Anharmonic phonon properties: electron-phonon coupling and stress

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Outline

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Principal axes approximation to the BO energy surface

- Harmonic approximation:

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

- Principal axes approximation to the BO energy surface:

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

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

Vibrational self-consistent field (I)

- Phonon Schrödinger equation:

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

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

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

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

Vibrational self-consistent field (II)

- Approximate 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 $S_{\mathbf{k}s}$.

General phonon expectation value

- Phonon expectation value at inverse temperature β:

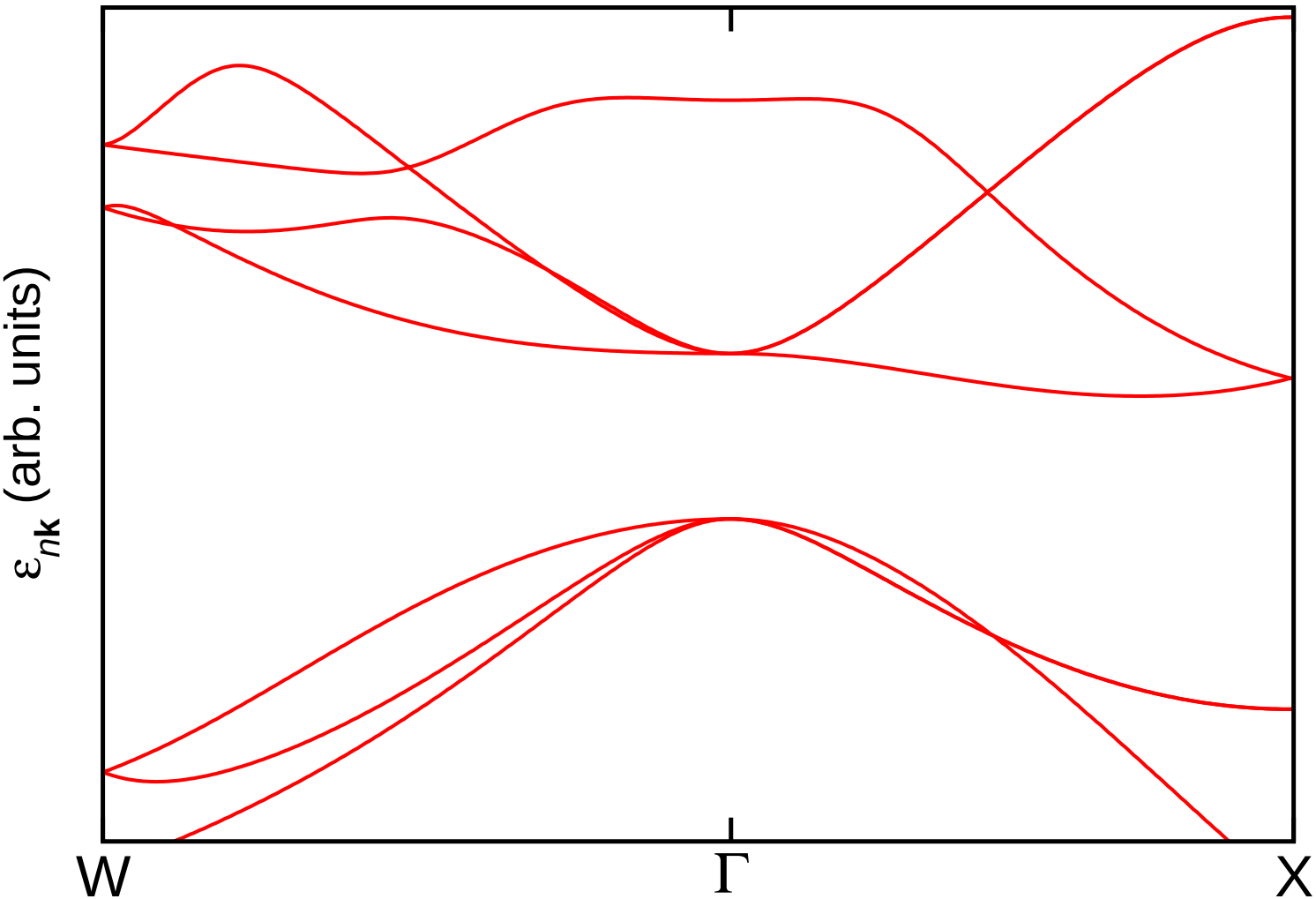
$$\langle \hat{O}(\mathbf{Q}) \rangle_{\Phi,\beta} = \frac{1}{\mathcal{Z}} \sum_{\mathbf{S}} \langle \Phi^{\mathbf{S}}(\mathbf{Q}) | \hat{O}(\mathbf{Q}) | \Phi^{\mathbf{S}}(\mathbf{Q}) \rangle e^{-\beta E_{\mathbf{S}}}$$

- Operator expansion:

$$\hat{O}(\mathbf{Q}) = \hat{O}(\mathbf{0}) + \sum_{\mathbf{k},s} \hat{O}_{\mathbf{k}s}(q_{\mathbf{k}s}) + \frac{1}{2} \sum_{\mathbf{k},s} {\sum_{\mathbf{k}',s'}}' \hat{O}_{\mathbf{k}s;\mathbf{k}'s'}(q_{\mathbf{k}s}, q_{\mathbf{k}'s'}) + \cdots$$

Outline

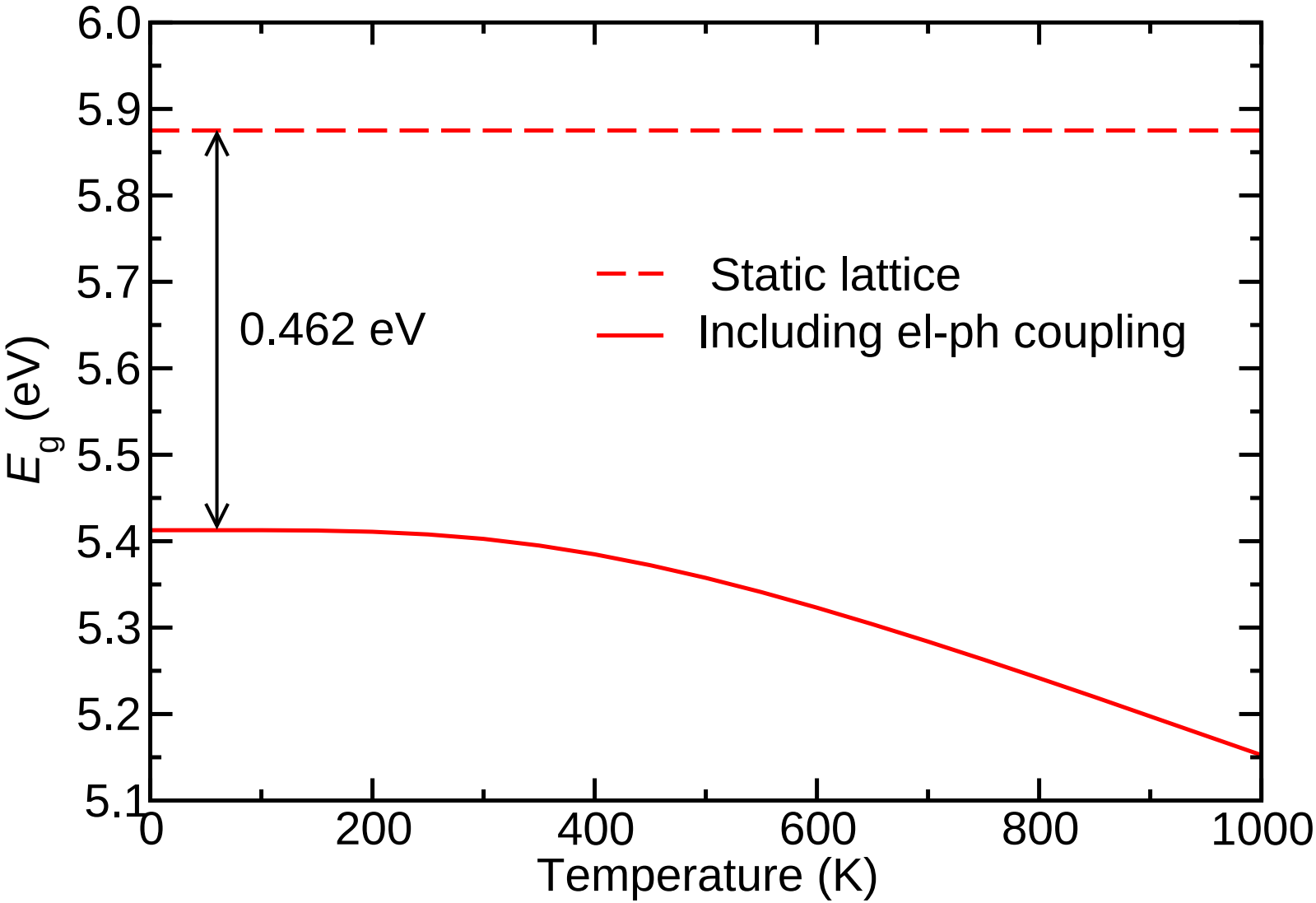
Band gap renormalisation



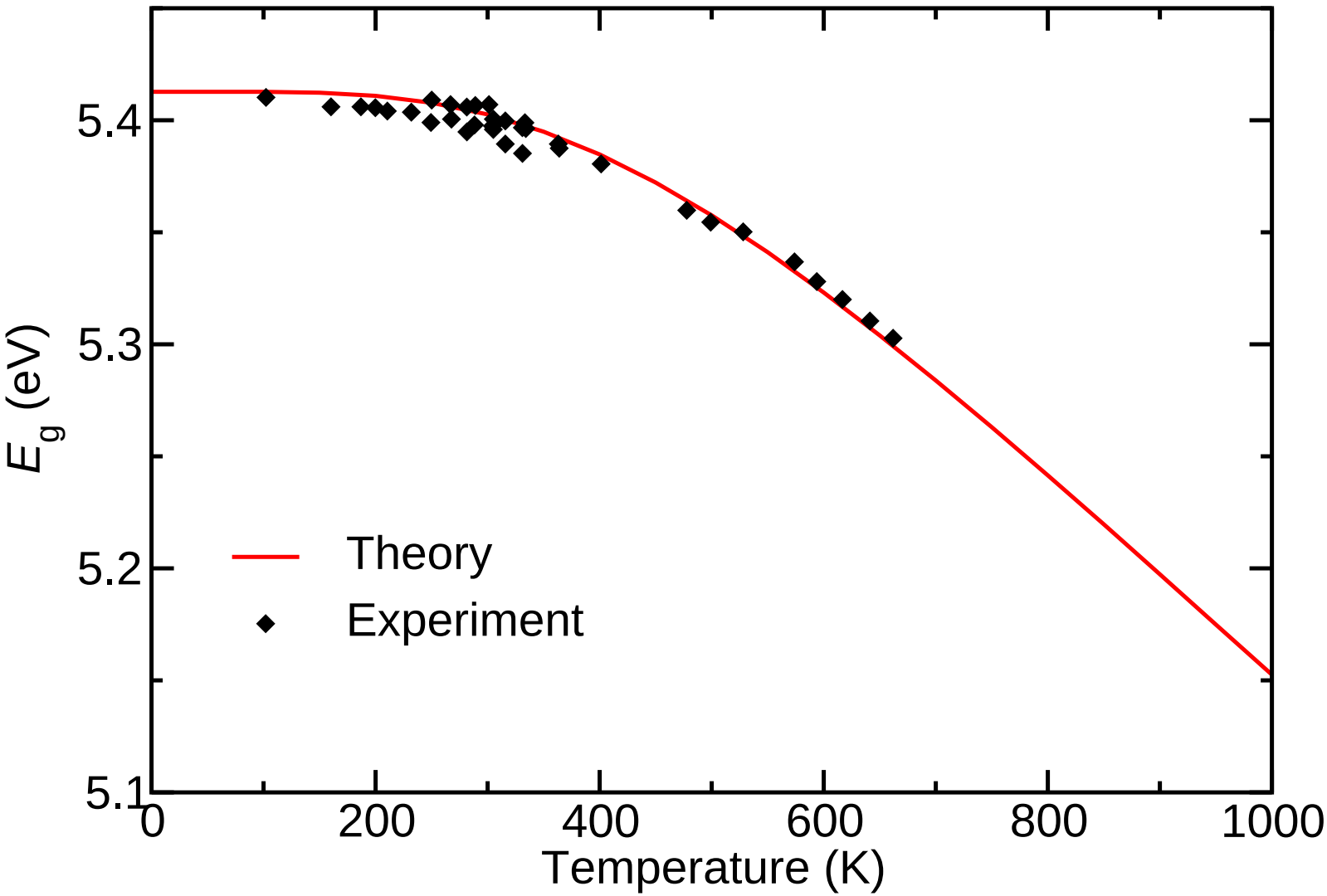
Standard exchange-correlation functionals

- Band gap problem (LDA, PBE, . . .): underestimation of gaps.
- Caused by the lack of a discontinuity in approximate *xc*-functionals with respect to particle number: correction Δ_{xc} to band gap.
- Approximate systematic shift in *all* displaced configurations.
- Error disappears in *change* in band gap.

Diamond thermal band gap (I)

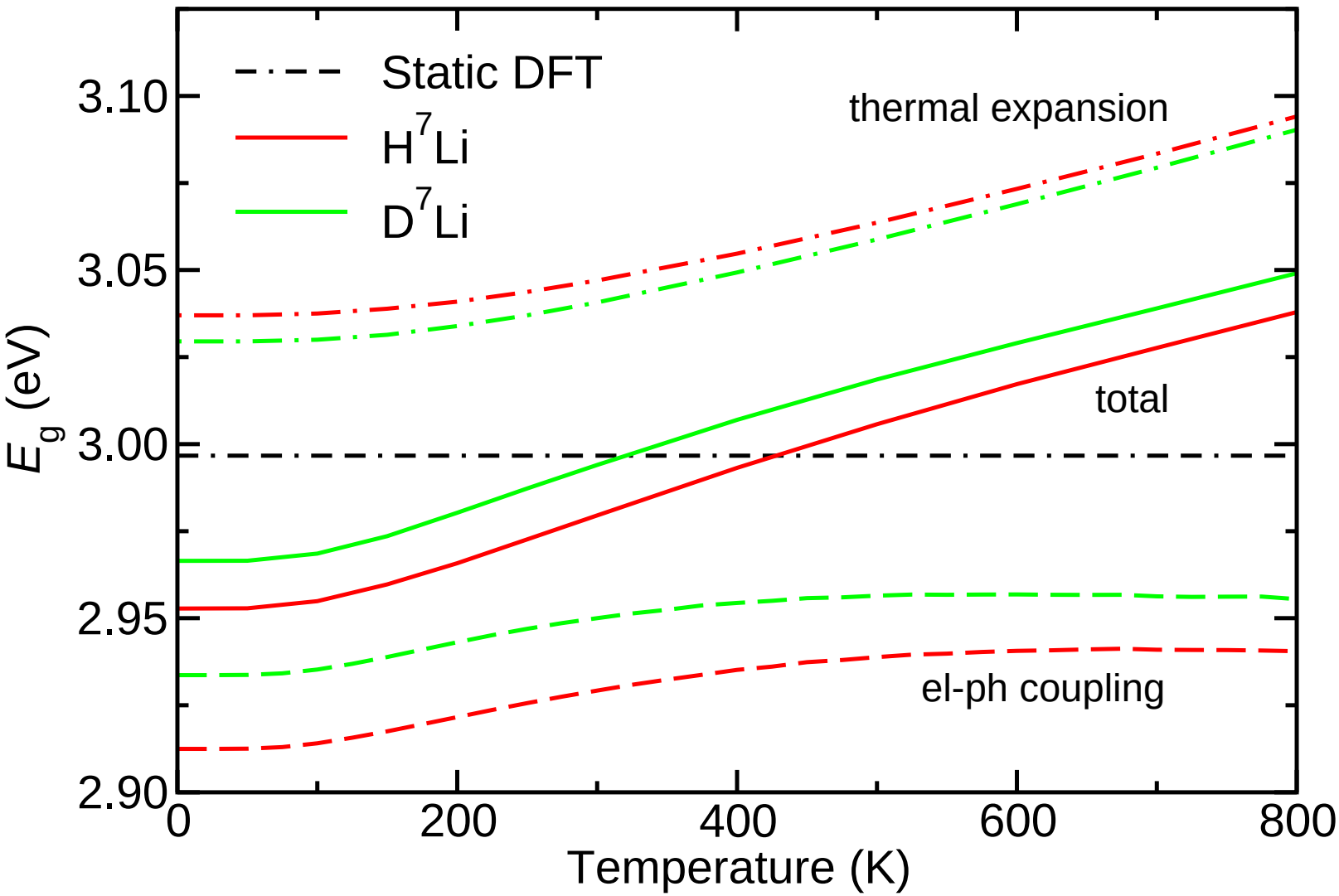


Diamond thermal band gap (II)



Experimental data from Proc. R. Soc. London, Ser. A **277**, 312 (1964)

LiH and LiD thermal band gaps



Outline

Gibbs free energy

- Gibbs free energy:

$$\mathrm{d}G = \mathrm{d}F_{\mathrm{el}} + \mathrm{d}F_{\mathrm{vib}} - \Omega \sum_{i,j} \sigma_{ij}^{\mathrm{ext}} \mathrm{d}\epsilon_{ij}$$

- Vibrational stress:

$$\sigma_{ij}^{\mathrm{vib}} = -\frac{1}{\Omega} \frac{\partial F_{\mathrm{vib}}}{\partial \epsilon_{ij}}$$

- Effective stress:

$$\mathrm{d}G = \mathrm{d}F_{\mathrm{el}} - \Omega \sum_{i,j} \sigma_{ij}^{\mathrm{eff}} \mathrm{d}\epsilon_{ij}$$

where $\sigma_{ij}^{\mathrm{eff}} = \sigma_{ij}^{\mathrm{ext}} + \sigma_{ij}^{\mathrm{vib}}$.

Vibrational stress tensor

- Potential part of vibrational stress tensor:

$$\sigma_{ij}^{\mathrm{vib,V}} = \langle \Phi(\mathbf{Q}) | \sigma_{ij}^{\mathrm{el}} | \Phi(\mathbf{Q}) \rangle$$

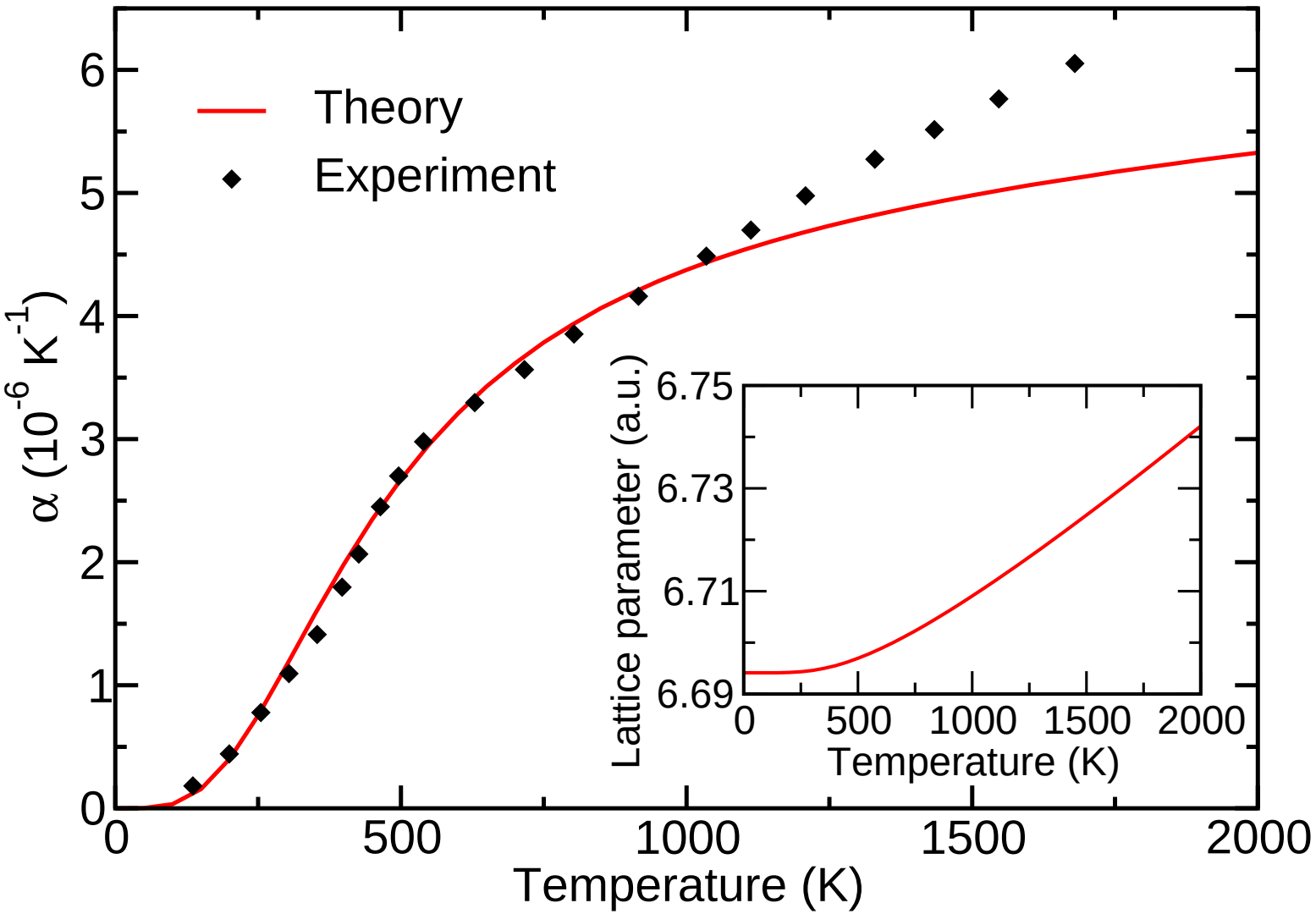
- Kinetic part of vibrational stress tensor:

$$\sigma_{ij}^{\mathrm{vib,T}} = -\frac{1}{\Omega} \left\langle \Phi \left| \sum_{\mathbf{R}_p,\alpha} m_\alpha \dot{u}_{p\alpha;i} \dot{u}_{p\alpha;j} \right| \Phi \right\rangle$$

- Total vibrational stress tensor:

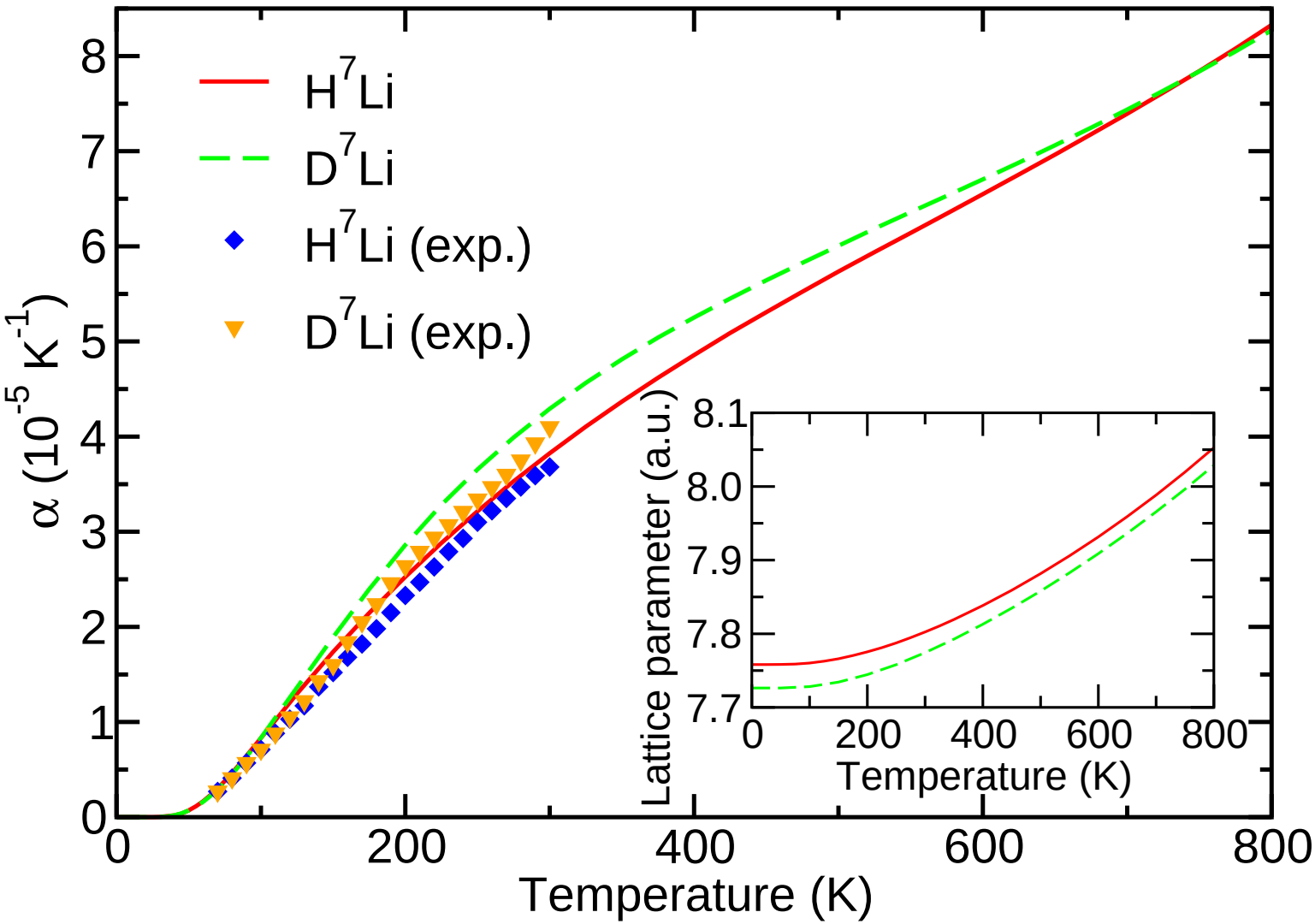
$$\sigma_{ij}^{\mathrm{vib}} = \sigma_{ij}^{\mathrm{vib,V}} + \sigma_{ij}^{\mathrm{vib,T}}$$

Diamond thermal expansion coefficient



Experimental data from J. Appl. Phys. **46**, 89 (1975)

LiH and LiD thermal expansion coefficient



Experimental data from J. Phys. C **15**, 6321 (1982)

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Conclusions

Summary:

- Principal axes approximation to the Born-Oppenheimer energy surface.
- VSCF method for the solution of the vibrational equation.
- General phonon expectation values.

Extended framework:

- All static DFT properties can be renormalised.
- Examples: mean atomic positions, hyperfine tensor, ...

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- References:
  - B. Monserrat, N.D. Drummond, R.J. Needs
    Physical Review B **87**, 144302 (2013)