Anharmonic Effects in Superconductors, Metallic Hydrides, and Layered Materials from the SSCHA

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Outline

1. Introduction
2. The stochastic self-consistent harmonic approximation (SSCHA)
3. Applications
   - The inverse isotope effect in palladium hydrides
   - Phonon spectra and CDW in 2H-$NbSe_2$
4. Conclusions

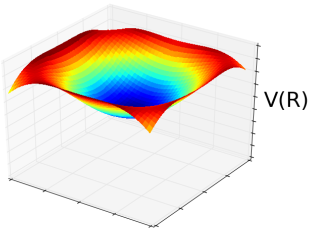
Vibrational properties of solids

The potential for the ions $V(\mathbf{R})$

Determined by the Born-Oppenheimer energy surface

$$V(\mathbf{R}) = V_0 + \sum_{n=2}^{\infty} V_n(\mathbf{R})$$

$$V_n(\mathbf{R}) = \frac{1}{n!} \sum_{s_1 \dots s_n} \sum_{\alpha_1 \dots \alpha_n} \left[\frac{\partial^{(n)} V(\mathbf{R})}{\partial R^{s_1\alpha_1} \dots \partial R^{s_n\alpha_n}} \right]_0 (R^{s_1\alpha_1} - R_{eq}^{s_1\alpha_1}) \dots (R^{s_n\alpha_n} - R_{eq}^{s_n\alpha_n})$$



The harmonic approximation

- Truncation of the potential at second order

$$V(\mathbf{R}) \sim V_0 + V_2(\mathbf{R}) = V_0 + \frac{1}{2}(\mathbf{R} - \mathbf{R}_{eq}) \left[\frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}^2} \right]_0 (\mathbf{R} - \mathbf{R}_{eq})$$

- The Hamiltonian can be exactly diagonalized
- Phonons well-defined quasiparticles

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- The Hamiltonian can be exactly diagonalized
- Phonons well-defined quasiparticles

Failures of the harmonic approximation

- Phonon intrinsic lifetime
- Lattice thermal conductivity
- Non-trivial temperature frequency-shift
- Stabilization of unstable structures due to thermal/quantum fluctuations (ferroelectrics, CDWs, . . .)

Anharmonic effects

$$V(\mathbf{R}) \sim V_0 + V_2(\mathbf{R}) + V_3(\mathbf{R}) + V_4(\mathbf{R}) + \dots$$

Properties

- Finite lifetime of phonons
- Thermal conductivity explained
- Temperature dependence explained

Anharmonic effects

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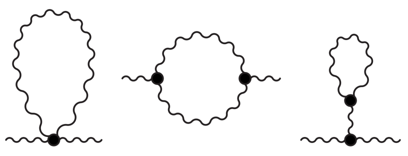
Perturbation theory

Valid when

$$V_3(\mathbf{R}) + V_4(\mathbf{R}) + \dots \ll V_2(\mathbf{R})$$



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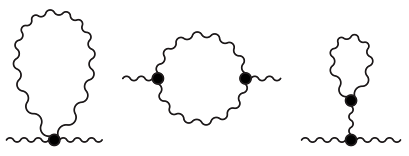


Properties

- Finite lifetime of phonons
- Thermal conductivity explained
- Temperature dependence explained

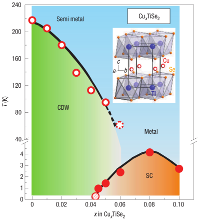
When $V_3(\mathbf{R}) + V_4(\mathbf{R}) + \cdots \sim V_2(\mathbf{R})$

Breakdown of perturbation theory

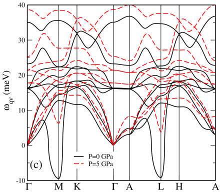
The non-perturbative regime

Transition Metal Dichalcogenides

$TiSe_2$



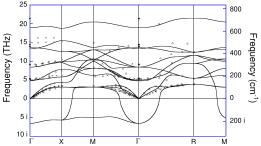
Morosan *et al.*, Nat. Physics 2, 544 (2006)



Calandra *et al.*, PRL 106, 196406 (2011)

Ferroelectrics

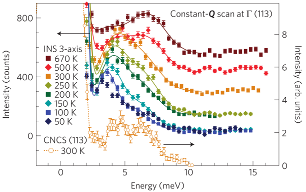
$BaTiO_3$



Ghosez *et al.*, Ferroelectrics 206, 205 (1998)

Thermoelectrics

PbTe



Delaire *et al.*, Nat. Materials 10, 614 (2010)

Hydrides

AlH_3

PHYSICAL REVIEW B **82**, 104504 (2010)

Giant anharmonicity suppresses superconductivity in AlH_3 under pressure

Bruno Rousseau[1,2,*] and Aitor Bergara[1,2,3,†]

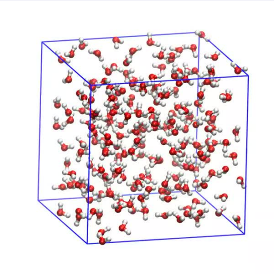
The non-perturbative regime

How to treat it?

- $k_B T >> \hbar\omega$

  Molecular Dynamics

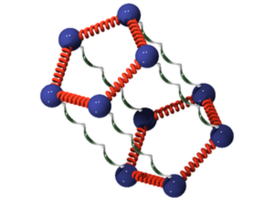
  - Newtonian mechanics for the ions



- $k_B T \sim \hbar\omega$

  Path Integral Monte-Carlo

  - exact
  - expensive
  - difficult to obtain vibrational spectra



The non-perturbative regime

The self-consistent harmonic approximation

The best *harmonic* potential that mimics the *anharmonic* one

LI. *A New Treatment of Anharmonicity in Lattice Thermodynamics : I*

By D. J. Hooton

Hooton, Philos. Mag. 46, 522 (1955)

Hartree-Fock for phonons

Electrons:

Effective non-interacting electrons that minimize the total energy including the e-e interaction

Phonons:

Effective non-interacting phonons that minimize the free energy with the exact (anharmonic) interaction

The self-consistent harmonic approximation (SCHA)

The vibrational free energy

- The vibrational Hamiltonian

$$H = \frac{\mathbf{P}^2}{2M} + V \quad \rho_H = e^{-\frac{H}{k_B T}}/Z_H$$

- The free energy

$$F_H = \mathrm{tr}[\rho_H H] + k_B T \mathrm{tr}[\rho_H \ln \rho_H]$$

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The free energy functional of a trial Hamiltonian

- Trial density matrix $\rho_{\mathcal{H}}$ from a trial Hamiltonian

$$\mathcal{H} = \frac{\mathbf{P}^2}{2M} + \mathcal{V} \qquad \rho_{\mathcal{H}} = e^{-\frac{\mathcal{H}}{k_B T}}/Z_{\mathcal{H}}$$

- The free energy functional

$$\mathcal{F}_H[\mathcal{H}] = \mathrm{tr}[\rho_{\mathcal{H}} H] + k_B T \mathrm{tr}[\rho_{\mathcal{H}} \ln \rho_{\mathcal{H}}]$$

The self-consistent harmonic approximation (SCHA)

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- The free energy functional

$$\mathcal{F}_H[\mathcal{H}] = \mathrm{tr}[\rho_{\mathcal{H}} H] + k_B T \mathrm{tr}[\rho_{\mathcal{H}} \ln \rho_{\mathcal{H}}]$$

Variational principle

$$\boxed{\mathcal{F}_H[\mathcal{H}] = F_{\mathcal{H}} + \mathrm{tr}[\rho_{\mathcal{H}}(V - \mathcal{V})] \geq F_H}$$

The SSCHA

$$\mathcal{F}_H[\mathcal{H}] = F_{\mathcal{H}} + \mathrm{tr}[\rho_{\mathcal{H}}(V - \mathcal{V})] \qquad \rho_{\mathcal{H}} = e^{-\frac{\mathcal{H}}{k_B T}}/Z_{\mathcal{H}}$$

$$\mathcal{H} = \frac{\mathbf{P}^2}{2M} + \frac{1}{2}(\mathbf{R} - \mathbf{R}_{eq})\Phi(\mathbf{R} - \mathbf{R}_{eq})$$

The Stochastic Self-Consistent Harmonic Approximation (SSCHA)

Stochastic implementation of the SCHA that **minimizes the number of calls to the ab initio total-energy-and-force engine**

Conjugate-gradient (CG) minimization of the free energy functional $\mathcal{F}_H[\mathcal{H}]$

- Minimization $\Rightarrow$ trajectory in the parameter space $(\mathbf{R}_{eq};\Phi)$

$$\begin{array}{ccccccccc} \mathcal{H}_0 & \rightarrow & \mathcal{H}_1 & \rightarrow & \mathcal{H}_2 & \rightarrow & \dots & \rightarrow & \mathcal{H}_n \\ (\mathbf{R}_{eq};\Phi)_0 & \rightarrow & (\mathbf{R}_{eq};\Phi)_1 & \rightarrow & (\mathbf{R}_{eq};\Phi)_2 & \rightarrow & \dots & \rightarrow & (\mathbf{R}_{eq};\Phi)_n \end{array}$$

- We need the gradient of the functional

The gradient of the functional

$$\begin{aligned}
\boldsymbol{\nabla}_{\mathbf{R}_{\rm eq}}\mathcal{F}_H[\mathcal{H}] &= -\int \mathrm{d}\mathbf{R}[\mathbf{f}(\mathbf{R}) - \mathbf{f}_{\mathcal{H}}(\mathbf{R})]\rho_{\mathcal{H}}(\mathbf{R}) \\
\boldsymbol{\nabla}_{\Phi}\mathcal{F}_H[\mathcal{H}] &= -\int \mathrm{d}\mathbf{R}[\mathbf{f}(\mathbf{R}) - \mathbf{f}_{\mathcal{H}}(\mathbf{R})] \times \boldsymbol{\nabla}_{\Phi}\mathbf{A} \times (\mathbf{R} - \mathbf{R}_{eq})\rho_{\mathcal{H}}(\mathbf{R}) \\
&\Downarrow \\
\boldsymbol{\nabla}\mathcal{F}_H[\mathcal{H}] &= \int \mathrm{d}\mathbf{R} O_{\mathcal{H}}[\mathbf{f}(\mathbf{R})]\rho_{\mathcal{H}}(\mathbf{R})
\end{aligned}$$

- $\mathbf{f}(\mathbf{R})$ **forces** on atomic configuration $\mathbf{R}$
- $\mathbf{f}_{\mathcal{H}}(\mathbf{R})$ **trial harmonic forces** on atomic configuration $\mathbf{R}$
- $\boldsymbol{\nabla}_{\Phi}\mathbf{A}$ analytic function of Φ and T

The probability distribution

$$\rho_{\mathcal{H}}(\mathbf{R}) = \langle \mathbf{R}|\rho_{\mathcal{H}}|\mathbf{R}\rangle = a\exp\left[-(\mathbf{R} - \mathbf{R}_{eq}) \times \mathbf{B} \times (\mathbf{R} - \mathbf{R}_{eq})\right]$$

- $\mathbf{B}$ analytic function of Φ and T

Stochastic evaluation of the gradient

$$\boldsymbol{\nabla}\mathcal{F}_H[\mathcal{H}] = \int \mathrm{d}\mathbf{R}\, O_{\mathcal{H}}[\mathbf{f}(\mathbf{R})]\rho_{\mathcal{H}}(\mathbf{R})$$

Importance sampling

- Create N_c ionic configurations in a supercell according to the initial $\rho_{\mathcal{H}_0}(\mathbf{R})$ probability distribution: $\{\mathbf{R}_I\}_{I=1,\dots,N_c}$
- Stochastic evaluation of the integral

$$\boldsymbol{\nabla}\mathcal{F}_H[\mathcal{H}_0] \simeq \frac{1}{N_c}\sum_{I=1}^{N_c} O_{\mathcal{H}_0}[\mathbf{f}(\mathbf{R}_I)]$$

- Requires to evaluate forces in supercells: $\mathbf{f}(\mathbf{R}_I)$
    - empirical potentials
    - DFT *ab initio*
    - Beyond DFT (Monte Carlo, GW, ...)

Stochastic evaluation of the gradient

Can we recycle the $\mathbf{f}(\mathbf{R}_I)$ forces on the configurations created with the initial $\rho_{\mathcal{H}_0}(\mathbf{R})$ in the CG trajectory?

$$\begin{array}{ccccccccc} \mathcal{H}_0 & \rightarrow & \mathcal{H}_1 & \rightarrow & \mathcal{H}_2 & \rightarrow & \dots & \rightarrow & \mathcal{H}_n \\ (\mathbf{R}_{eq};\Phi)_0 & \rightarrow & (\mathbf{R}_{eq};\Phi)_1 & \rightarrow & (\mathbf{R}_{eq};\Phi)_2 & \rightarrow & \dots & \rightarrow & (\mathbf{R}_{eq};\Phi)_n \end{array}$$

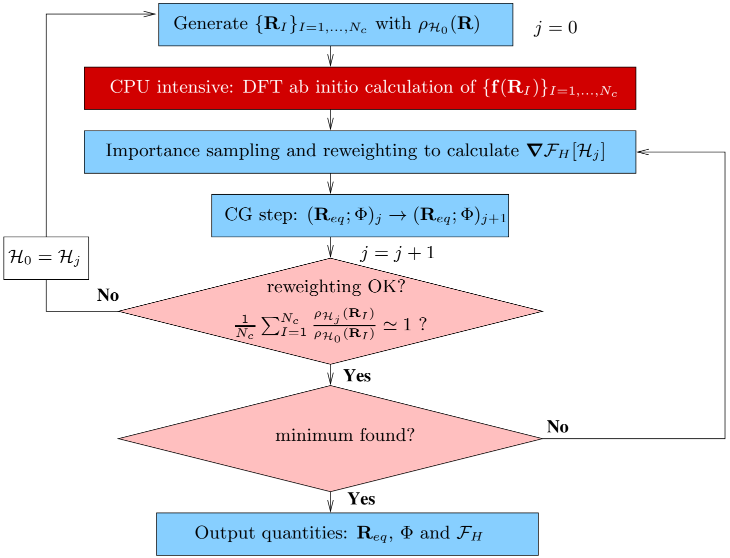
Reweighting

- Include the reweighting factor in the CG step $j > 0$

$$\begin{aligned} \boldsymbol{\nabla}\mathcal{F}_H[\mathcal{H}_0] &\simeq \frac{1}{N_c}\sum_{I=1}^{N_c} O_{\mathcal{H}_0}[\mathbf{f}(\mathbf{R}_I)] \\ &\Downarrow \\ \boldsymbol{\nabla}\mathcal{F}_H[\mathcal{H}_j] &\simeq \frac{1}{N_c}\sum_{I=1}^{N_c} O_{\mathcal{H}_j}[\mathbf{f}(\mathbf{R}_I)]\frac{\rho_{\mathcal{H}_j}(\mathbf{R}_I)}{\rho_{\mathcal{H}_0}(\mathbf{R}_I)} \end{aligned}$$

- The calculated forces can be used throughout the CG minimization

Practical recipe



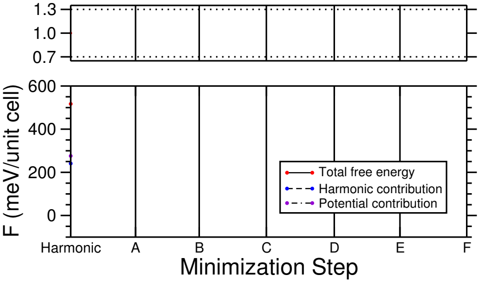
Model calculation: PtH, 100 GPa, 0 K

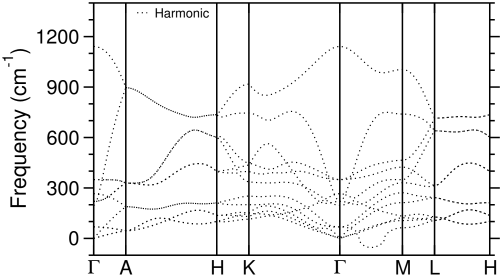
$$\frac{1}{N_c}\sum_{I=1}^{N_c}\frac{\rho_{\mathcal{H}_j}(\mathbf{R}_I)}{\rho_{\mathcal{H}_0}(\mathbf{R}_I)}$$

Free energy:

$$\mathcal{F}_H[\mathcal{H}_j] \simeq F_{\mathcal{H}_j} + \frac{1}{N_c}\sum_{I=1}^{N_c}[V(\mathbf{R}_I) - \mathcal{V}_j(\mathbf{R}_I)]\frac{\rho_{\mathcal{H}_j}(\mathbf{R}_I)}{\rho_{\mathcal{H}_0}(\mathbf{R}_I)}$$

- Forces computed on a 2 $\times$ 2 $\times$ 1 hcp supercell





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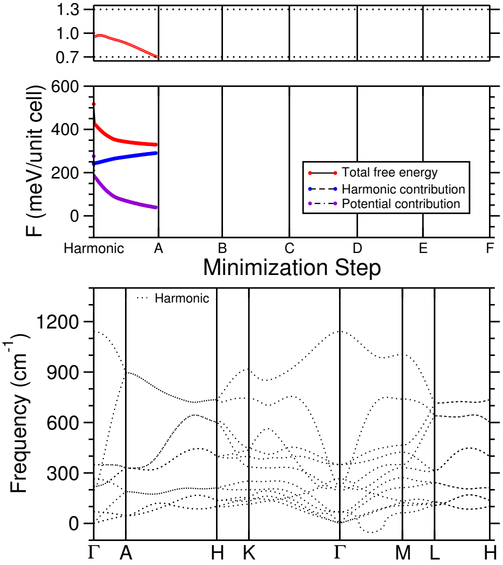

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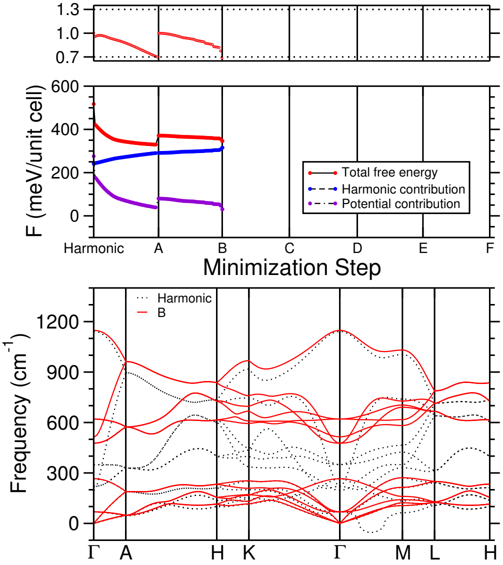

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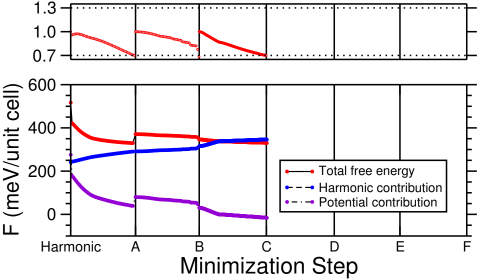

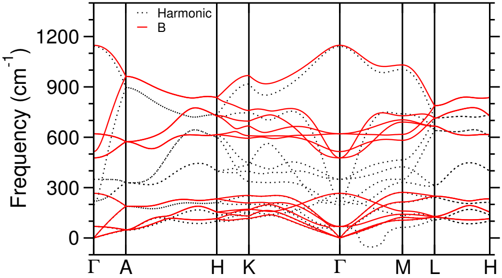

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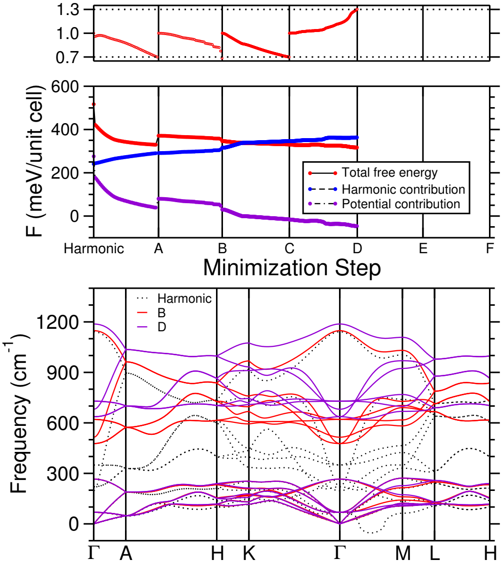

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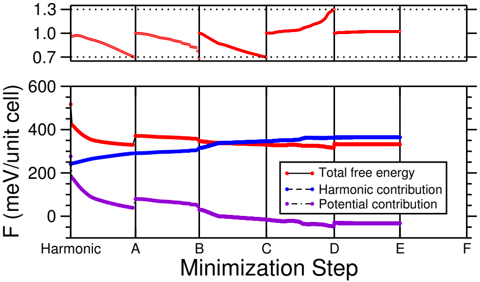

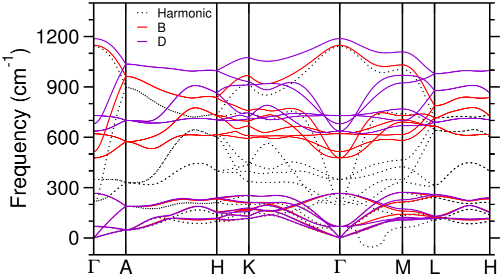

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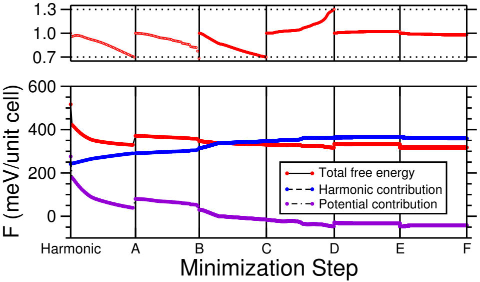

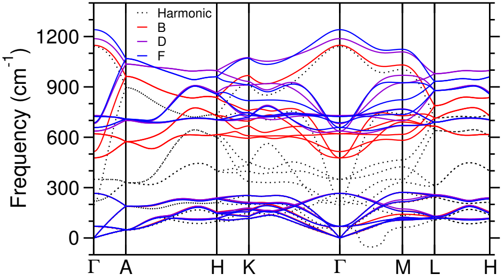

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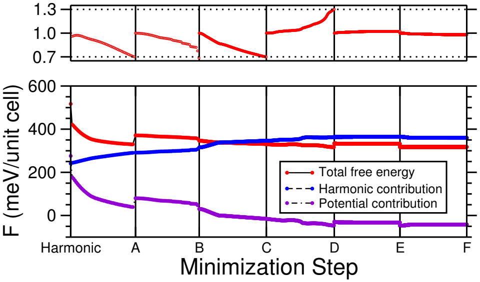
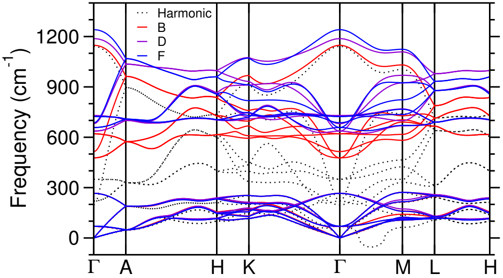
- Forces computed on a 2 × 2 × 1 hcp supercell
- 20 force calculations (CPU intensive) at Harmonic, A, B, C, D
- 380 force calculations (CPU intensive) at E





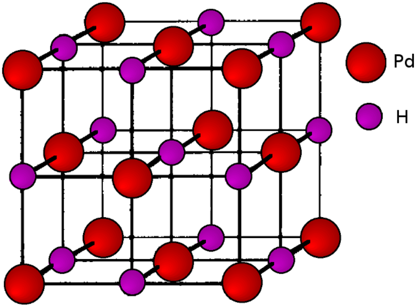
Features of the SSCHA

- Computational cost smaller than molecular dynamics
- Includes quantum and thermal fluctuations
- Direct access to free energy without thermodynamical integration
- Direct access to vibrational quasiparticles (phonons)
- It can deal with strong anharmonicity in the non-pertubative regime at any temperature

References:

1. Ion Errea, Matteo Calandra, and Francesco Mauri, Phys. Rev. Lett. 111, 177002 (2013)
2. Ion Errea, Matteo Calandra, and Francesco Mauri, Phys. Rev. B 89, 064302 (2014)

Palladium hydrides



- A superconducting hydride at ambient pressure
- Display the **most anomalous isotope effect** in the literature

The isotope effect in superconductors

McMillan's equation for superconducting T_c:

$$T_c = \frac{\omega_{log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1-0.62\lambda)} \right)$$

Mass dependence of T_c in BCS harmonic superconductors

$$\lambda \sim \mathrm{DOS}(\varepsilon_F) \frac{D^2}{M\omega^2}$$

- **In the harmonic approximation**:

$$\omega \propto 1/\sqrt{M} \Rightarrow \lambda \text{ mass independent } \Rightarrow T_c \propto 1/\sqrt{M}$$

- The isotope coefficient:

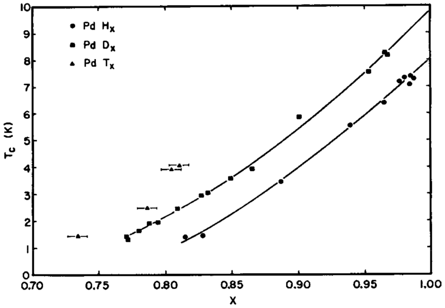
$$\alpha = -\frac{\mathrm{d}\ln(T_c)}{\mathrm{d}\ln M} \sim 0.5$$

The inverse isotope effect in palladium hydrides

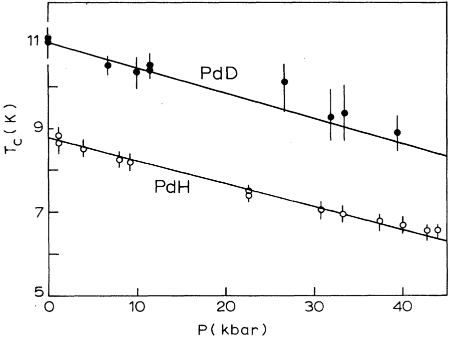
- T_c increases with increasing M

$$\alpha_{\mathrm{PdH/PdD}} \approx -0.3$$

- **Inconsistent with harmonic theory**

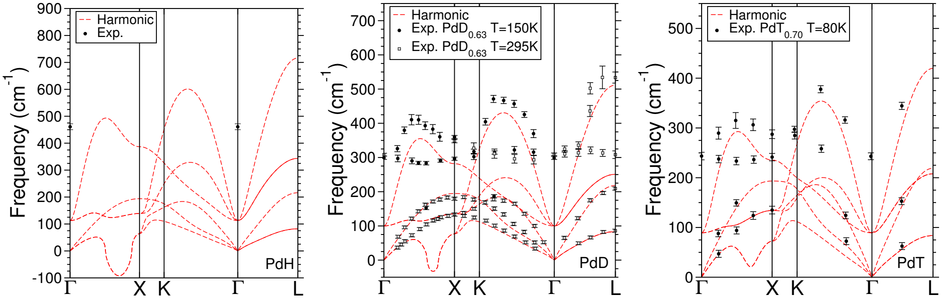


Schirber *et al.*, Solid State Comm. 52, 837 (1984)



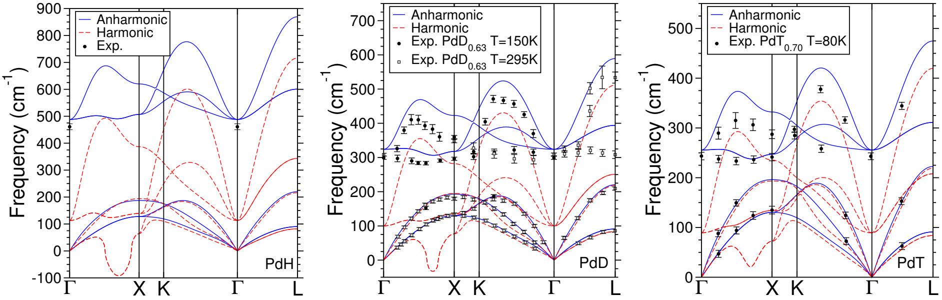
Hemmes *et al.*, Phys. Rev. B 39, 4110 (1989)

Harmonic and Anharmonic phonon spectra of palladium hydrides



Errea *et al.*, Phys. Rev. Lett. 111, 177002 (2013)

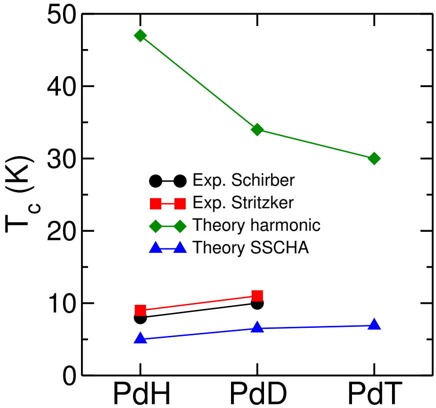
Harmonic and Anharmonic phonon spectra of palladium hydrides



Errea *et al.*, Phys. Rev. Lett. 111, 177002 (2013)

- Anharmonicity strongly renormalizes H-character optical modes
- Good agreement with experiments

Electron-phonon coupling and superconductivity



Errea *et al.*, Phys. Rev. Lett. 111, 177002 (2013)

The inverse isotope effect explained

$$\alpha_{\text{exp}} = -0.32$$

$$\alpha_{\text{harmonic}} = +0.47$$

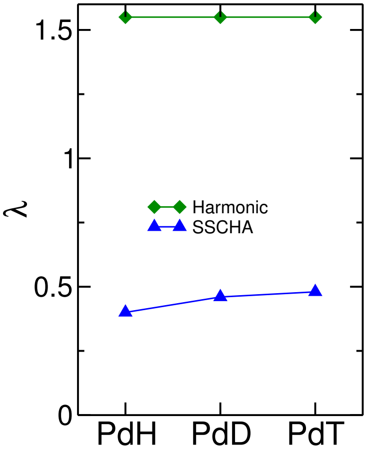
$$\alpha_{\text{SSCHA}} = -0.38$$

Electron-phonon coupling and superconductivity

- The enhancement of the phonon frequencies suppresses the electron-phonon coupling

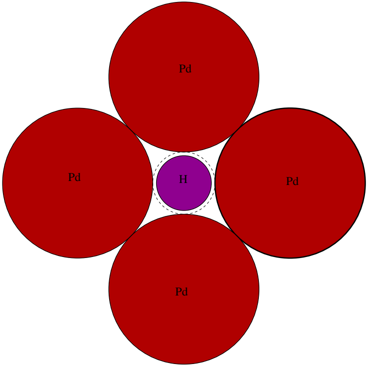
$$\lambda \sim \mathrm{DOS}(\varepsilon_F)\frac{D^2}{M\omega^2}$$

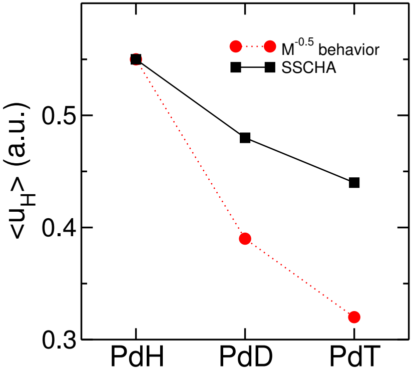
- The suppression is stronger the lighter the isotope



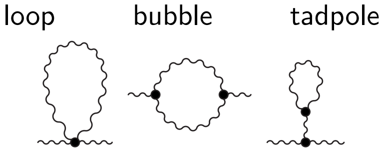
Origin of anharmonicity

- The H atom is smaller than the octahedral void $\Rightarrow$ **H vibrations are anharmonic rattling modes**
- The root mean square displacement does not scale as $1/\sqrt{M}$





Combining the SSCHA with perturbation theory



The SSCHA + perturbation theory

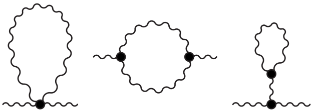
$$\mathcal{F}_H[\mathcal{H}] = F_{\mathcal{H}} + \mathrm{tr}[\rho_{\mathcal{H}}(V - \mathcal{V})]$$

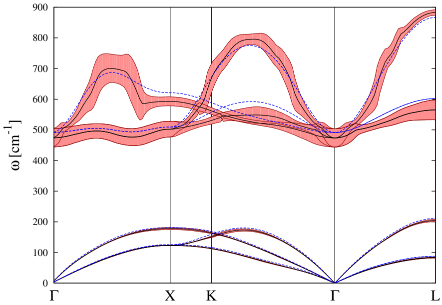
- SCHA in perturbative limit $\rightarrow$ loop
- Thermal expansion $\rightarrow$ tadpole
- Need to include the **bubble**
- Linewidth and frequency shift from the bubble :

$$\begin{aligned} \Pi_\nu(\mathbf{q},\Omega) &= \Delta_\nu(\mathbf{q},\Omega) + i\Gamma_\nu(\mathbf{q},\Omega) \\ \Omega_\nu(\mathbf{q}) &- \omega_\nu(\mathbf{q}) = \Delta_\nu(\mathbf{q},\omega_\nu(\mathbf{q})) \\ \gamma_\nu^{\mathrm{HWHM}}(\mathbf{q}) &= \Gamma_\nu(\mathbf{q},\omega_\nu(\mathbf{q})) \end{aligned}$$

Combining the SSCHA with perturbation theory

loop bubble tadpole





PdH at 295 K

The SSCHA + perturbation theory

$$\mathcal{F}_H[\mathcal{H}] = F_{\mathcal{H}} + \mathrm{tr}[\rho_{\mathcal{H}}(V - \mathcal{V})]$$

- SCHA in perturbative limit → loop
- Thermal expansion → tadpole
- Need to include the **bubble**
- Linewidth and frequency shift from the bubble :

$$\begin{aligned} \Pi_\nu(\mathbf{q},\Omega) &= \Delta_\nu(\mathbf{q},\Omega) + i\Gamma_\nu(\mathbf{q},\Omega) \\ \Omega_\nu(\mathbf{q}) &- \omega_\nu(\mathbf{q}) = \Delta_\nu(\mathbf{q},\omega_\nu(\mathbf{q})) \\ \gamma_\nu^{\mathrm{HWHM}}(\mathbf{q}) &= \Gamma_\nu(\mathbf{q},\omega_\nu(\mathbf{q})) \end{aligned}$$

Combining the SSCHA with perturbation theory

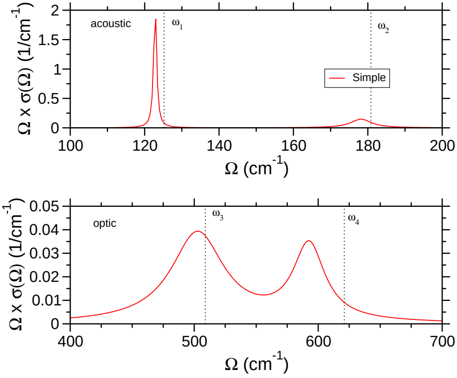
Inelastic Neutron Scattering spectra

$$\chi(\mathbf{q},\Omega) \propto \sigma(\mathbf{q},\Omega) = \sum_{\nu} \frac{2\omega_\nu(\mathbf{q})\Gamma_\nu(\mathbf{q},\Omega)}{[\Omega^2 - \omega_\nu^2(\mathbf{q}) - 2\omega_\nu(\mathbf{q})\Delta_\nu(\mathbf{q},\Omega)]^2 + 4\omega_\nu^2(\mathbf{q})\Gamma_\nu^2(\mathbf{q},\Omega)}$$

Combining the SSCHA with perturbation theory

Inelastic Neutron Scattering spectra

$$\chi(\mathbf{q},\Omega) \propto \sigma(\mathbf{q},\Omega) = \sum_{\nu} \frac{2\omega_\nu(\mathbf{q})\Gamma_\nu(\mathbf{q},\omega_\nu(\mathbf{q}))}{[\Omega^2 - \omega_\nu^2(\mathbf{q}) - 2\omega_\nu(\mathbf{q})\Delta_\nu(\mathbf{q},\omega_\nu(\mathbf{q}))]^2 + 4\omega_\nu^2(\mathbf{q})\Gamma_\nu^2(\mathbf{q},\omega_\nu(\mathbf{q}))}$$



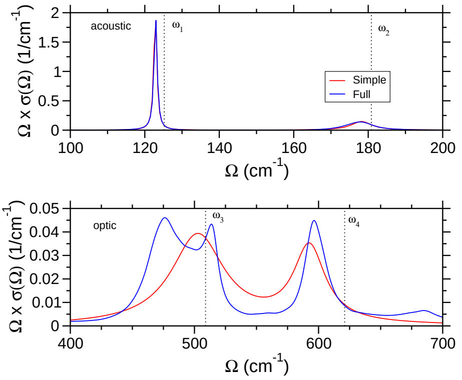
PdH at 295 K, X point

- Simple approach:
  $\Delta_\nu(\mathbf{q},\Omega) = \Delta_\nu(\mathbf{q},\omega_\nu(\mathbf{q}))$
  $\Gamma_\nu(\mathbf{q},\Omega) = \Gamma_\nu(\mathbf{q},\omega_\nu(\mathbf{q}))$

Combining the SSCHA with perturbation theory

Inelastic Neutron Scattering spectra

$$\chi(\mathbf{q},\Omega) \propto \sigma(\mathbf{q},\Omega) = \sum_{\nu} \frac{2\omega_{\nu}(\mathbf{q})\Gamma_{\nu}(\mathbf{q},\Omega)}{[\Omega^2 - \omega_{\nu}^2(\mathbf{q}) - 2\omega_{\nu}(\mathbf{q})\Delta_{\nu}(\mathbf{q},\Omega)]^2 + 4\omega_{\nu}^2(\mathbf{q})\Gamma_{\nu}^2(\mathbf{q},\Omega)}$$

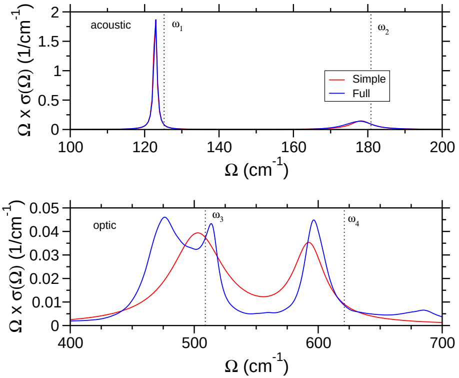


PdH at 295 K, X point

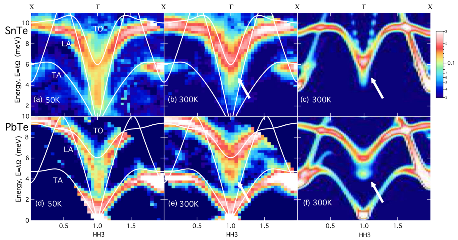
- Simple approach:
  $\Delta_{\nu}(\mathbf{q},\Omega) = \Delta_{\nu}(\mathbf{q},\omega_{\nu}(\mathbf{q})$
  $\Gamma_{\nu}(\mathbf{q},\Omega) = \Gamma_{\nu}(\mathbf{q},\omega_{\nu}(\mathbf{q})$
- Full approach:
  Keeping the Ω dependence in $\Delta_{\nu}(\mathbf{q},\Omega)$ and $\Gamma_{\nu}(\mathbf{q},\Omega)$

Anharmonicity induced satellite peaks

PdH at 295 K, X point



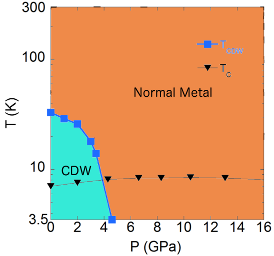
PbTe

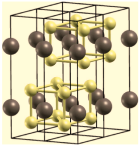


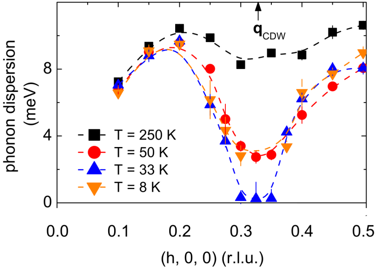
Li *et al.*, Phys. Rev. Lett. 112, 175501 (2014)

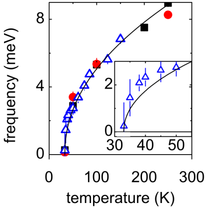
A prototypical transition metal dichalcogenide

- A CDW and superconductivity coexist
- The harmonic approximation completely breaks down

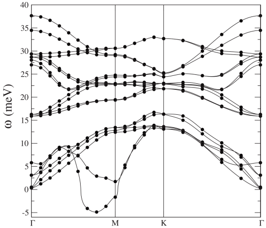






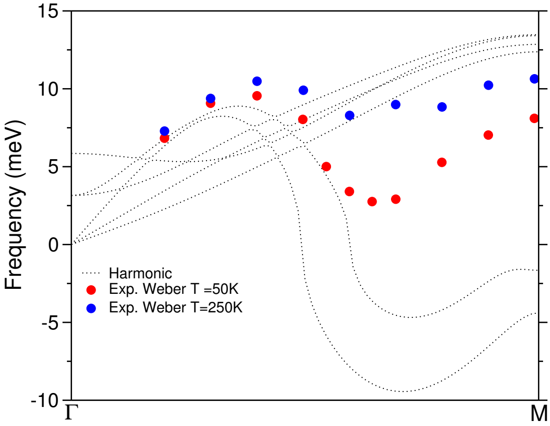


Weber *et al.*, Phys. Rev. Lett. 107, 107403 (2011)

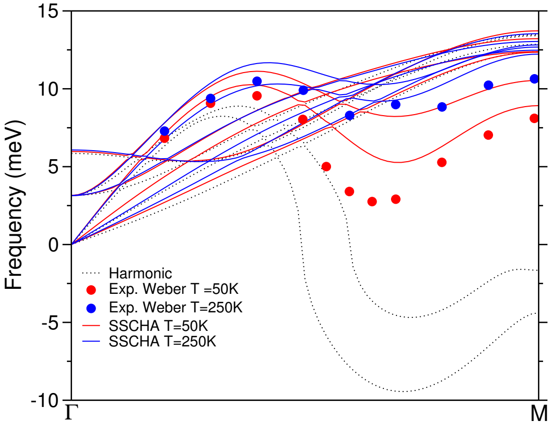


Calandra *et al.*, PRB 80, 241108(R) (2009)

The SSCHA in 2H-$NbSe_2$ at 0 GPa

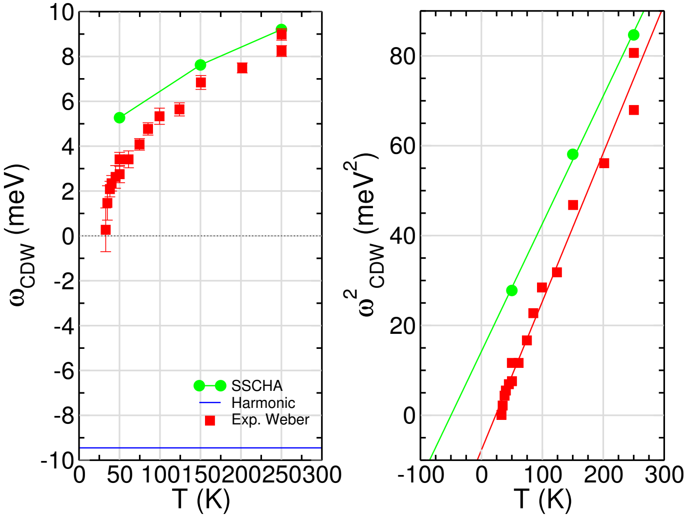


The SSCHA in 2H-$NbSe_2$ at 0 GPa



- The instabilities disappear in the SSCHA
- The temperature dependence is explained
- Good agreement with experiments

The SSCHA in 2H-$NbSe_2$ at 0 GPa



The prediction of T_{CDW} is possible with the SSCHA

Conclusions

1. Anharmonic effects important to explain many physical phenomena
2. The SSCHA:
   Efficient method to obtain anharmonic free energies and phonon dispersions
3. It can be combined with perturbation theory to obtain phonon linewidths
4. Possible to calculate temperature dependent soft-mode driven phase transitions

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EUSKO JAURLARITZA
GOBIERNO VASCO

- The Basque Government and Ikerbasque

ikerbasque
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