Hands-On Tutorial Workshop, July 29th 2014

Tutorial 6:
Phonons, Lattice Expansion, and Band-gap Renormalization

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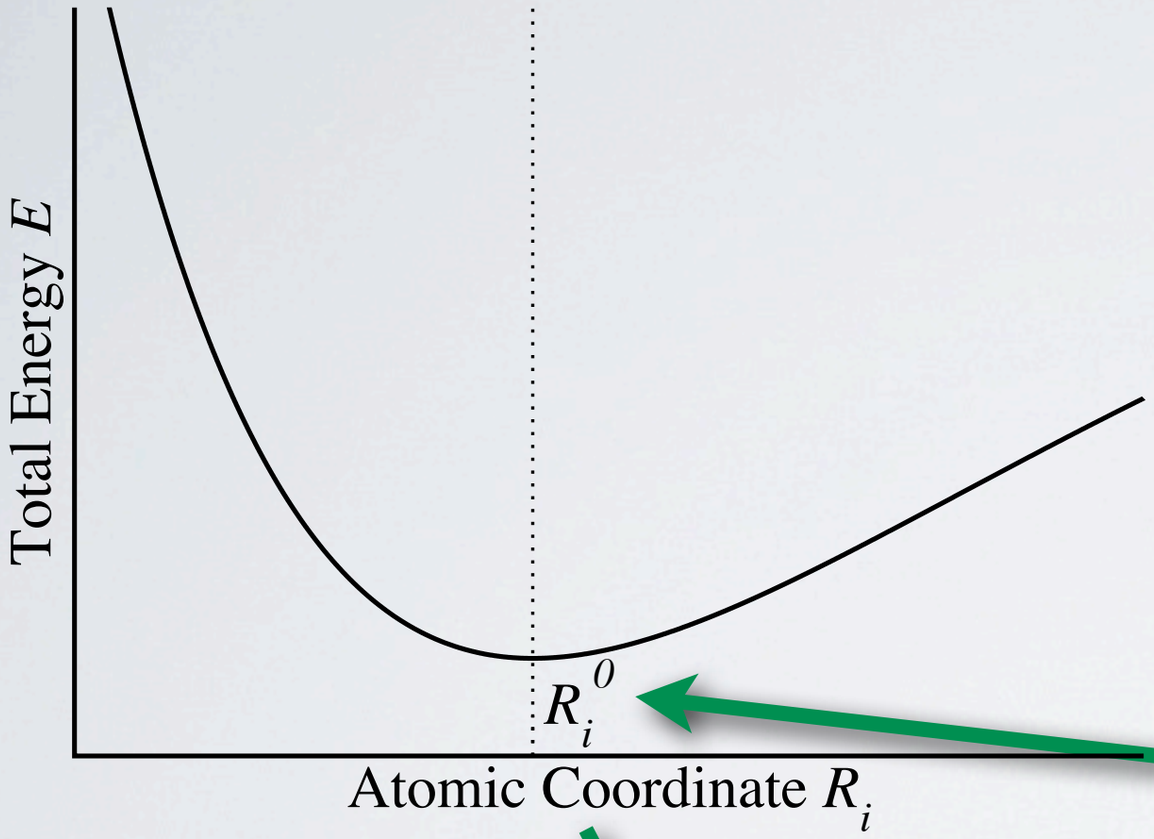
Institut für Physik, Universität Rostock

I. THE HARMONIC CRYSTAL

THE HARMONIC APPROXIMATION



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

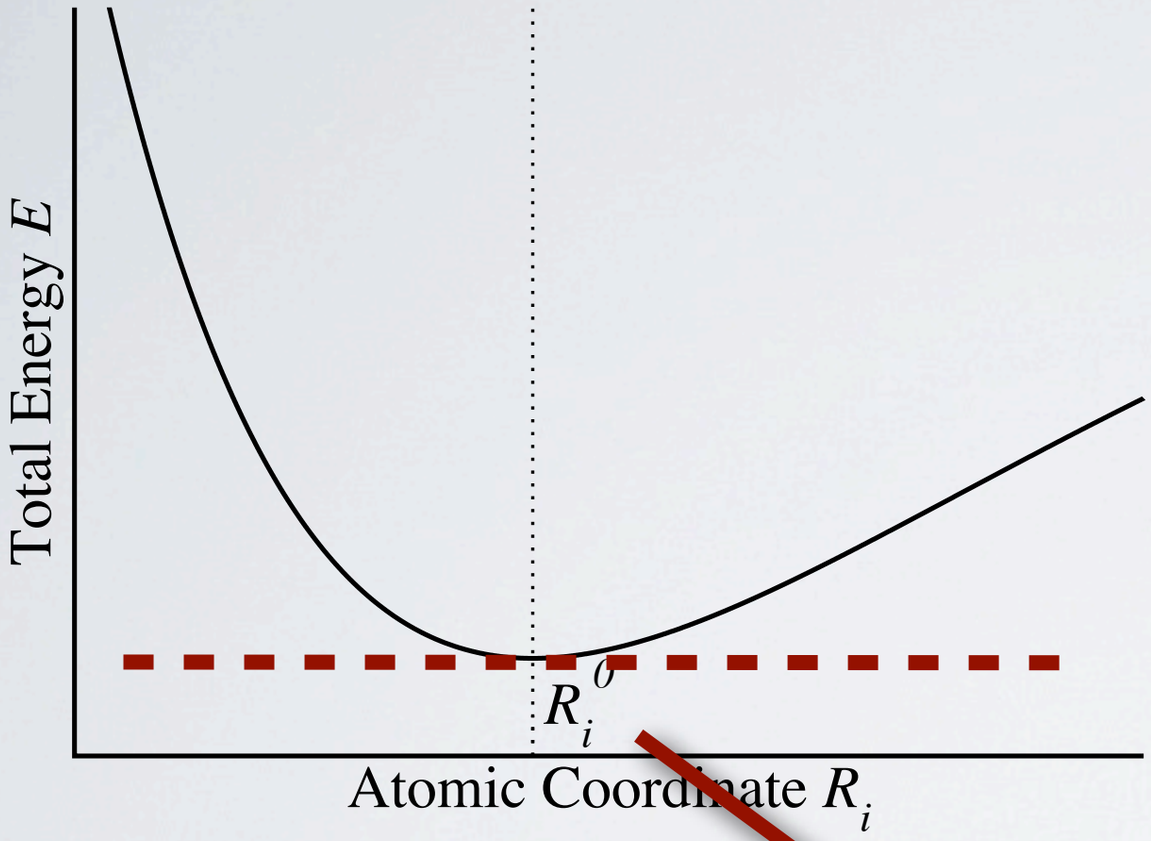
$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

Approximate by Taylor Expansion around the Static Equilibrium R_i^0

$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \cdots$$

Static Equilibrium Energy

THE HARMONIC APPROXIMATION



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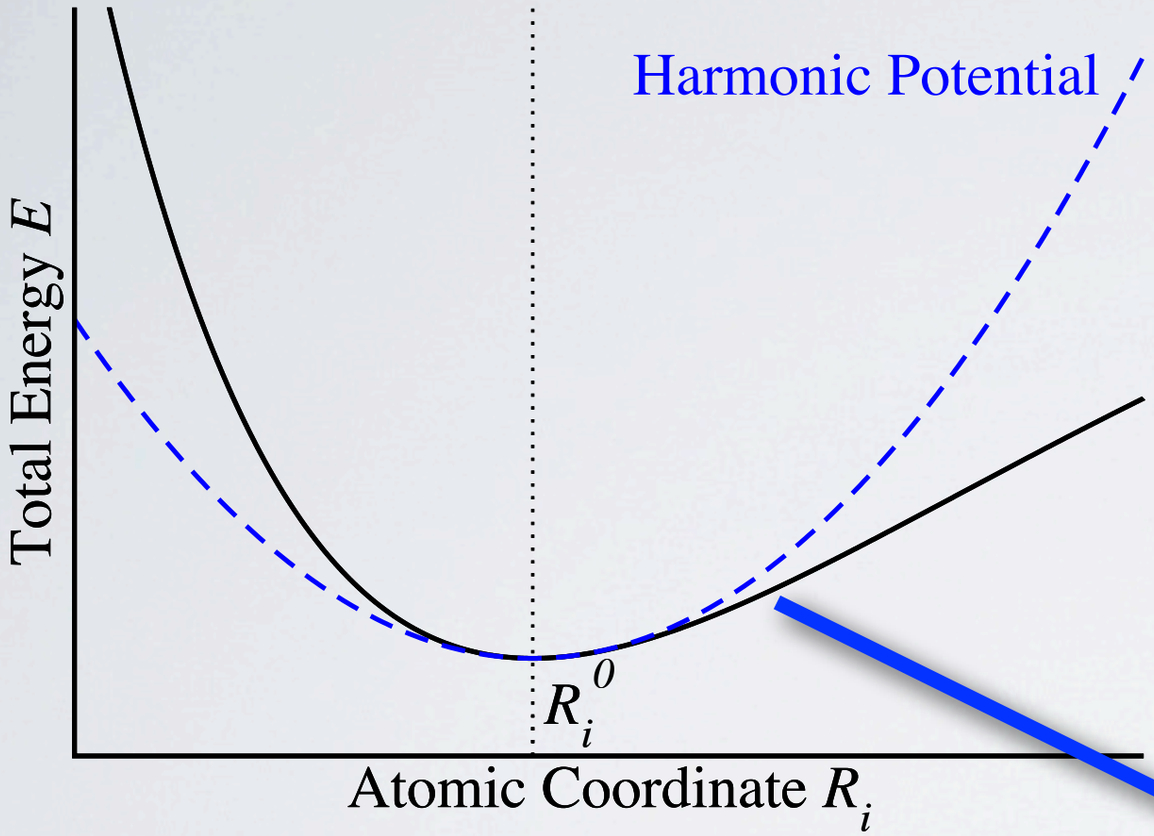
Approximate by Taylor Expansion around the Static Equilibrium R_i^0

$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \sum_i \frac{\partial E}{\partial \mathbf{R}_i}\bigg|_{\mathbf{R}_0} \Delta\mathbf{R}_i + \cdots$$

Forces vanish at $\mathbf{R_0}$

THE HARMONIC APPROXIMATION



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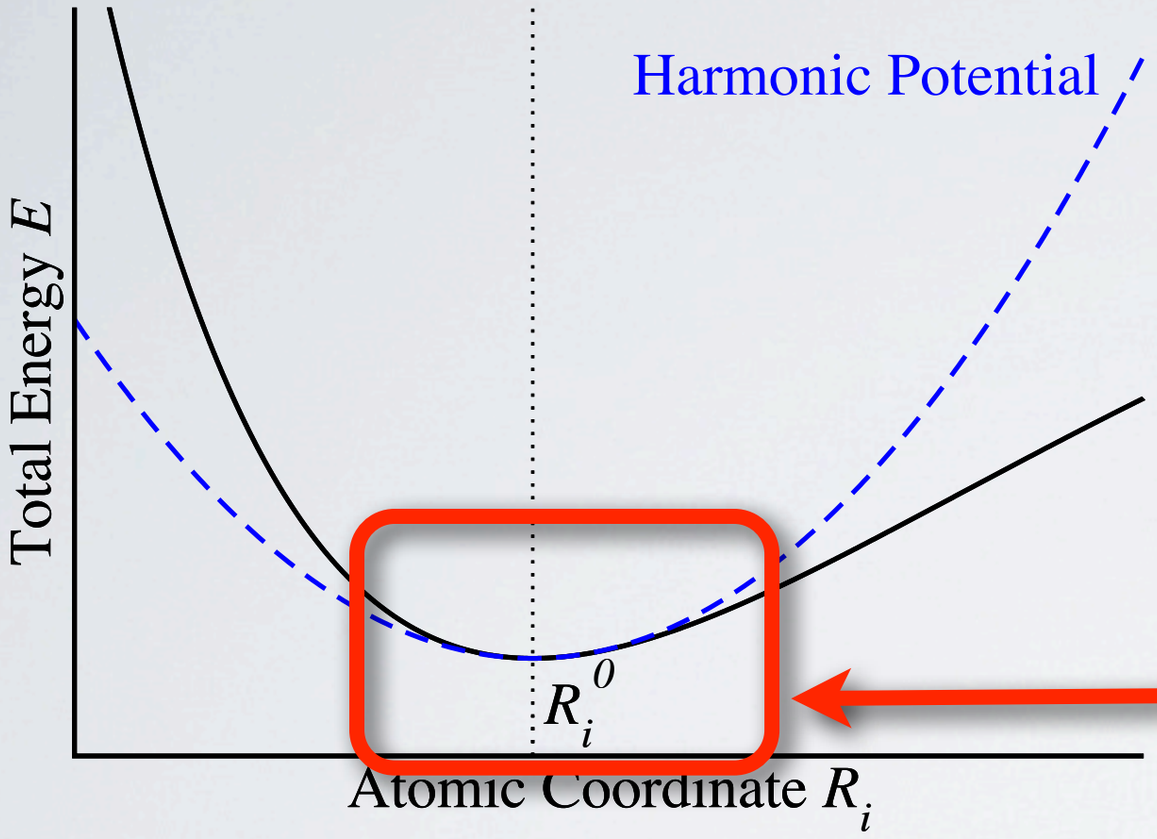
Hessian Φ_{ij}

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 from $\boldsymbol{R^0}$!

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

THE HARMONIC APPROXIMATION

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Static Equilibrium Energy from DFT

Hessian Φ_{ij}

Determine **Hessian** aka the **Harmonic Force Constants** Φ_{ij}:

- from **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).

- from **Finite Differences**
  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).

THE HARMONIC APPROXIMATION

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

Static Equilibrium Energy from DFT

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Determine **Hessian** aka the **Harmonic Force Constants** Φ_{ij}:

`phonopy-FHI-aims`

A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* **78**, 134106 (2008).

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  K. Kunc, and R. M. Martin, *Phys. Rev. Lett.* **48**, 406 (1982) &
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THE FINITE DIFFERENCE APPROACH

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Finite differences using **normalized displacements *d*:**

$$\Phi_{ij} = \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}^0} = -\left.\frac{\partial}{\partial \mathbf{R}_i}\mathbf{F}_j\right|_{\mathbf{R}^0} \approx -\frac{\mathbf{F}_j(\mathbf{R}_i^0 + \varepsilon\,\mathbf{d}_i)}{\varepsilon}$$

Example: Diamond Si (2 atoms in the basis):

$$\begin{pmatrix}
\Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & \Phi_{12}^{xx} & \Phi_{12}^{xy} & \Phi_{12}^{xz} \\
\Phi_{11}^{yx} & \Phi_{11}^{yy} & \Phi_{11}^{yz} & \Phi_{12}^{yx} & \Phi_{12}^{yy} & \Phi_{12}^{yz} \\
\Phi_{11}^{zx} & \Phi_{11}^{zy} & \Phi_{11}^{zz} & \Phi_{12}^{zx} & \Phi_{12}^{zy} & \Phi_{12}^{zz} \\
\Phi_{21}^{xx} & \Phi_{21}^{xy} & \Phi_{21}^{xz} & \Phi_{22}^{xx} & \Phi_{22}^{xy} & \Phi_{22}^{xz} \\
\Phi_{21}^{yx} & \Phi_{21}^{yy} & \Phi_{21}^{yz} & \Phi_{22}^{yx} & \Phi_{22}^{yy} & \Phi_{22}^{yz} \\
\Phi_{21}^{zx} & \Phi_{21}^{zy} & \Phi_{21}^{zz} & \Phi_{22}^{zx} & \Phi_{22}^{zy} & \Phi_{22}^{zz}
\end{pmatrix}$$

Hessian has **36** entries:
⇒ 6 displacements ***d*** required

THE FINITE DIFFERENCE APPROACH

K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997).
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Example: Diamond Si (2 atoms in the basis):

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\Phi_{21}^{xx} & \Phi_{21}^{xy} & \Phi_{21}^{xz} & \Phi_{22}^{xx} & \Phi_{22}^{xy} & \Phi_{22}^{xz} \\
\Phi_{21}^{yx} & \Phi_{21}^{yy} & \Phi_{21}^{yz} & \Phi_{22}^{yx} & \Phi_{22}^{yy} & \Phi_{22}^{yz} \\
\Phi_{21}^{zx} & \Phi_{21}^{zy} & \Phi_{21}^{zz} & \Phi_{22}^{zx} & \Phi_{22}^{zy} & \Phi_{22}^{zz}
\end{pmatrix}$$

Space Group Analysis ⇒

$$\begin{pmatrix}
\Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & -\Phi_{11}^{xx} & \Phi_{12}^{xy} & 0 \\
0 & \Phi_{11}^{xx} & \Phi_{11}^{yz} & \Phi_{11}^{yz} & -\Phi_{11}^{xx} & 0 \\
0 & \Phi_{12}^{xy} & \Phi_{11}^{xx} & -\Phi_{11}^{xz} & -\Phi_{11}^{xy} & -\Phi_{11}^{xx} \\
-\Phi_{11}^{xx} & -\Phi_{11}^{xy} & -\Phi_{11}^{xz} & \Phi_{11}^{xx} & -\Phi_{12}^{xy} & 0 \\
0 & -\Phi_{11}^{xx} & -\Phi_{11}^{yz} & -\Phi_{11}^{yz} & \Phi_{11}^{xx} & 0 \\
0 & -\Phi_{12}^{xy} & -\Phi_{11}^{xx} & \Phi_{11}^{xz} & \Phi_{11}^{xy} & \Phi_{11}^{xx}
\end{pmatrix}$$

Hessian has **5 unique, non-zero** entries:
⇒ Only **1** displacement ***d*** required

(a) Edit your file *control.in* so that it contains the following lines

```
phonon displacement    0.01
```

(b) Run *phonopy-FHI-aims* by typing

```
phonopy-FHI-aims
```

(c) Change into the directory *phonopy-FHI-aims-displacement-01* and run *FHI-aims*:

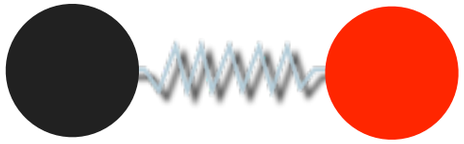
```
cd phonopy-FHI-aims-displacement-01
mpirun -np 4 aims.x > phonopy-FHI-aims-displacement-01.out
```

(d) Change into parent directory and run *phonopy-FHI-aims* again

```
cd ..
phonopy-FHI-aims
```

THE HARMONIC APPROXIMATION

...in Molecules:



N ... Number of atoms

⇓

Degrees of Freedom: ***3N***
Dimension of Hessian: $9N^2$

Tuesday July 22:

⇒ *Björn Lange, Nuts and Bolts of DFT II*

⇒ *O. Hofmann & L. Nemec, Tutorial 1*

...in Crystalline Solids:

N ... Number of atoms

⇓

Degrees of Freedom: ***3N***
Dimension of Hessian: $9N^2$

BUT:

$N \rightarrow \infty$

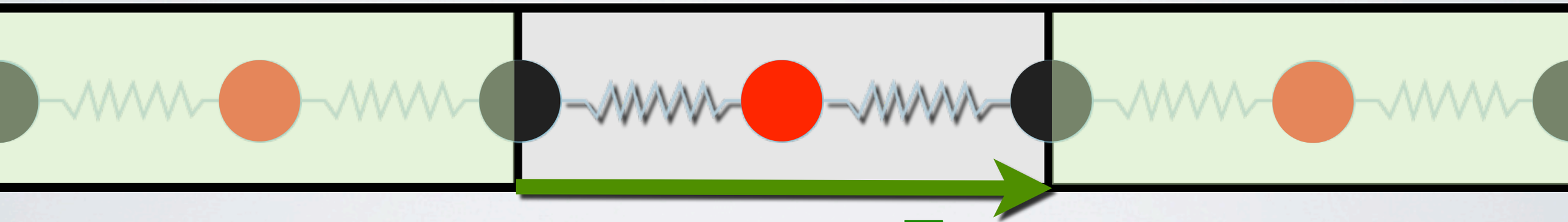
PERIODIC BOUNDARY CONDITIONS

cf. Christian Ratsch, "Electronic Structure Theory for Periodic Systems: The Concepts", Tuesday July 22

Unit Cell with N_p atoms

Periodic Images

Periodic Images



Lattice vector: $\mathbf{E}_0$

Real Space:
Hessian Φ_{ij}
with $i,j \rightarrow \infty$

Fourier Transform

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}\cdot(\mathbf{R}_j^0 - \mathbf{R}_{j'}^0)\right)}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}$$

Reciprocal Space:
Dynamical Matrix $D_{i'j'}(q)$
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:
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$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}\cdot(\mathbf{R}_j^0 - \mathbf{R}_{j'}^0)\right)}}{\sqrt{M_{i'}M_{j'}}}\,\Phi_{i'j}$$

Reciprocal Space:
Dynamical Matrix $D_{i'j'}(q)$
with $i',j' \leq N_p$

Fourier Transform can be truncated since
$\Phi_{ij} = 0$ for large $|R_j^0 - R_{j'}^0|$

Hessian Φ_{ij}
with **finite** number
of non-zero entries

Dynamical Matrix $D_{i'j'}(q)$
known for the **whole**
reciprocal space

VIBRATIONS IN A CRYSTAL 101

e.g. N. W Ashcroft and N. D. Mermin, "*Solid State Physics*" (1976)
also see Björn Lange, *Nuts and Bolts of DFT II,* Tuesday July 22

Dynamical matrix:

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}\cdot(\mathbf{R}_j^0 - \mathbf{R}_{j'}^0)\right)}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}$$

Equation of Motion becomes an **Eigenvalue** Problem:

$$\mathbf{D}(\mathbf{q})\ [\nu(\mathbf{q})] = \omega^2(\mathbf{q})\ [\nu(\mathbf{q})]$$

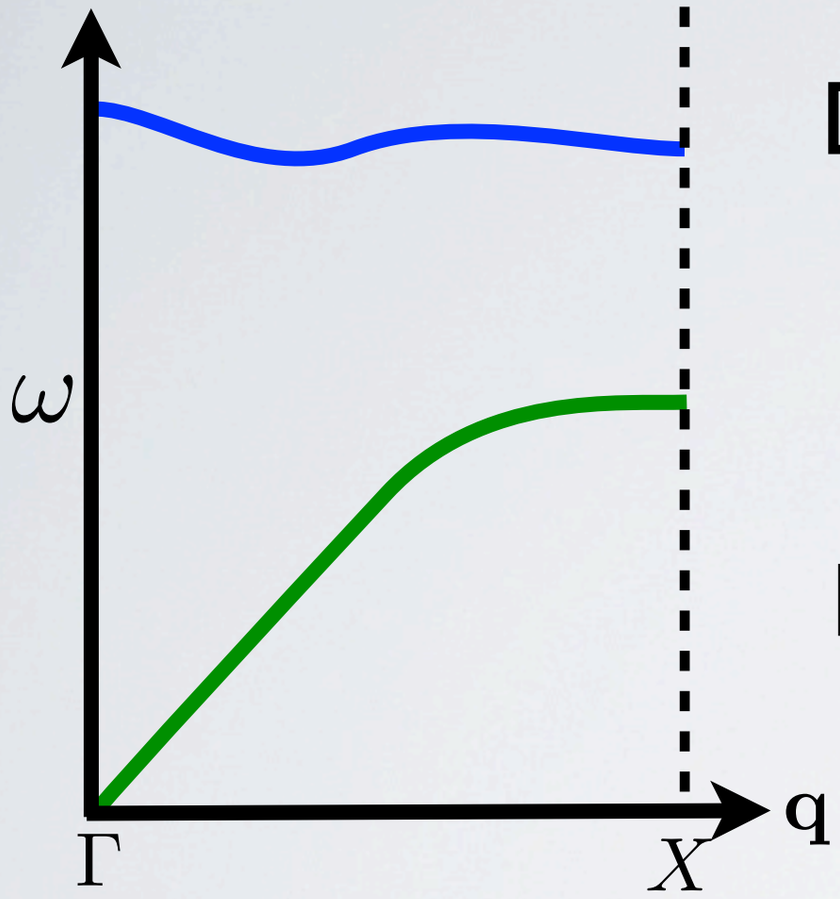
Analytical Solution in Real Space:

Superposition of Harmonic Oscillations

$$\mathbf{R}_j(t) \quad = \quad \mathbf{R}_j^0 + \mathfrak{Re}\left(\sum_s \frac{A_s}{\sqrt{M_i}} e^{i\left(\mathbf{q}\cdot(\mathbf{R}_j^0 - \mathbf{R}_{j'}^0) - \omega_s(\mathbf{q})t\right)} \cdot [\nu_s(\mathbf{q})]_{j'}\right)$$

VIBRATIONS IN A CRYSTAL 101

e.g. N.W Ashcroft and N. D. Mermin, "*Solid State Physics*" (1976)
Björn Lange, *Nuts and Bolts of DFT II*, Tuesday July 22



Dynamical matrix:

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}\cdot(\mathbf{R}_j - \mathbf{R}_{j'})\right)}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}$$

Eigenvalue problem:

$$\mathbf{D}(\mathbf{q})\ [\nu(\mathbf{q})] = \omega^2(\mathbf{q})\ [\nu(\mathbf{q})]$$

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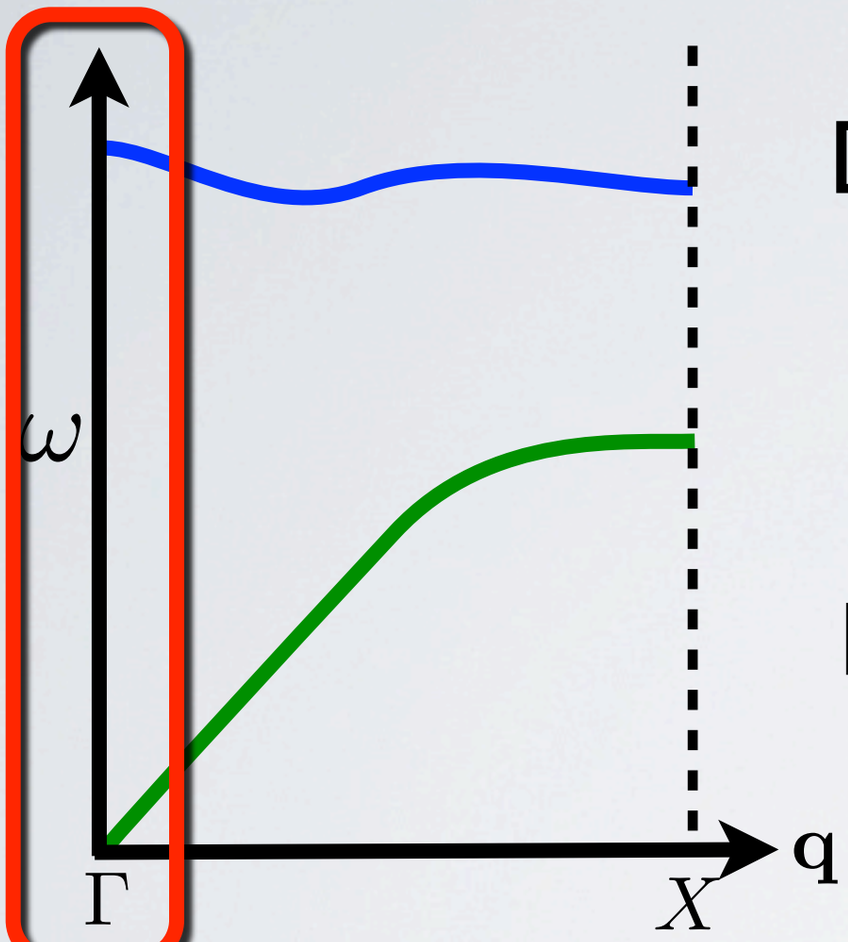
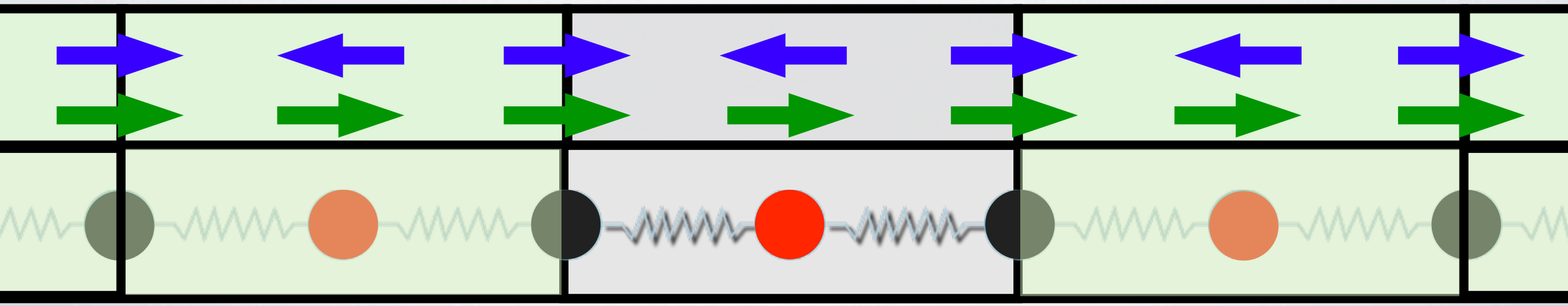


Dynamical matrix:

$$D_{i'j'}(\mathbf{\Gamma}) = \sum_j \frac{e^{i\left(\mathbf{q}\cdot(\mathbf{R}_{j'}-\mathbf{R}_{j'})\right)}}{\sqrt{M_{i'}M_{j'}}}\,\Phi_{i'j} \quad = 1$$

Eigenvalue problem:

$$\mathbf{D}(\mathbf{\Gamma})\,[\nu(\mathbf{\Gamma})] = \omega^2(\mathbf{\Gamma})\,[\nu(\mathbf{\Gamma})]$$



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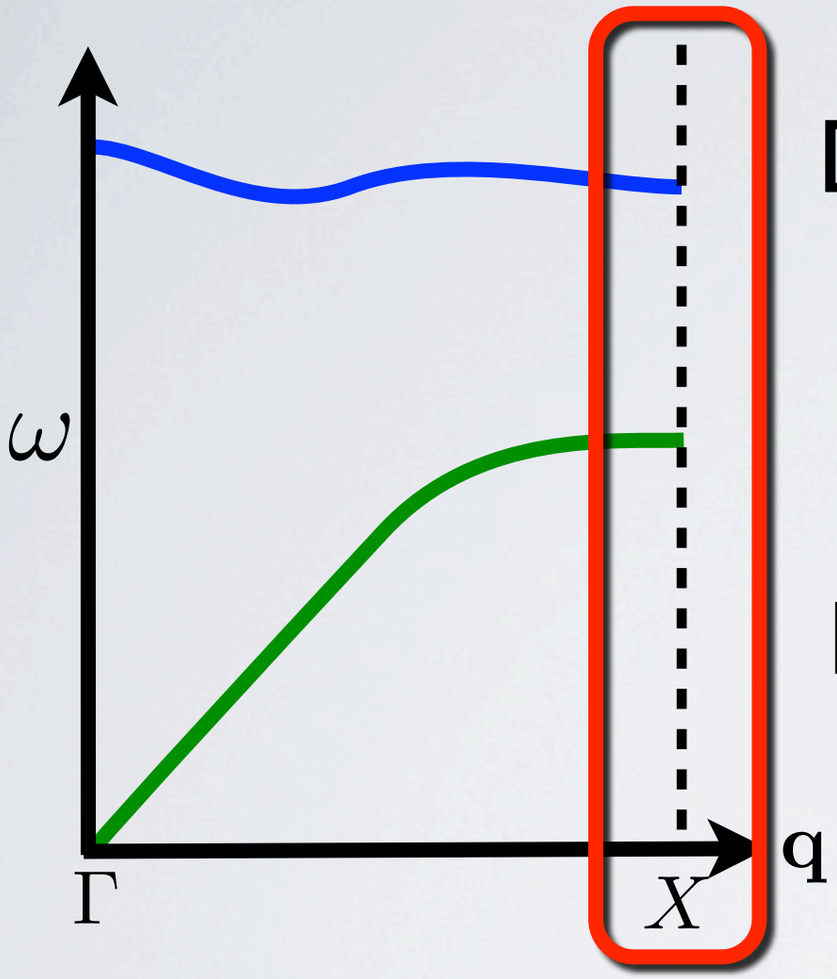

Dynamical matrix:

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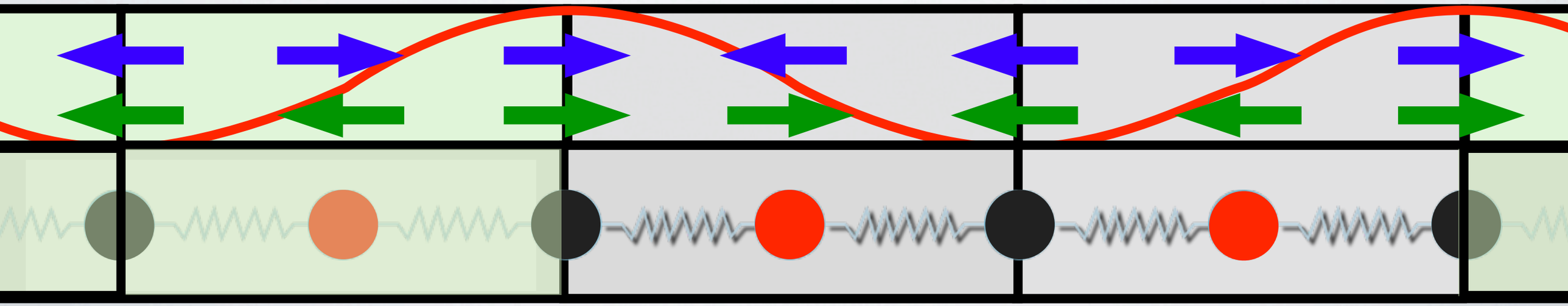
Eigenvalue problem:

$$\mathbf{D}(X)\ [\nu(X)] = \omega^2(X)\ [\nu(X)]$$



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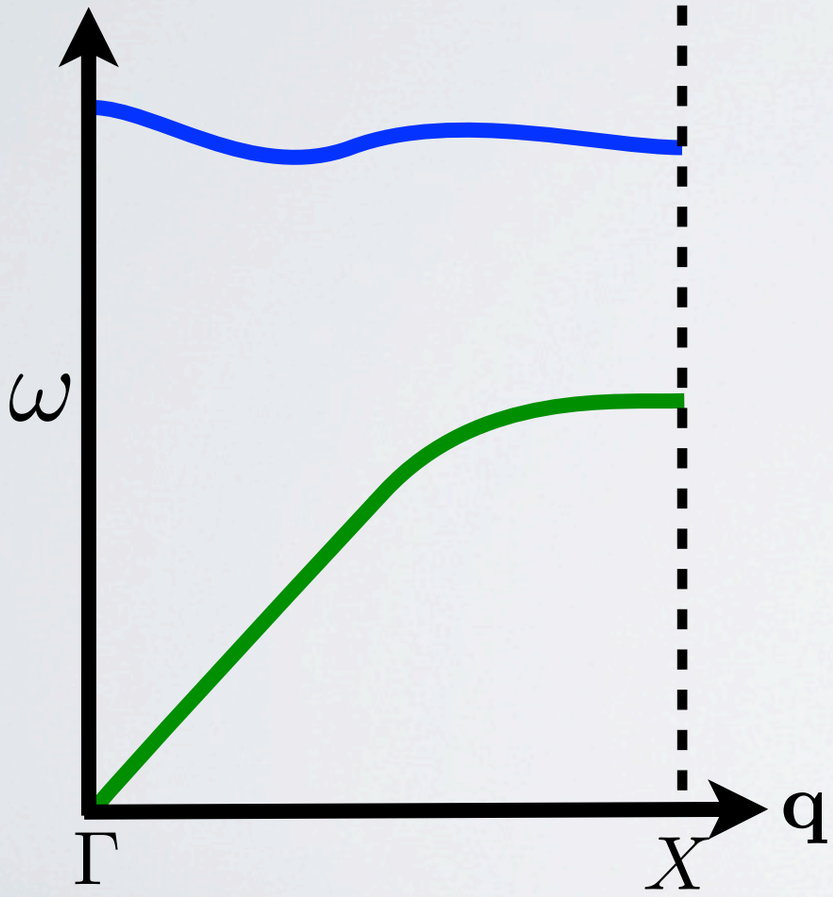
For N_p atoms in the unit cell there are:



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
- **ω > 0** at **Γ** (and everywhere else)
- Weak dispersion

CONVERGING THE SUPERCELL

Fourier Transform can be truncated since $\Phi_{ij} = 0$ for large $R_{ij}^0 = |R_j^0 - R_{j'}^0|$

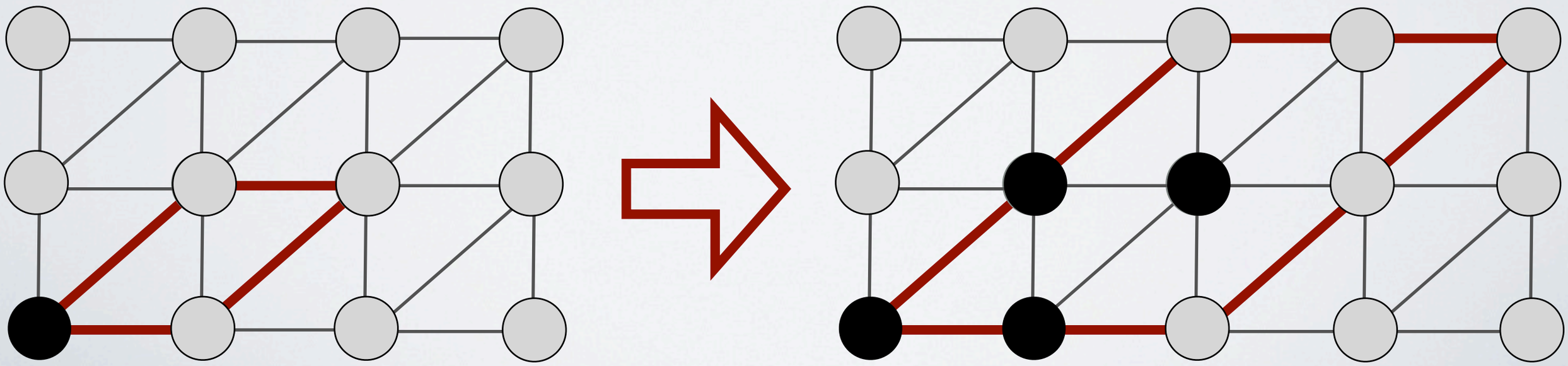
$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}\cdot(\mathbf{R}_j^0 - \mathbf{R}_{j'}^0)\right)}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}$$

```
phonon displacement 0.01
phonon supercell    1  1  1

k_grid              4  4  4
```

```
phonon displacement 0.01
phonon supercell    2  2  2

k_grid              2  2  2
```



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phonon displacement 0.01
phonon supercell    1  1  1

k_grid              4  4  4
```

```
phonon displacement 0.01
phonon supercell    2  2  2

k_grid              2  2  2
```

To achieve convergence, it is **essential** to have a **consistent** description of the electronic structure **for all supercell sizes**:

#atoms • #k-points ≈ ***constant***

CONVERGING THE SUPERCELL

Fourier Transform can be truncated since $\Phi_{ij} = 0$ for large $R_{ij}^0 = |R_j^0 - R_{j'}^0|$

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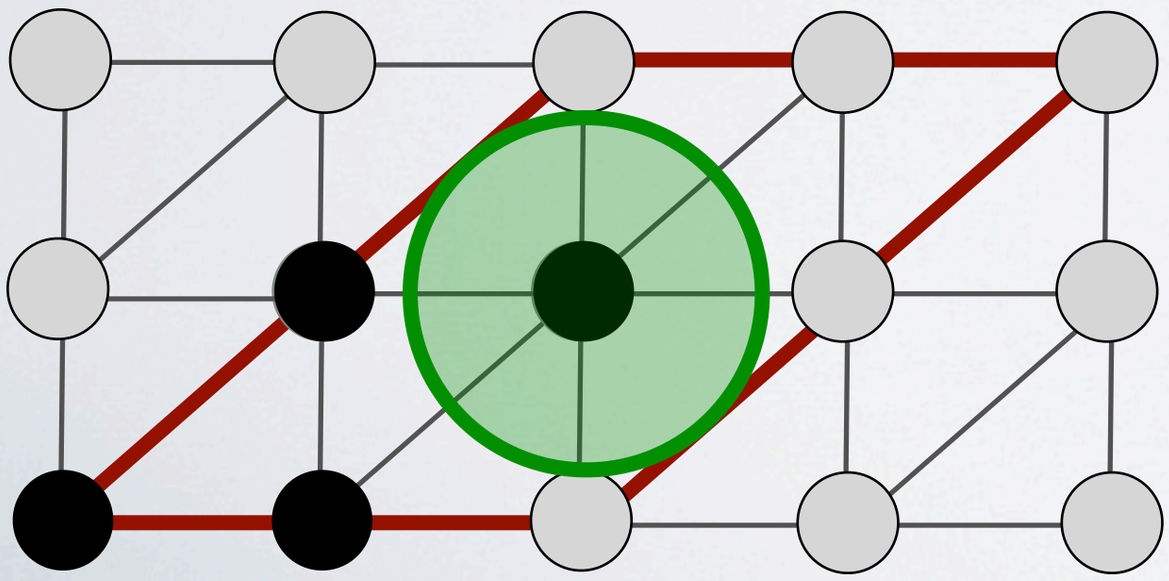
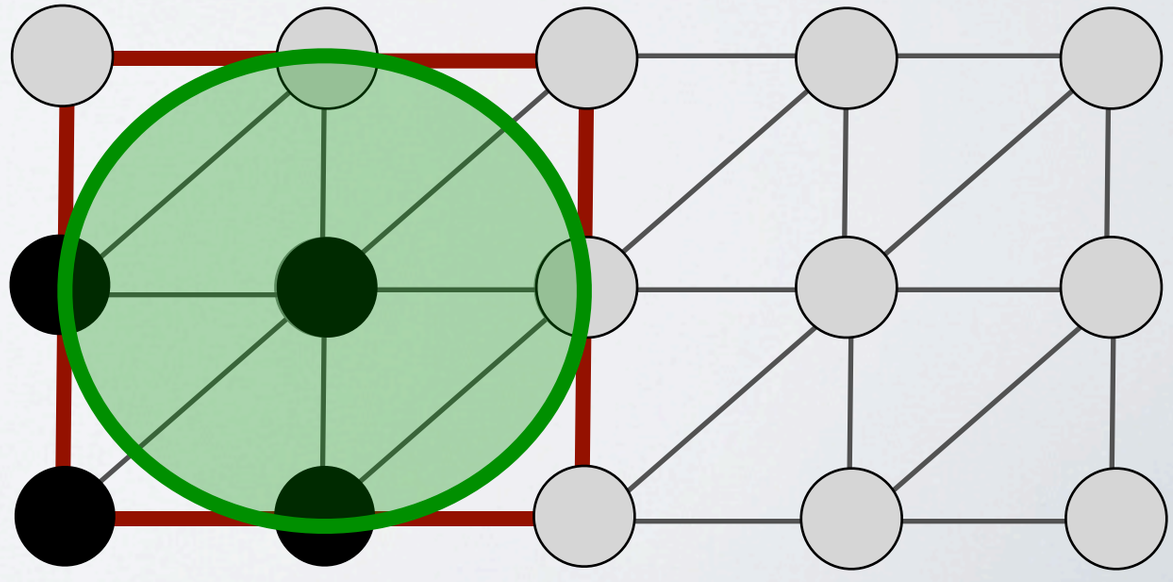
Oblique Cell:

Not all Cartesian directions are treated **consistently**!



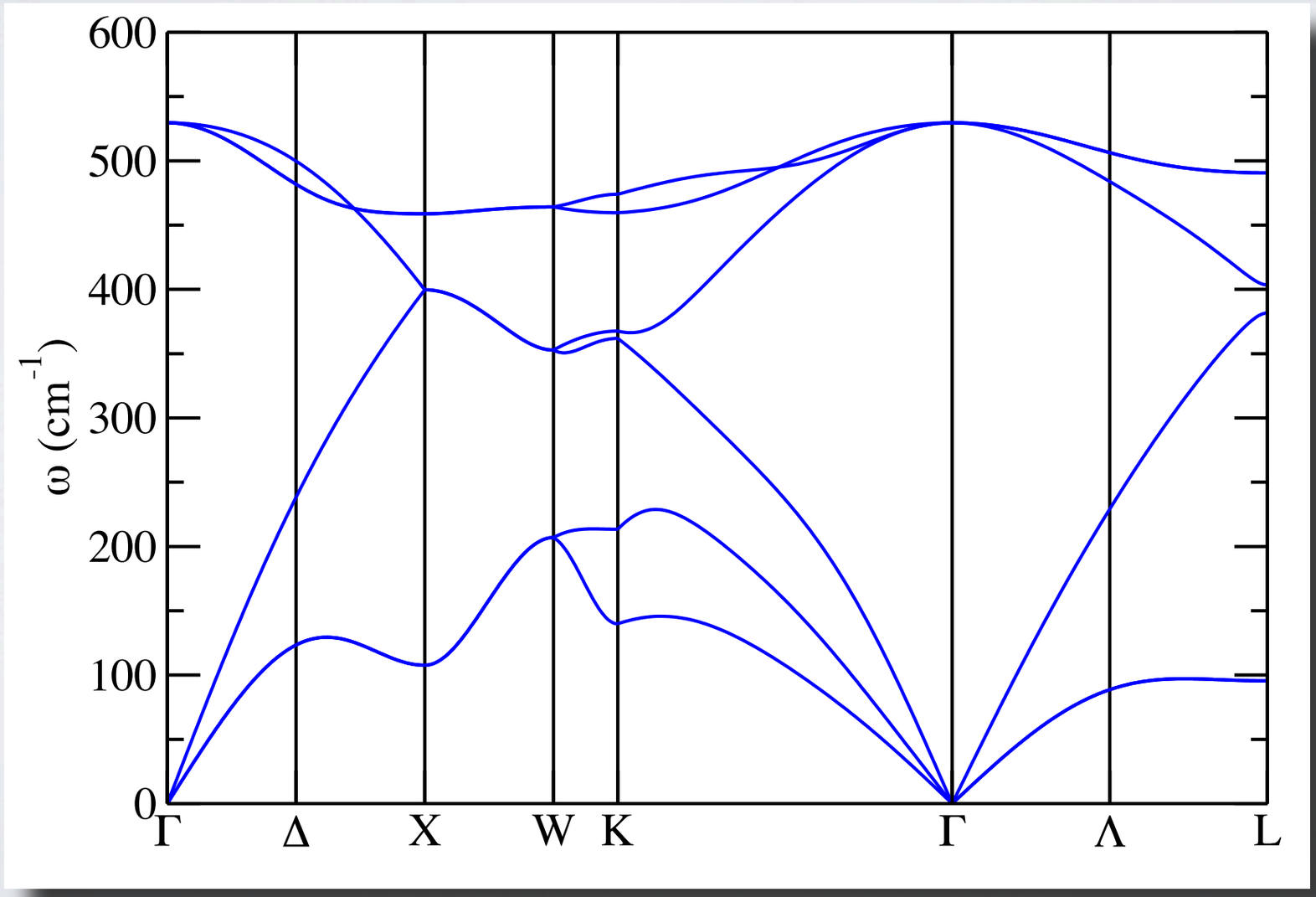
Cubic ("spherical") Cell:

Consistent assessment of **all** cartesian directions!



VIBRATIONAL BAND STRUCTURE

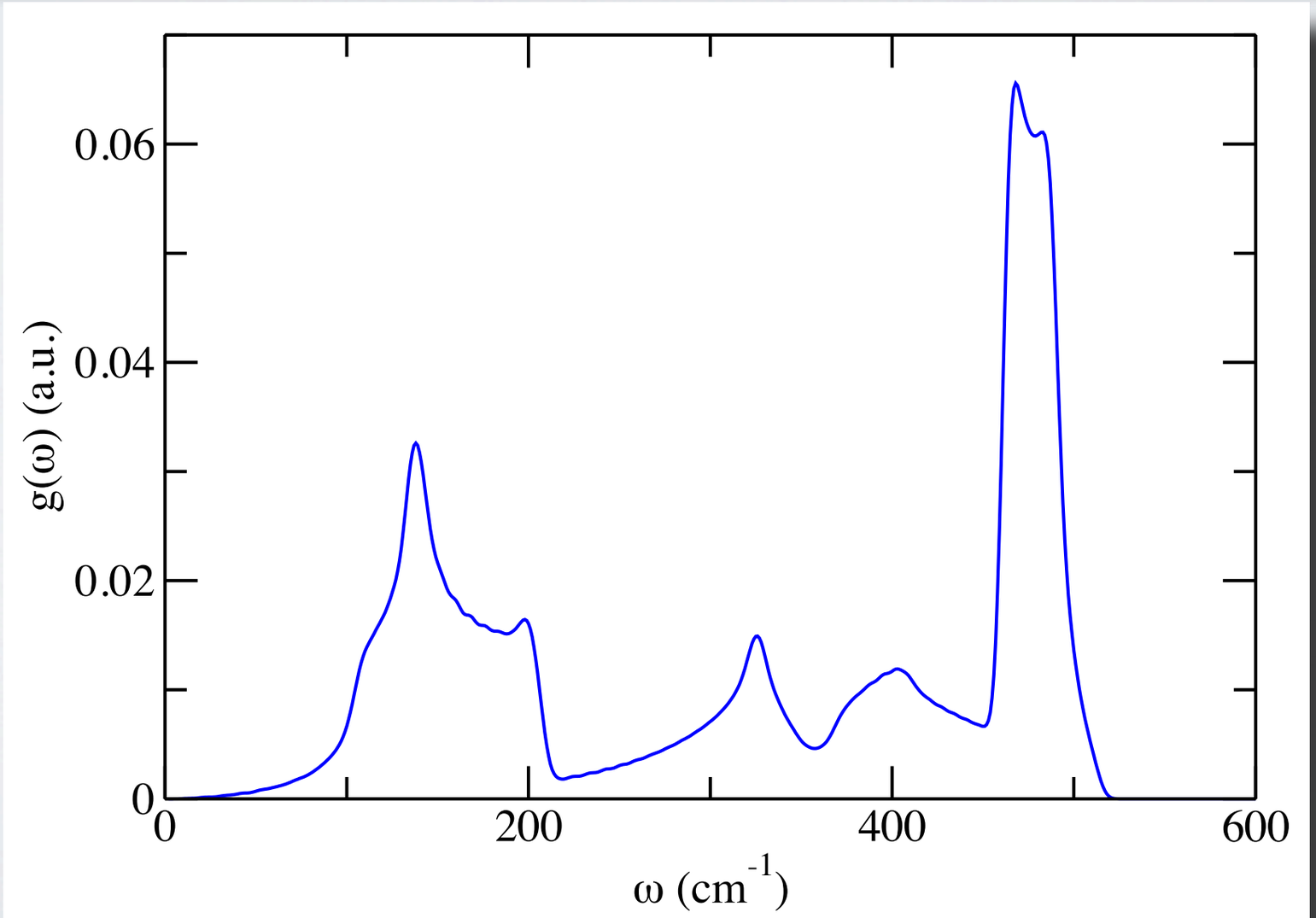
```
# control.in : Plot vibrational band structure
phonon band  0     0     0     0.00  0.25  0.25  100   Gamma  Delta
phonon band  0.00  0.25  0.25  0     0.5   0.5   100   Delta  X
phonon band  0     0.5   0.5   0.25  0.50  0.75  100   X      W
phonon band  0.25  0.50  0.75  0.375 0.375 0.75  100   W      K
phonon band  0.375 0.375 0.75  0     0     0     100   K      Gamma
phonon band  0     0     0     0.25  0.25  0.25  100   Gamma  Lambda
phonon band  0.25  0.25  0.25  0.5   0.5   0.5   100   Lambda L
```



VIBRATIONAL DENSITY OF STATES

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

```
# control.in : Plot vibrational density of states
phonon dos          0   800   800   3 45
```



THE HARMONIC FREE ENERGY

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

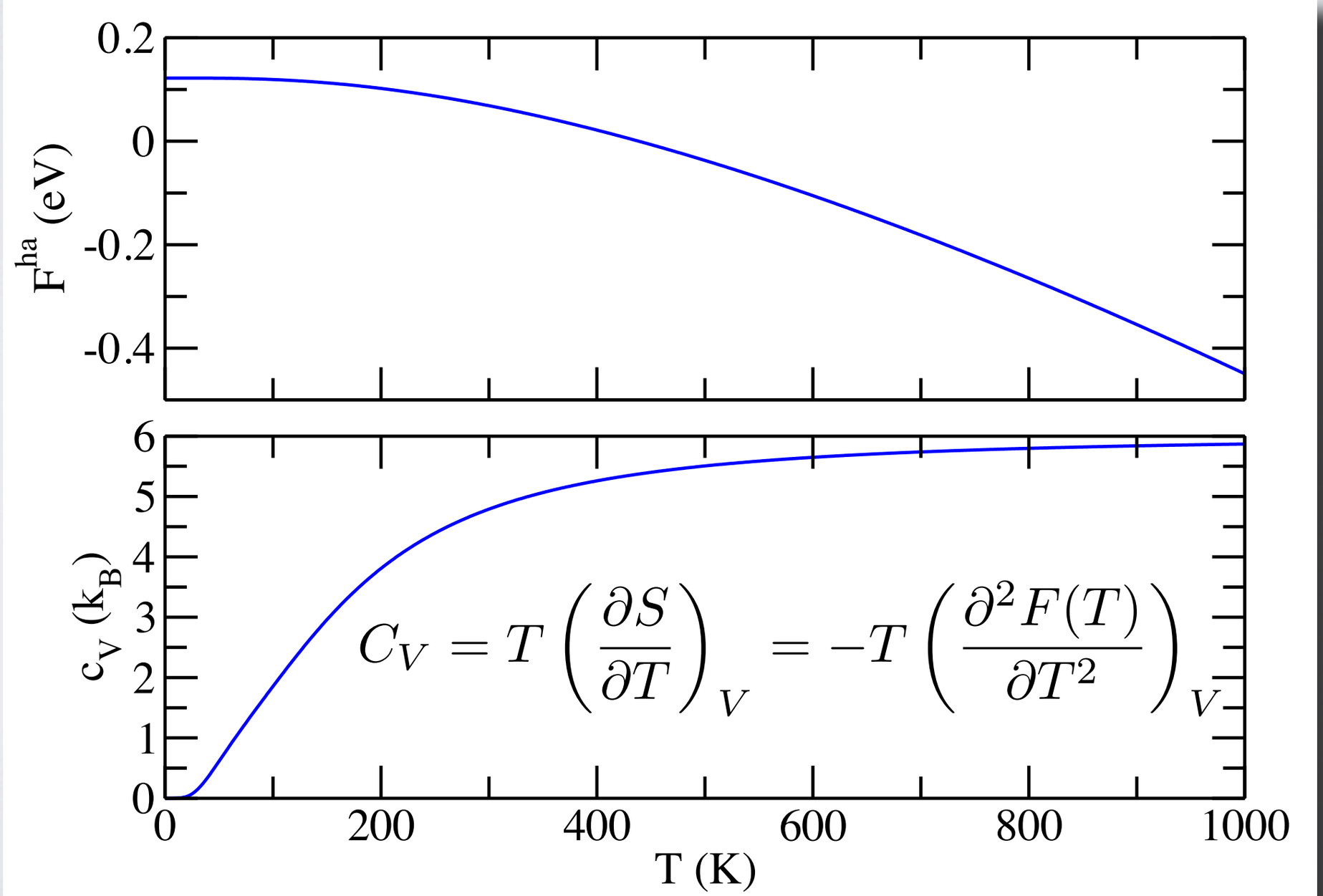
Static Equilibrium Energy

Zero-point vibration

Thermally induced vibrations

FREE ENERGY AND HEAT CAPACITY

```
# control.in : Plot harmonic contribution to F(T)
phonon free_energy 0  1010  1010     45
```



THE QUASI-HARMONIC APPROXIMATION

THE HARMONIC APPROXIMATION

$$\mathbb{H} = \sum_i T_i + \frac{1}{2}\sum_{i,j} \Phi_{ij}\Delta\mathbf{R}_i\Delta\mathbf{R}_j \quad \Rightarrow \quad \frac{\partial \mathbb{H}}{\partial V} = 0$$

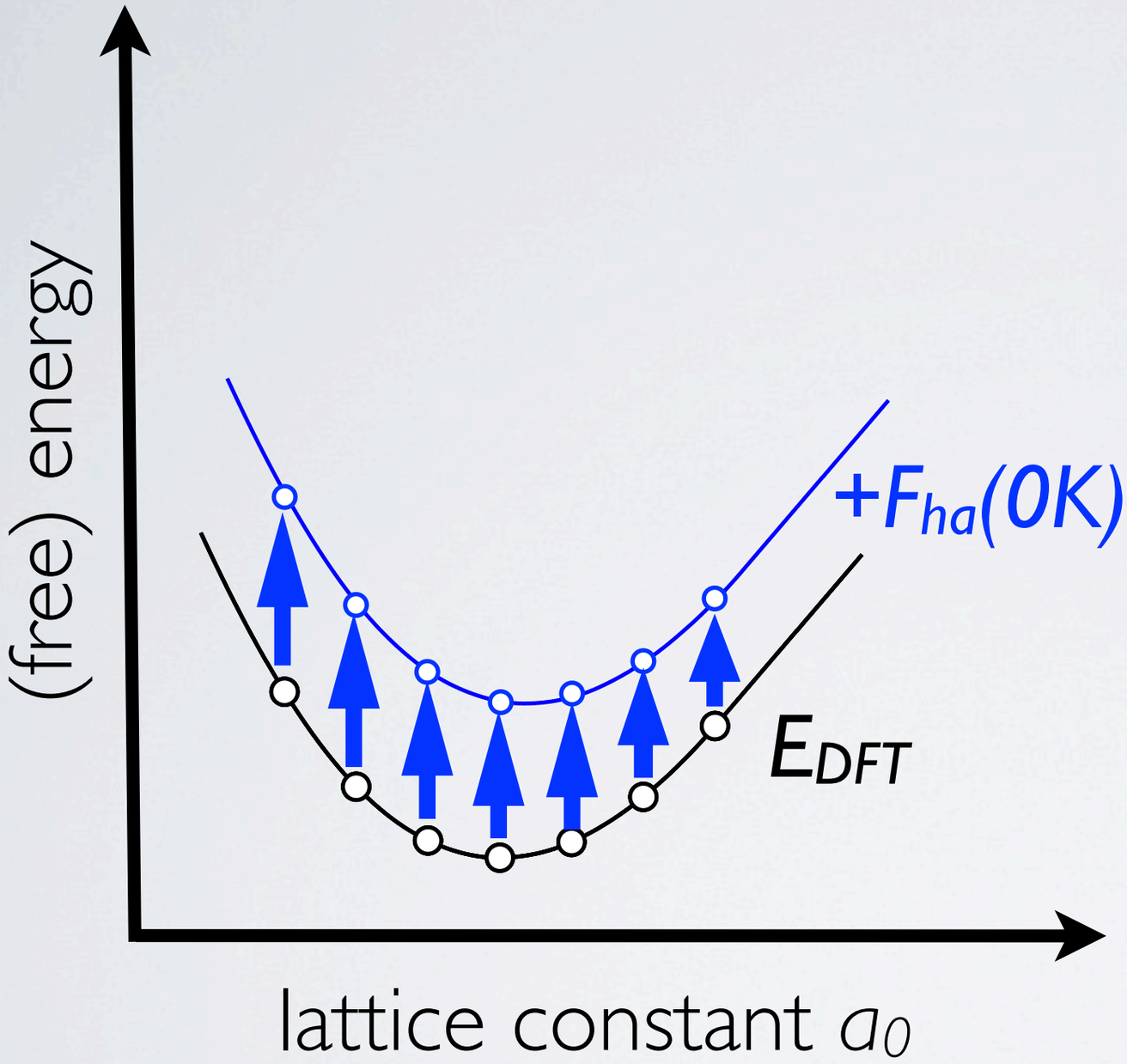
Lattice expansion *vanishes in the* **harmonic** *approximation.*

THE **QUASI**-HARMONIC APPROACH

$$\mathbb{H} = \sum_i T_i + \frac{1}{2}\sum_{i,j} \Phi_{ij}(V)\,\Delta\mathbf{R}_i\Delta\mathbf{R}_j \quad \Rightarrow \quad \frac{\partial \mathbb{H}}{\partial V} \neq 0$$

Assess **lattice expansion** *by explicitly accounting for the* ***volume dependence*** *of the* ***Hessian****.*

THE QUASI-HARMONIC APPROACH

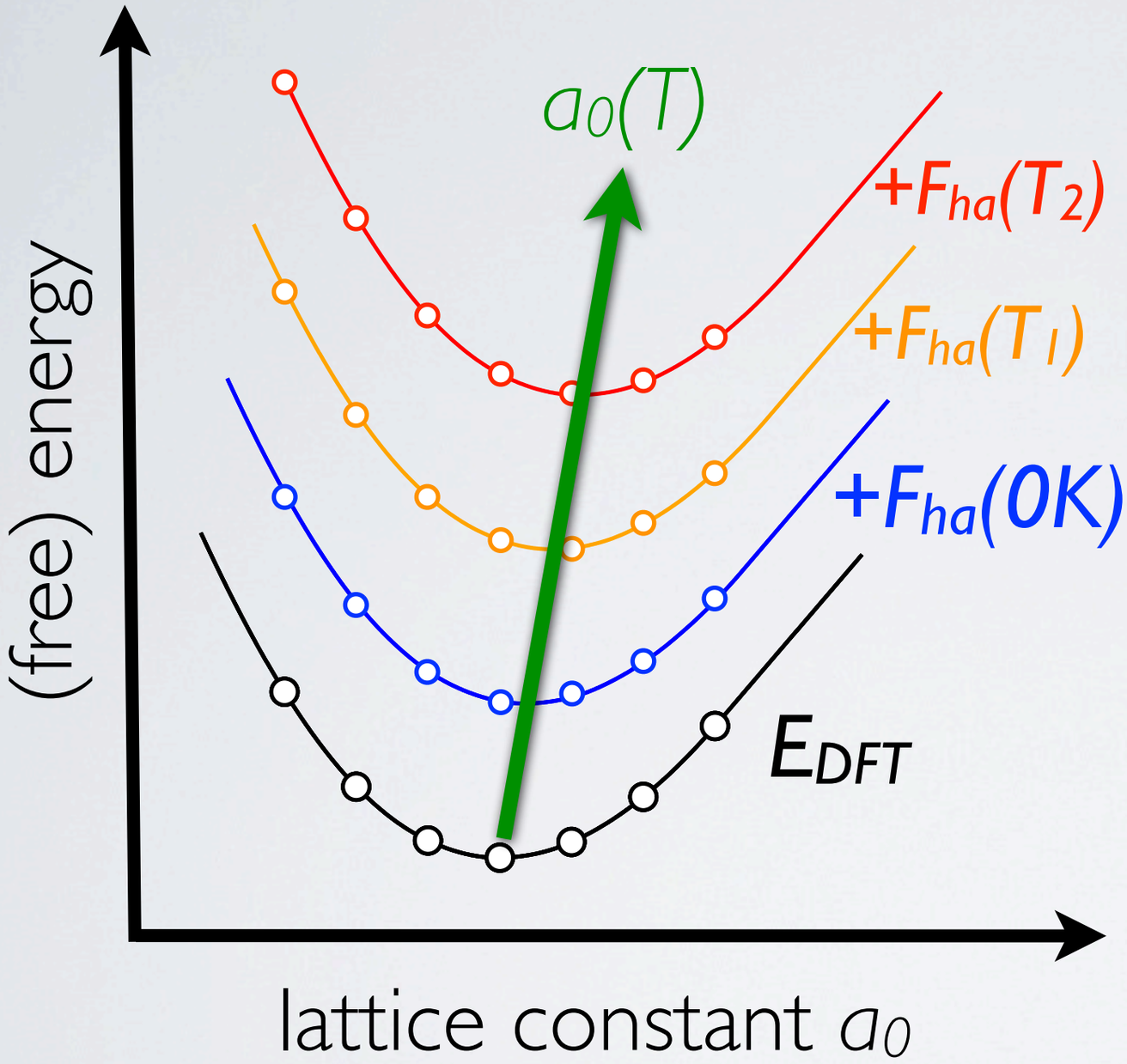


Lattice constant a_0 can be determined from *Birch-Murnaghan* fit of $E(a_0)$

cf. L. Nemec & B. Bienik, Tutorial 2

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

THE QUASI-HARMONIC APPROACH



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

cf. L. Nemec & B. Bienik, Tutorial 2

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** $a_0(T)$.

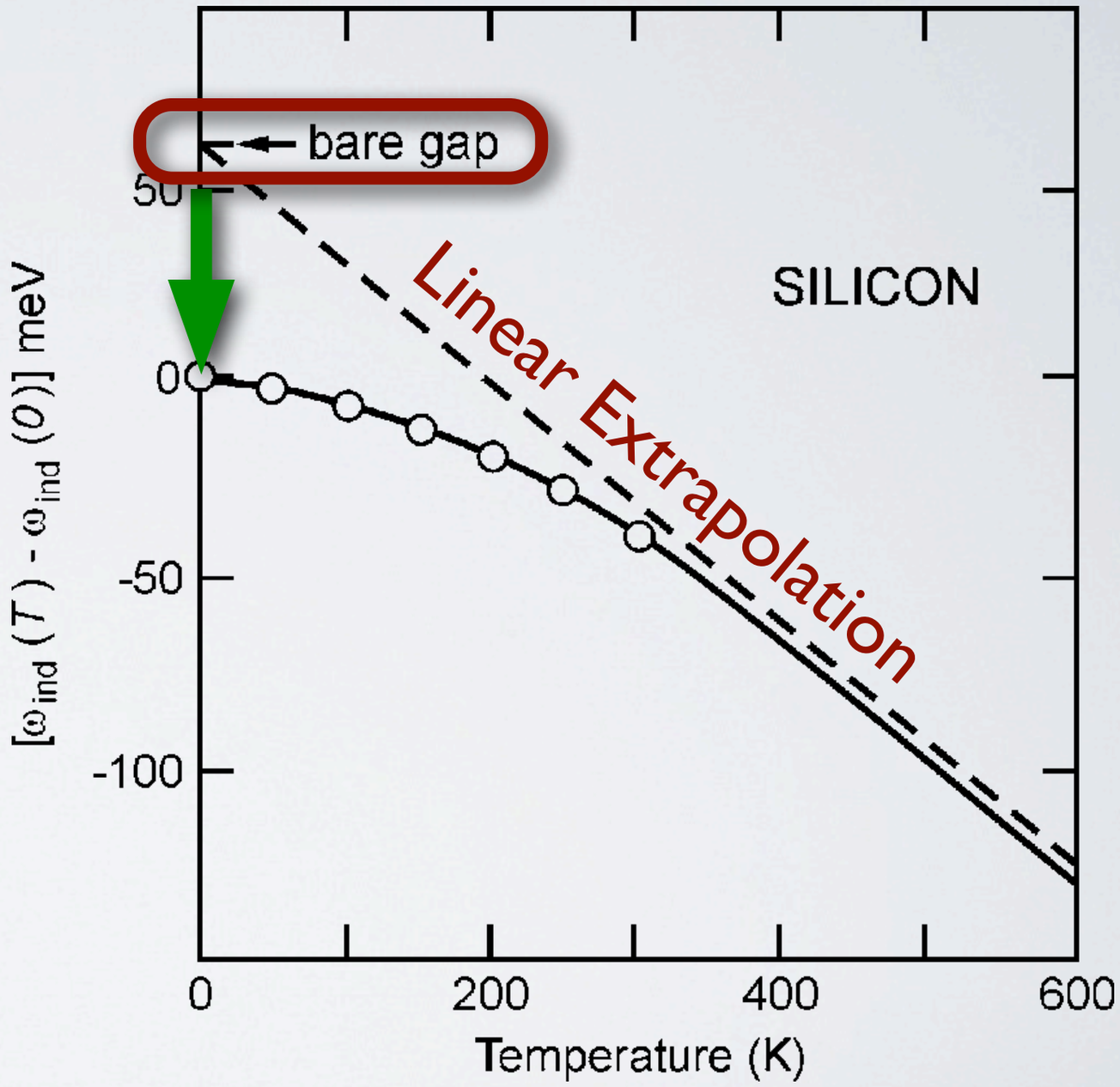
ELECTRON-PHONON COUPLING

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**



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

BAND GAP TEMPERATURE DEPENDENCE

What is the physical mechanism?

Exercise 4:
Lattice Expansion?

Use results from **exercise 3**

Exercise 5:
Atomic Motion?

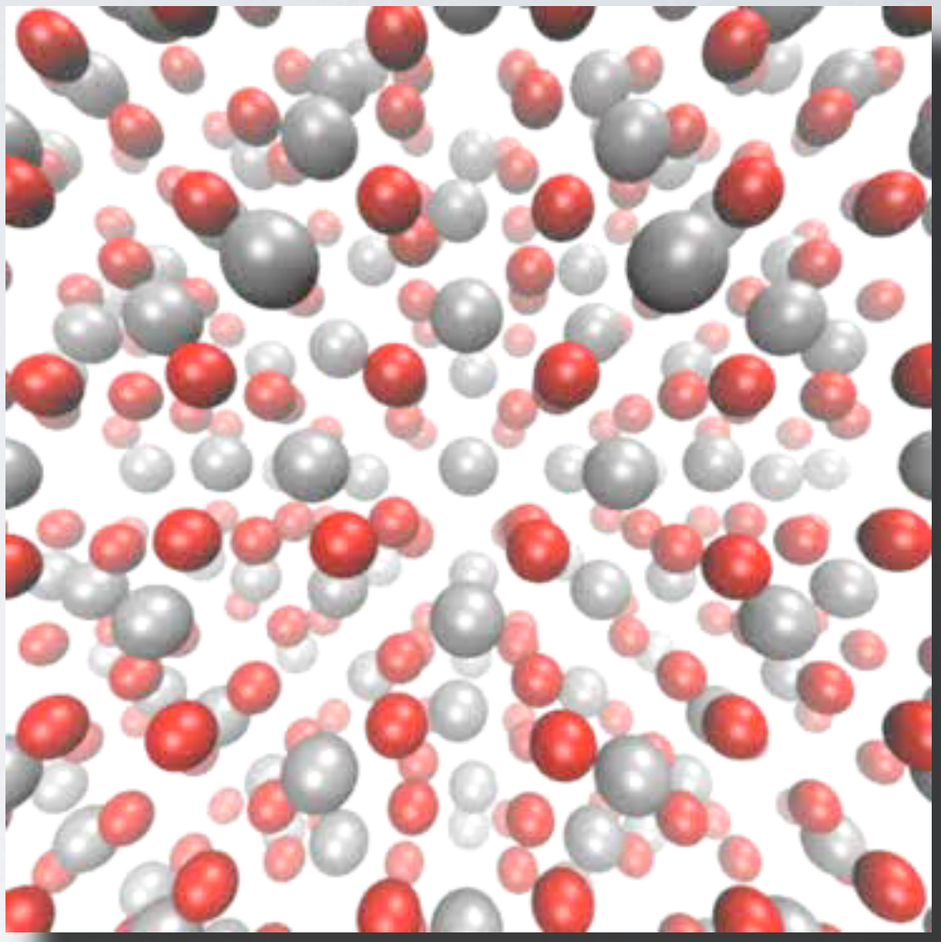
Molecular Dynamics

MOLECULAR DYNAMICS

Numerical Integration of the **equations of motion**

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

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_{\mathbf{R}_i} E_{DFT}$$



cf. Mariana Rossi & Luca Ghiringhelli,
Tutorial 4: Molecular Dynamics

HARMONIC MOLECULAR DYNAMICS

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_{\mathbf{R}_i} E_{DFT} \qquad M_I \ddot{\mathbf{R}}_I(t) = -\sum_j \Phi_{ij} \Delta \mathbf{R}_j$$

Harmonic Approximation

```
# Molecular Dynamics
MD_MB_init   300.000
MD_time_step 0.001
MD_clean_rotations .false.
MD_schedule
MD_segment  5.0 NVT_parrinello 300.000 0.050   # Equilibration
  harmonic_potential_only fc_constants.dat
MD_segment 20.0 NVT_parrinello 300.000 0.050   # Sample phase space
  harmonic_potential_only fc_constants.dat
```

WARNING:

In the following exercises, the computational settings, in particular the reciprocal space grid (tag `k_grid`), the basis set, and supercells, have been chosen to allow a rapid computation of the exercises in the limited time and within the CPU resources available during the tutorial session. In a "real" production calculation, the reciprocal space grid, the basis set, and the supercells would all have to be converged with much more care, but the qualitative trends hold already with the present settings

Happy Computing!

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