonic effects.

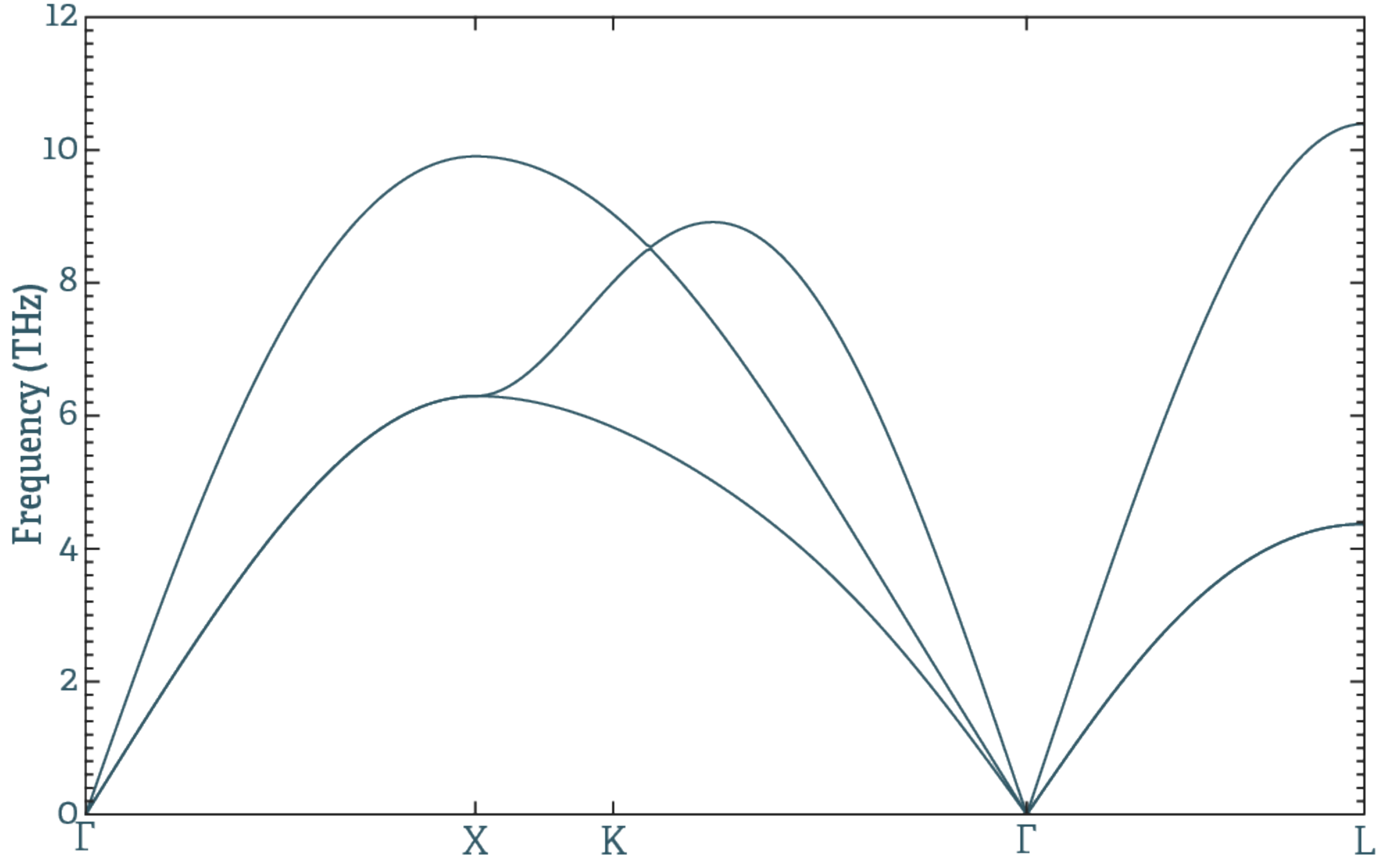
What is the Effect of Anharmonicity?

https://ollehellman.github.io/page/workflows/minimal_example_1.html

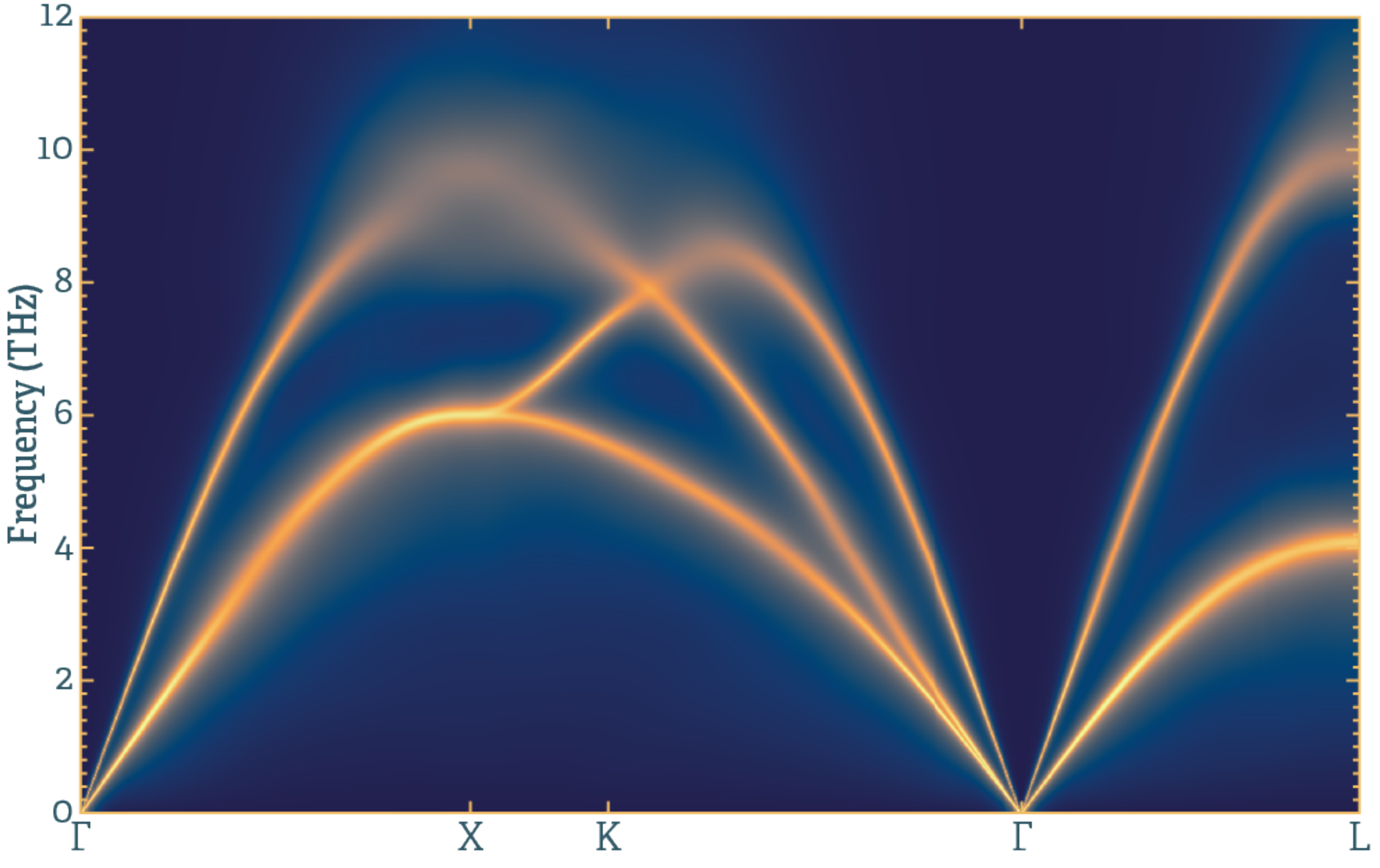
$$E^{\mathrm{harm}} = \frac{1}{2}\sum_{I,J}\sum_{abc,lmn}\Phi_{Iabc,Jlmn}\Delta\mathbf{R}_{Iabc}\Delta\mathbf{R}_{Jlmn}$$

$$E^{\mathrm{anh}} = \frac{1}{2}\sum_{I,J}\sum_{abc,lmn}\Phi_{Iabc,Jlmn}\Delta\mathbf{R}_{Iabc}\Delta\mathbf{R}_{Jlmn} + \frac{1}{6}\sum_{I,J,K}\sum_{\substack{abc,\\lmn,\\xyz}}\Psi_{Iabc,Jlmn,Kxyz}\Delta\mathbf{R}_{Iabc}\Delta\mathbf{R}_{Jlmn}\Delta\mathbf{R}_{Kxyz}$$

Harmonic fcc Al at 0K



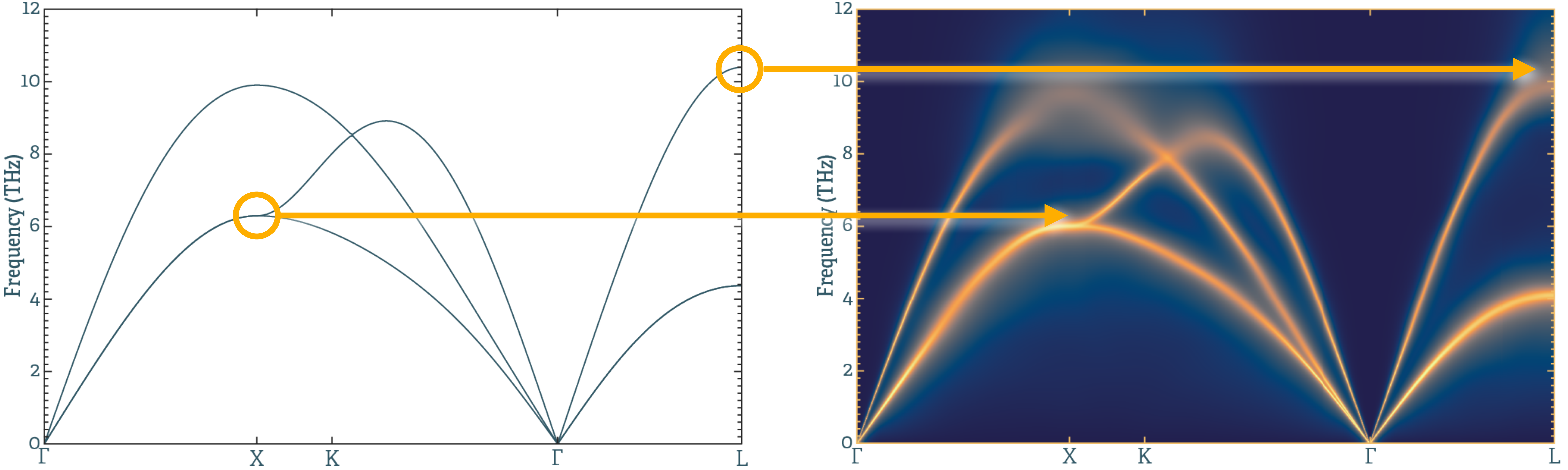
Anharmonic fcc Al at 800K



What is the Effect of Anharmonicity?

https://ollehellman.github.io/page/workflows/minimal_example_1.html

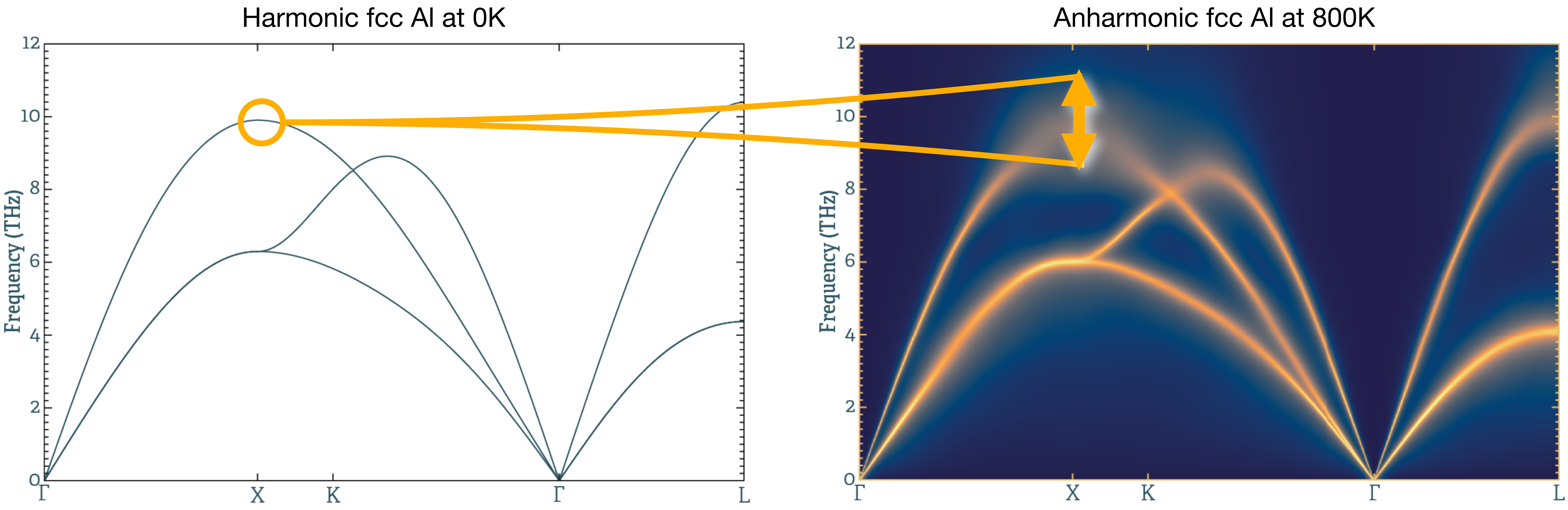
Harmonic fcc Al at 0K   Anharmonic fcc Al at 800K



⇒ **Anharmonicity** can **alter** the phonon frequencies!

What is the Effect of Anharmonicity?

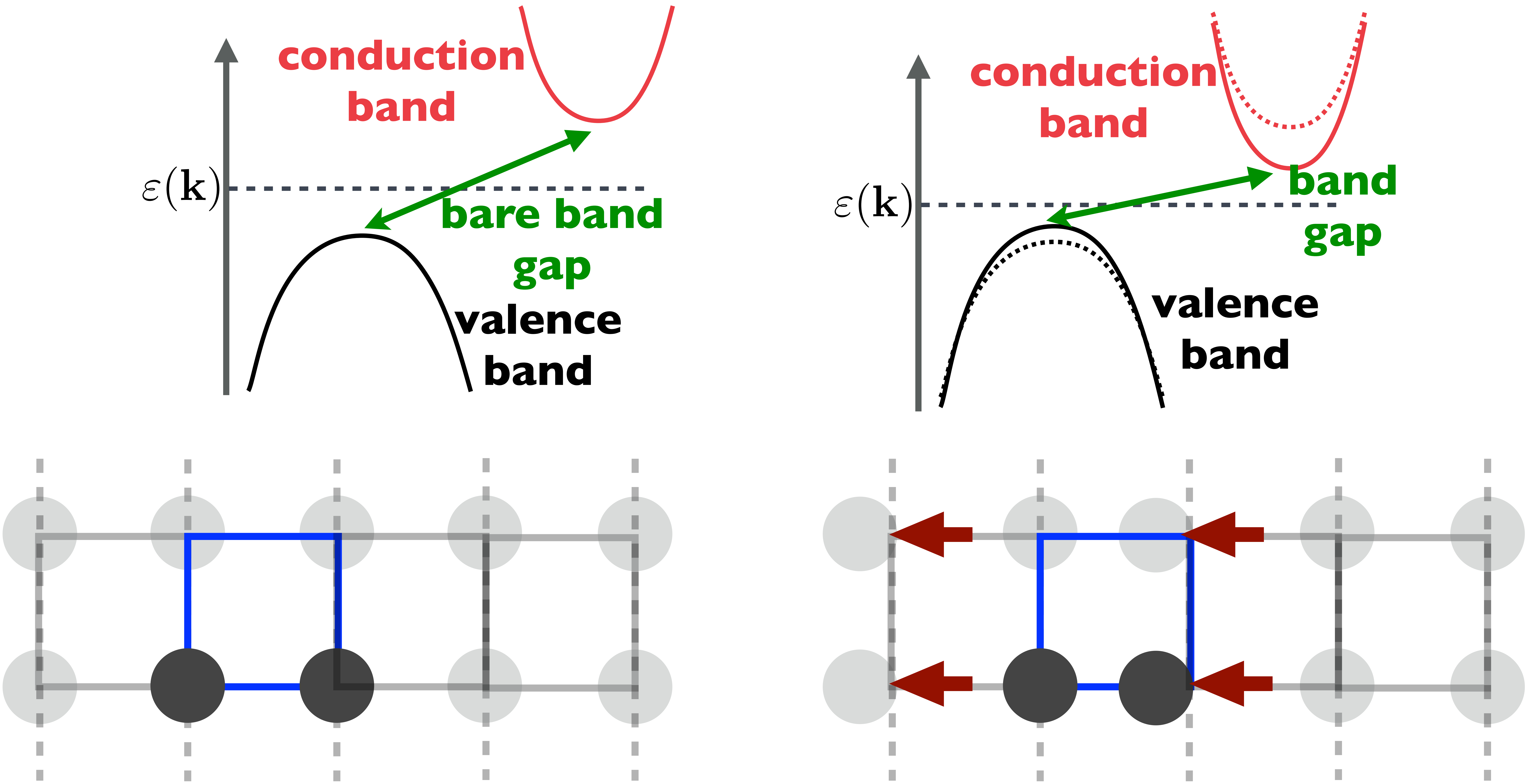
https://ollehellman.github.io/page/workflows/minimal_example_1.html



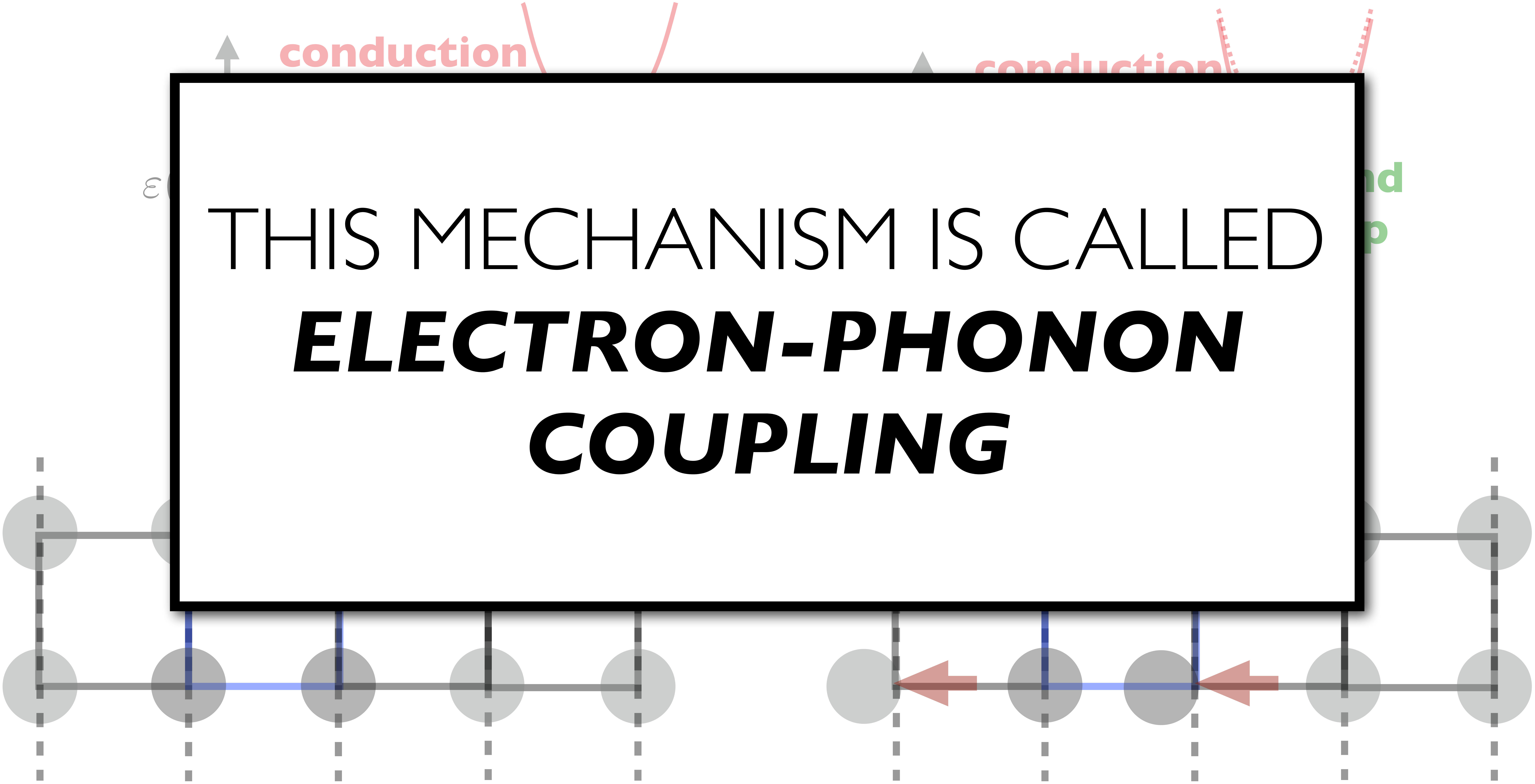
⇒ **Anharmonicity** can **alter** the phonon frequencies!

⇒ **Anharmonicity** introduces **finite** line-widths!

Exercise 4: What about Electrons?



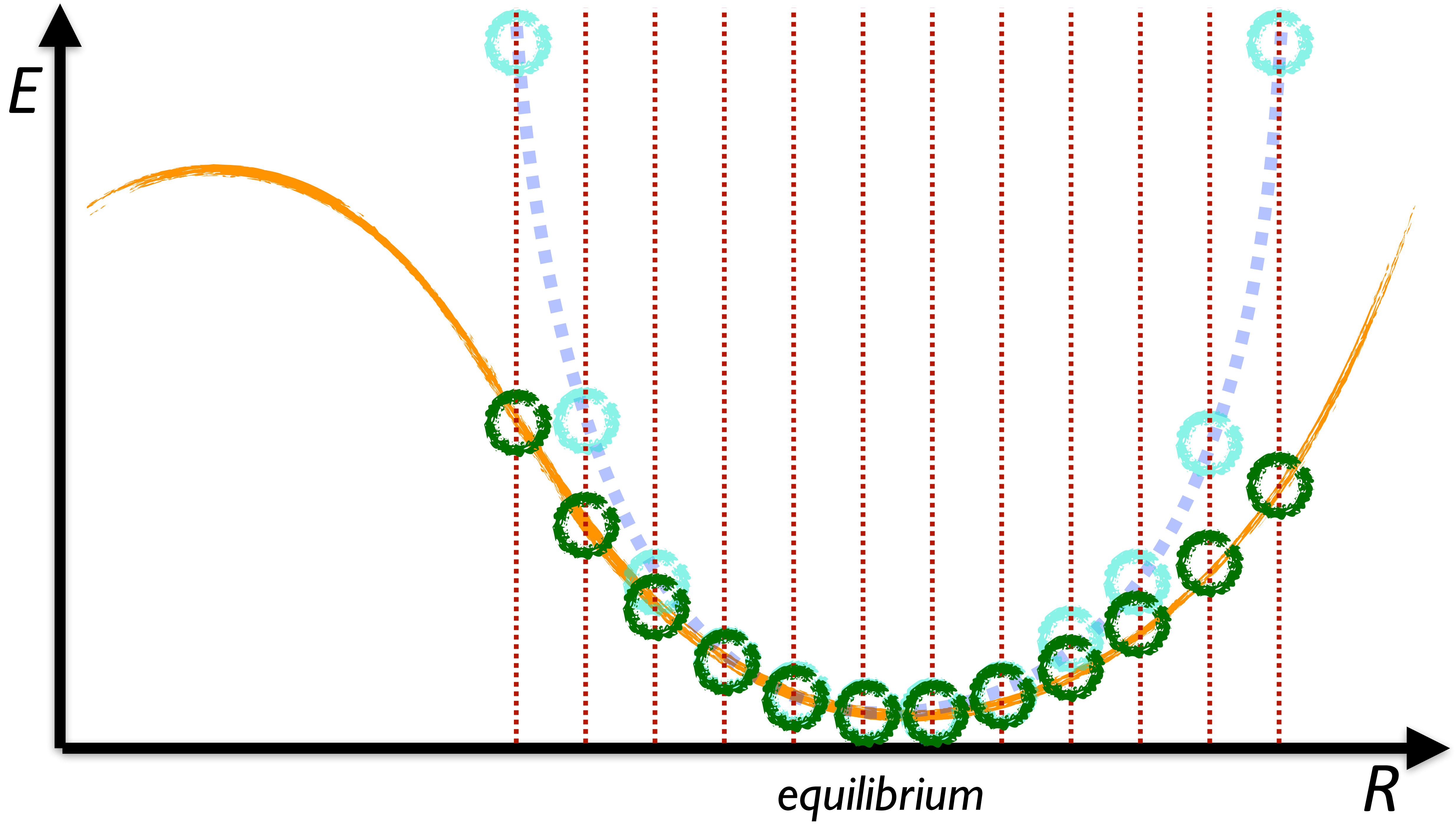
Exercise 4: What about Electrons?



THIS MECHANISM IS CALLED

ELECTRON-PHONON COUPLING

Exercise 4: What about Electrons?



1) Approximately sample the *real* dynamics using the harmonic approximation.

2) Store the potential energies $E^{harm}(t)$ observed along $\boldsymbol{R}_I^{harm}(t)$.

3) Compute the potential energies $E^{DFT}(t)$ and band gaps for these samples.

4) Calculate the average band gap!

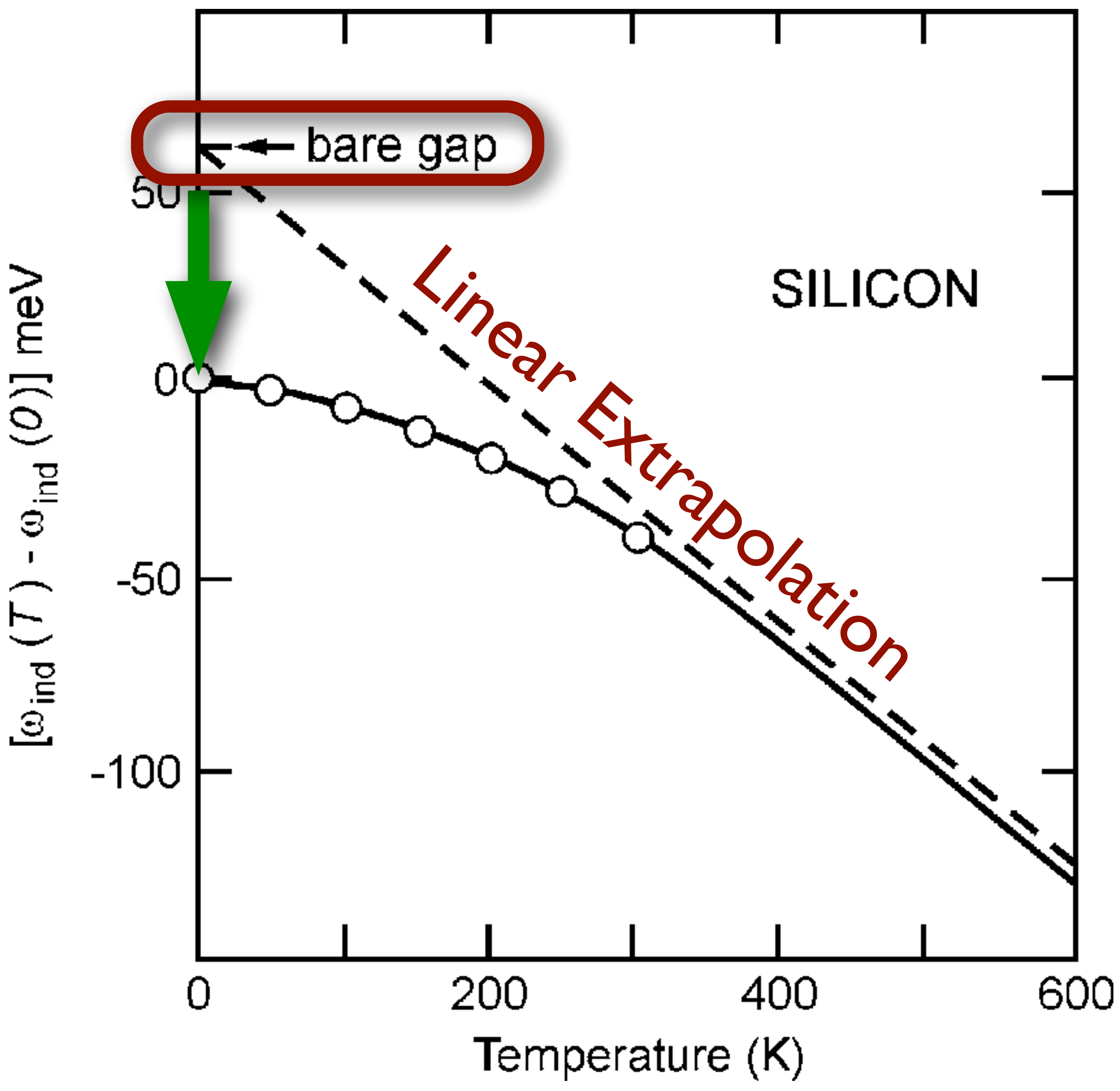
BAND GAP RENORMALIZATION

Electronic band gaps often exhibit a distinct **temperature dependence**

Linear extrapolation yields the **bare gap at 0K**, i.e., the gap for immobile nuclei **(classical limit)**

Actual band gap at 0K differs from the **bare gap**:
⇒ **Band gap renormalization**

due to 0K phonon motion



M. Cardona,
Solid State Comm. **133**, 3 (2005).

Attention:
Quantum-Nuclear Effects

Classical Limit: Equipartition Theorem

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

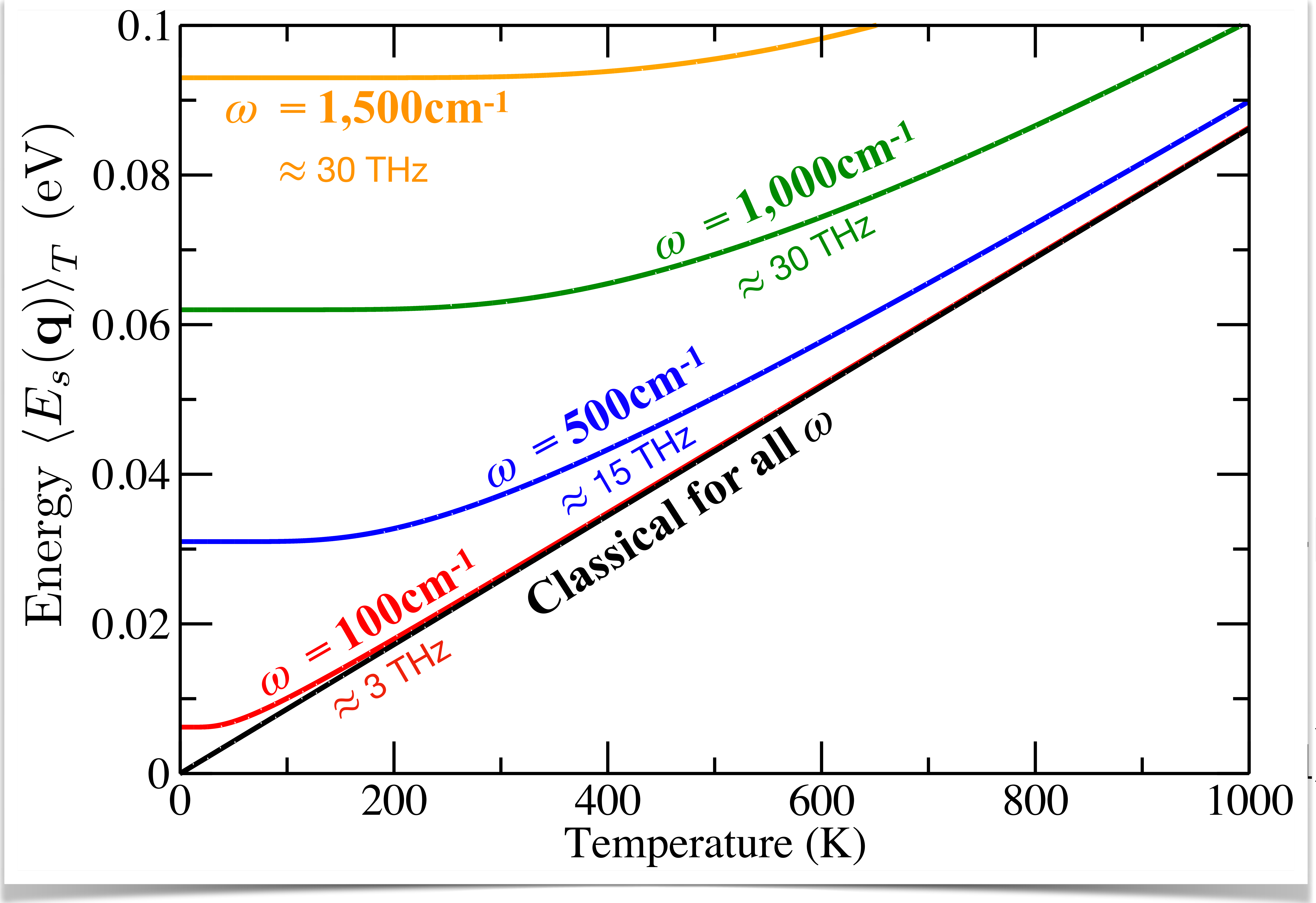
Quantum-mechanical Solution: Bose-Einstein

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:

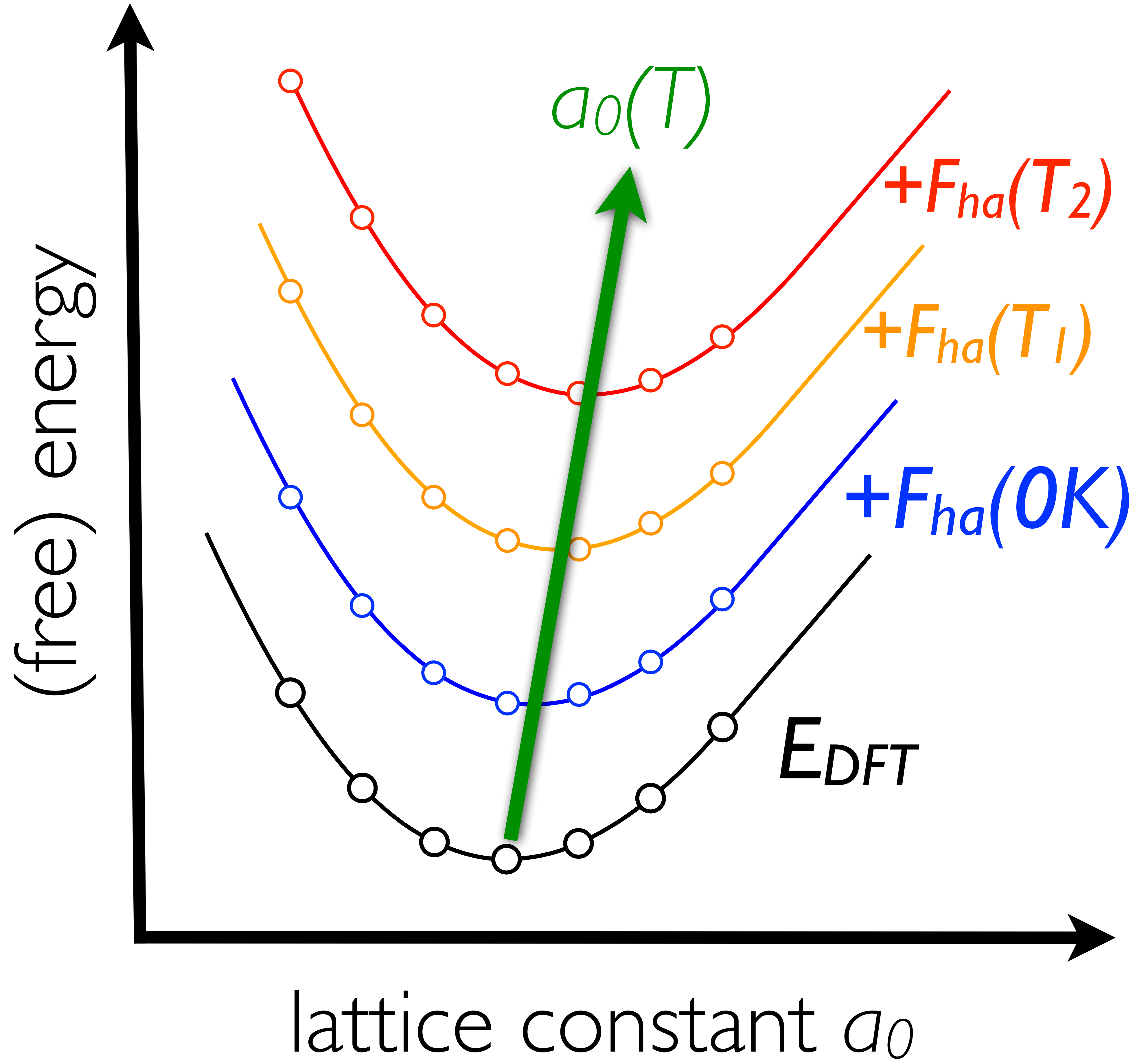
Quantum-Nuclear Effects



Einstein

$$),T)) + \frac{1}{2}\Big)$$

Exercise 5: Quasi-Harmonic Approach



Lattice constant a_0 can be determined from *Birch-Murnaghan* fit of $E(a_0)$

Add **vibrational free energy** for each individual value of a_0

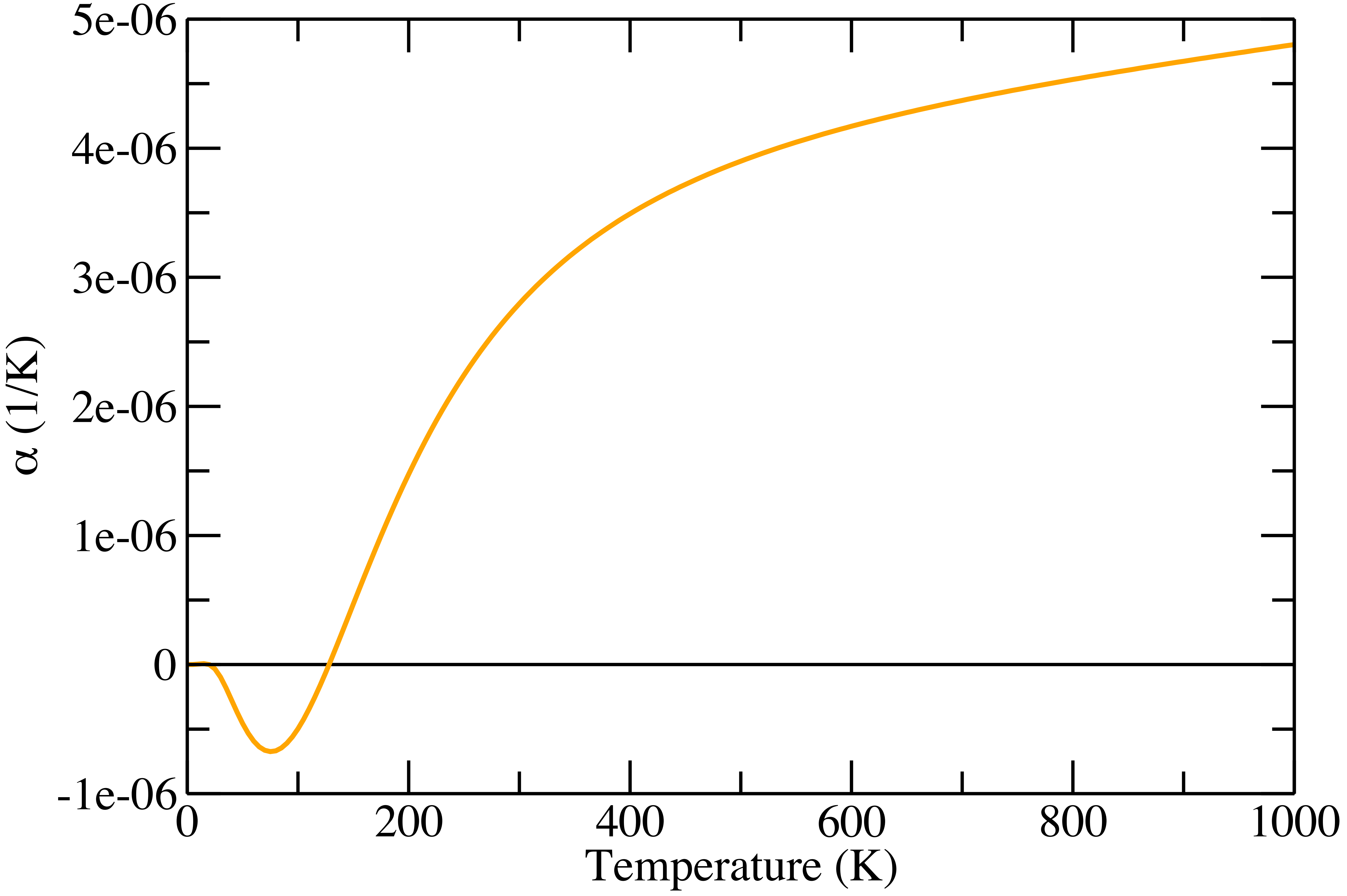
Repeat for **each** temperature
0K < T_1 < T_2

Birch-Murnaghan fits for **each individual temperature** allow to determine **temperature dependence of lattice constant** $a_0(T)$.

LATTICE EXPANSION

S. Biernacki and M. Scheffler, *Phys. Rev. Lett.* **63**, 290 (1989).

$$\alpha(T) = \frac{1}{a}\left(\frac{\partial a}{\partial T}\right)_p$$



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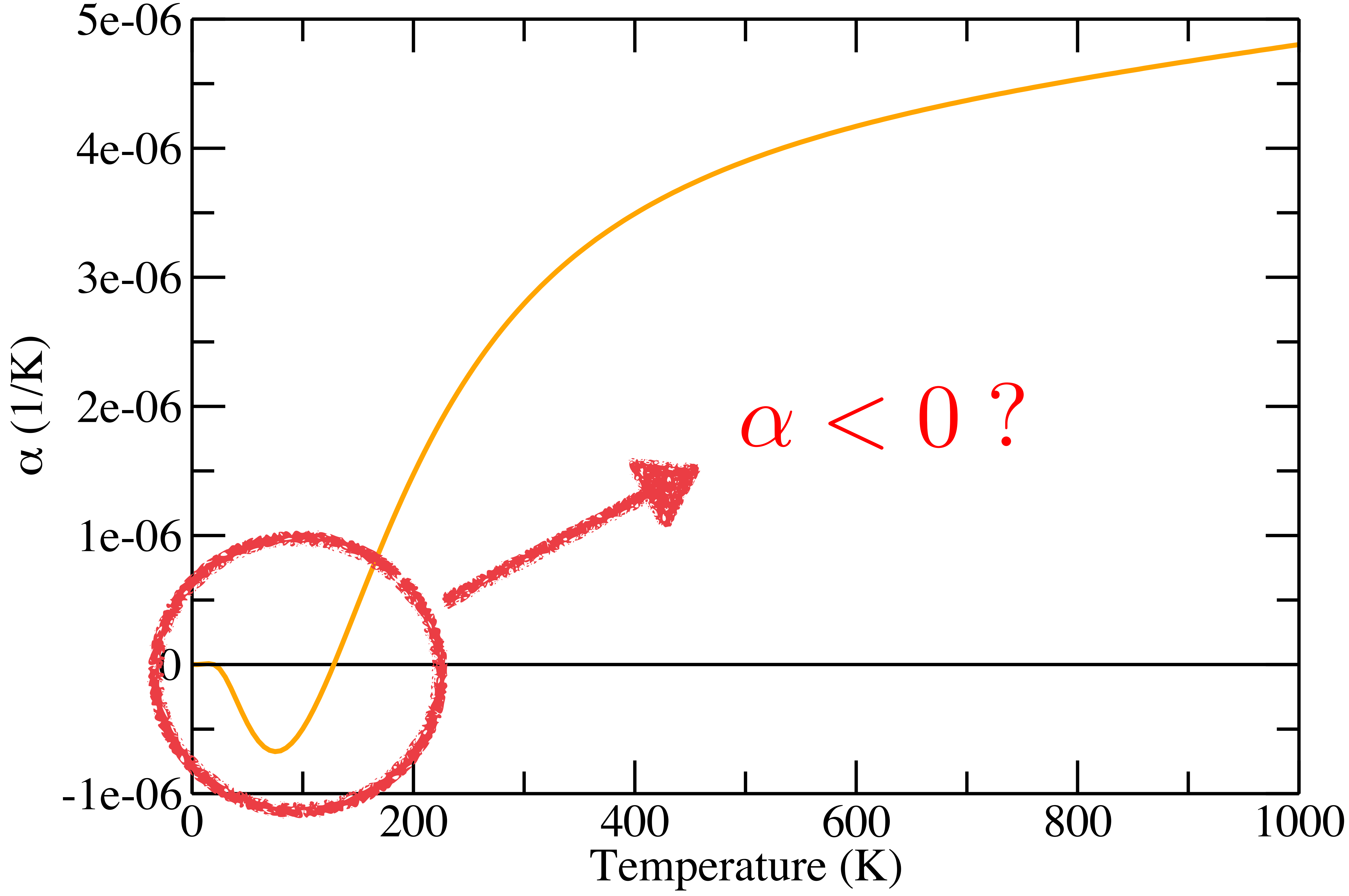

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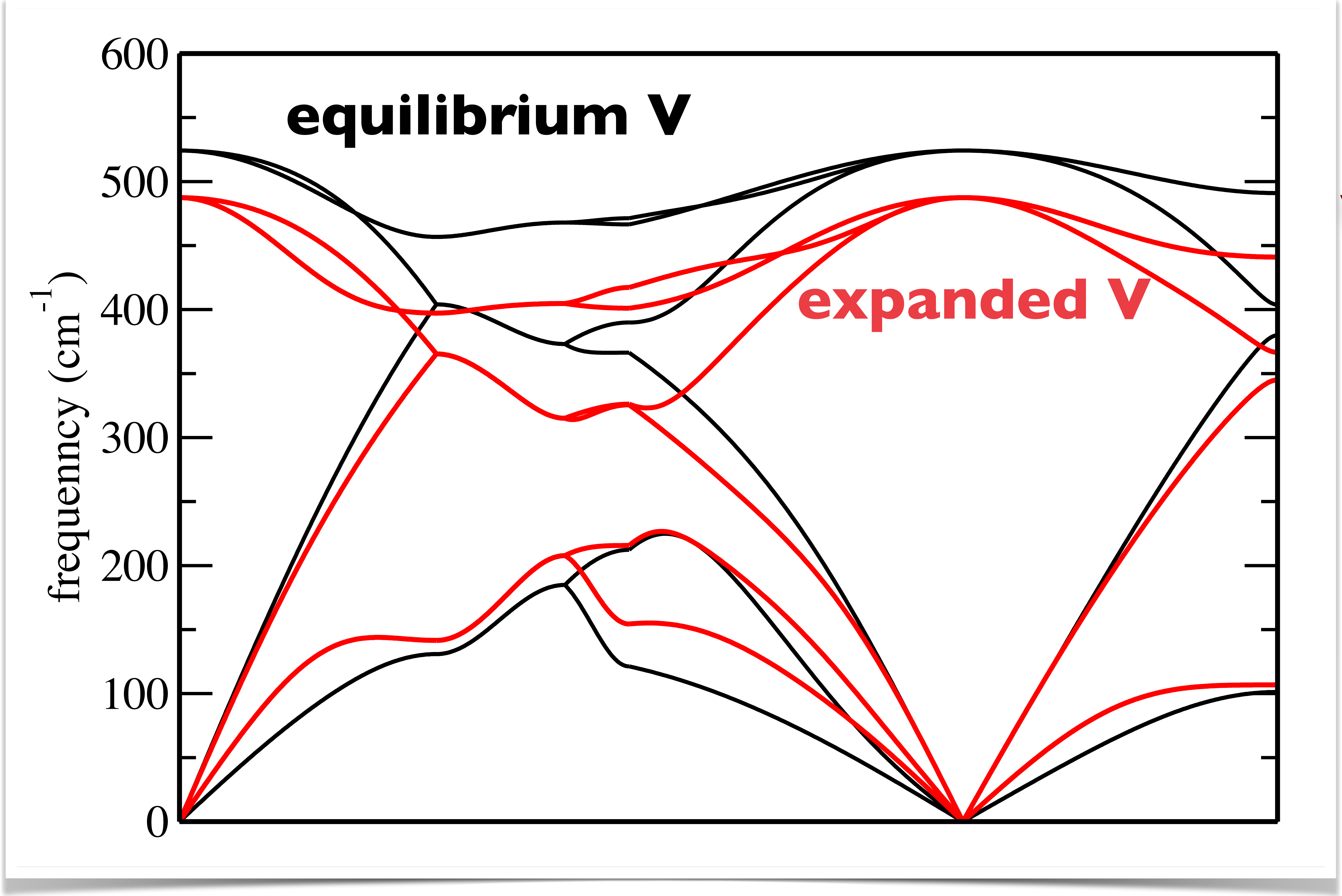
Free energy definition: $F^{ha}(T \to 0) \quad \propto \quad \int d\omega \; g(\omega) \frac{\hbar\omega}{2}$



Frequencies **lowered** at **larger** volumes!

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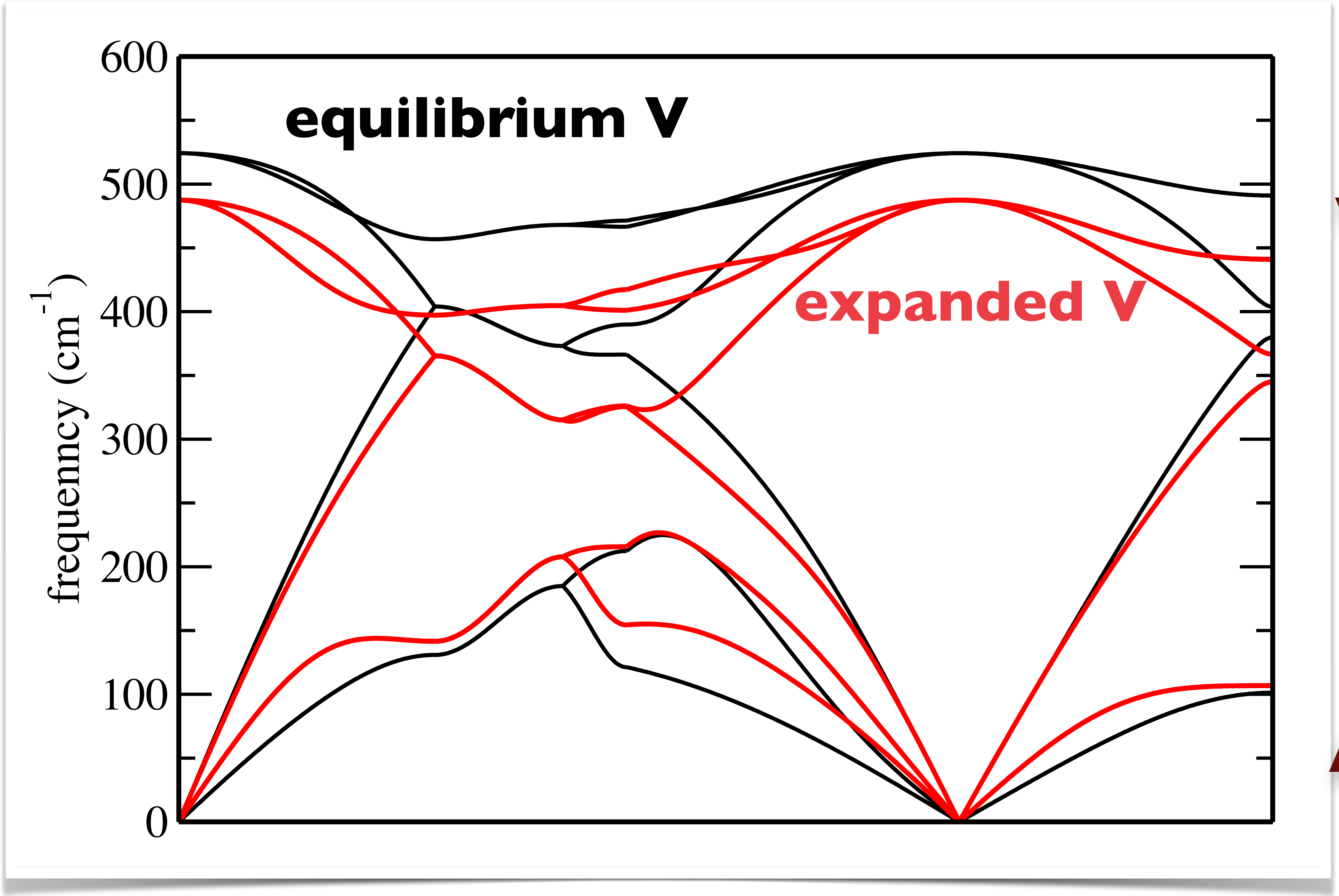

Frequencies **lowered** at **larger** volumes!

Acoustic frequencies **increased** at **larger** volumes!

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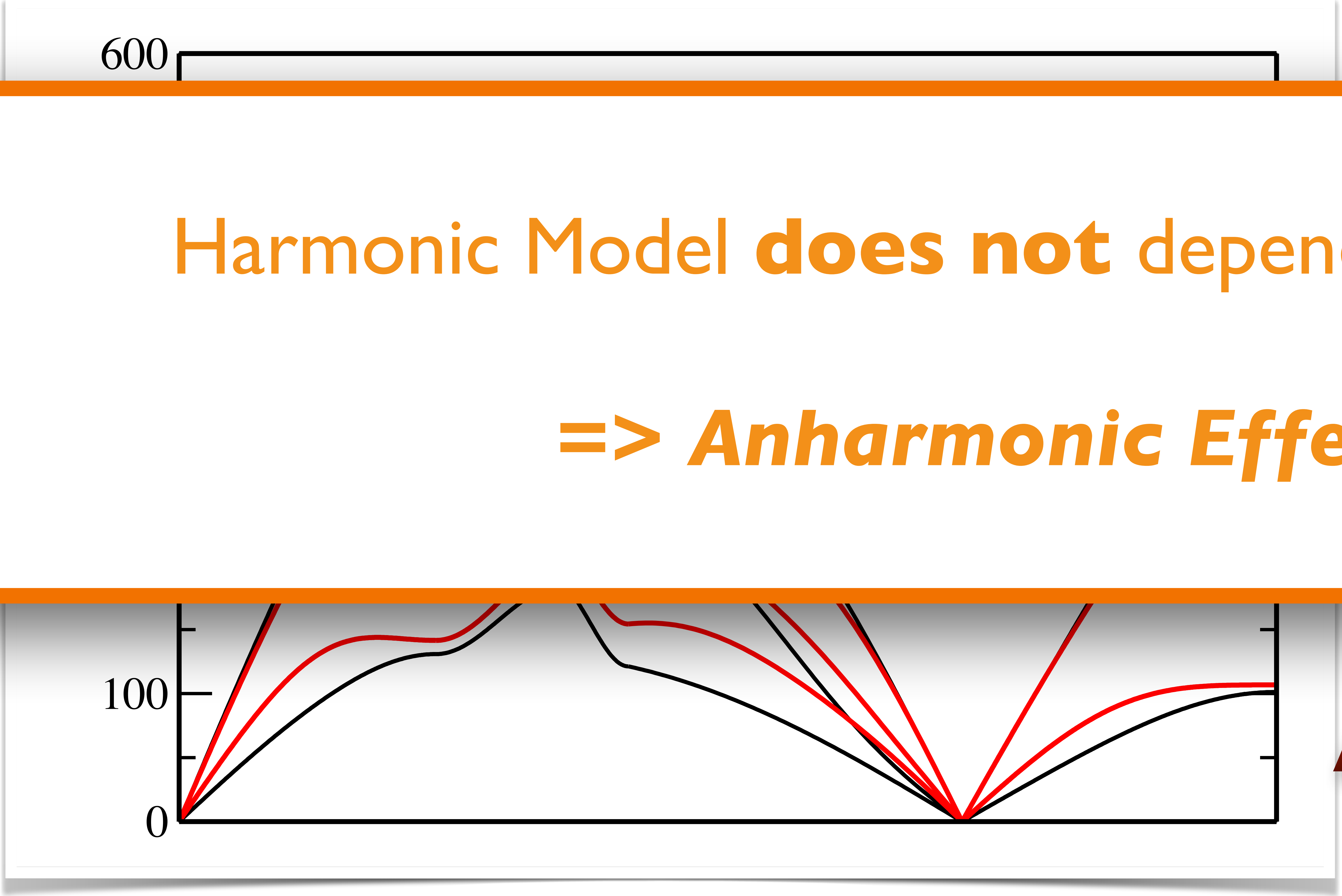

Harmonic Model **does not** depend on **volume:**

=> Anharmonic Effect!

red
s!

Acoustic frequencies **increased** at **larger** volumes!

Karsten Reuter

Christoph Dähn

Matteo Rinaldi

Elena Gelžinytė

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