An overview of vibrations in solids

Bartomeu Monserrat

QMC in the Apuan Alps IX
27 July 2014

Why vibrations in a QMC conference?

- If the required accuracy makes QMC necessary, then vibrations could also be important.
- QMC band gaps are static, the effects of electron-phonon coupling may be important.

Outline

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Why is the vibrational problem difficult?

$$\hat{H}_{\text{vib}} = -\frac{1}{2} \sum_{\mathbf{R}_p, \alpha} \frac{1}{m_\alpha} \nabla^2_{p\alpha} + V(\mathbf{r}_\alpha)$$

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- $3N$-dimensional function

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- $3N$-dimensional function
- Each data point requires an electronic energy calculation

Harmonic approximation

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

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

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

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

Principal axes approximation to the BO energy surface

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

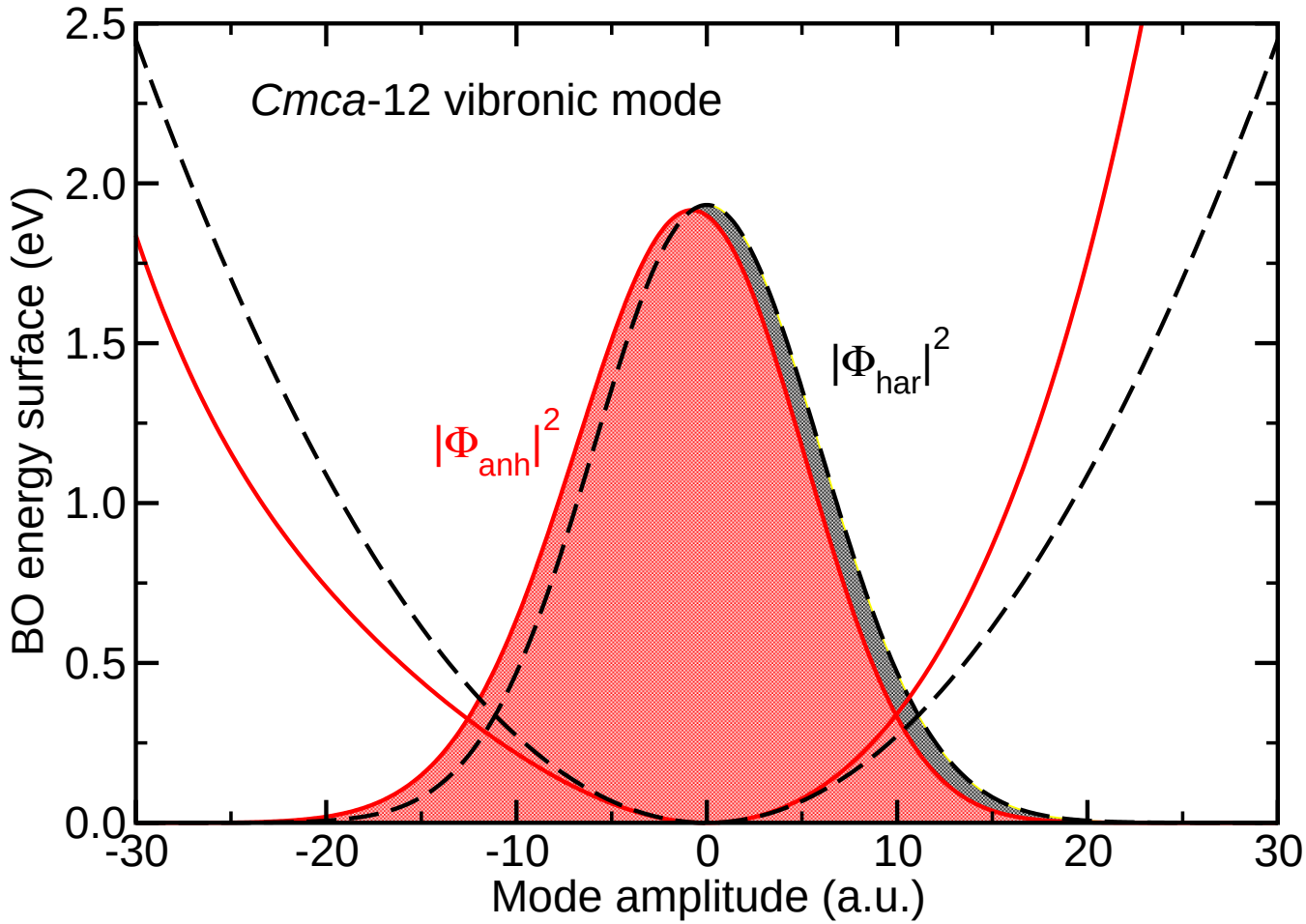
- Static lattice DFT total energy.
- DFT total energy along frozen independent mode.
- DFT total energy along frozen coupled modes.

Features:

- Can be improved systematically.
- Subspace with higher N-body terms (e.g. perovskites).
- Estimate of error in anharmonic energy.

Independent term (I)

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



Independent term (II)

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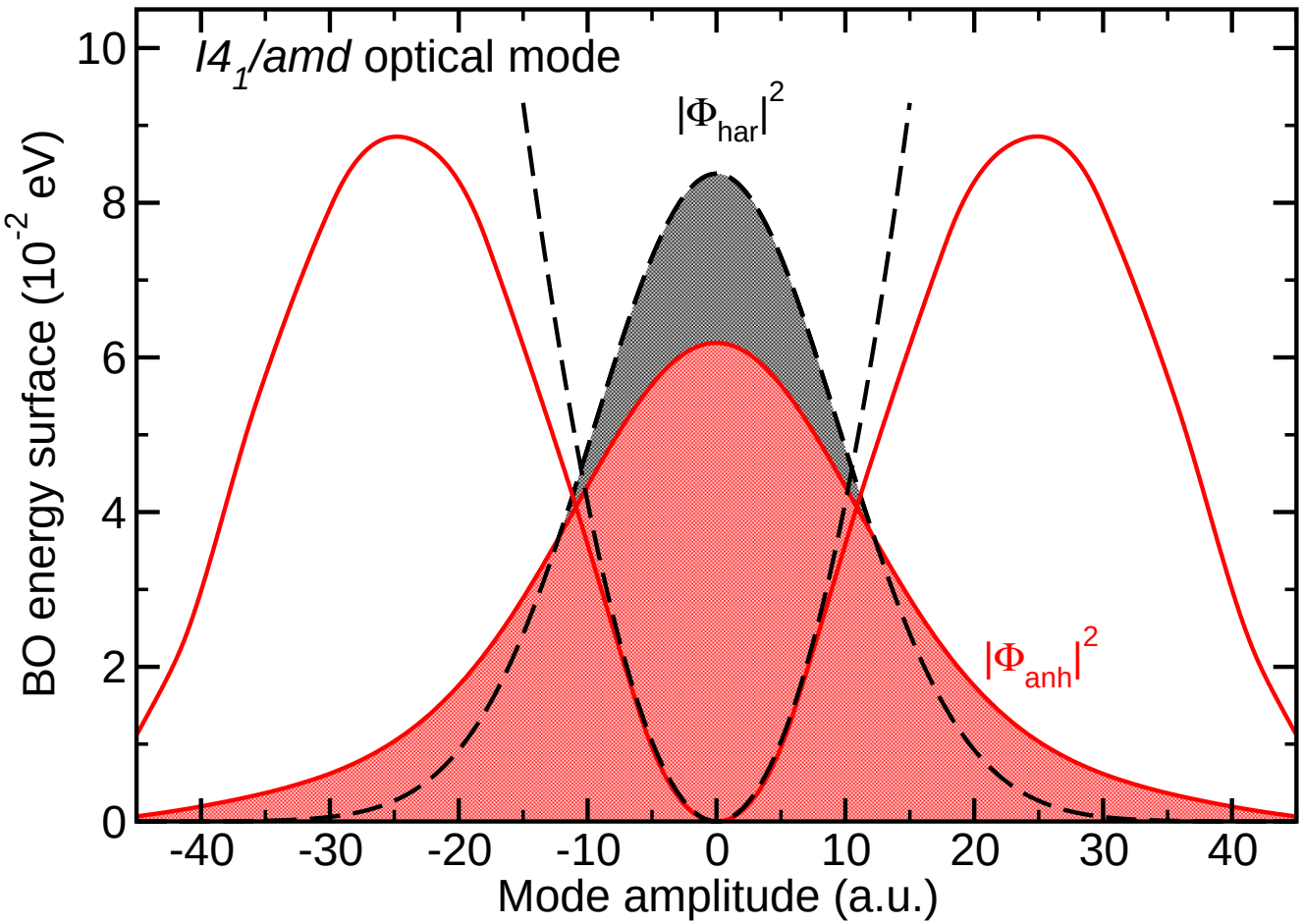

Coupled term (I)

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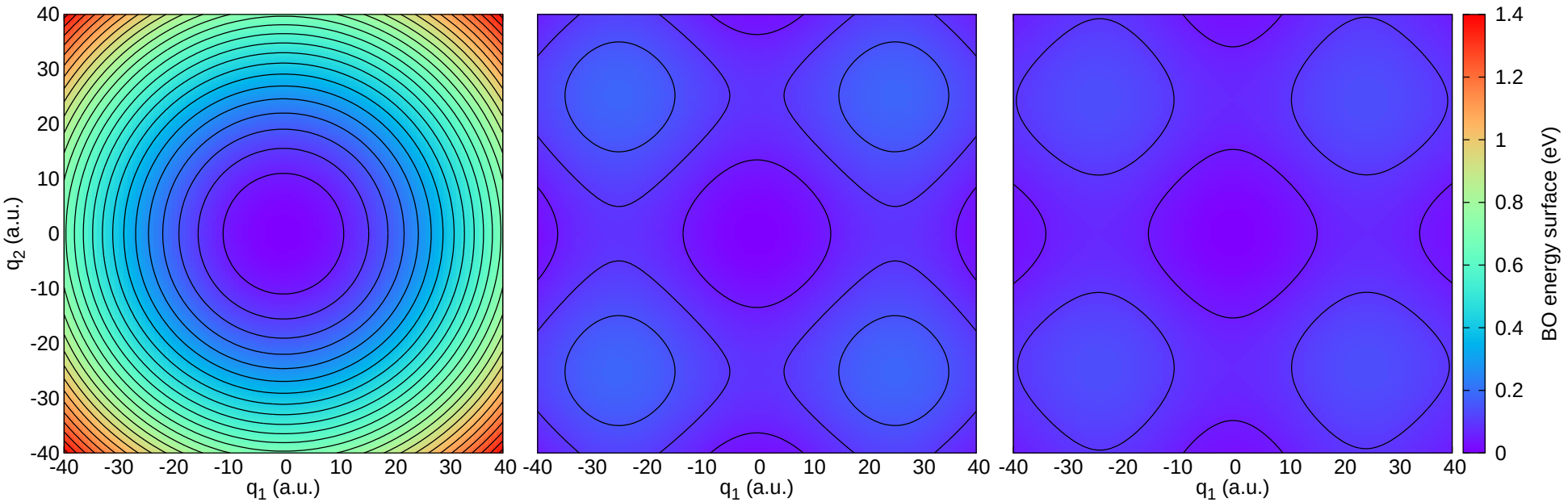

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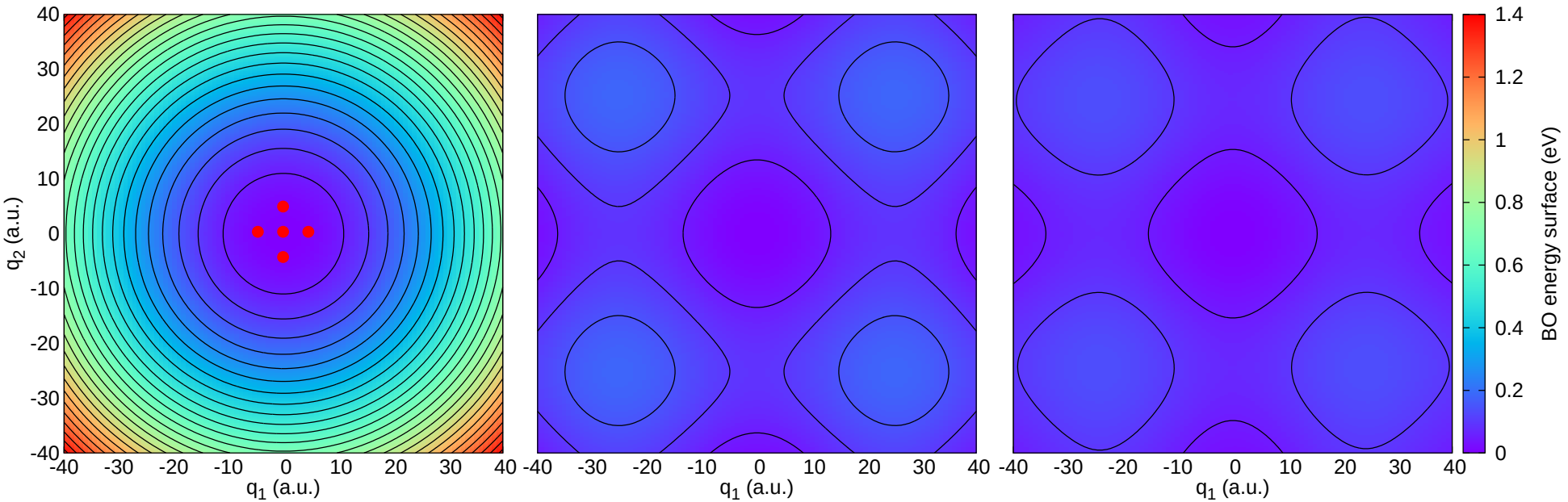

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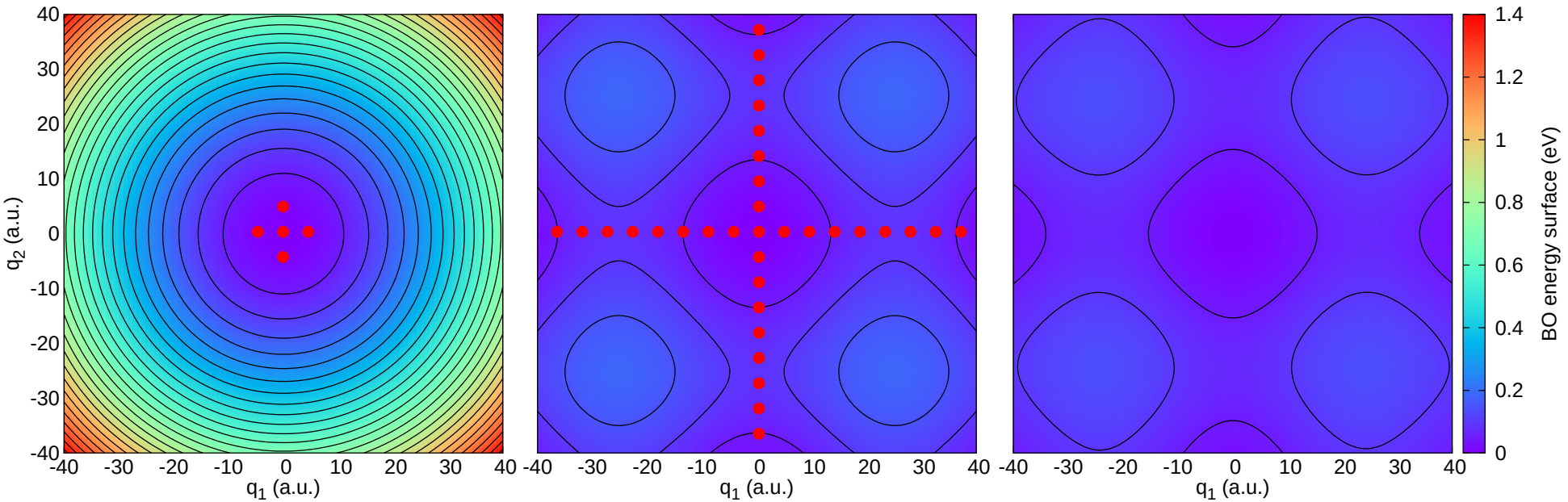

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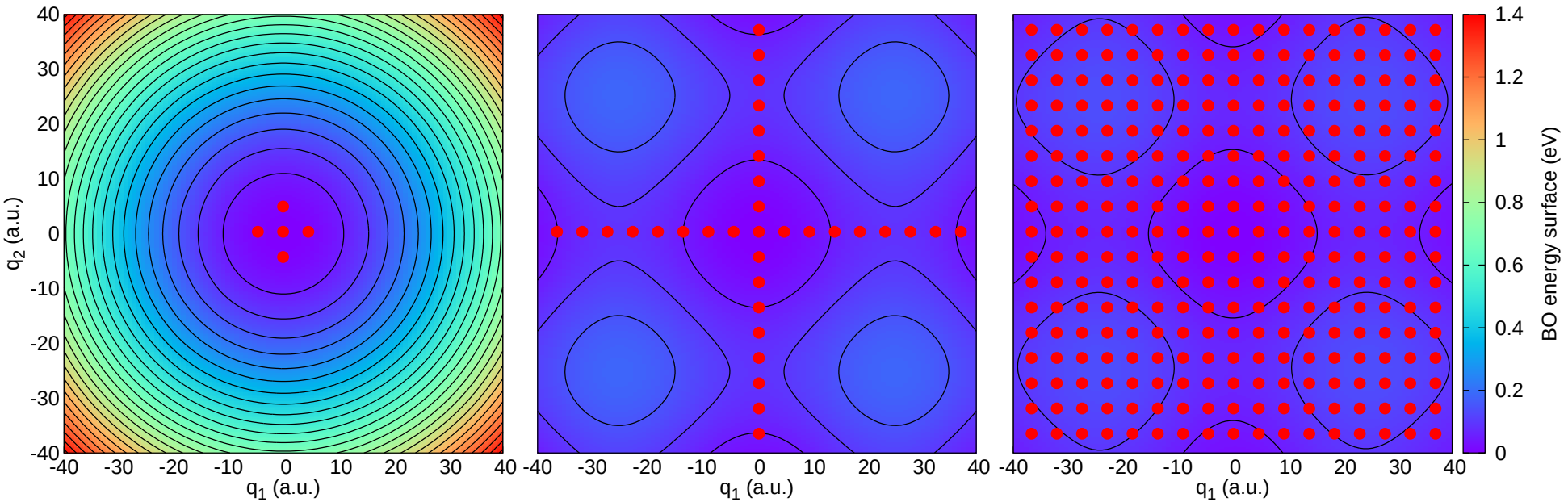

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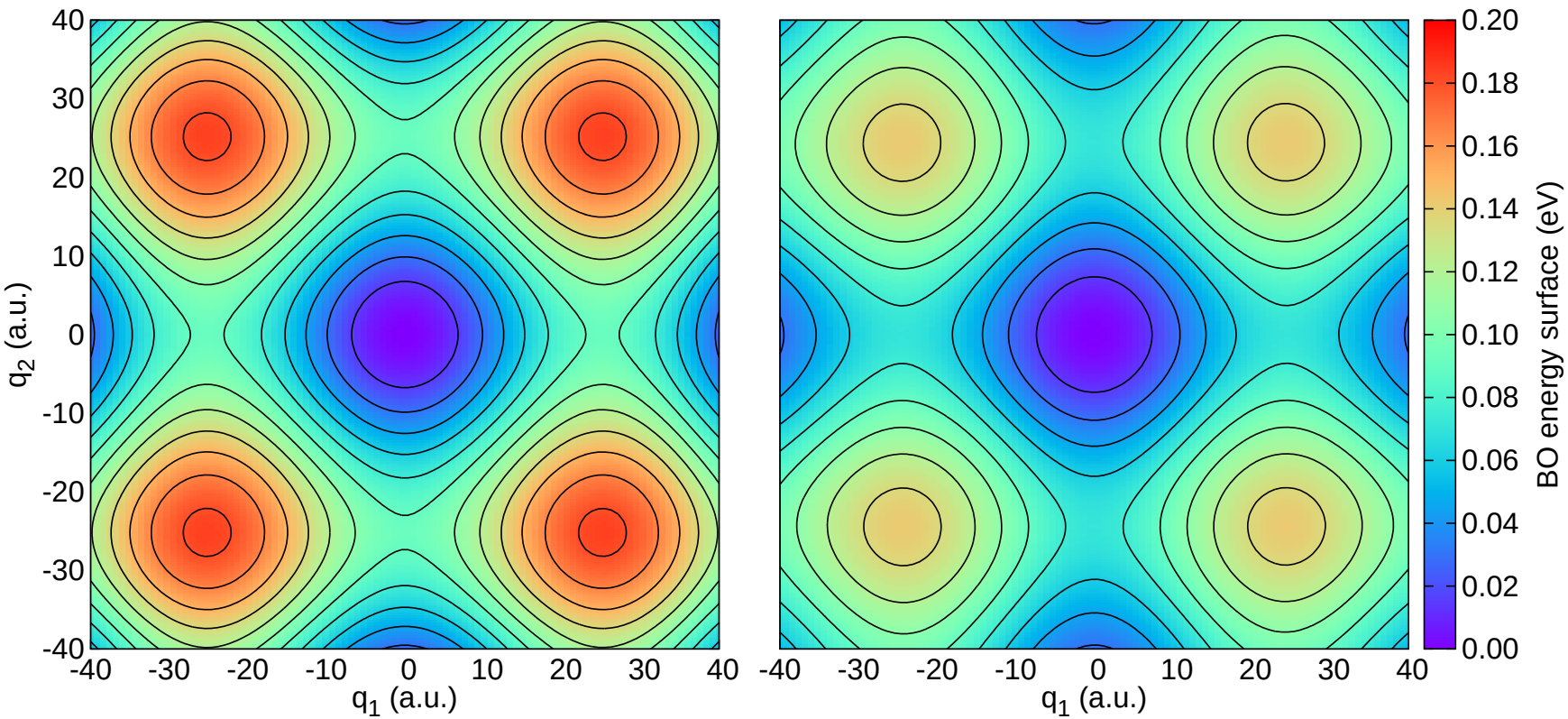


Vibrational self-consistent field equations

- Vibrational Schrödinger equation:

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

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

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

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

Second order perturbation theory

- Second order perturbation theory (similar to MP2).
- Measures the accuracy of the mean-field approach.
- So far small MP2 corrections.
- Can use other methods: whole electronic structure hierarchy.

Anharmonic free energy

- Anharmonic vibrational excited states:

$$|\Phi^{\mathbf{S}}(\mathbf{q})\rangle = \prod_{\mathbf{k},s} |\phi_{\mathbf{k}s}^{S_{\mathbf{k}s}}(q_{\mathbf{k}s})\rangle$$

  where $\mathbf{S}$ is a vector with elements $S_{\mathbf{k}s}$.

- Anharmonic free energy:

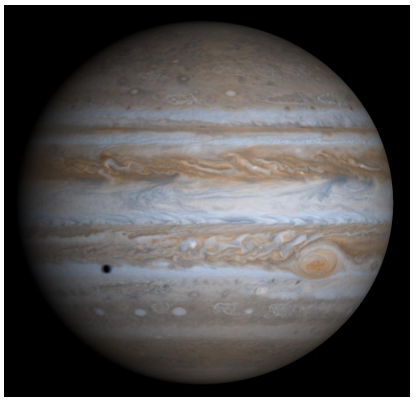
$$\mathcal{F}_{\text{anh}} = -\frac{1}{\beta} \ln \sum_{\mathbf{S}} e^{-\beta E_{\mathbf{S}}}$$

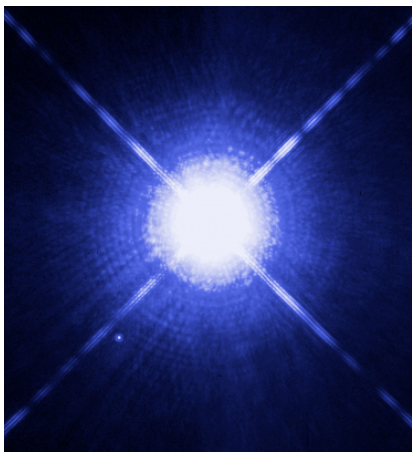
  Single calculation for insulators.

Outline

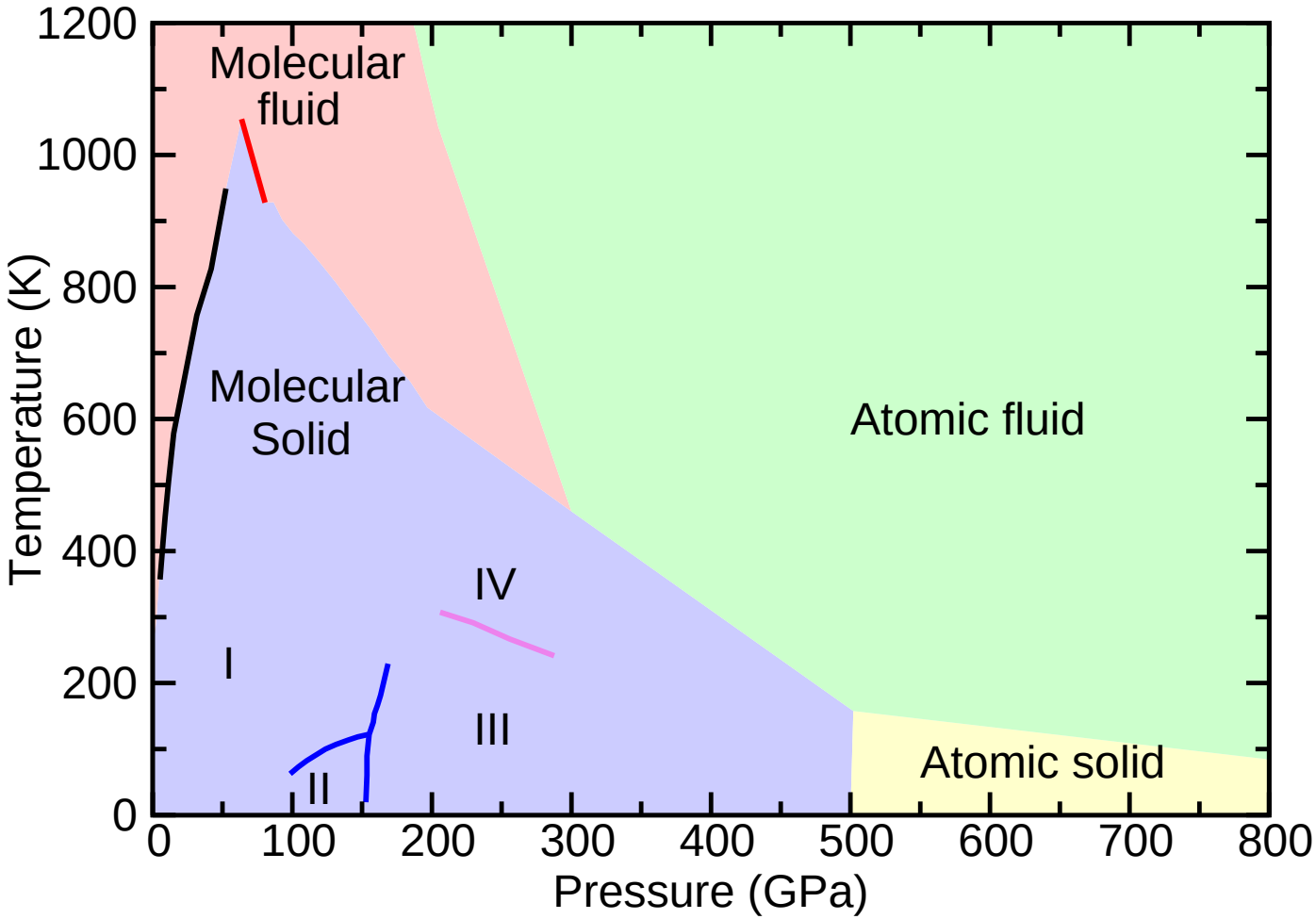
Solid hydrogen

- Most abundant element in the Universe.
- Hydrogen at high pressure in planetary interiors and stars.
- Possibility of exotic phases: high-temperature superconductivity, zero-temperature quantum fluid, ...



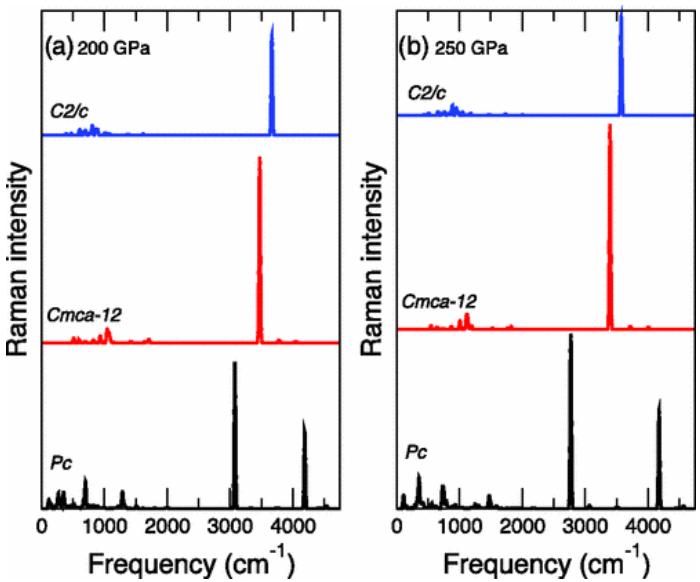


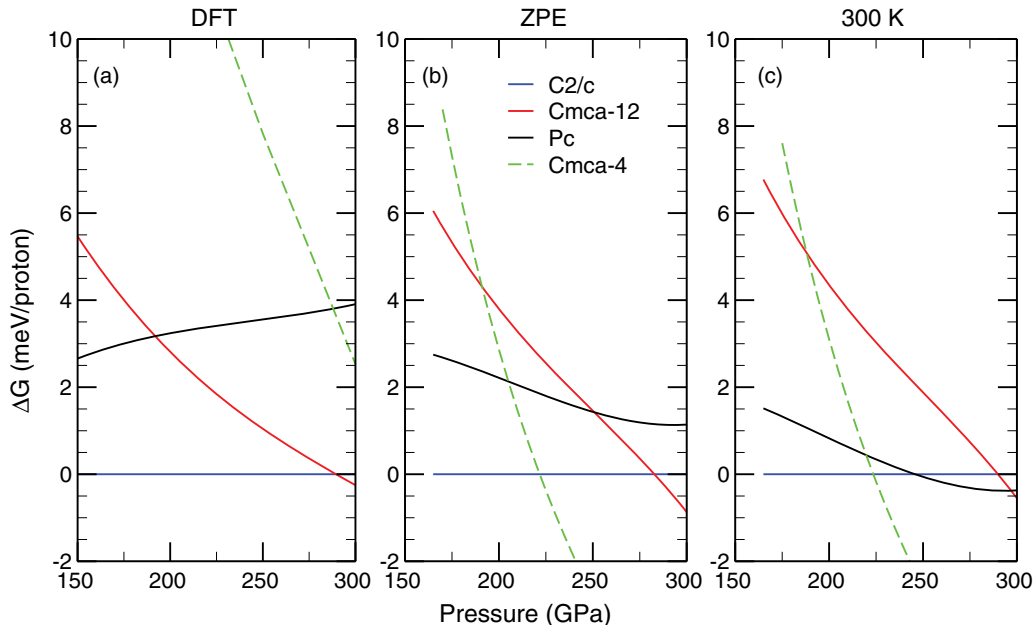
The phase diagram of high pressure hydrogen



↦ Goncharov *et al.*, Phys. Rev. Lett. **80**, 101 (1998)
↦ Datchi *et al.*, Phys. Rev. B **61**, 6535 (2000)
↦ Gregoryanz *et al.*, Phys. Rev. Lett. **90**, 175701 (2003)
↦ Deemyad and Silvera, Phys. Rev. Lett. **100**, 155701 (2008)
↦ Howie *et al.*, Phys. Rev. Lett. **108**, 125501 (2012)

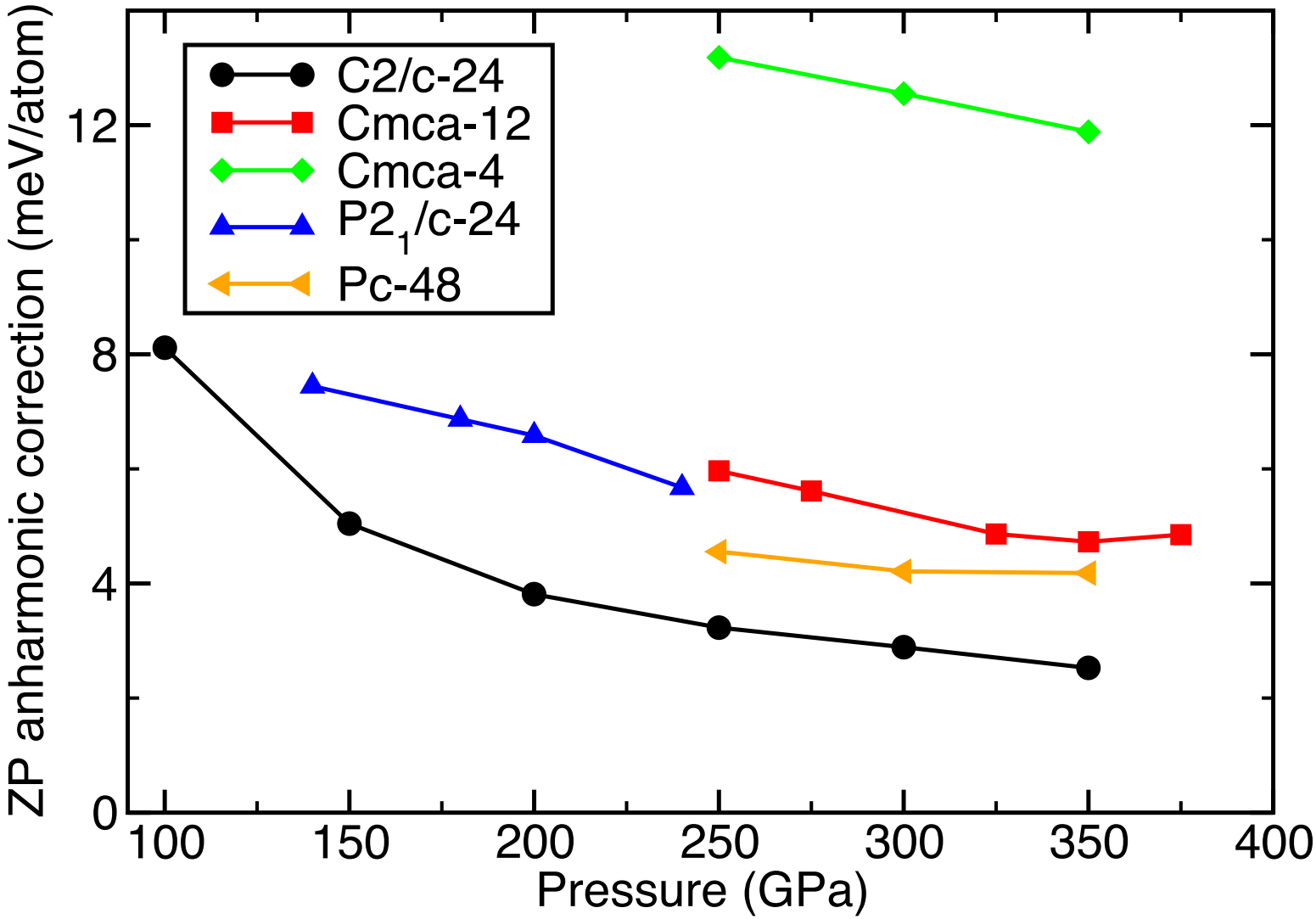
The determination of phase IV





↦ Pickard, Martinez-Canales, and Needs, Phys. Rev. B **85**, 214114 (2012)
↦ Pickard, Martinez-Canales, and Needs, Phys. Rev. B **86**, 059902 (2012)

Anharmonic vibrations in solid molecular hydrogen



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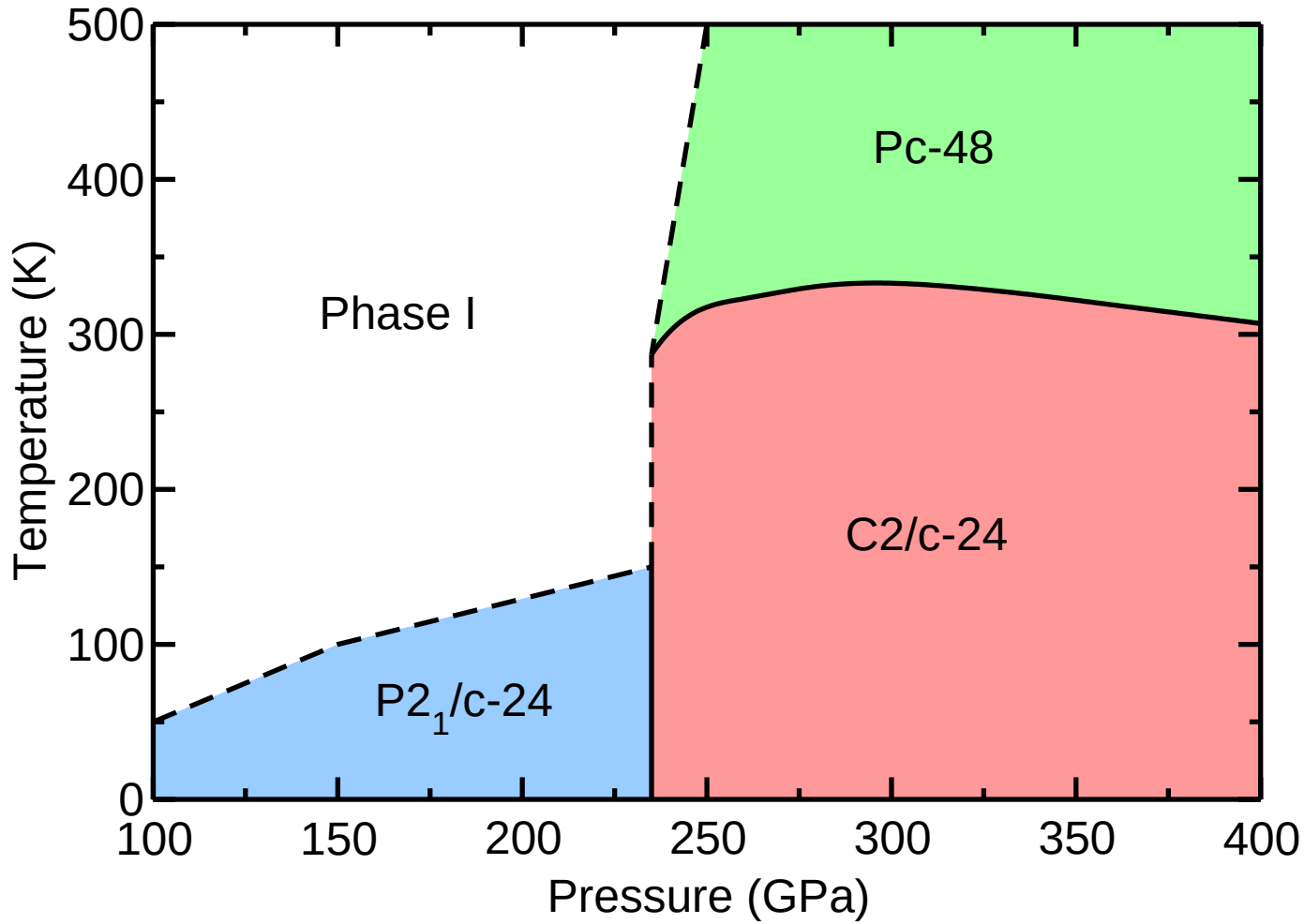
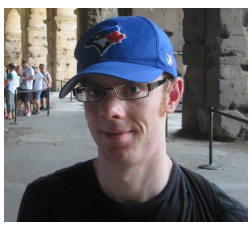




Lloyd-Williams, Monserrat, López Ríos, Drummond, and Needs

See talk on Tuesday at 12:00am:

DFT and QMC calculations of solid molecular hydrogen

Why are snowflakes hexagonal?

$-30°\mathrm{C}$

$-25°\mathrm{C}$

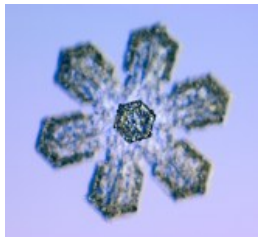
$-20°\mathrm{C}$

$-15°\mathrm{C}$

$-10°\mathrm{C}$

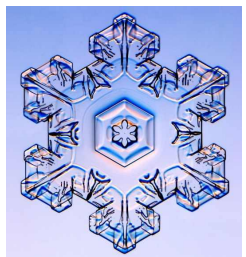
$-5°\mathrm{C}$

$0°\mathrm{C}$



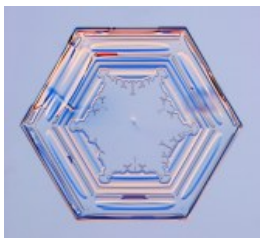
Plates and columns

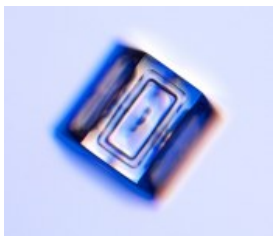
$T < -22°\mathrm{C}$



Plates

$-22°\mathrm{C} < T < -10°\mathrm{C}$





Columns

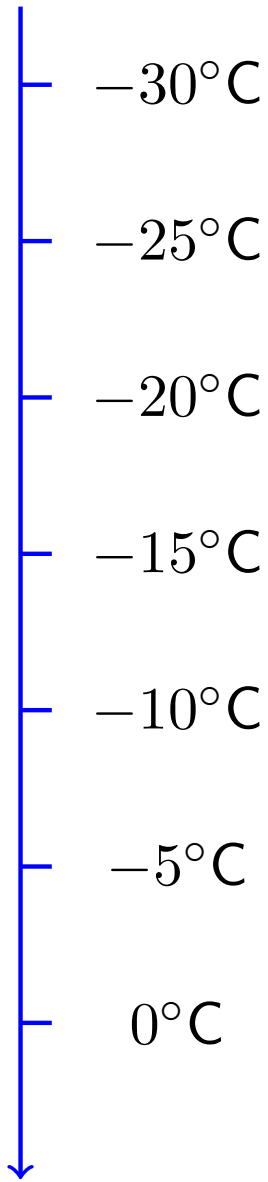
$-10°\mathrm{C} < T < -4°\mathrm{C}$

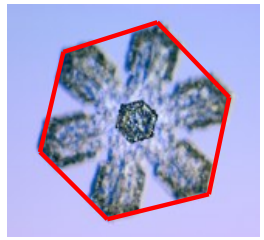
Plates

$-4°\mathrm{C} < T < 0°\mathrm{C}$

Pictures by Kenneth G. Libbrecht (SnowCrystals.com)

Why are snowflakes hexagonal?





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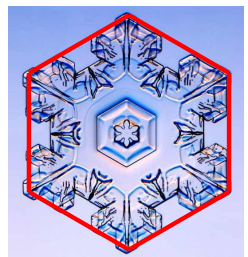

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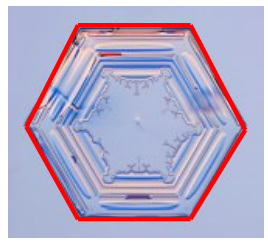

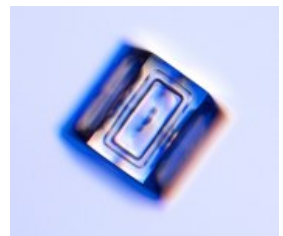

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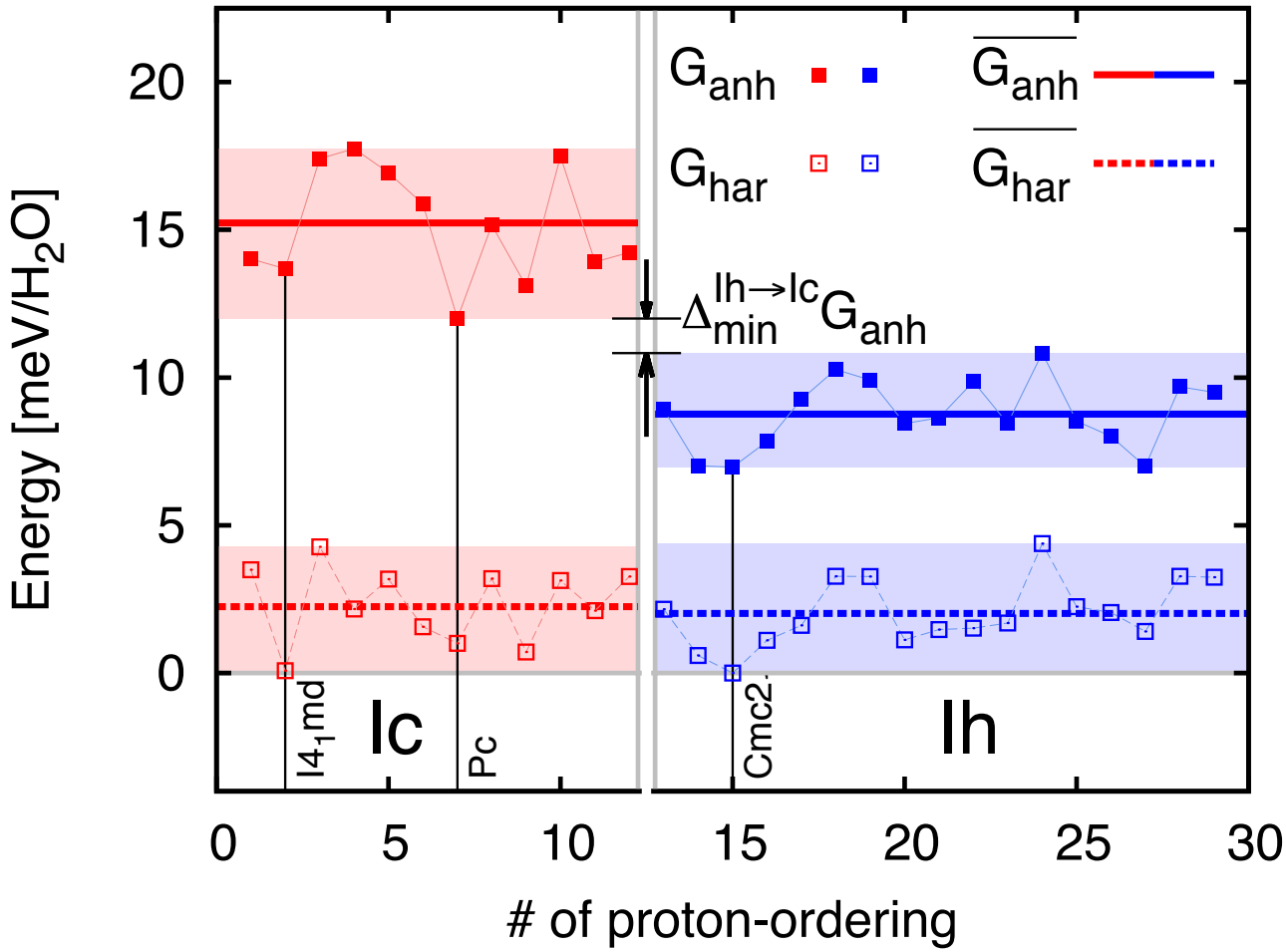
The relative stability of hexagonal and cubic ice



Engel, Monserrat, and Needs

See talk on Wednesday at 12:00am:

Anharmonic nuclear motion and the relative stability of hexagonal and cubic ice

Outline

Vibrational coupling to generic physical observables

$$\langle \mathcal{A} \rangle = \langle \Phi(\mathbf{q}) | \mathcal{A}(\mathbf{q}) | \Phi(\mathbf{q}) \rangle$$

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Vibrational coupling to generic physical observables

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- Vibrational wave function: harmonic or anharmonic
- Observable coupling:
  - Expansion:

$$\mathcal{A}(\mathbf{q}) = \sum_{n,\mathbf{k}} a^{(1)}_{n\mathbf{k}} q_{n\mathbf{k}} + \sum_{n,\mathbf{k}} \sum_{n',\mathbf{k}'} a^{(2)}_{n\mathbf{k};n'\mathbf{k}'} q_{n\mathbf{k}} q_{n'\mathbf{k}'} + \cdots$$

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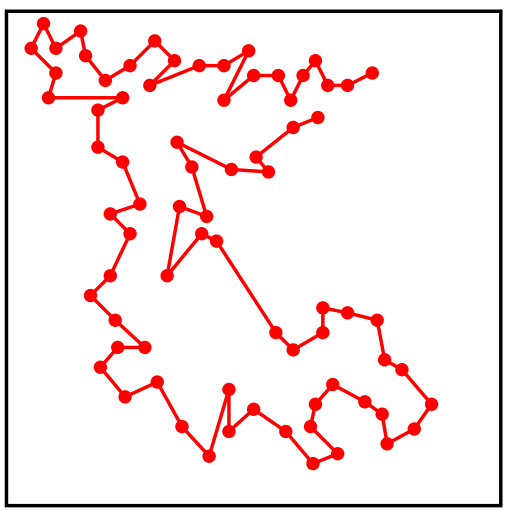
  - Monte Carlo sampling
- Examples: electronic band gaps, chemical shielding tensor

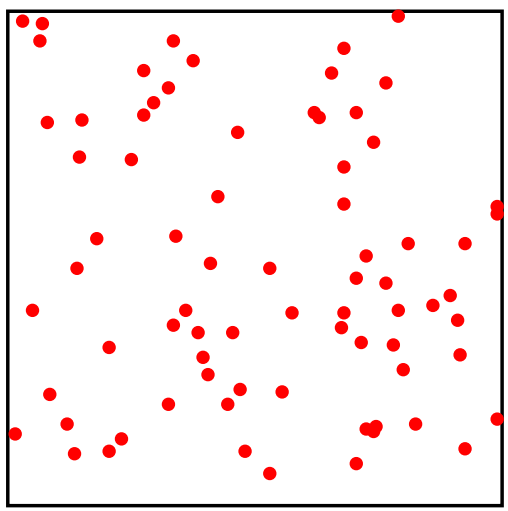
Vibrational phase space sampling

$$\langle \mathcal{A} \rangle = \langle \Phi(\mathbf{q}) | \mathcal{A}(\mathbf{q}) | \Phi(\mathbf{q}) \rangle$$

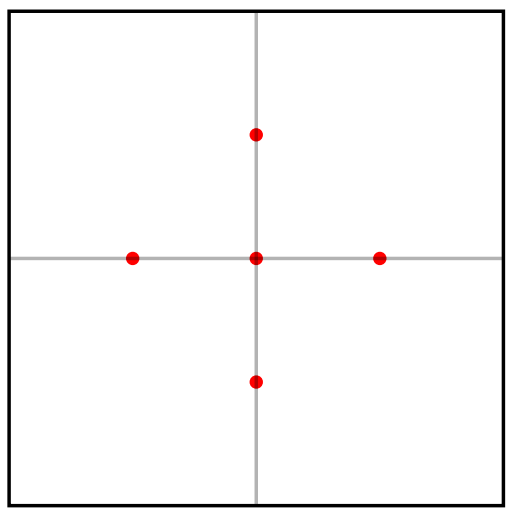
MD/PIMD



Random



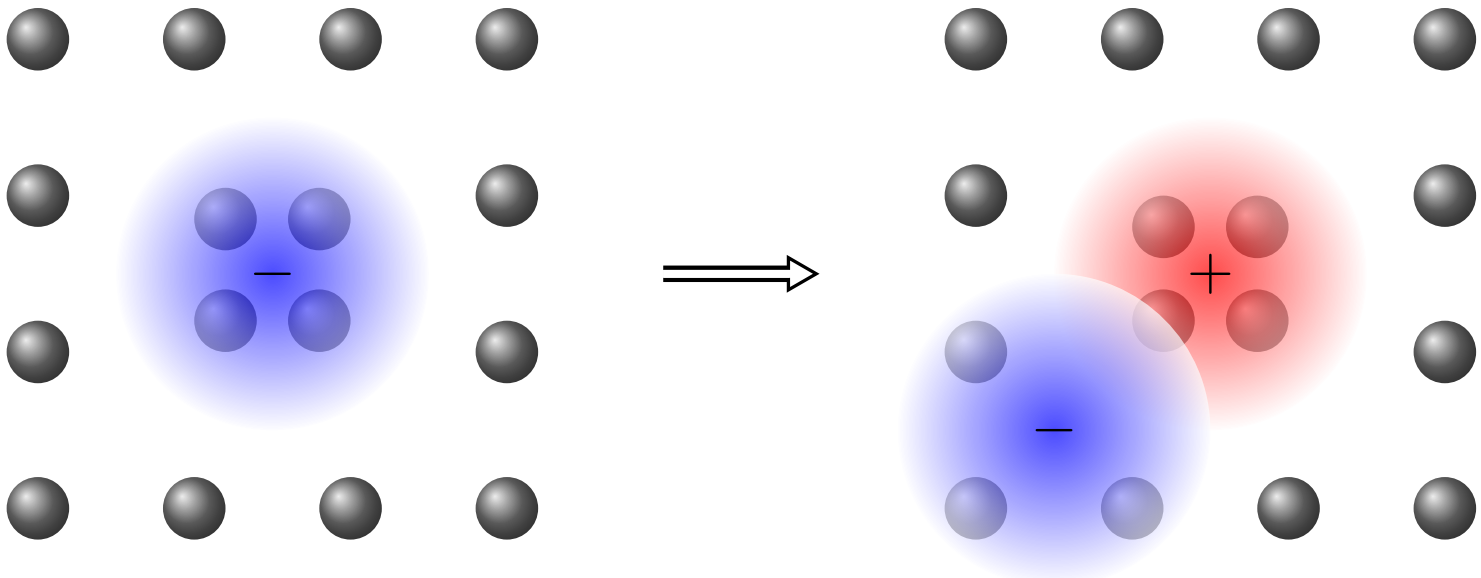
Quadratic



Outline

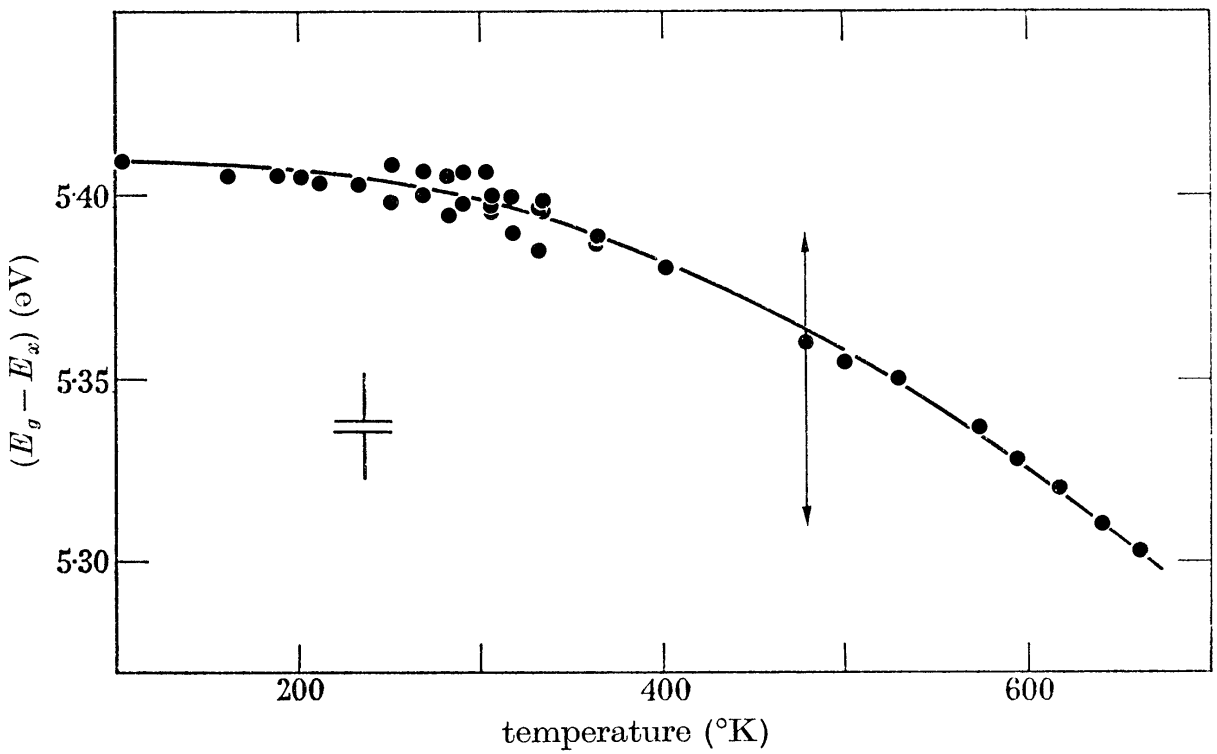
Electron-phonon coupling in condensed matter

- Coupling to form Cooper pairs in standard superconductivity



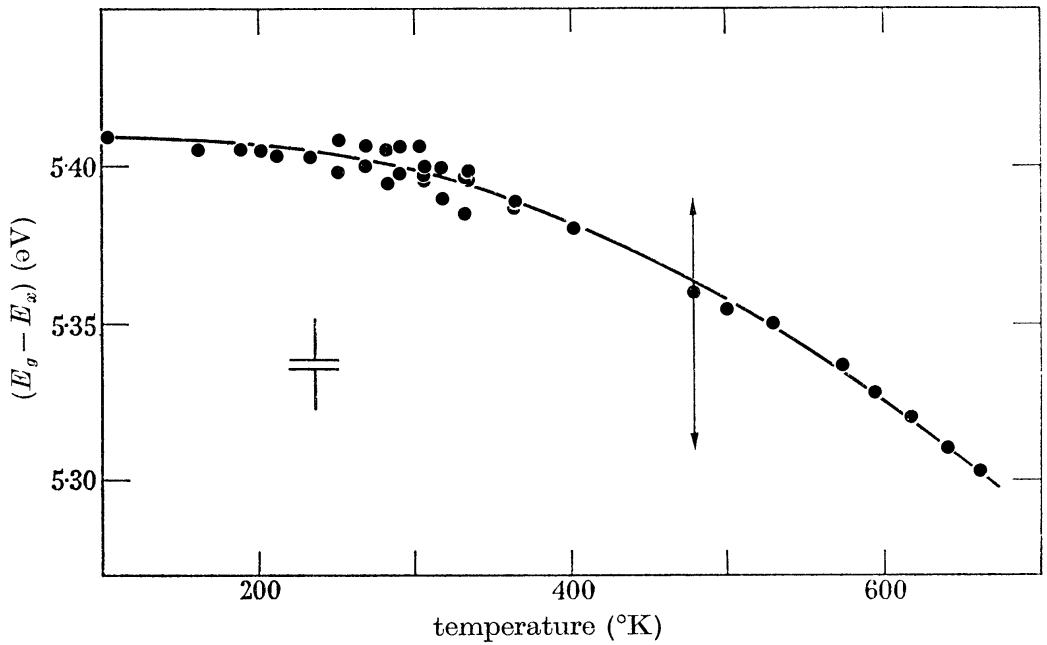
Electron-phonon coupling in condensed matter

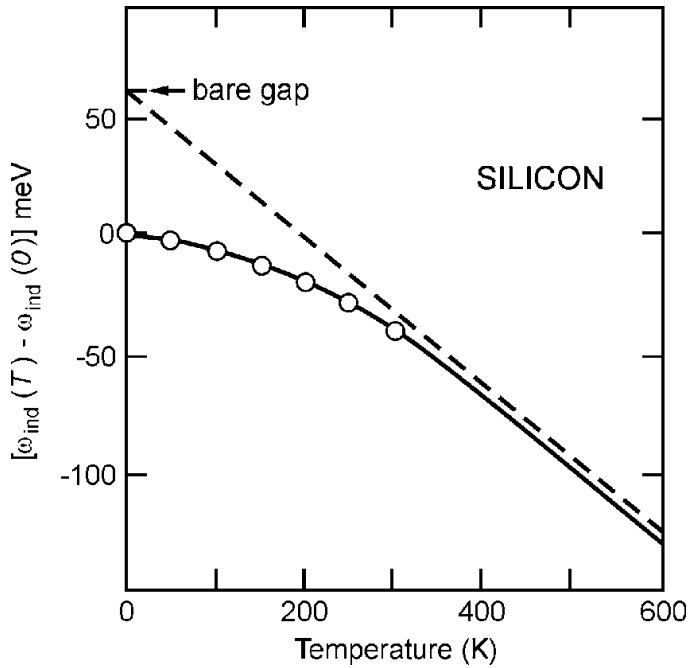
- Coupling to form Cooper pairs in standard superconductivity
- Temperature dependence of band gaps in semiconductors



↦ Clark, Dean, and Harris, Proc. R. Soc. Lond. A **277**, 312 (1964)

Electron-phonon coupling in diamond and silicon



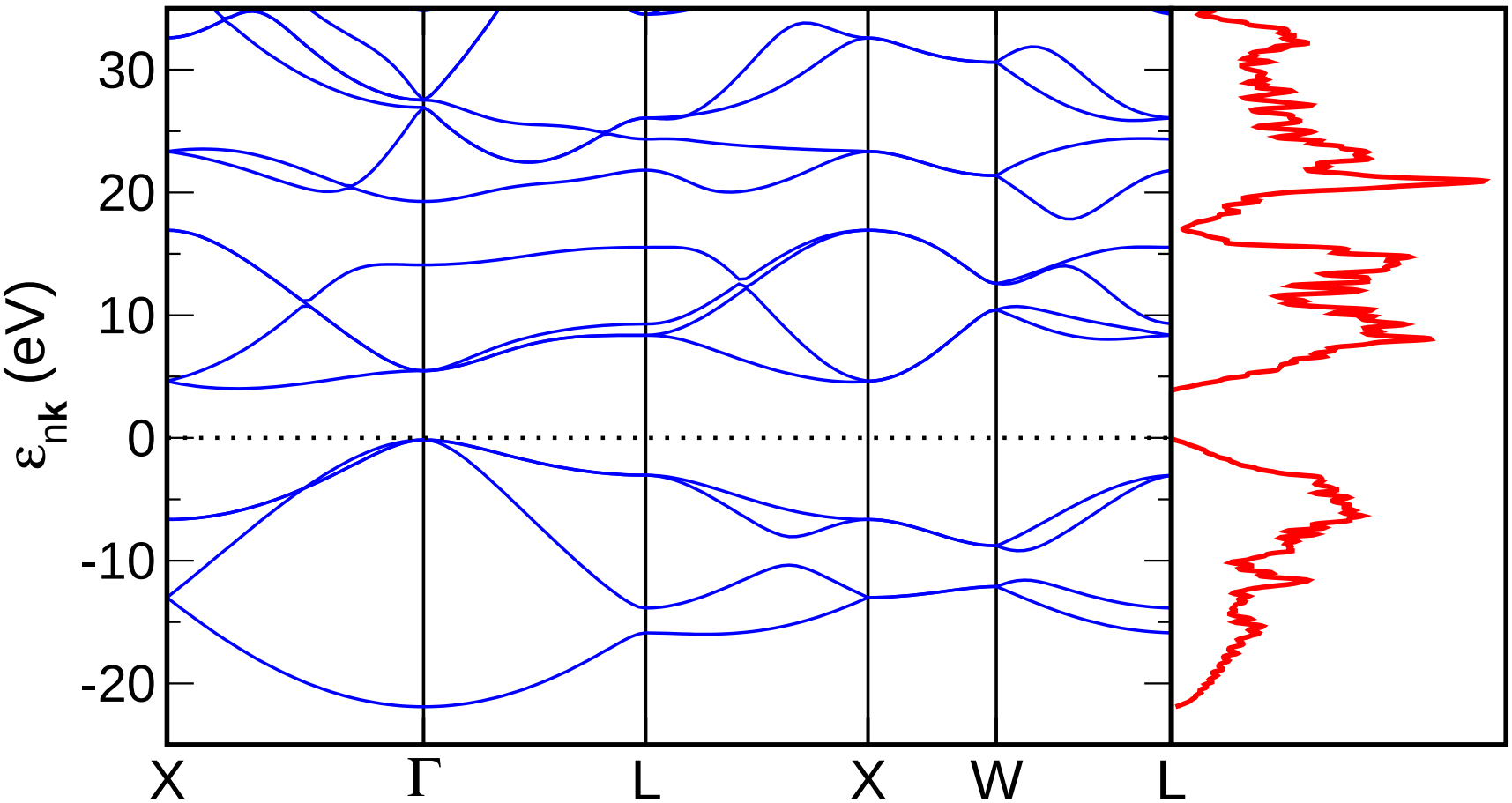


ZP band gap corrections:

- Silicon: -53 meV
- Diamond: about -370 meV

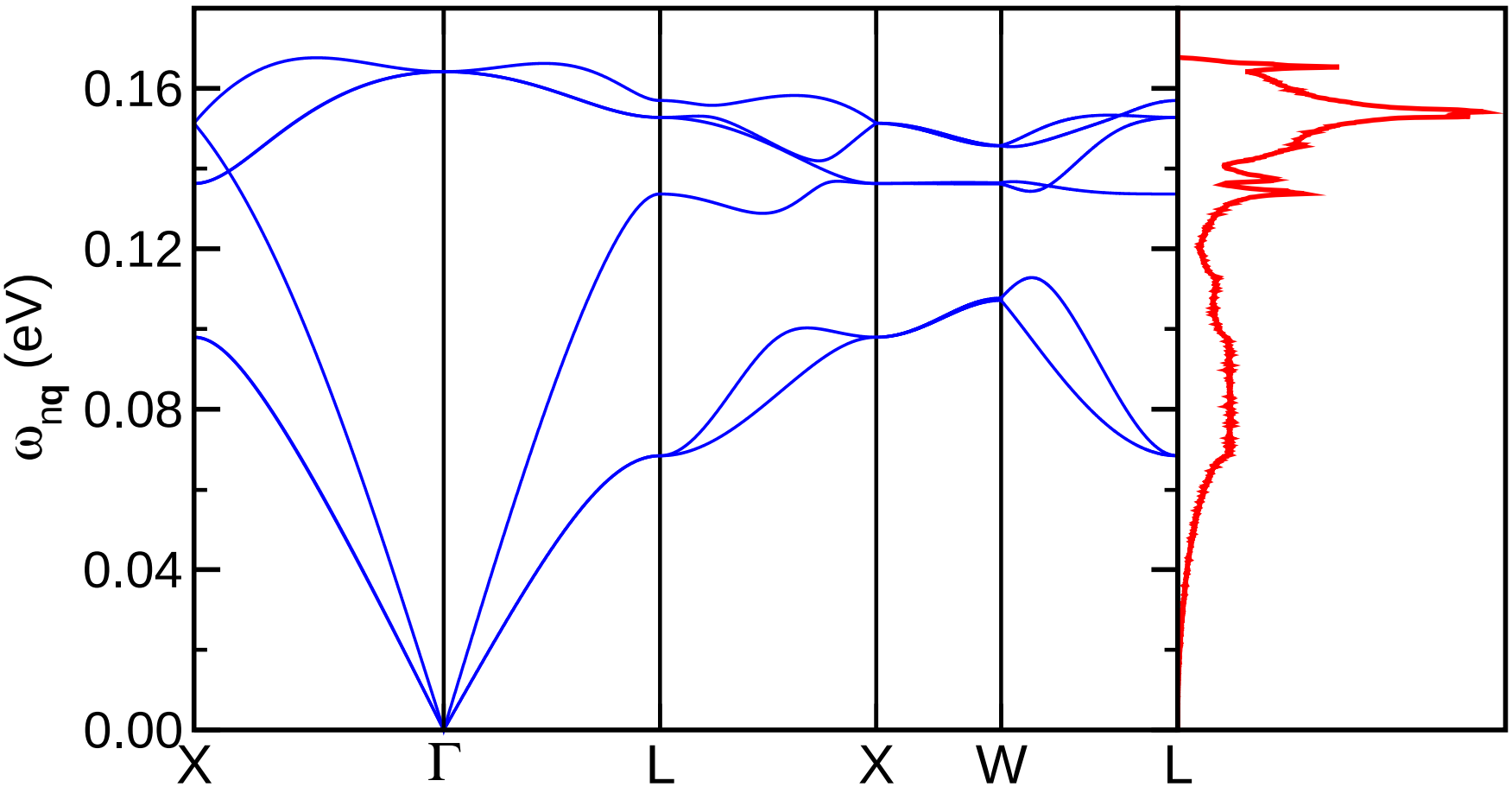
↦ Clark, Dean, and Harris, Proc. R. Soc. Lond. A **277**, 312 (1964)
↦ Cardona, Solid State Comm. **133**, 3 (2005)

Diamond band structure



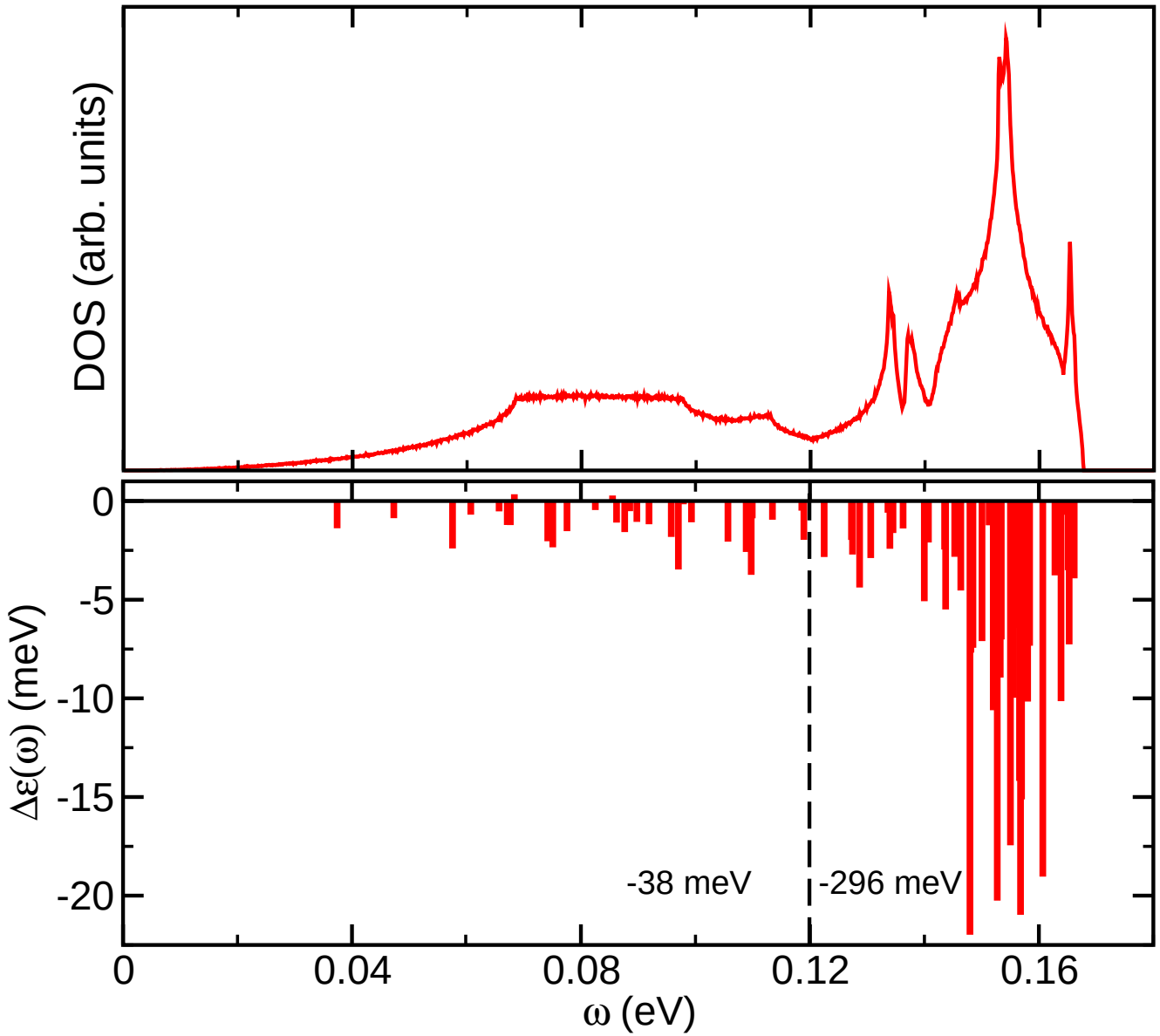
↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

Diamond phonon dispersion



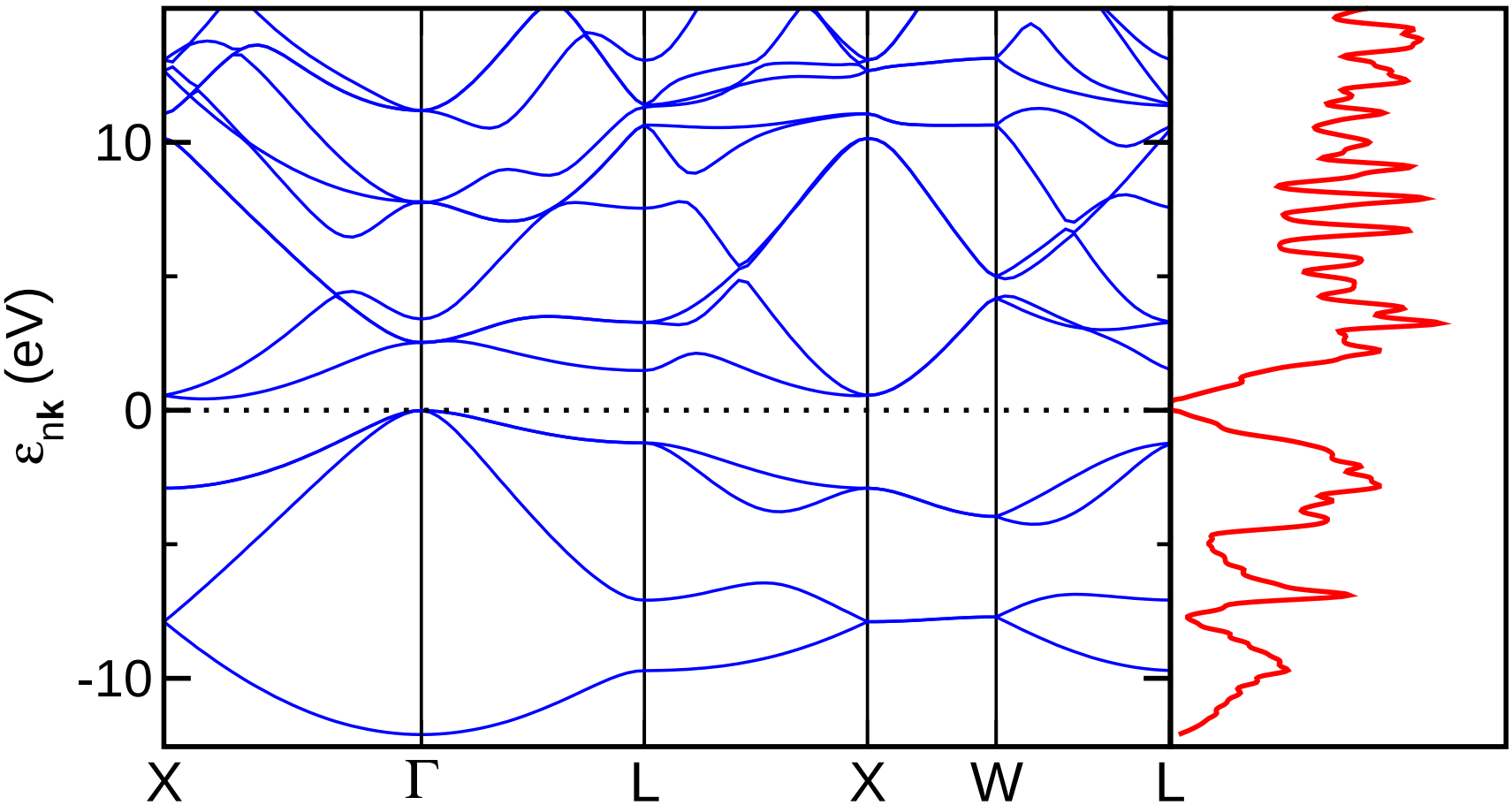
↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

Diamond electron-phonon coupling



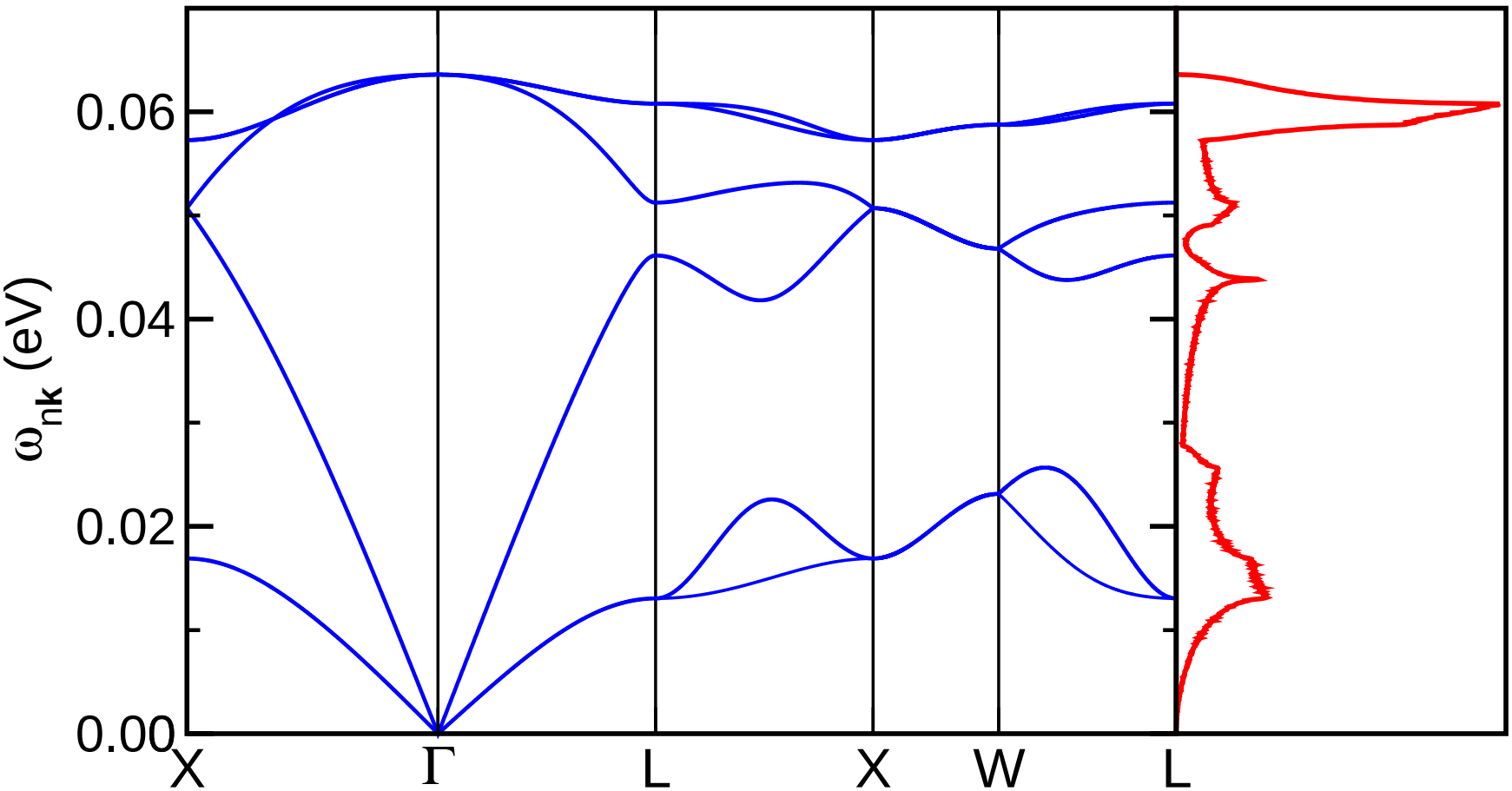
↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

Silicon band structure



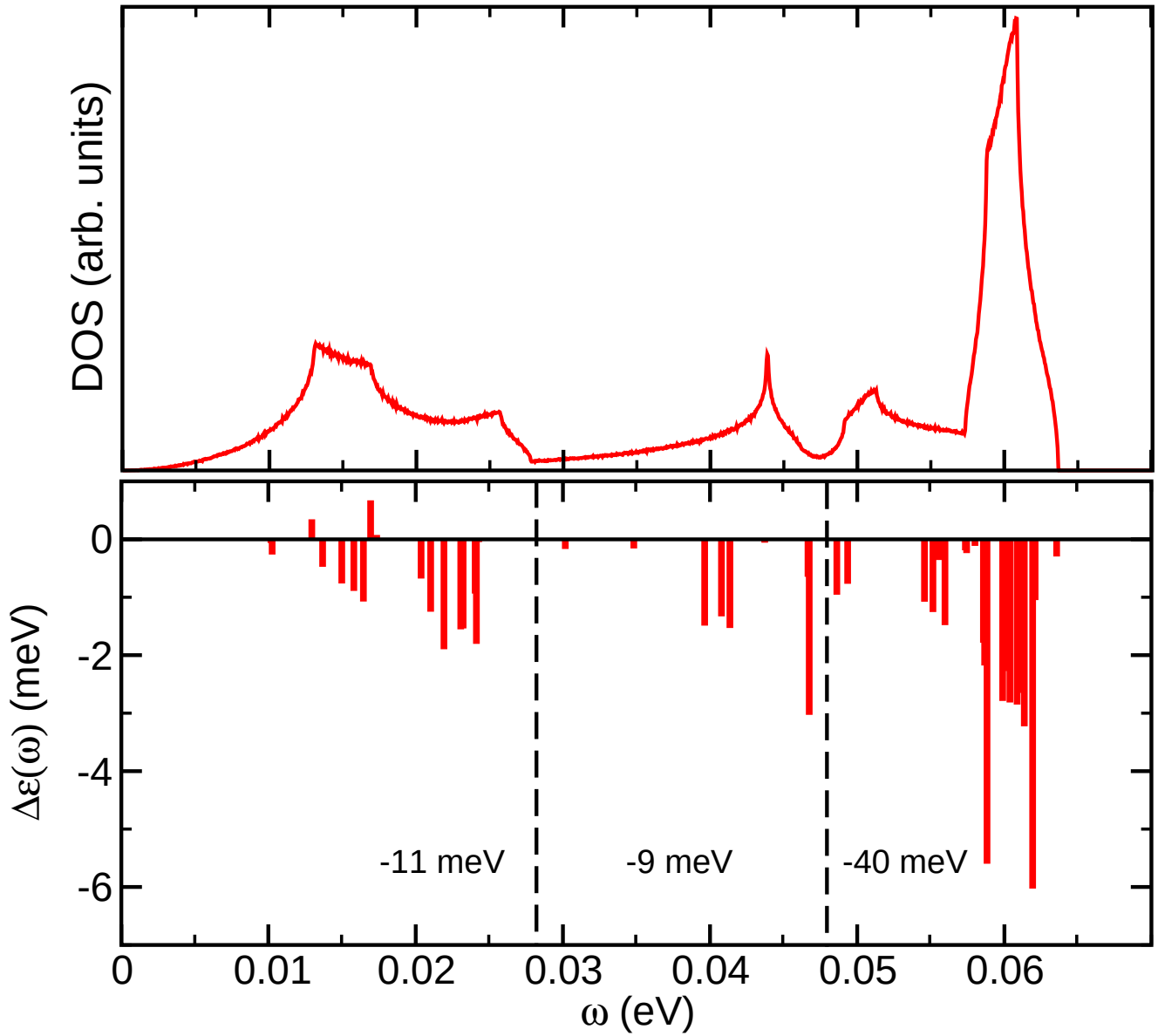
↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

Silicon phonon dispersion



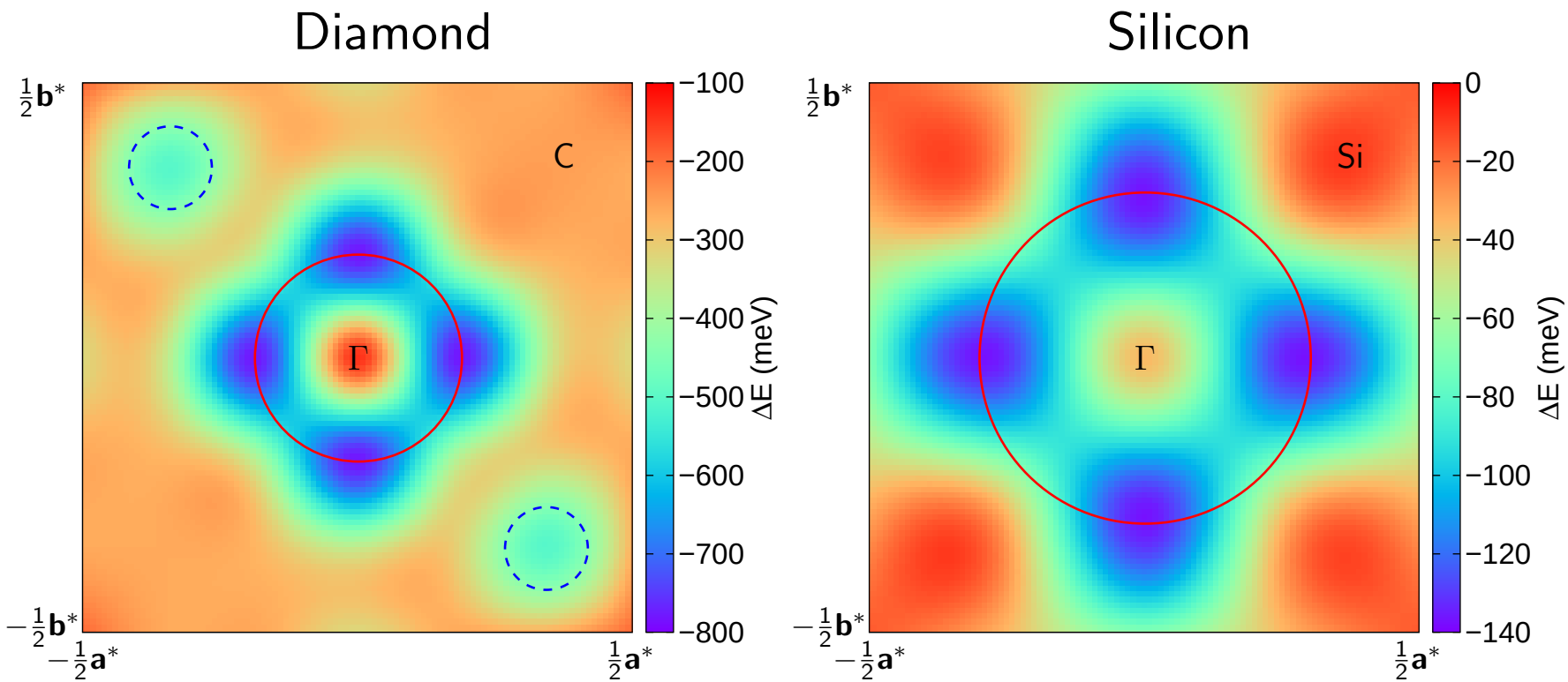
↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

Silicon electron-phonon coupling



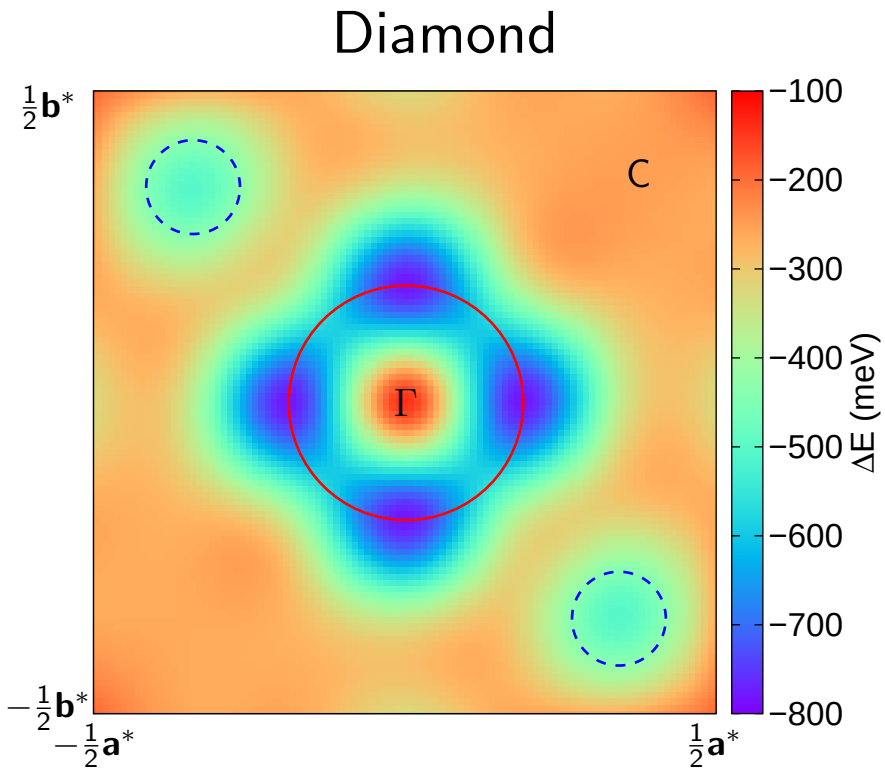
↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

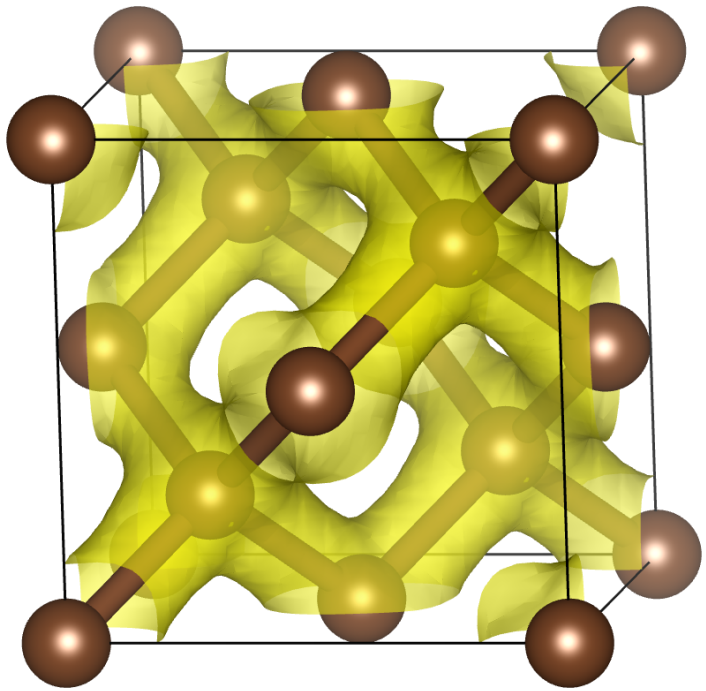
Electron-phonon coupling in diamond and silicon



↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

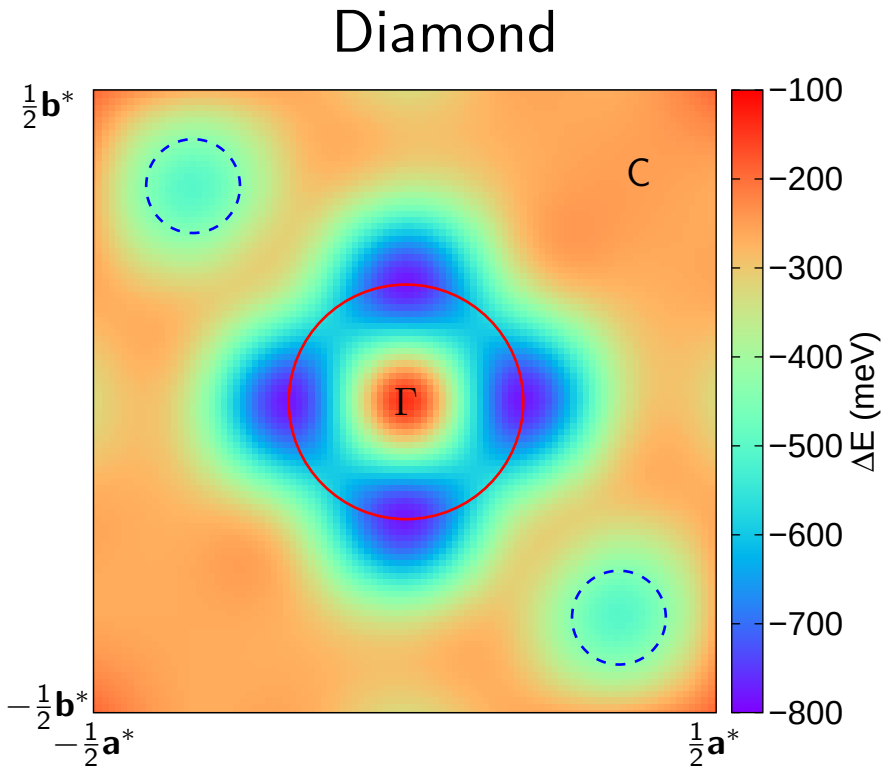
Electron-phonon coupling in diamond and silicon

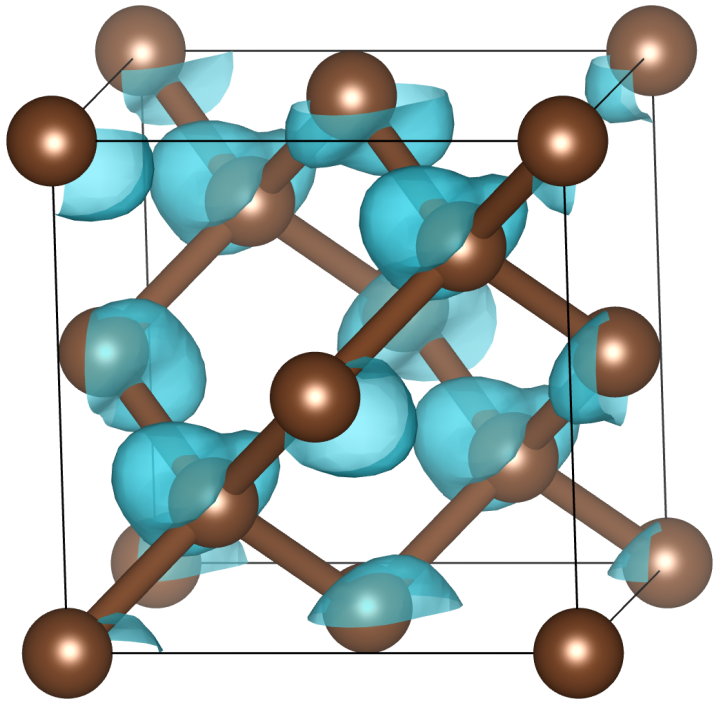




↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

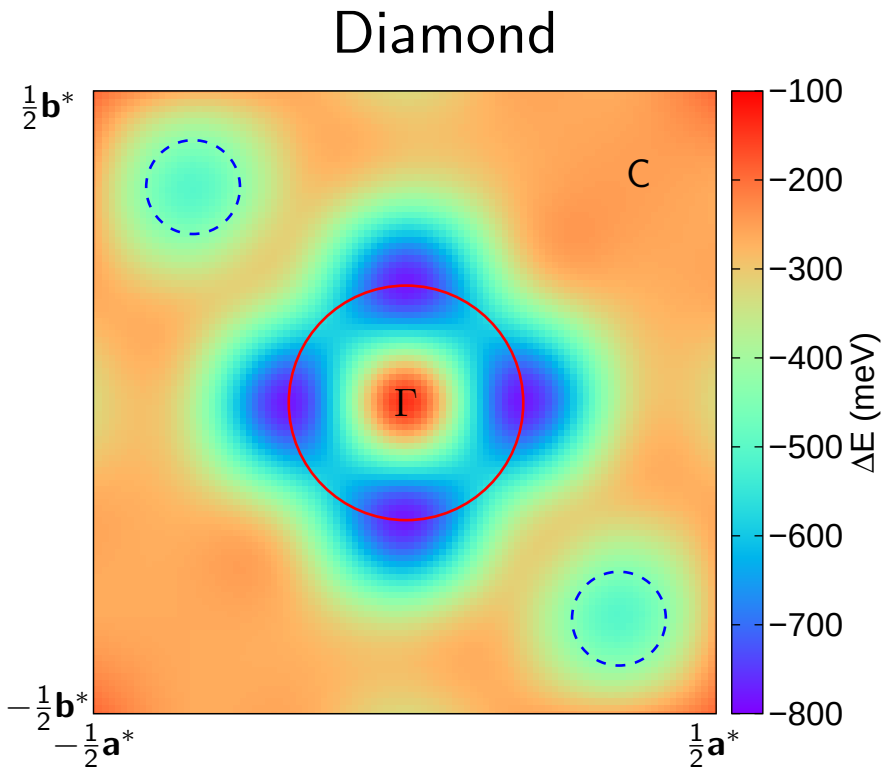
Electron-phonon coupling in diamond and silicon

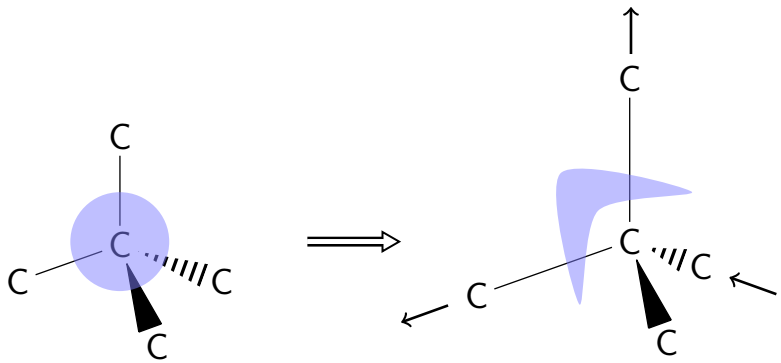




↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

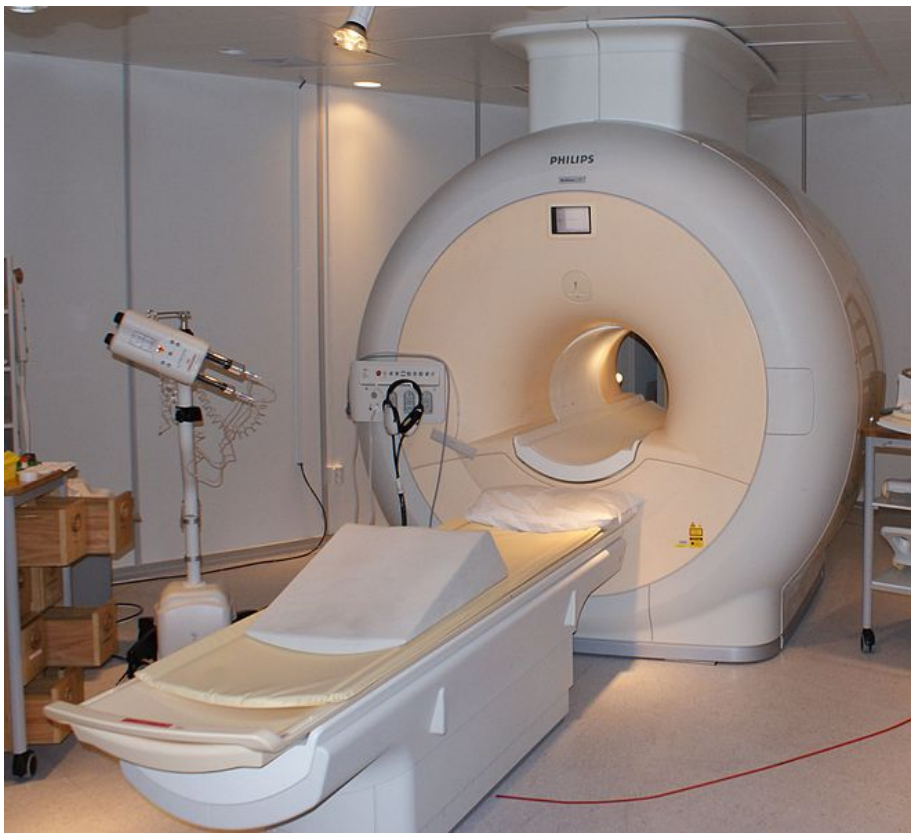
Electron-phonon coupling in diamond and silicon

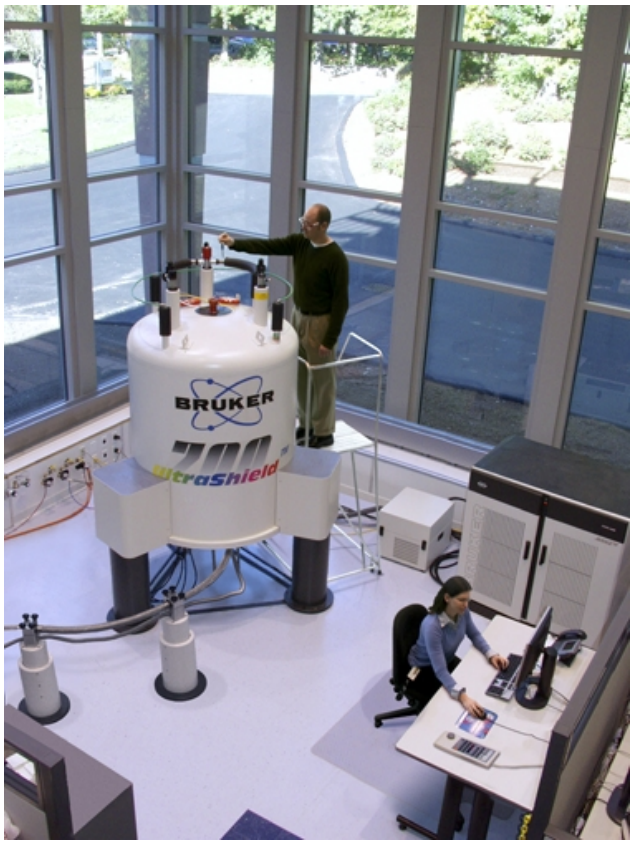




↦ Monserrat and Needs, Phys. Rev. B **89**, 214304 (2014)

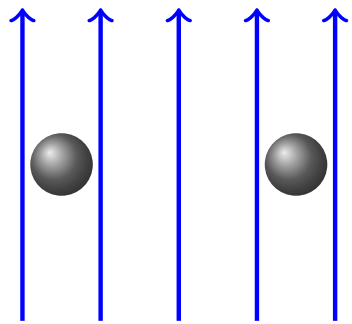
Nuclear magnetic resonance (NMR)





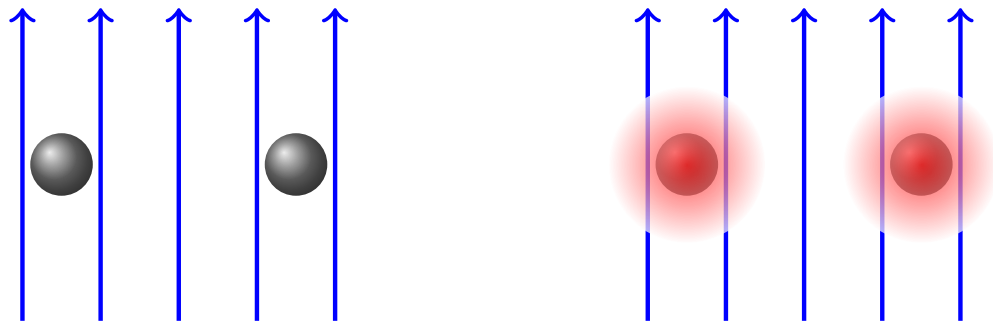
Nuclear magnetic resonance (NMR)

Magnetic field



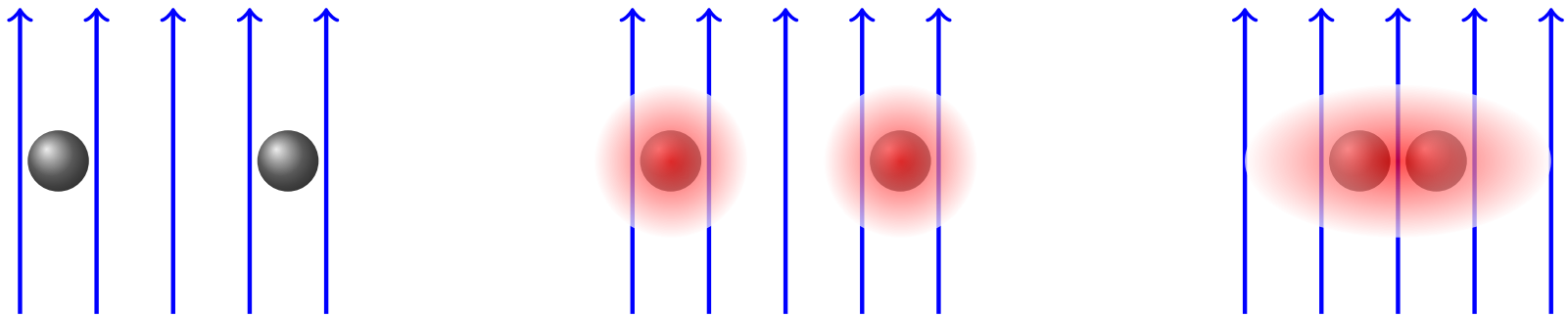
Nuclear magnetic resonance (NMR)

Magnetic field



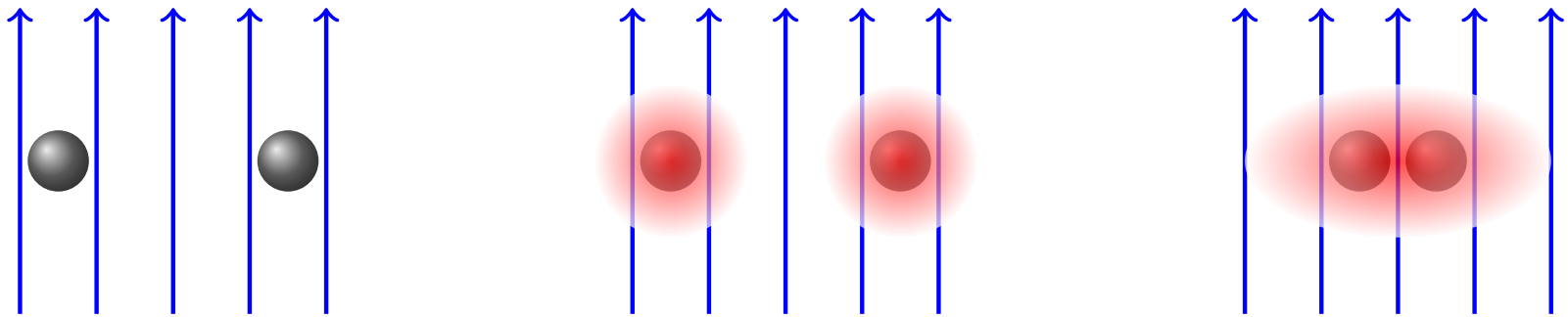
Nuclear magnetic resonance (NMR)

Magnetic field



Nuclear magnetic resonance (NMR)

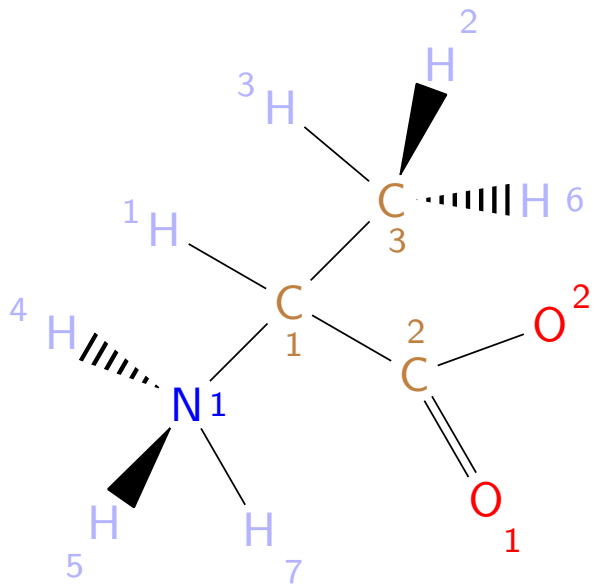
Magnetic field



$$\begin{aligned}
\mathbf{B} &= \mathbf{B}_{\text{ext}} - \mathbf{B}_{\text{ind}} = (\mathbf{1} - \boldsymbol{\sigma})\mathbf{B}_{\text{ext}} \\
\mathbf{B}_{\text{ind}} &= \boldsymbol{\sigma}\mathbf{B}_{\text{ext}} \\
\mathbf{B}_{\text{ind}}(\mathbf{r}) &= \frac{1}{c}\int \mathrm{d}^3\mathbf{r}'\mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}
\end{aligned}$$

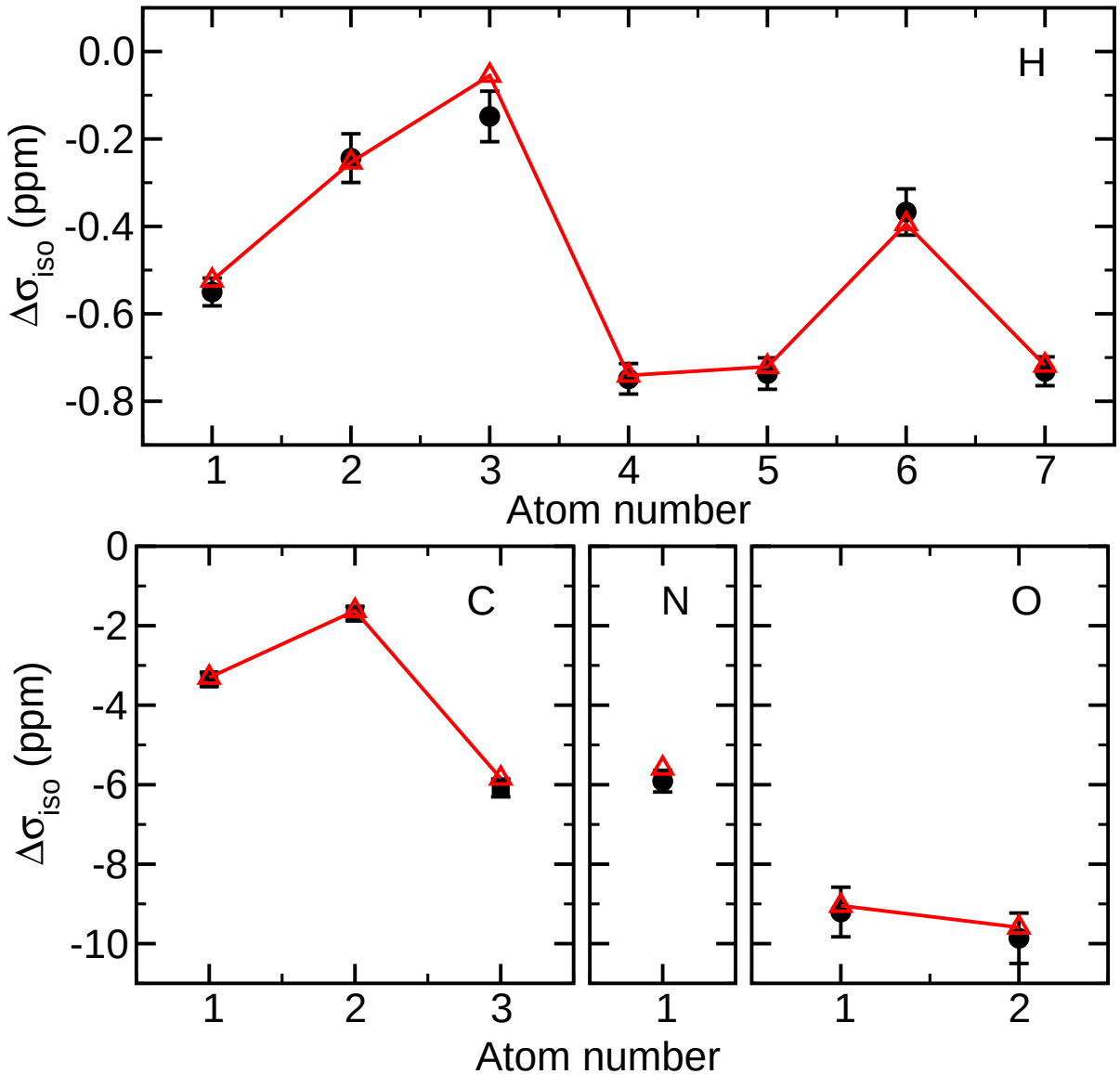
L-alanine molecular crystal

L-alanine

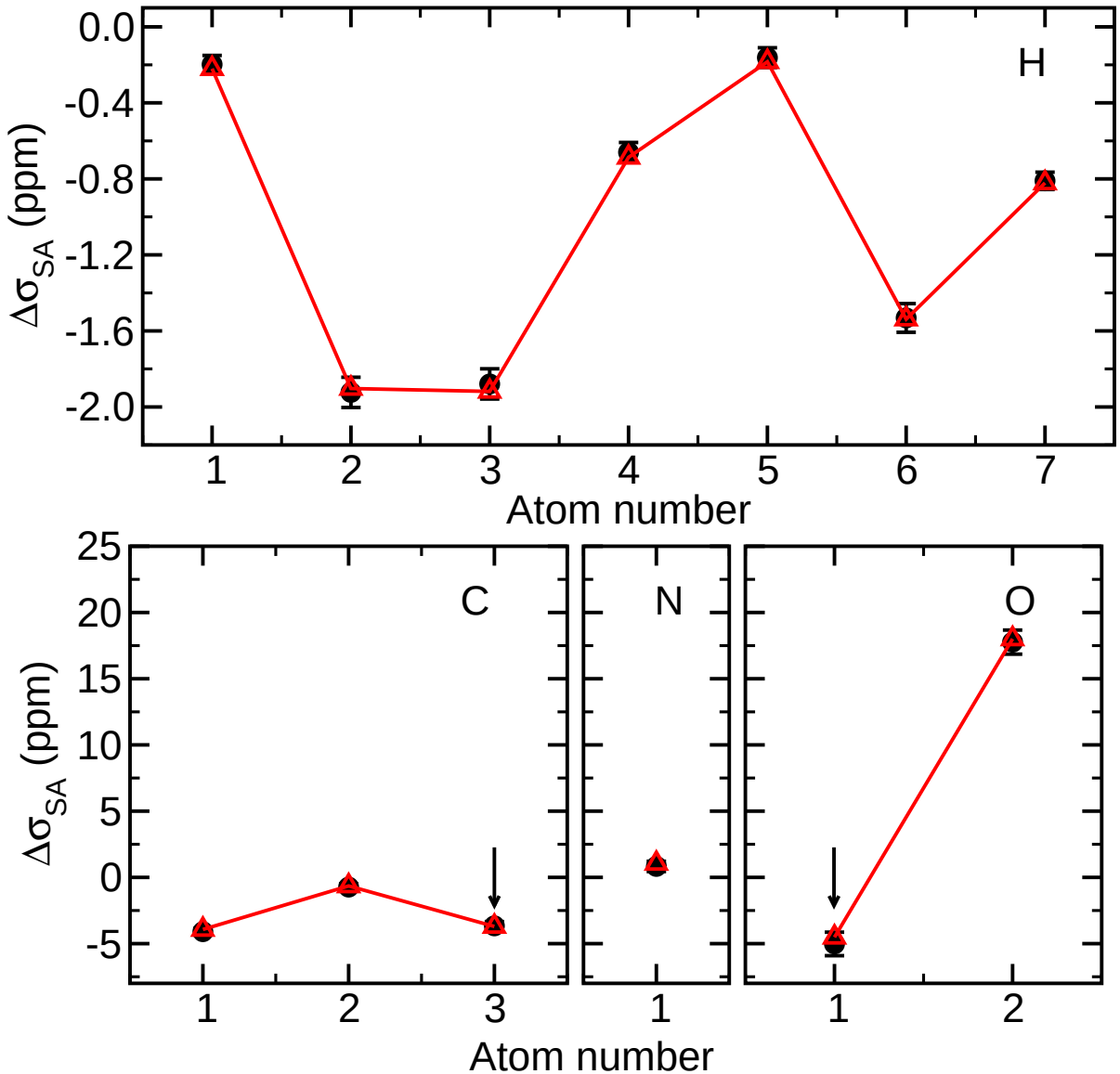


- Orthorhombic space group $P2_12_12_1$ (4 molecules).
- L-alanine ($C_3H_7NO_2$) has 52 atoms in the primitive cell.

Isotropic shift

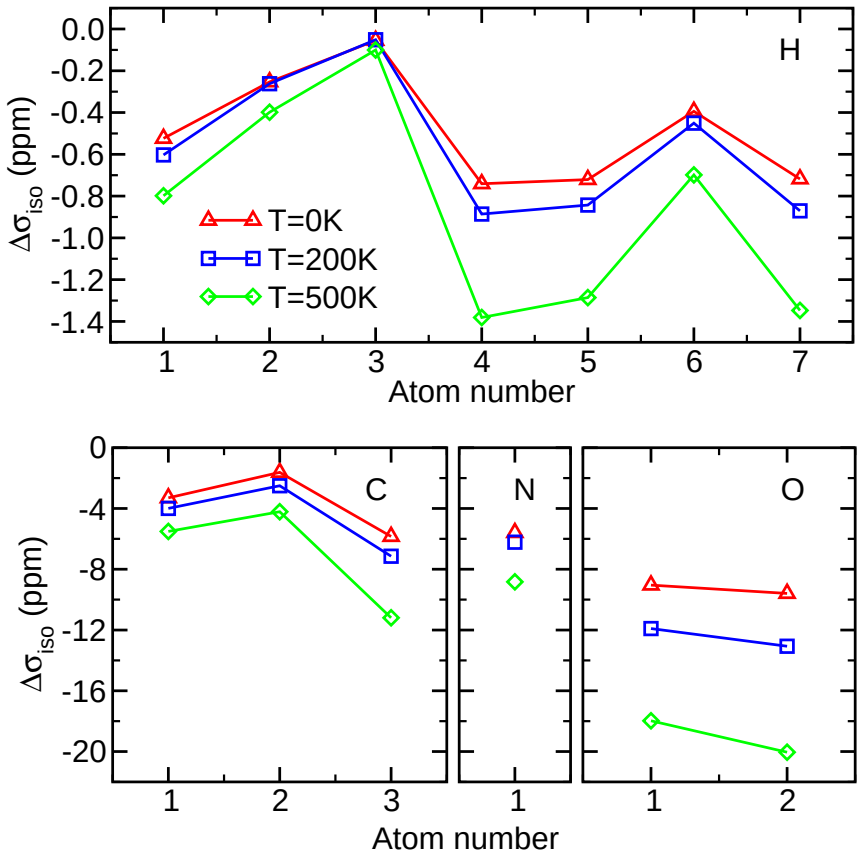


Shielding anisotropy

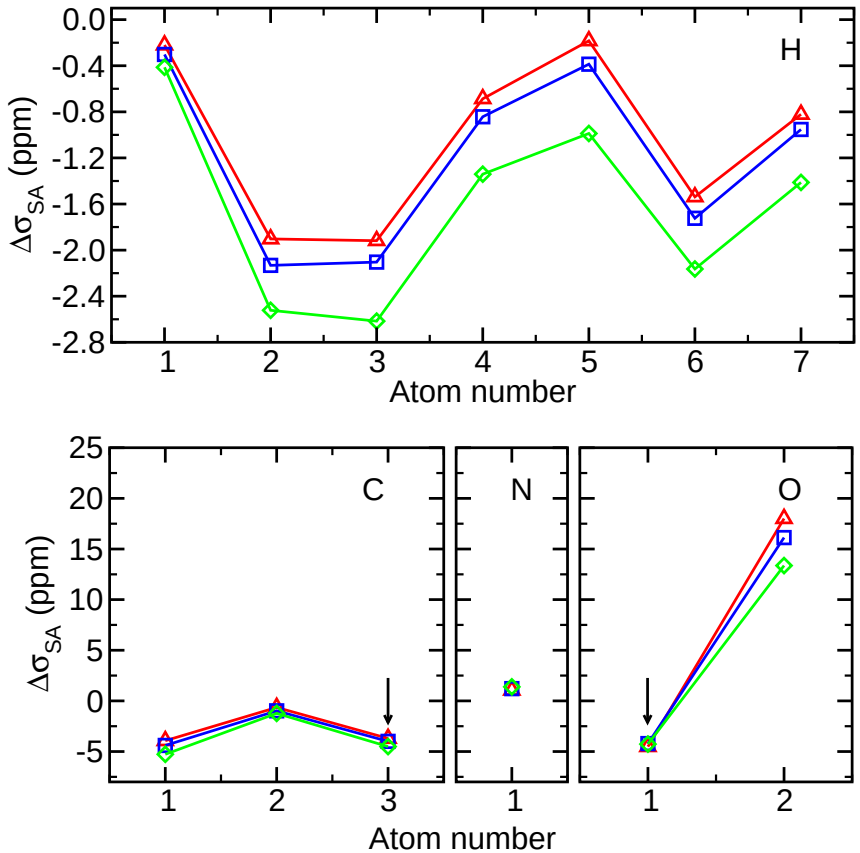


Temperature dependence

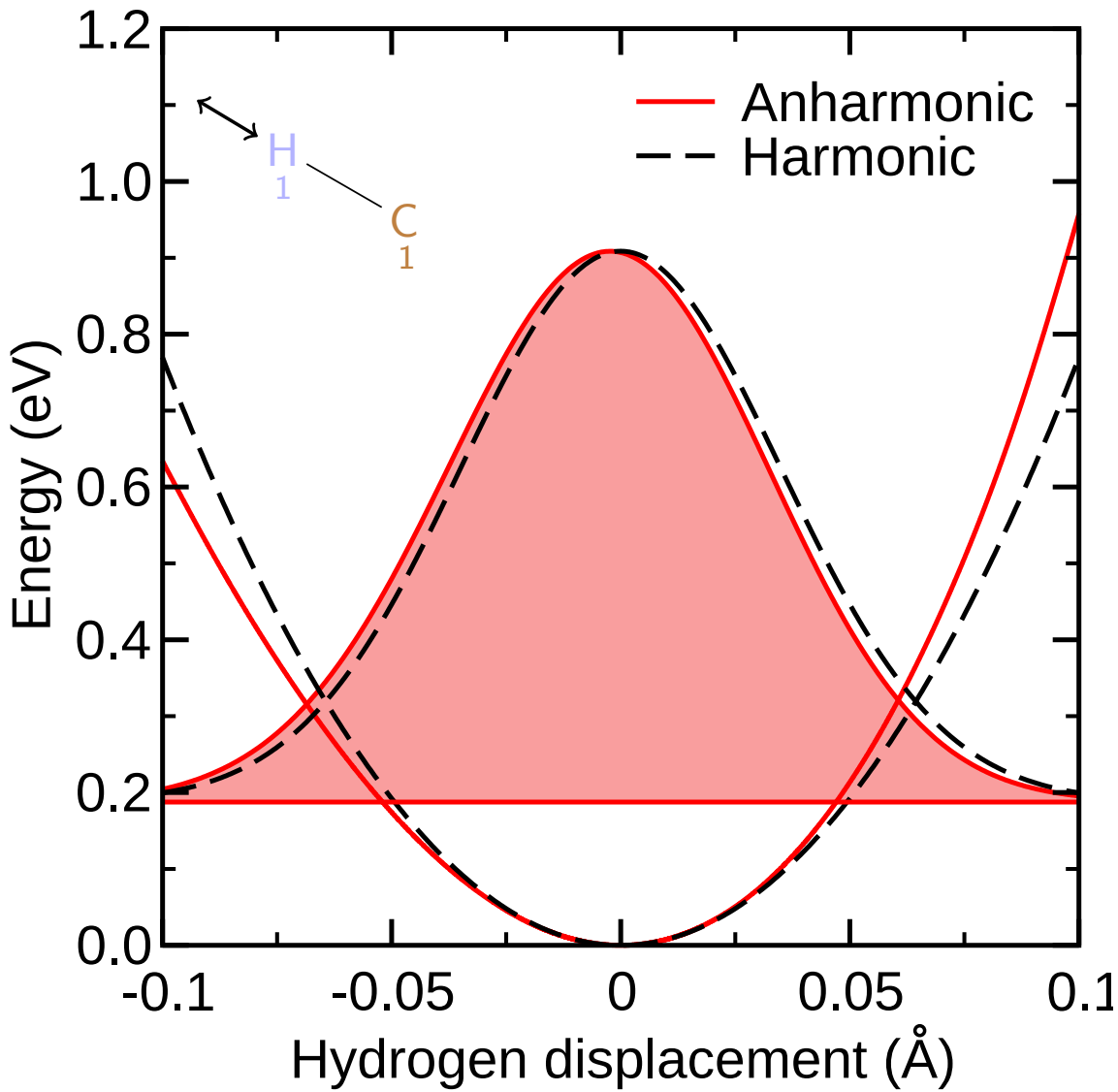
Isotropic shift



Shielding anisotropy

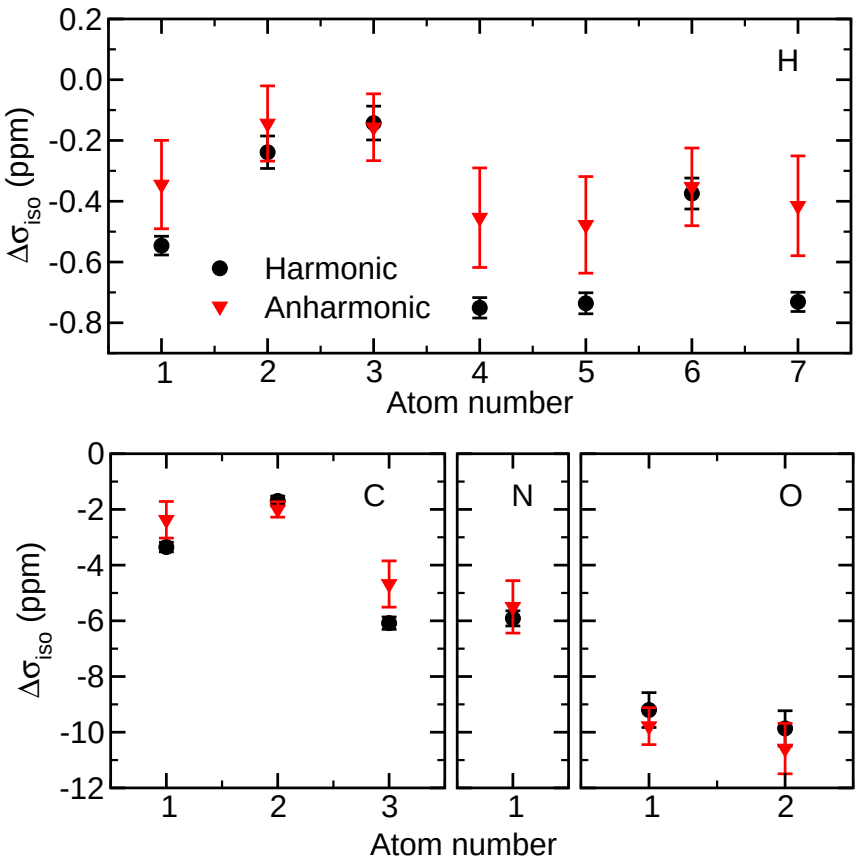


Anharmonic vibrations

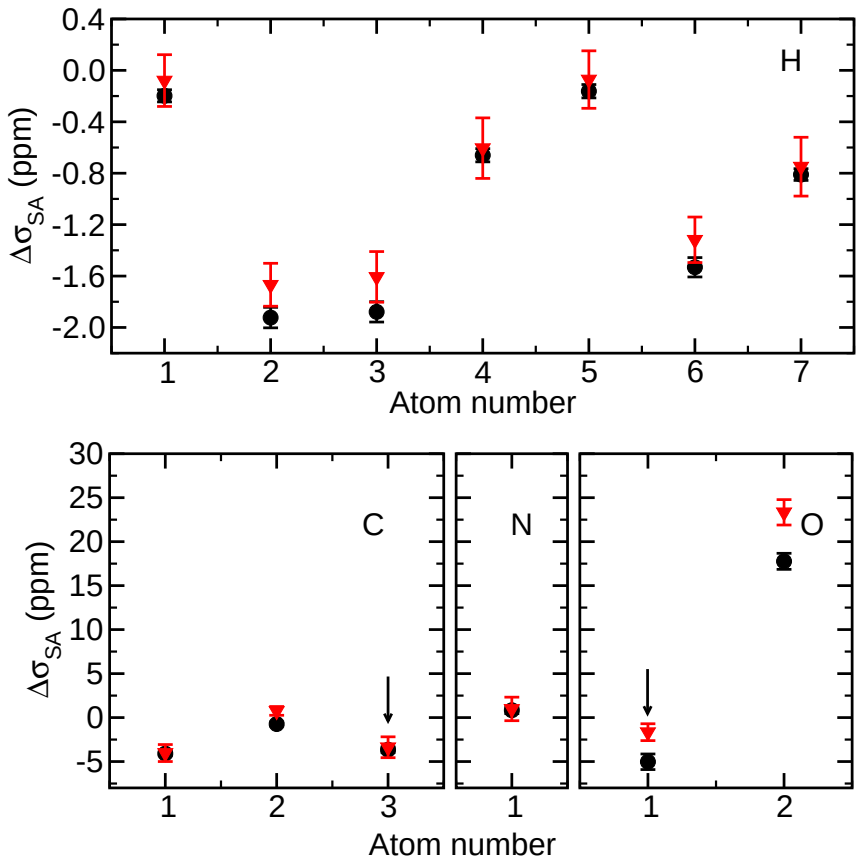


Anharmonic coupling to the shielding tensor

Isotropic shift



Shielding anisotropy



Summary

- Anharmonic energy:
  - Vibrational self-consistent field method for solids.
  - Phase diagram of high-pressure solid molecular hydrogen.
  - Relative stability of hexagonal and cubic ice.

- Vibrational coupling:
  - Quandratic expansion and Monte Carlo.
  - Electron-phonon coupling in semiconductors.
  - Vibrational effects on the chemical shielding tensor.

Outlook

- Anharmonic vibrations can be important:
  - Small enthalpy differences between competing phases.
  - Harmonic instabilities.
  - High temperatures.
  - ...
- Vibrational coupling can be important:
  - Zero-point correction and finite temperature.
  - Any quantity available at the static level can be coupled to vibrations.
  - Electronic band gaps, NMR, ...

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  Physical Review Letters **112**, 165501 (2014)
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