Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation
Lecture 9: Quantum and Anharmonic Effects in Superhydrides

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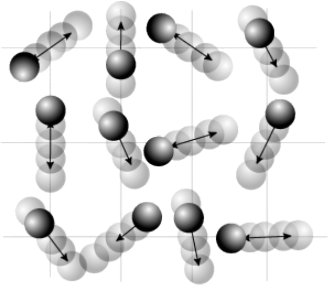
March and April 2022



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Universidad del País Vasco
Euskal Herriko Unibertsitatea

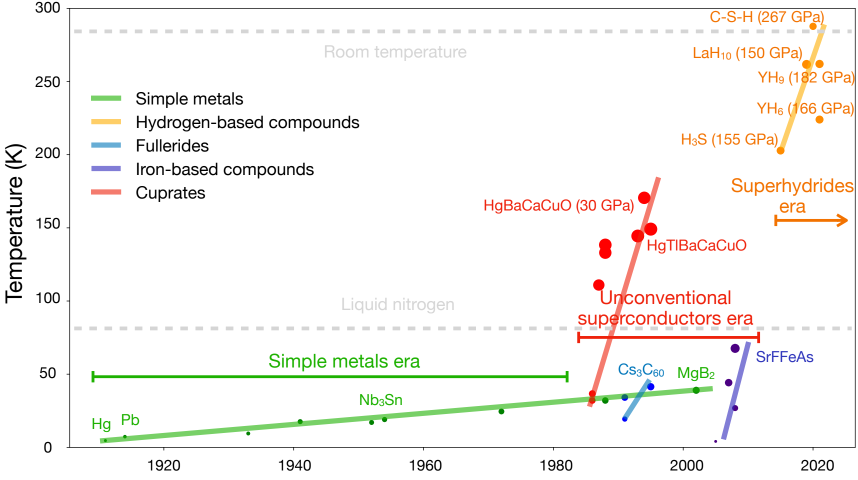
CFM
Materials Physics Center
Centro de Física de Materiales
Materialen Fisika Zentroa

Donostia International Physics Center

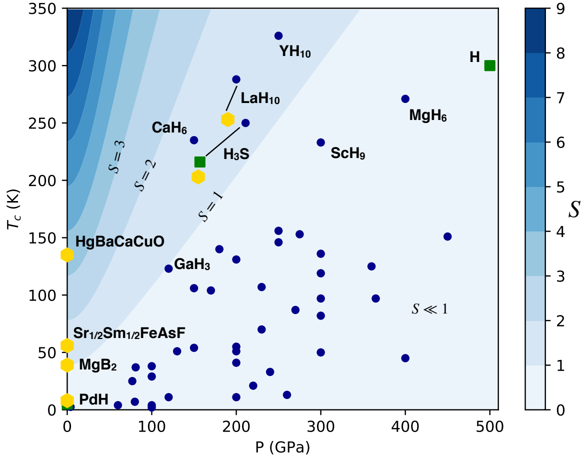
Outline

1. High-temperature superconductivity in hydrogen-based superconductors
2. Electron-phonon interaction in anharmonic crystals
3. Palladium Hydrides
4. H_3S
5. LaH_{10}
6. Conclusions

Superconductivity in hydrogen-based superconductors



Superconductivity in hydrogen-based superconductors



$$S = \frac{T_c}{\sqrt{T_{c,\mathrm{MgB_2}}^2 + P^2}}$$

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Electron-phonon interaction in anharmonic crystals

- The superconducting properties of materials can be calculated from the Eliashberg spectral function $\alpha^2 F(\omega)$

$$\alpha^2 F(\omega) = \frac{1}{N(E_F)N^2} \sum_{\substack{\mu \boldsymbol{q} \\ \boldsymbol{k} nm}} |g^{\mu}_{m\boldsymbol{k}+\boldsymbol{q},n\boldsymbol{k}}|^2 \delta(E_{\boldsymbol{k}n}) \delta(E_{\boldsymbol{k}+\boldsymbol{q}m}) \delta(\omega - \omega_{\mu}(\boldsymbol{q}))$$

where $N(E_F)$ is the electronic DOS at the Fermi level and

$$g^{\mu}_{m\mathrm{k}+\mathrm{q},n\mathrm{k}} = \sum_a \frac{e^a_{\mu}(\boldsymbol{q})}{\sqrt{2M_a \omega_{\mu}(\boldsymbol{q})}} \langle \psi_{m\boldsymbol{k}+\boldsymbol{q}} | \left[\frac{\partial V_{KS}}{\partial u_a(\boldsymbol{q})} \right]_{\boldsymbol{R}=\boldsymbol{R}_0} | \psi_{n\boldsymbol{k}} \rangle$$

- If we want to include anharmonic effects in the Eliashberg function, we substitute the harmonic phonon frequencies and polarization vectors by the anharmonic ones (auxiliary of those coming from the free energy Hessian)

$$\alpha^2 F(\omega) = \frac{1}{N(E_F^{\boldsymbol{\mathcal{R}}_0})N^2} \sum_{\substack{\mu \boldsymbol{q} \\ \boldsymbol{k} nm}} |\mathrm{g}^{\mu}_{m\boldsymbol{k}+\boldsymbol{q},n\boldsymbol{k}}|^2 \delta(E^{\boldsymbol{\mathcal{R}}_0}_{\boldsymbol{k}n}) \delta(E^{\boldsymbol{\mathcal{R}}_0}_{\boldsymbol{k}+\boldsymbol{q}m}) \delta(\omega - \mathtt{w}_{\mu}(\boldsymbol{q}))$$

with the electron-phonon coupling calculated at the $\boldsymbol{\mathcal{R}}_0$ positions

$$\mathrm{g}^{\mu}_{m\mathrm{k}+\mathrm{q},n\mathrm{k}} = \sum_a \frac{\mathrm{e}^a_{\mu}(\boldsymbol{q})}{\sqrt{2M_a \mathtt{w}_{\mu}(\boldsymbol{q})}} \langle \psi^{\boldsymbol{\mathcal{R}}_0}_{m\boldsymbol{k}+\boldsymbol{q}} | \left[\frac{\partial V_{KS}}{\partial u_a(\boldsymbol{q})} \right]_{\boldsymbol{R}=\boldsymbol{\mathcal{R}}_0} | \psi^{\boldsymbol{\mathcal{R}}_0}_{n\boldsymbol{k}} \rangle$$

Calculating the critical temperature

- With $\alpha^2 F(\omega)$ the electron-phonon coupling constant can be calculated

$$\lambda = 2 \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega}$$

- The superconducting critical temperature can also be calculated with Allen-Dynes modified McMillan equation

$$T_c = \frac{f_1 f_2 \omega_{\log}}{1.2} \exp\left[- \frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right]$$

with μ^* the effective repelling electron-electron interaction and

$$\omega_{\log} = \exp\left(\frac{2}{\lambda} \int d\omega \frac{\alpha^2 F(\omega)}{\omega} \log \omega \right)$$

$$f_1 = \left[1 + (\lambda/\Lambda_1)^{3/2} \right]^{1/3} \qquad f_2 = 1 + \frac{(\bar{\omega}_2/\omega_{\log} - 1)\lambda^2}{\lambda^2 + \Lambda_2^2}$$

$$\Lambda_1 = 2.46(1 + 3.8\mu^*) \qquad \Lambda_2 = 1.82(1 + 6.3\mu^*)(\bar{\omega}_2/\omega_{\log})$$

$$\bar{\omega}_2 = \left[\frac{2}{\lambda} \int d\omega \alpha^2 F(\omega) \omega \right]^{1/2}$$

Migdal-Eliashberg equations

- With $\alpha^2F(\omega)$ the Migdal-Eliashberg (isotropic) equations can be solved alternatively (more exact theory)

$$\begin{aligned} Z_n &= 1 + \frac{\pi T}{\omega_n} \sum_m \frac{\omega_m}{\sqrt{\omega_m^2 + \Delta_m^2}} \lambda_{nm} \\ \Delta_n &= \frac{\pi T}{Z_n} \sum_m \frac{\Delta_m}{\sqrt{\omega_m^2 + \Delta_m^2}} (\lambda_{nm} - \mu^*) \end{aligned}$$

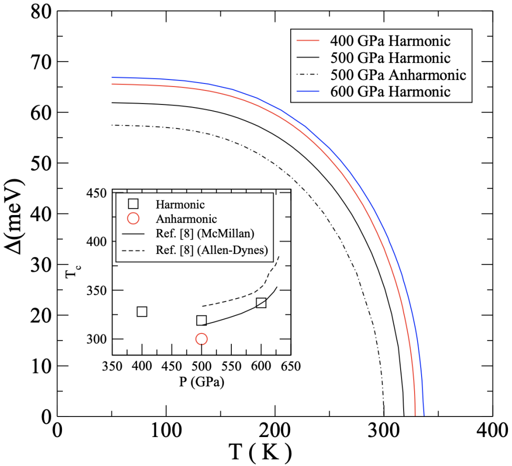
where

$$\omega_n = (2n+1)T\pi \quad \text{and} \quad \lambda_{nm} = \int d\Omega \frac{2\Omega}{(\omega_n - \omega_m)^2 + \Omega^2} \alpha^2 F(\Omega)$$

- The temperature at which Δ_0 vanishes determines the superconducting critical temperature

Migdal-Eliashberg equations

Atomic hydrogen



Borinaga *et al.*, PRB (2016)

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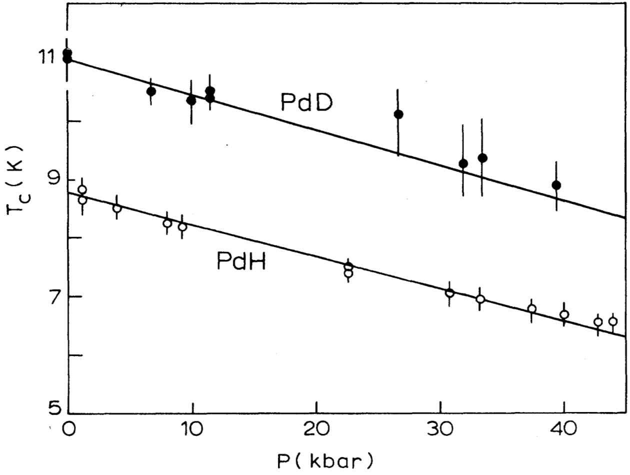
Inverse isotope effects in palladium hydrides

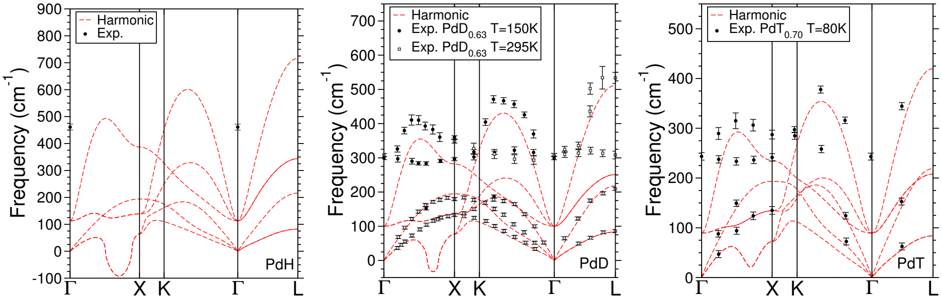
PdD has a higher T_c than PdH



Hemmes *et al.*, PRB (1989)

Anharmonic effects in palladium hydrides

PdH (0 GPa, 0 K)



Errea *et al.*, PRL (2013)

Anharmonic effects in palladium hydrides

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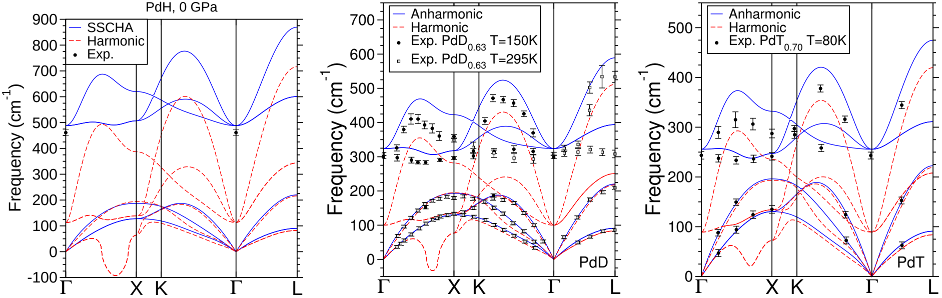
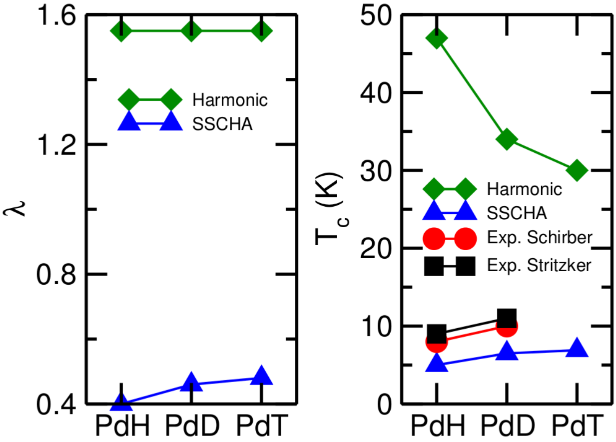


Errea *et al.*, PRL (2013)

Anharmonic effects in palladium hydrides induce the inversion of the isotope effect



Errea *et al.*, PRL (2013)

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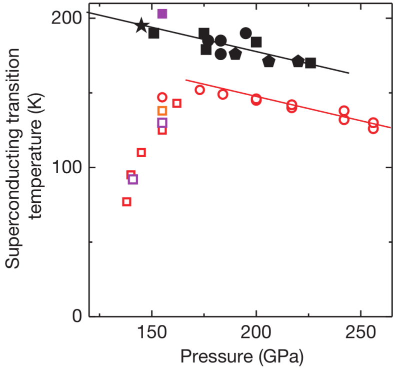
Record superconductivity in hydrogen sulfide

LETTER

doi:10.1038/nature14964

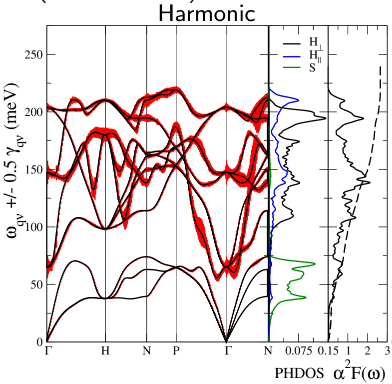
Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

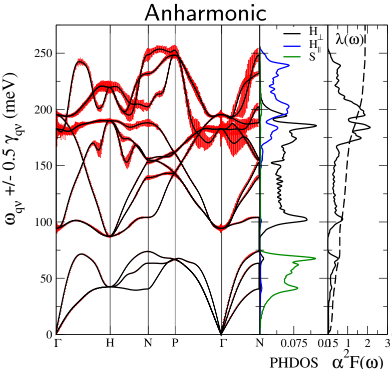
A. P. Drozdov[1]*, M. I. Eremets[1]*, I. A. Troyan[1], V. Ksenofontov[2] & S. I. Shylin[2]



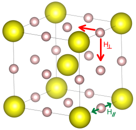
H_3S is an anharmonic electron-phonon superconductor

H_3S (200 GPa, 0 K)





	$\bar{\omega}_{H_\perp}$ (meV)	$\bar{\omega}_{H_\parallel}$ (meV)
Harmonic	157.0	158.1
Anharmonic	147.9	203.3



Errea *et al.*, PRL (2015)

The quantum nature of the proton symmetrizes the hydrogen bonds in H_3S

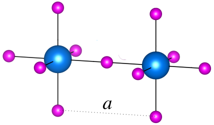
- Total energy as a function of $\mathcal{R}$

$$E(\mathcal{R}) = E_{BO}(\mathcal{R}) + E_{vib}(\mathcal{R})$$

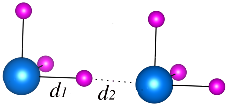
- The total energy calculated along the path defined by the reaction coordinate Q:

$$\mathcal{R}(Q) = \boldsymbol{R}_{Im\bar{3}m} + Q(\boldsymbol{R}_{R3m} - \boldsymbol{R}_{Im\bar{3}m})$$

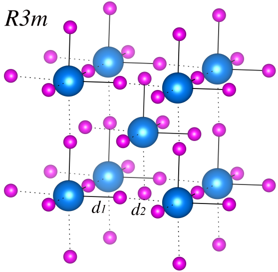
$Q = 0$:

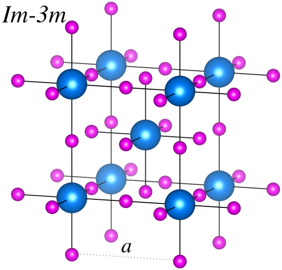


$Q = 1$:



Off-centering: $x = (d_2 - a/2)/(a/2)$





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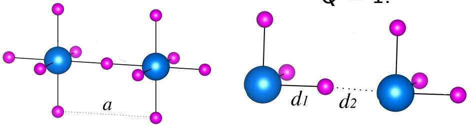

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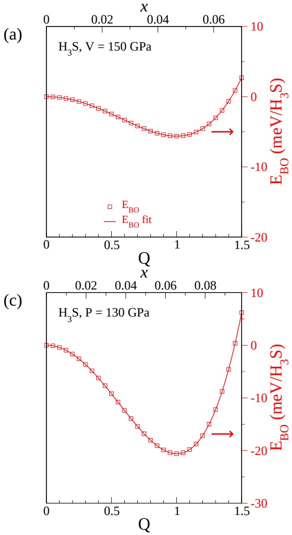

Errea *et al.*, Nature (2016)

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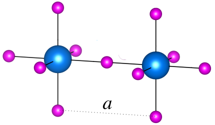

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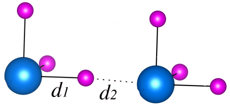

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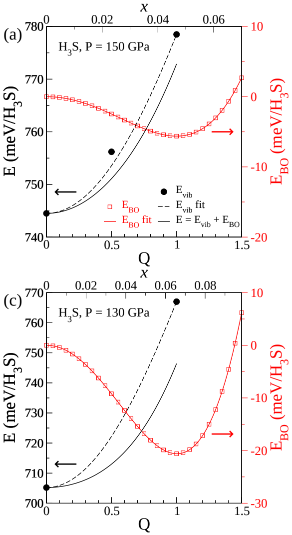
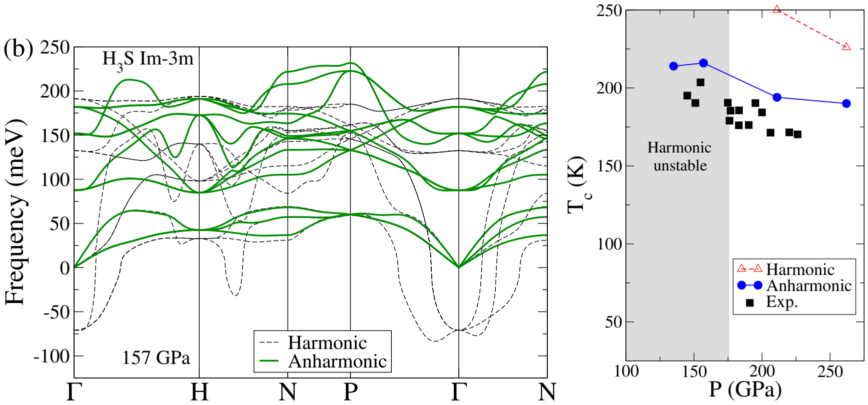


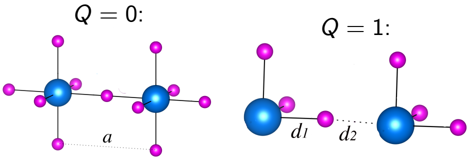
Errea *et al.*, Nature (2016)

The quantum symmetrization has a large impact on phonons and the superconducting T_c



Errea *et al.*, Nature (2016)

We determine the transition pressure by interpolating the obtained energies



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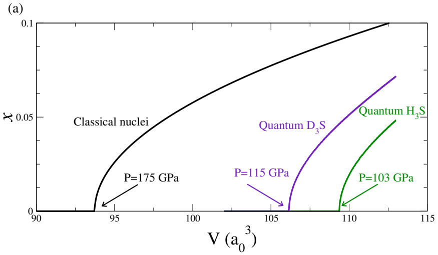

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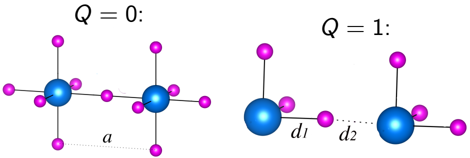

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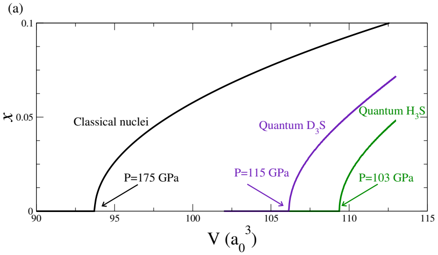

Isotope shift for the transition pressure: **12 GPa**

Errea *et al.*, Nature (2016)

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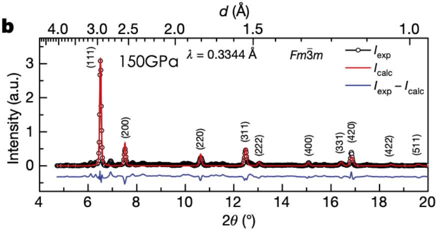
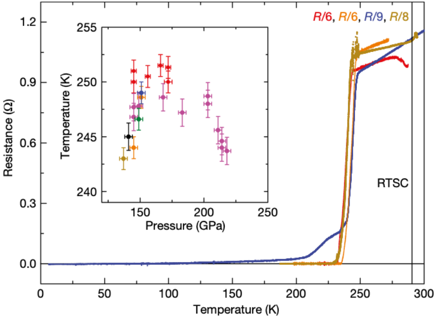
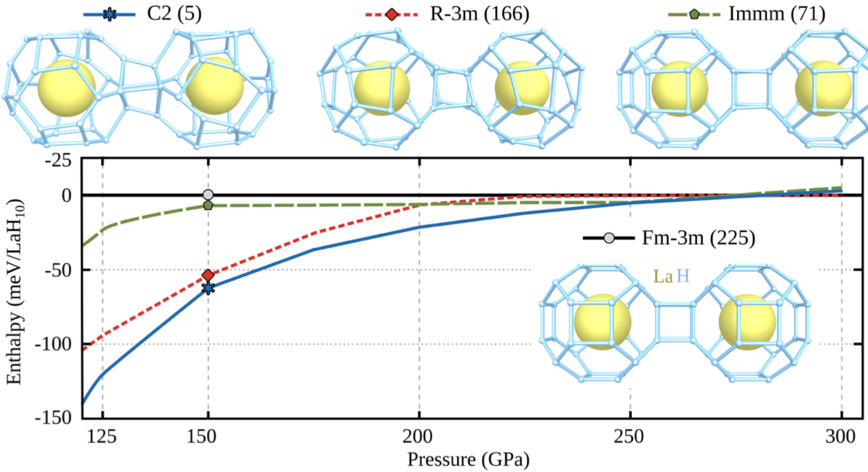
LaH_{10} a record superconductor





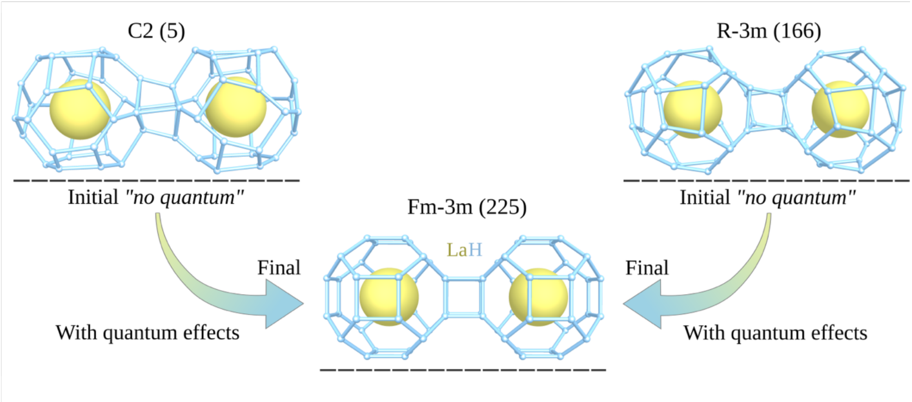
Drozdov *et al.*, Nature (2019)

Strongly distorted phases of LaH_{10}



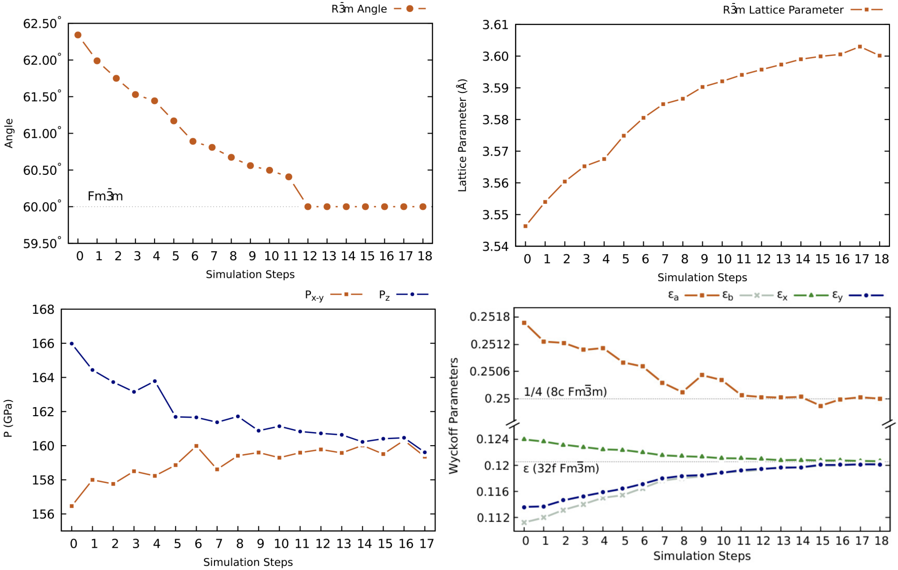
Errea *et al.*, Nature (2020)

Quantum structural relaxations in LaH_{10}



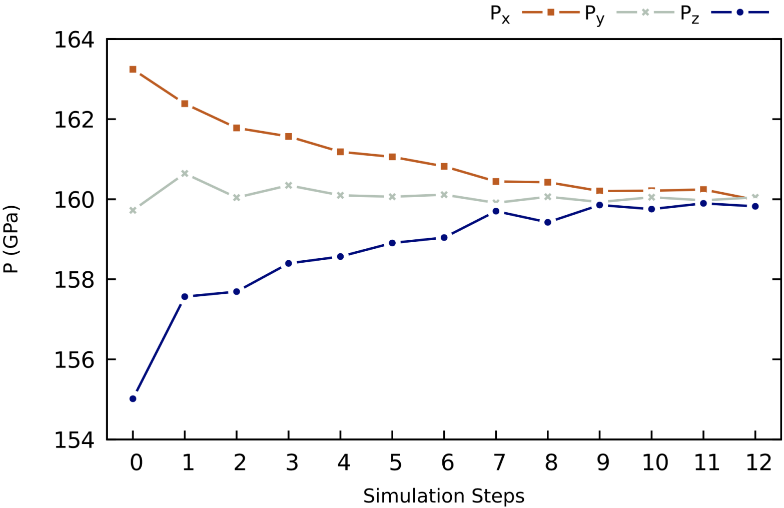
Errea *et al.*, Nature (2020)

Quantum structural relaxations in LaH_{10} $R\bar{3}m$



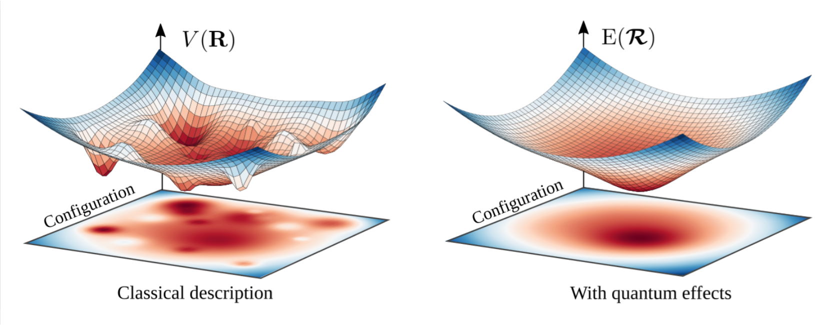
Errea *et al.*, Nature (2020)

Quantum structural relaxations in LaH_{10} $C2$



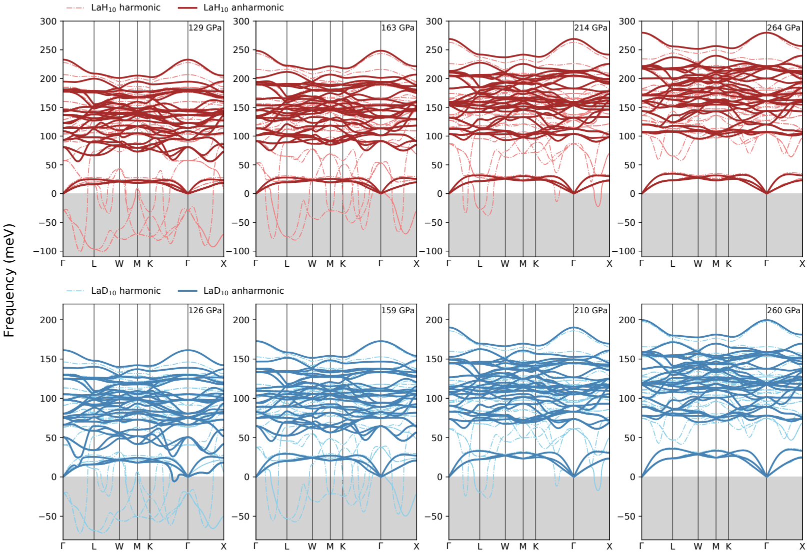
Errea *et al.*, Nature (2020)

The energy landscape is quantum



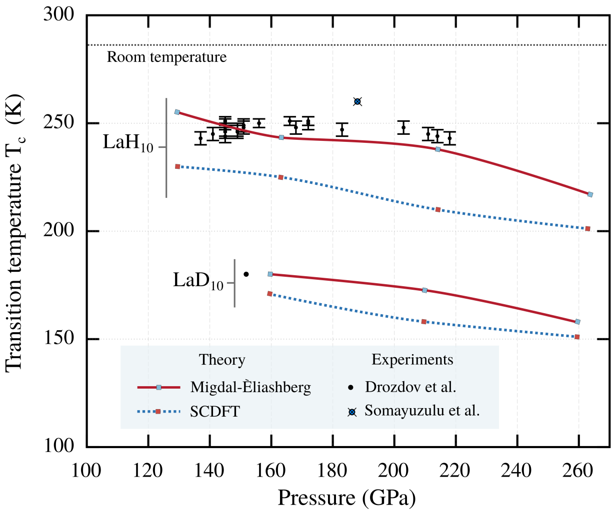
Errea *et al.*, Nature (2020)

Anharmonic phonons for $Fm\bar{3}m$ LaH_{10}



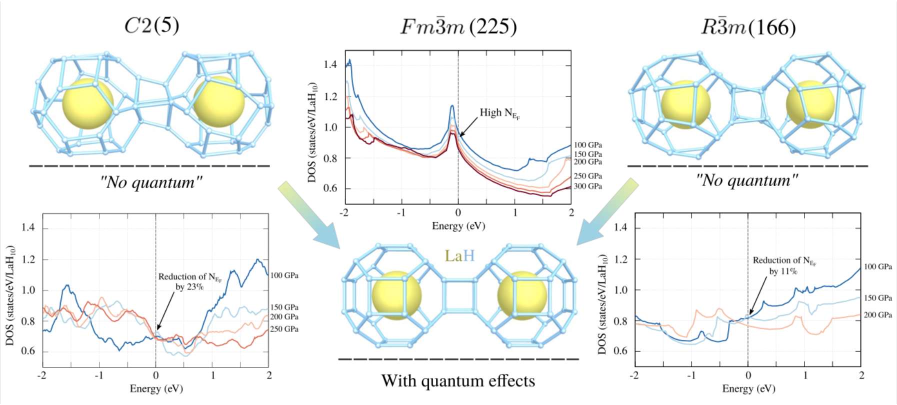
Errea *et al.*, Nature (2020)

T_c in agreement with experiments



Errea *et al.*, Nature (2020)

Quantum anharmonic enhancement of superconductivity



Errea *et al.*, Nature (2020)

Conclusions

1. Superhydrides are strongly affected by anharmonicity and quantum effects, both in the crystal structure and the phonon spectra, strongly affecting the superconducting properties
2. Quantum anharmonic effects can enhance the superconductivity by stabilizing structures that would otherwise be unstable classically at much lower pressures