



QUANTUM ESPRESSO
FOUNDATION

density-functional perturbation theory

response functions, phonons, and all that

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response functions

$$\text{property} = \frac{\partial(\text{variable})}{\partial(\text{strength})}$$



response functions

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👉 polarizability, dielectric constant

$$\frac{\partial P_i}{\partial E_j}$$

👉 elastic constants

$$\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}$$

👉 piezoelectric constants

$$\frac{\partial P_i}{\partial \epsilon_{kl}}$$

👉 interatomic force constants

$$\frac{\partial f_i^s}{\partial u_j^t}$$

👉 Born effective charges

$$\frac{\partial d_i^s}{\partial u_j^s}$$

👉 ...

...



susceptibilities as energy derivatives

$$\hat{H}_\alpha = \hat{H}^\circ + \alpha \hat{A}$$

$$\chi_{BA} = \frac{\partial \langle \hat{B} \rangle_\alpha}{\partial \alpha}$$



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$$\langle \hat{B} \rangle = \frac{\partial E_\beta}{\partial \beta}$$

(Hellmann & Feynman)

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(Hellmann & Feynman)

$$\hat{H}_\beta = \hat{H}^\circ + \beta \hat{B}$$

$$\chi_{BA} = \frac{\partial^2 E_{\alpha\beta}}{\partial \alpha \partial \beta}$$

$$\hat{H}_{\alpha\beta} = \hat{H}^\circ + \alpha \hat{A} + \beta \hat{B}$$



energy derivatives

$$H = H_0 + \sum_i \lambda_i v_i$$



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$$H = H_0 + \sum_i \lambda_i v_i$$
$$E[\lambda] = E_0 - \sum_i f_i \lambda_i + \frac{1}{2} \sum_{ij} h_{ij} \lambda_i \lambda_j + \dots$$



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- 👉 structural optimization & molecular dynamics



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- 👉 structural optimization & molecular dynamics
- 👉 (static) response functions
 - elastic constants
 - dielectric tensor
 - piezoelectric tensor
 - ...
- 👉 vibrational modes in the adiabatic approximation
 - interatomic force constants
 - Born effective charges
 - ...



energy derivatives from perturbation

$$H = H_0 + \sum_i \lambda_i v_i \quad E[\lambda] = E_0 - \sum_i f_i \lambda_i + \frac{1}{2} \sum_{ij} h_{ij} \lambda_i \lambda_j + \dots$$



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the “2n+1” theorem

$$\Phi = \Phi_0 + \mathcal{O}(\epsilon) \Rightarrow E = E_0 + \mathcal{O}(\epsilon^2)$$



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$$E^{(3)} = \langle \Phi' | V' | \Phi' \rangle - \langle \Phi' | \Phi' \rangle \langle \Phi_0 | V' | \Phi_0 \rangle$$



density-functional perturbation theory

$$V_\lambda(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i \lambda_i v_i(\mathbf{r})$$



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$$\frac{\partial^2 E(\lambda)}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda_j} v_i(\mathbf{r}) d\mathbf{r} \quad \text{DFPT}$$



calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$n'(\mathbf{r}) = 2\text{Re} \sum_v \phi_v^{\circ*}(\mathbf{r}) \phi'_v(\mathbf{r})$$



calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

$$\begin{aligned} n'(\mathbf{r}) &= 2\text{Re} \sum_v \phi_v^{\circ*}(\mathbf{r}) \phi'_v(\mathbf{r}) \\ &= 2\text{Re} \sum_{cv} \rho'_{vc} \phi_v^{\circ*}(\mathbf{r}) \phi_c^{\circ}(\mathbf{r}) \end{aligned}$$

$$\phi'_v = \sum_c \phi_c^{\circ} \frac{\langle \phi_c^{\circ} | V' | \phi_v^{\circ} \rangle}{\epsilon_v^{\circ} - \epsilon_c^{\circ}}$$



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$$(H^{\circ} - \epsilon_v^{\circ}) \phi'_v = -P_c V' \phi_v^{\circ}$$



calculating the response

$$n'(\mathbf{r}) = 2\text{Re} \sum_v \phi_v^{\circ*}(\mathbf{r}) \phi_v'(\mathbf{r})$$

$$(H^\circ - \epsilon_v^\circ) \phi_v' = -P_c V' \phi_v^\circ$$



DFPT: the equations

DFT

$$V_0(\mathbf{r}) \Leftarrow n(\mathbf{r})$$

$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

$$(-\Delta + V_{SCF}(\mathbf{r}))\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r})$$



DFPT: the equations

DFT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

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$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

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DFPT

$$V'(\mathbf{r}) \leftrightarrows n'(\mathbf{r})$$

$$V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \frac{n'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu'_{xc}(\mathbf{r})$$

$$n'(\mathbf{r}) = 2 \operatorname{Re} \sum_{\epsilon_v < E_F} \phi_v^*(\mathbf{r}) \phi'_v(\mathbf{r})$$

$$(-\Delta + V_{SCF}(\mathbf{r}) - \epsilon_v) \phi'_v(\mathbf{r}) = P_c V'_{SCF}(\mathbf{r}) \phi_v(\mathbf{r})$$

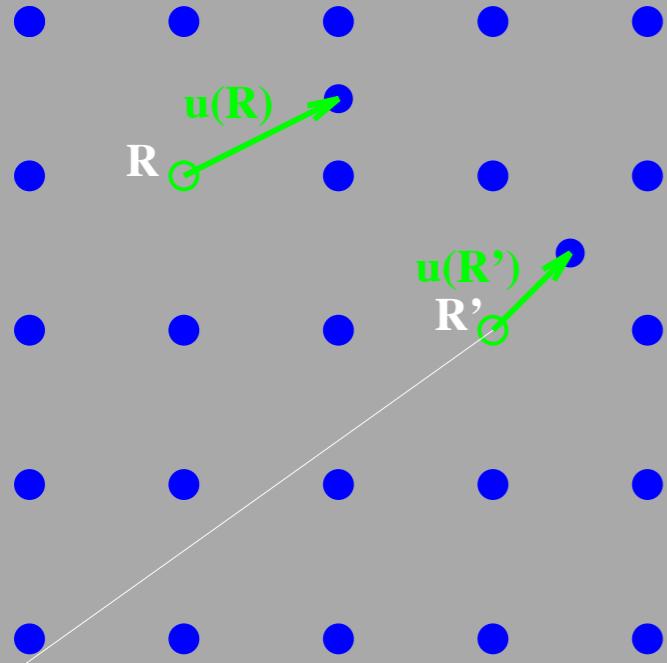


SB, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)

simulating atomic vibrations ...

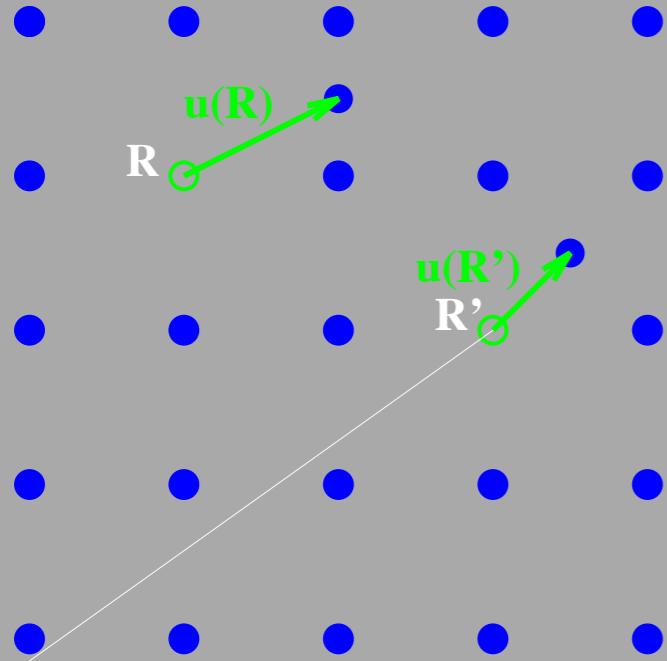


lattice dynamics



$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r} - \mathbf{R})}{\partial \mathbf{R}} + \dots$$

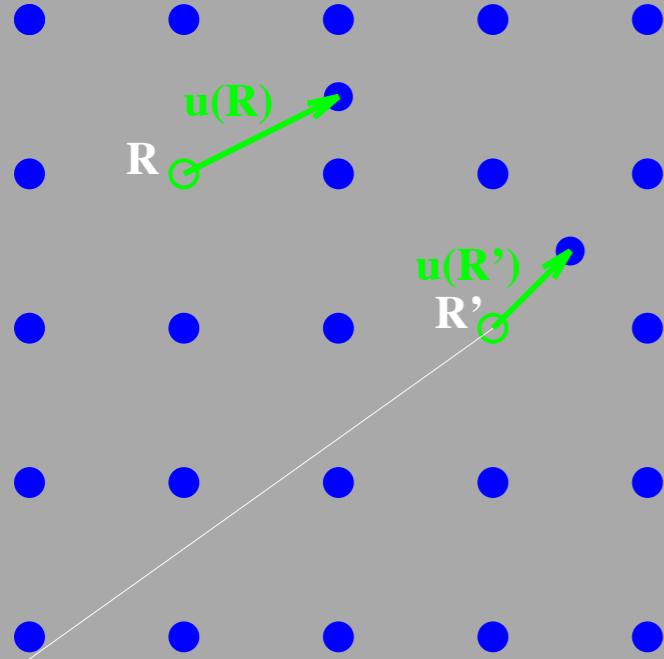
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$$E = E_0 + \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}') + \dots$$

lattice dynamics

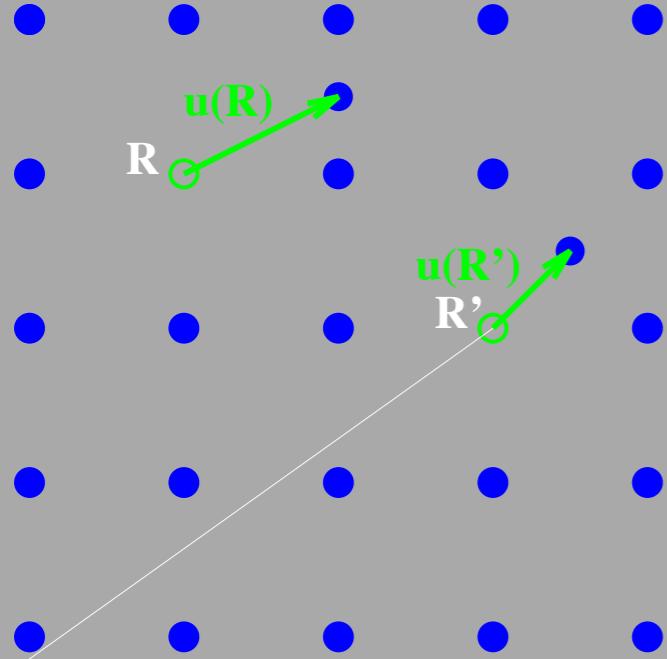


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$-\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{u}(\mathbf{R}')}$

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lattice dynamics

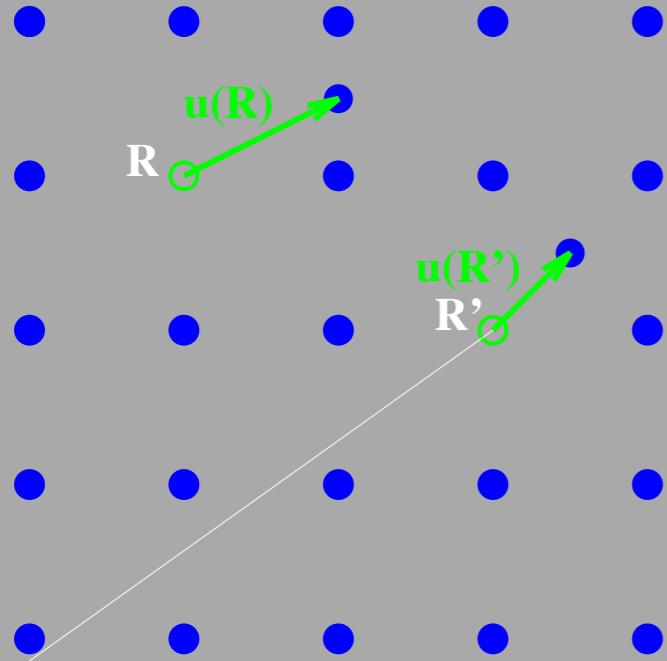


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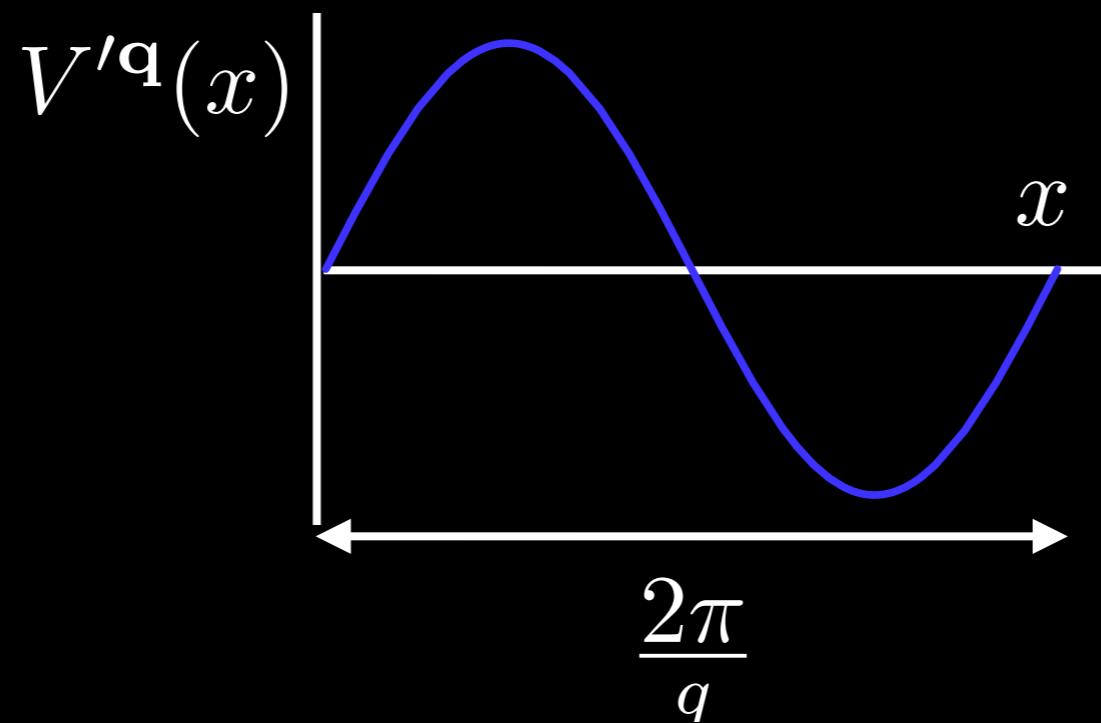
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$$\det \left[\frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')} - \omega^2 M(\mathbf{R}) \delta_{\mathbf{R}, \mathbf{R}'} \right] = 0$$

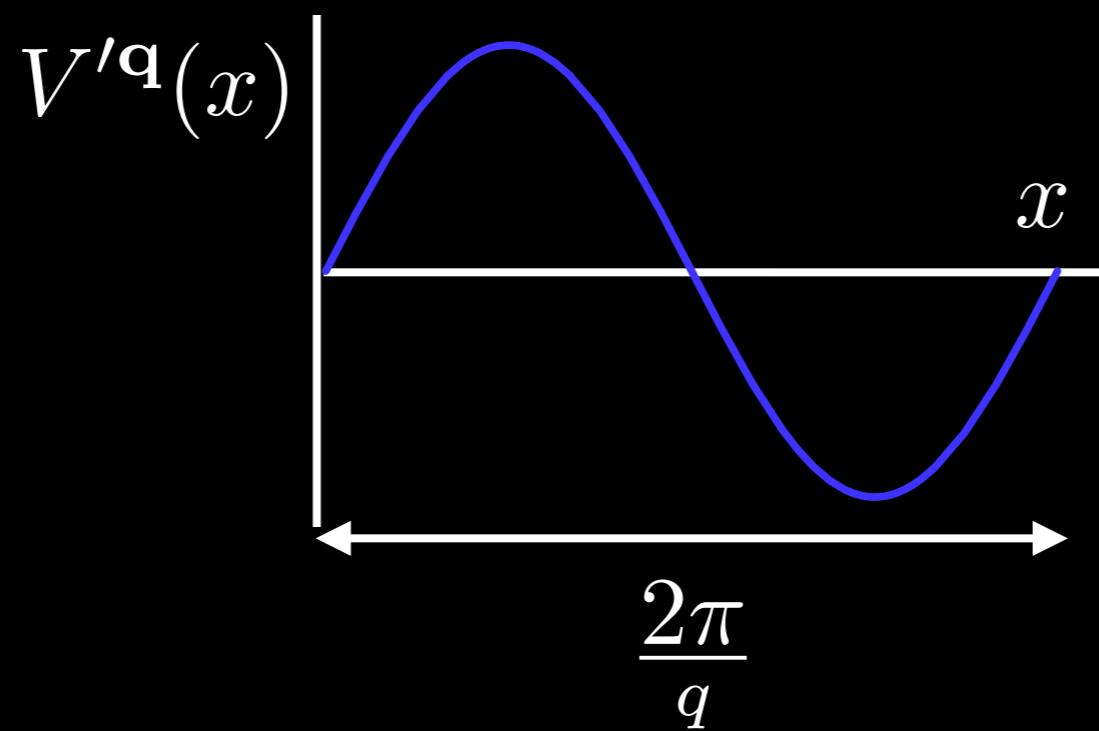
monochromatic perturbations



DFPT rhs:

$$-P_c V'^{\mathbf{q}}_{SCF} \phi_v^{\mathbf{k}}(\mathbf{r})$$

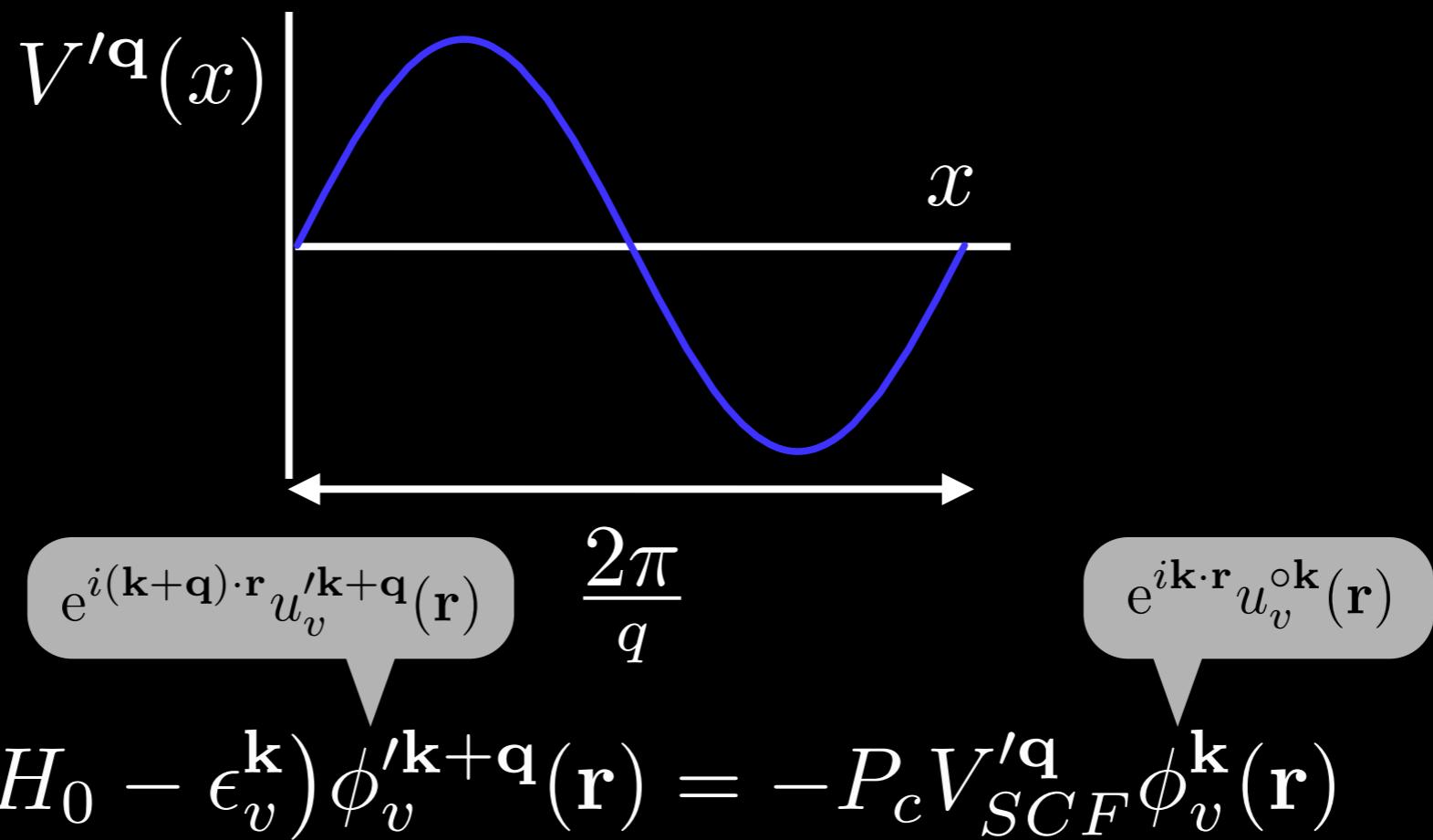
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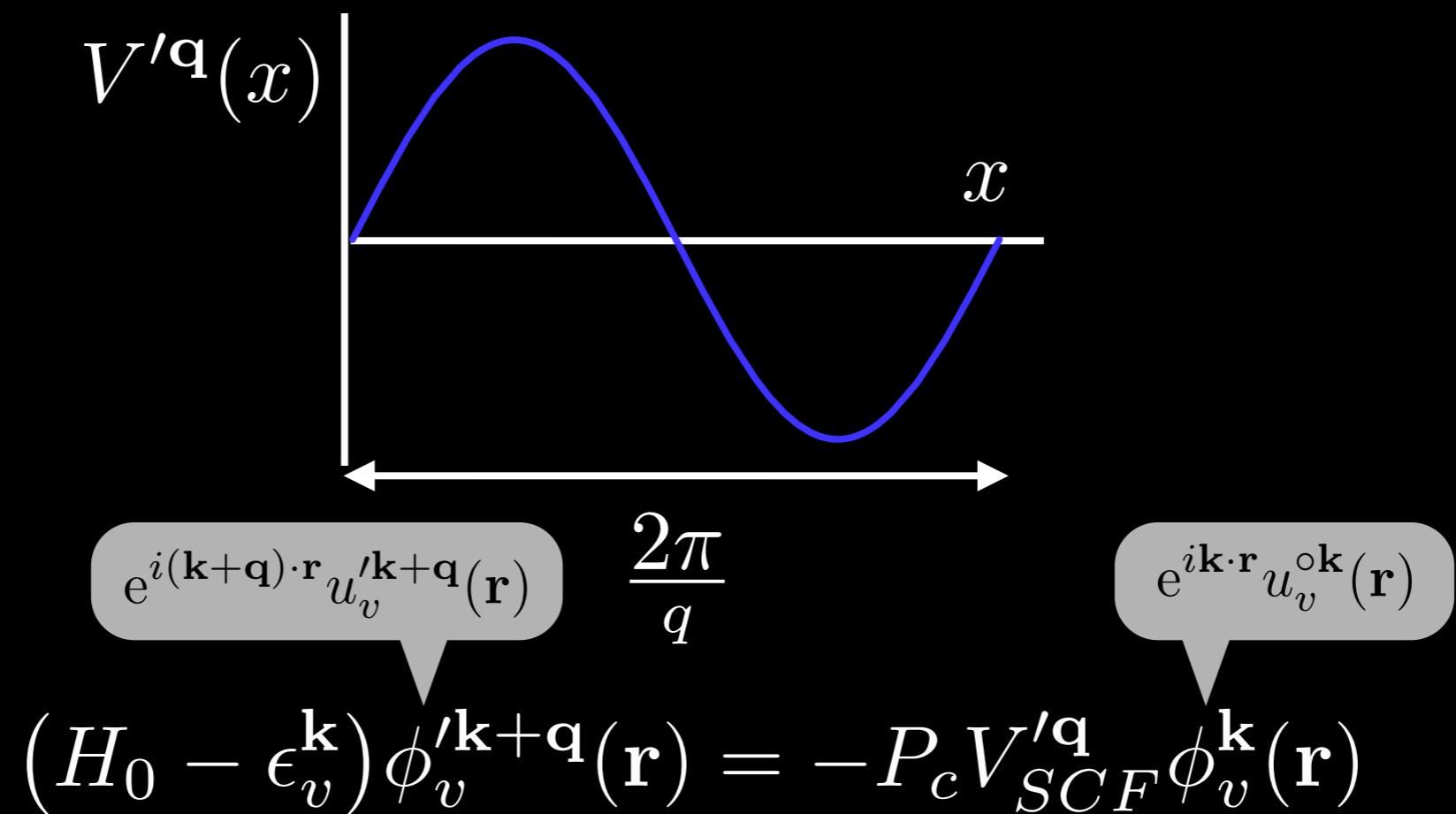
$$(H_0 - \epsilon_v^{\mathbf{k}}) \phi_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r}) = -P_c V_{SCF}'^{\mathbf{q}} \phi_v^{\mathbf{k}}(\mathbf{r})$$



monochromatic perturbations

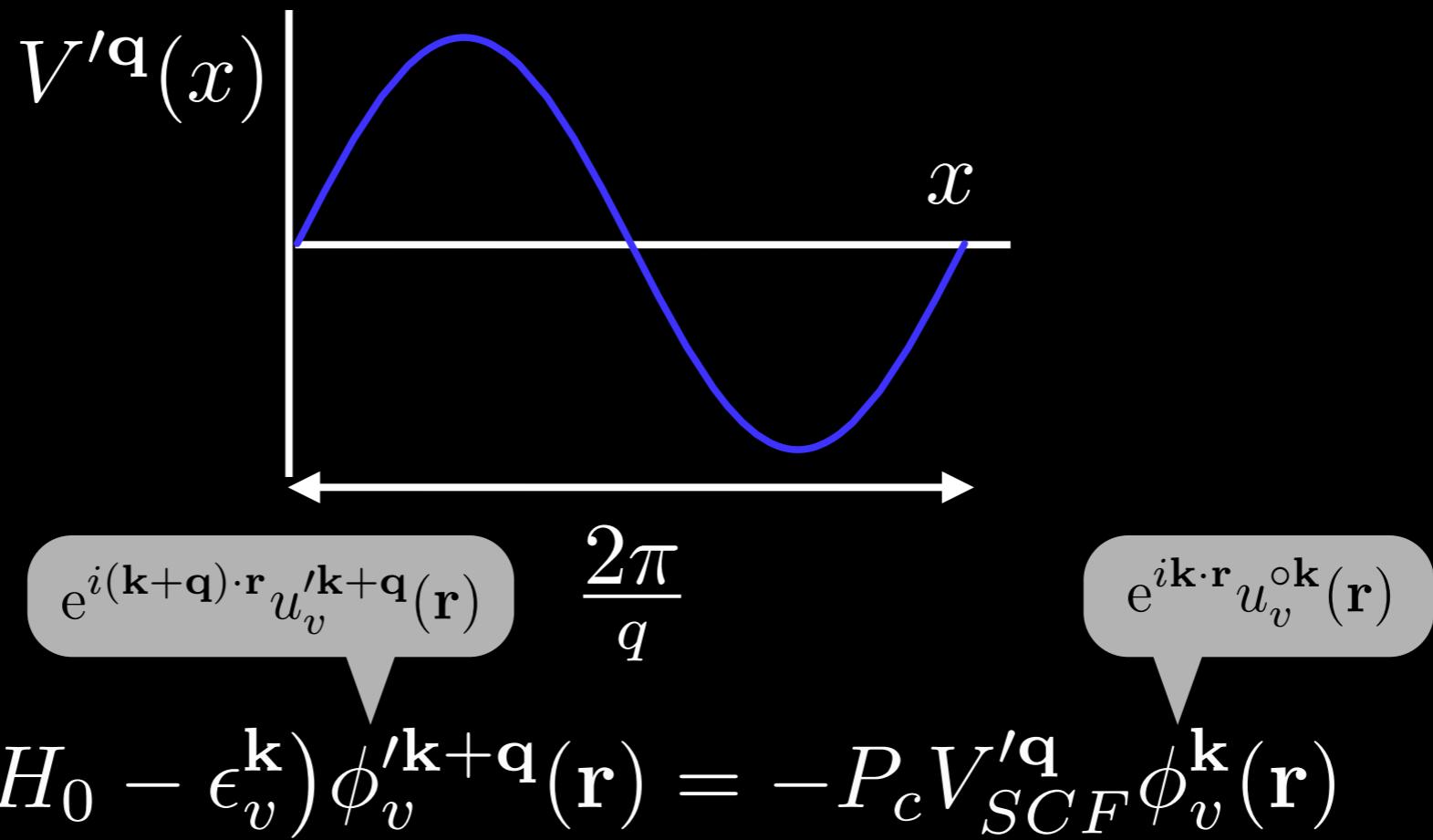


monochromatic perturbations



$$n'^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \sum_{v,\mathbf{k}} u_v^{\circ\mathbf{k}*}(\mathbf{r}) u_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

monochromatic perturbations



$$n'^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \sum_{v,\mathbf{k}} u_v^{\circ \mathbf{k}*}(\mathbf{r}) u_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

$$V'^{\mathbf{q}}(\mathbf{r}) = V_{ext}'^{\mathbf{q}}(\mathbf{r}) + \int \left(\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \kappa_{xc}(\mathbf{r}, \mathbf{r}') \right) n'^{\mathbf{q}}(\mathbf{r}') d\mathbf{r}'$$

phonons in polar materials

$$E(\mathbf{u}) = \frac{1}{2} M \omega_0^2 u^2$$



phonons in polar materials

$$E(\mathbf{u}, \mathbf{E}) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi} \epsilon_\infty \mathbf{E}^2 - e Z^* \mathbf{u} \cdot \mathbf{E}$$



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$$\mathbf{F} \equiv -\frac{\partial E}{\partial \mathbf{u}} = -M \omega_0^2 \mathbf{u} + Z^* \mathbf{E}$$

$$\mathbf{D} \equiv -\frac{4\pi}{\Omega} \frac{\partial E}{\partial \mathbf{E}} = \frac{4\pi}{\Omega} Z^* \mathbf{u} + \epsilon_\infty \mathbf{E}$$



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phonons in polar materials

$$E(\mathbf{u}, \mathbf{E}) = \frac{1}{2} M \omega_0^2 u^2 - \frac{\Omega}{8\pi} \epsilon_\infty \mathbf{E}^2 - e Z^* \mathbf{u} \cdot \mathbf{E}$$

$$\mathbf{F} \equiv -\frac{\partial E}{\partial \mathbf{u}} = -M \omega_0^2 \mathbf{u} + Z^* \mathbf{E}$$

$$\mathbf{D} \equiv -\frac{4\pi}{\Omega} \frac{\partial E}{\partial \mathbf{E}} = \frac{4\pi}{\Omega} Z^* \mathbf{u} + \epsilon_\infty \mathbf{E}$$

$$\text{rot } \mathbf{E} \sim i \mathbf{q} \times \mathbf{E} = 0 \quad \mathbf{u} \perp \mathbf{q} \Rightarrow \mathbf{E} = 0 \quad (\text{T})$$

$$\text{div } \mathbf{D} \sim i \mathbf{q} \cdot \mathbf{D} = 0 \quad \mathbf{u} \parallel \mathbf{q} \Rightarrow \mathbf{D} = 0 \quad (\text{L})$$

$$\mathbf{F}_{\textcolor{red}{T}} = -M \omega_0^2 \mathbf{u}$$



phonons in polar materials

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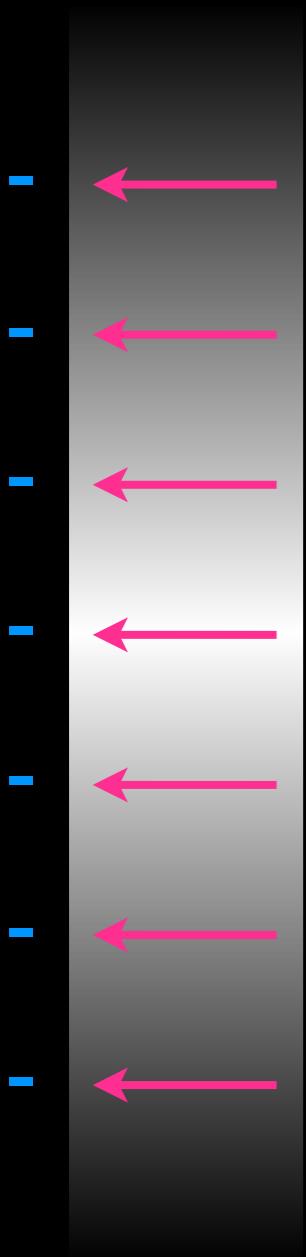
$$\mathbf{F}_T = -M \omega_0^2 \mathbf{u}$$

$$\mathbf{F}_L = -M \left(\omega_0^2 + \frac{4\pi Z^*}{M \Omega \epsilon_\infty} \right) \mathbf{u}$$



macroscopic electric fields

$$\mathbf{E} = \text{const}$$

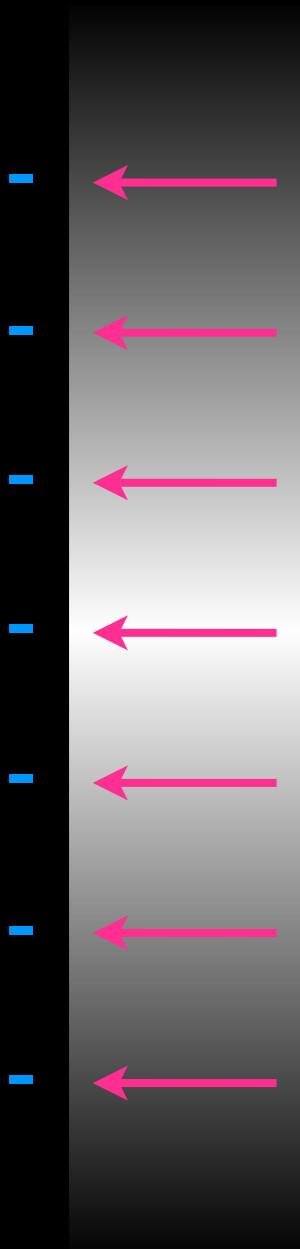


$$V'(\mathbf{r}) = \mathbf{E} \cdot \mathbf{r}$$

macroscopic electric fields

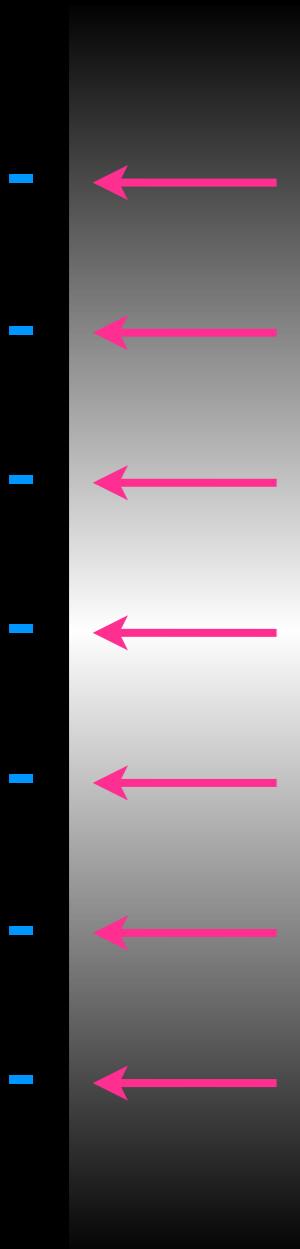
$$\mathbf{E} = \text{const}$$

$$\phi_v^0(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r})$$



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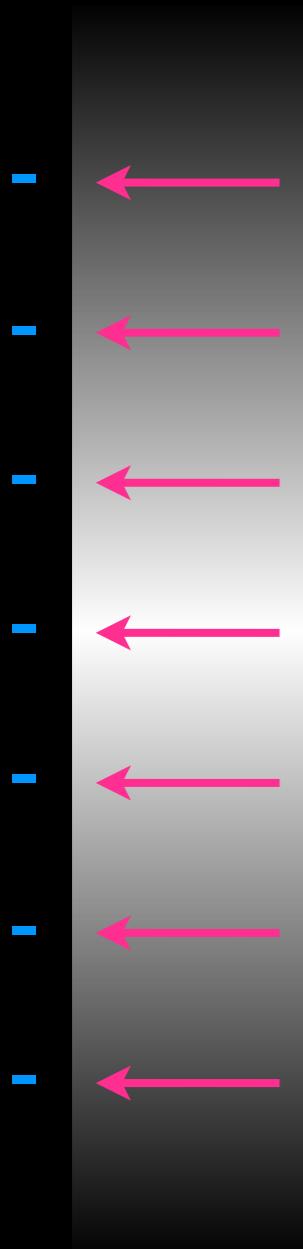
$$V'(\mathbf{r})\phi_v^0(\mathbf{r}) = ??$$



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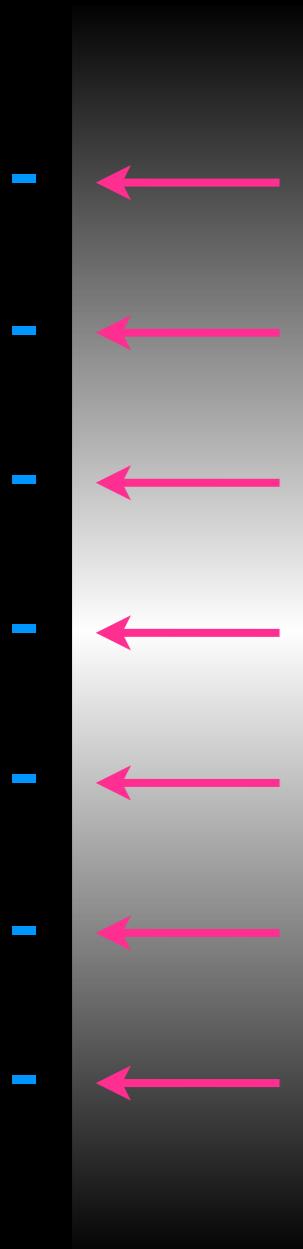


$$\begin{aligned}\phi_v^0(\mathbf{r}) &= e^{i\mathbf{k} \cdot \mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r}) \\ V'(\mathbf{r}) \phi_v^0(\mathbf{r}) &= ??\end{aligned}$$

$$-P_c V' \phi_v^0 = -\mathsf{E} \sum_c \phi_c^0 \langle \phi_c^0 | x | \phi_v^0 \rangle$$

macroscopic electric fields

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$$\phi_v^0(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{v,\mathbf{k}}(\mathbf{r})$$
$$V'(\mathbf{r})\phi_v^0(\mathbf{r}) = ??$$

$$\langle \phi_v^0 | x | \phi_u^0 \rangle = \frac{\langle \phi_v^0 | [H, x] | \phi_u^0 \rangle}{\epsilon_v^0 - \epsilon_u^0} \quad [H, x] = -\frac{\hbar^2}{m} \frac{\partial}{\partial x} + [H, V_{nl}]$$

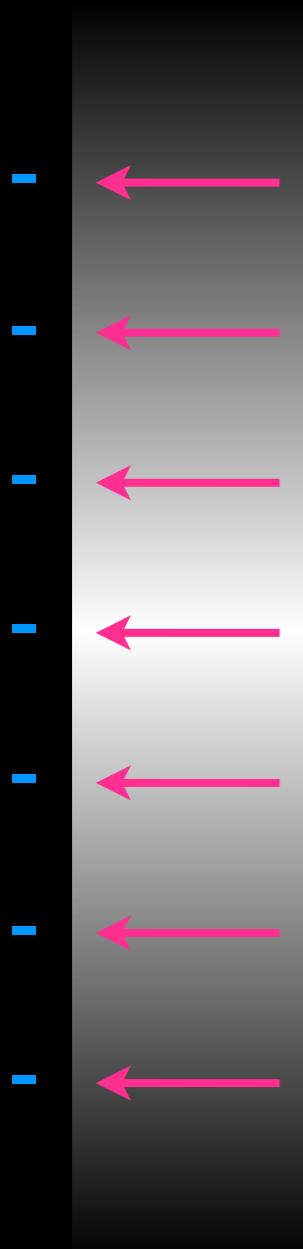
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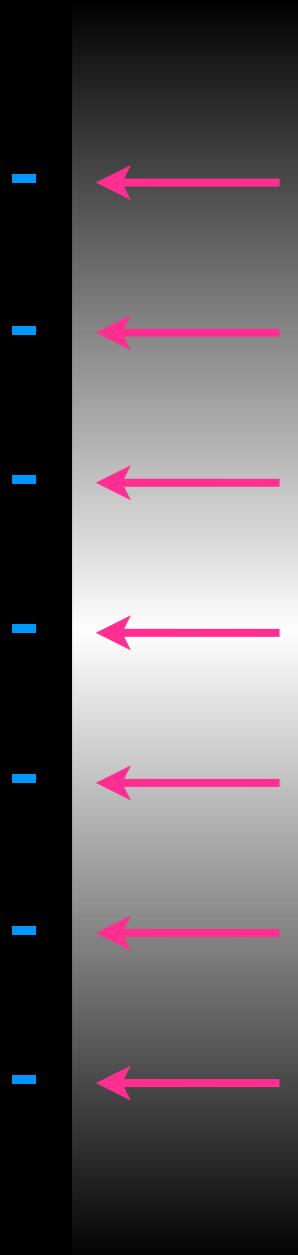
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macroscopic electric fields

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$$V'(\mathbf{r}) = \mathbf{E} \cdot \mathbf{r}$$

$$(H_0 - \epsilon_v^0) \psi'_v = -\mathsf{E} P_c [H_0, x] \phi_v^0$$

DFPT rhs

interatomic force constants

$$\Phi_{st}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') = -\frac{\partial^2 E}{\partial u_s^\alpha(\mathbf{R}) \partial u_t^\beta(\mathbf{R}')}$$



interatomic force constants

$$\begin{aligned}\Phi_{st}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') &= -\frac{\partial^2 E}{\partial u_s^\alpha(\mathbf{R}) \partial u_t^\beta(\mathbf{R}')} \\ &= \frac{\Omega}{(2\pi)^3} \int e^{i\mathbf{q} \cdot (\mathbf{R} - \mathbf{R}')} D_{st}^{\alpha\beta}(\mathbf{q}) d\mathbf{q}\end{aligned}$$



interatomic force constants

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short ranged +
dipole-dipole



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short ranged +
dipole-dipole

- remove singularities in $D(\mathbf{q})$
- do FFT's (# R's = # q's - the shorter the range, the coarser the grid)
- store information
- interpolate $D(\mathbf{q})$ on any finer mesh (pad Φ with 0's and do FFT^{-1} : # q's = # R's)
- calculate phonon bands



DFPT: the main features

- ☞ response functions calculated in terms of response orbitals, $\{\phi'_v\}$



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- non-periodic perturbations: OK



DFPT: the main features

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- calculate the response to the perturbation you want, only
- non-local perturbations: OK
- non-periodic perturbations: OK
- macroscopic electric fields: OK



Piezoelectric Properties of III-V Semiconductors from First-Principles Linear-Response Theory

Stefano de Gironcoli^(a)

Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I-34014 Trieste, Italy

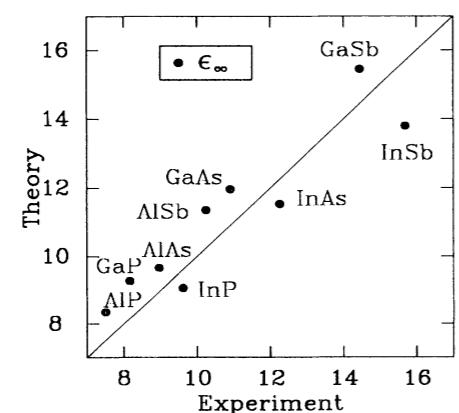
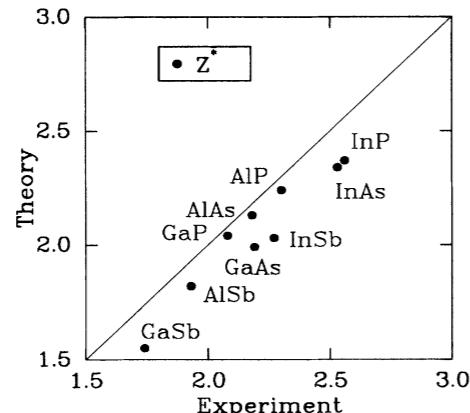
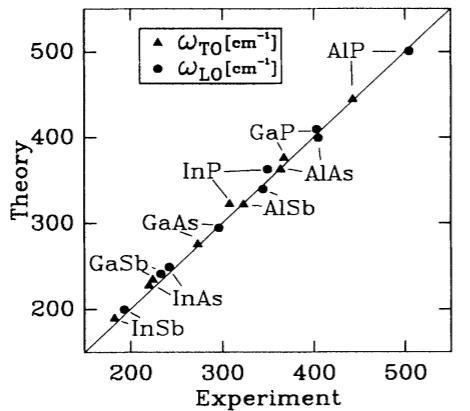
Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati (SISSA), Strada Costiera 11, I-34014 Trieste, Italy

Raffaele Resta^(b)

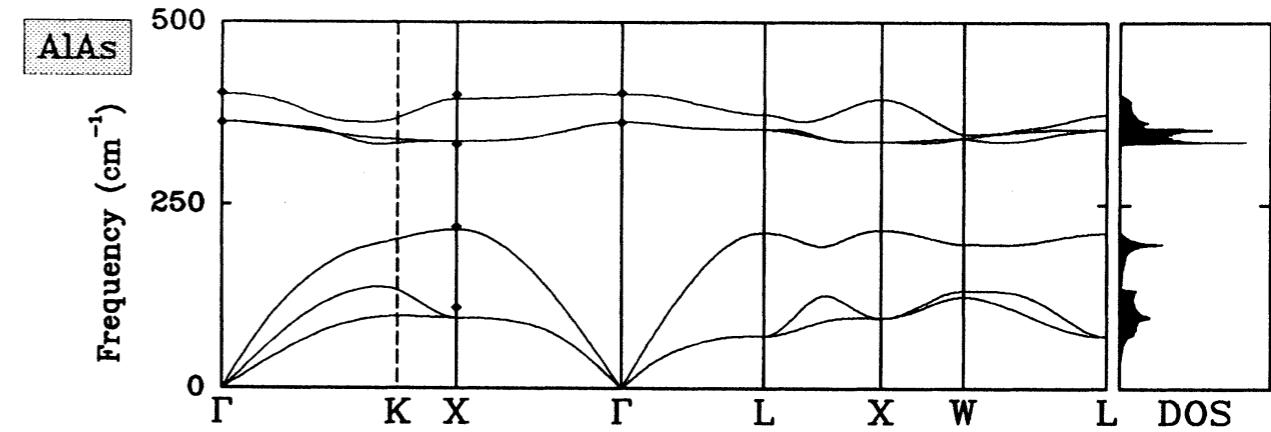
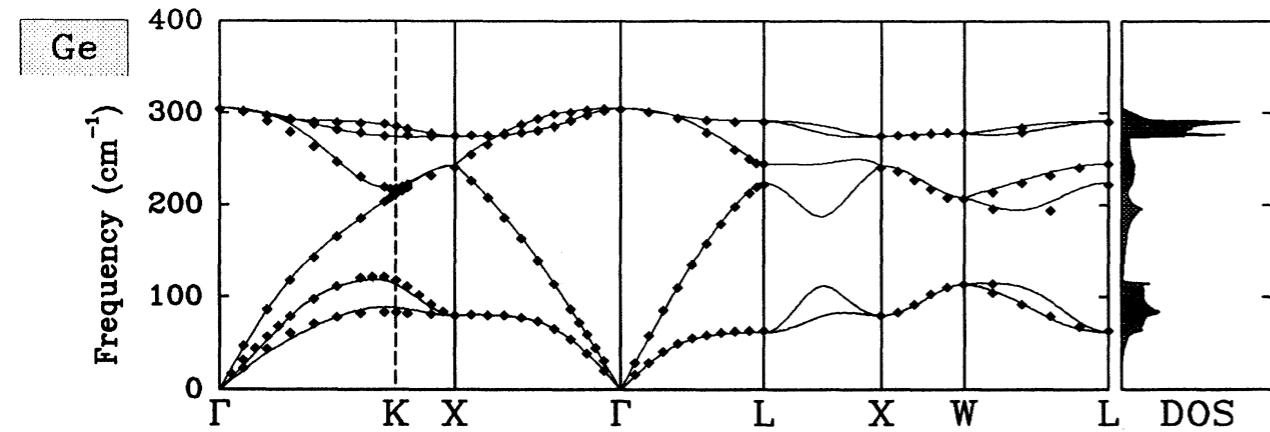
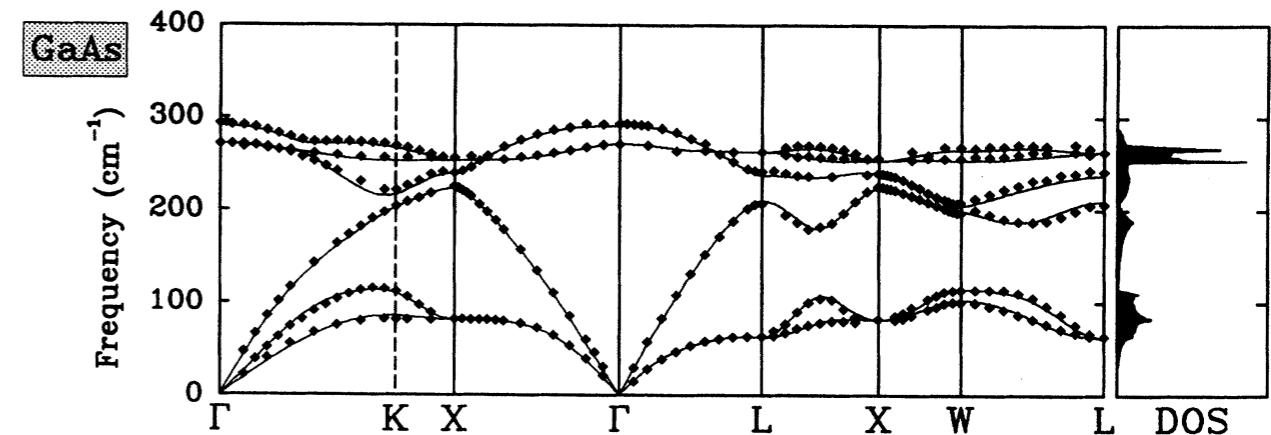
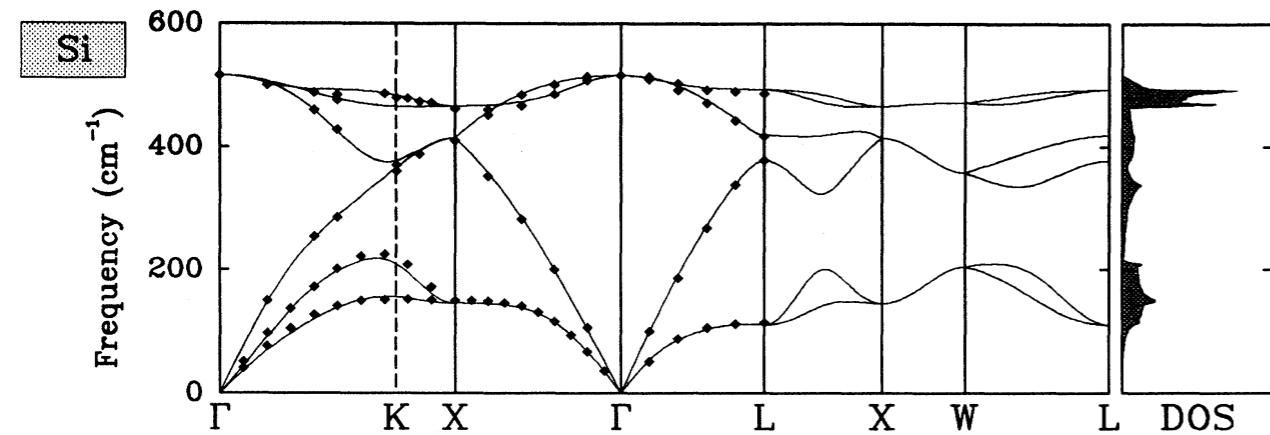
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMa), Ecole Polytechnique
Fédérale de Lausanne, CH-1015, Lausanne, Switzerland

(Received 7 November 1988)



$\bar{\gamma}_{14}$	P	As	Sb
Al	0.11 (...)	-0.03 (...)	-0.13 (-0.16)
Ga	-0.18 (-0.18)	-0.35 (-0.32)	-0.40 (-0.39)
In	0.12 (0.09)	-0.08 (-0.10)	-0.20 (-0.18)

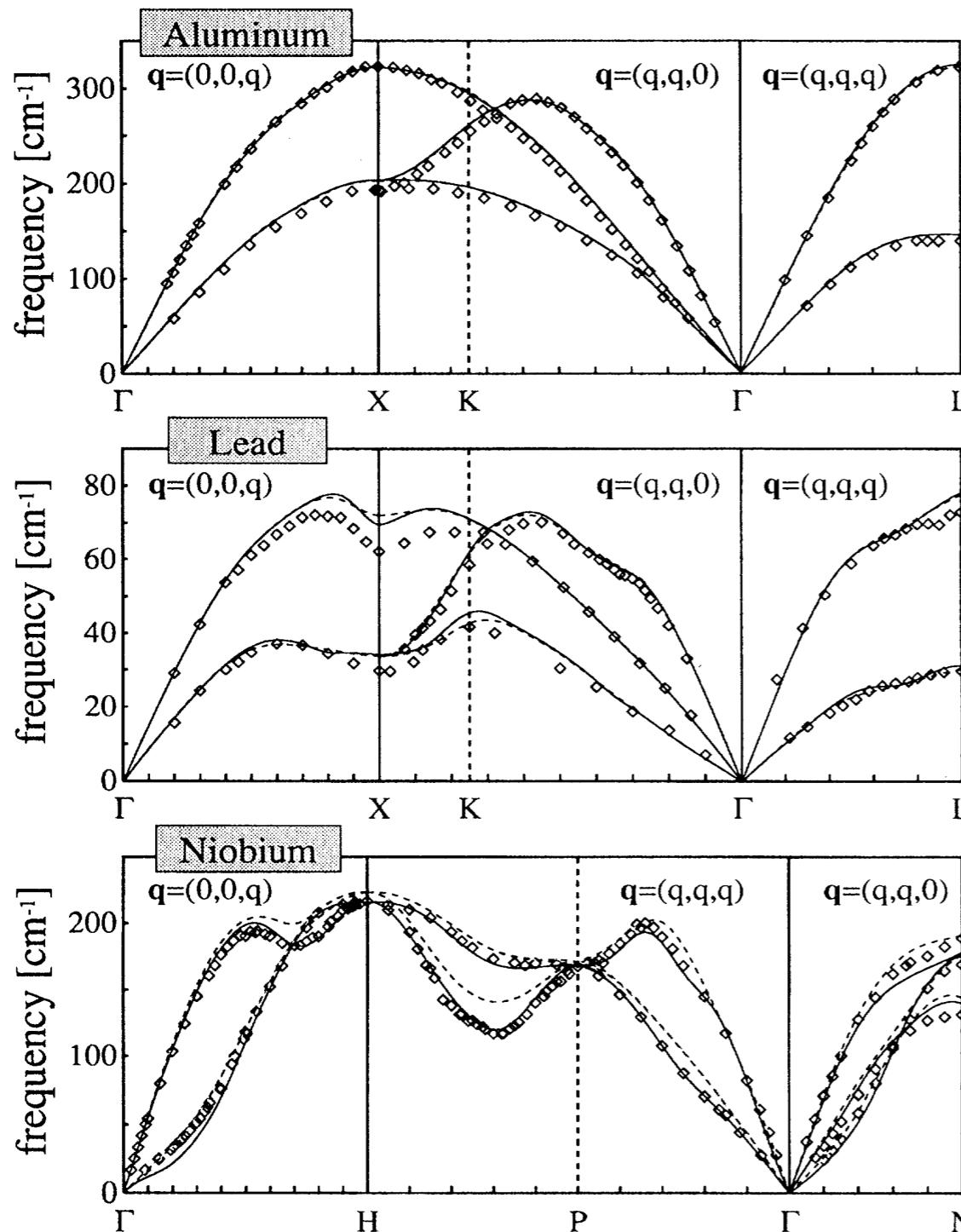
phonons from DFPT



P. Giannozzi, S. de Gironcoli, P. Pavone, and SB, Phys. Rev. B **43**, 7231 (1991)



DFPT phonons in metals



Stefano de Gironcoli,
Phys. Rev. B **51**, 6773 (1995)

applications done so far

- Dielectric properties
- Piezoelectric properties
- Elastic properties
- Phonon in crystals and alloys
- Phonon at surfaces, interfaces, super-lattices, and nano-structures
- Raman and infrared activities
- Anharmonic couplings and vibrational line widths
- Mode softening and structural transitions
- Electron-phonon interaction and superconductivity
- Thermal expansion
- Isotopic effects on structural and dynamical properties
- Thermo-elasticity and other thermal properties of minerals
- ...

SB, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, *Phonons and related crystal properties from density-functional perturbation theory*, Rev. Mod. Phys. **73**, 515 (2001)



a sampler of recent applications

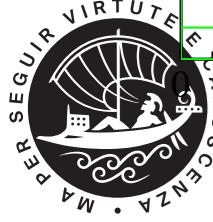
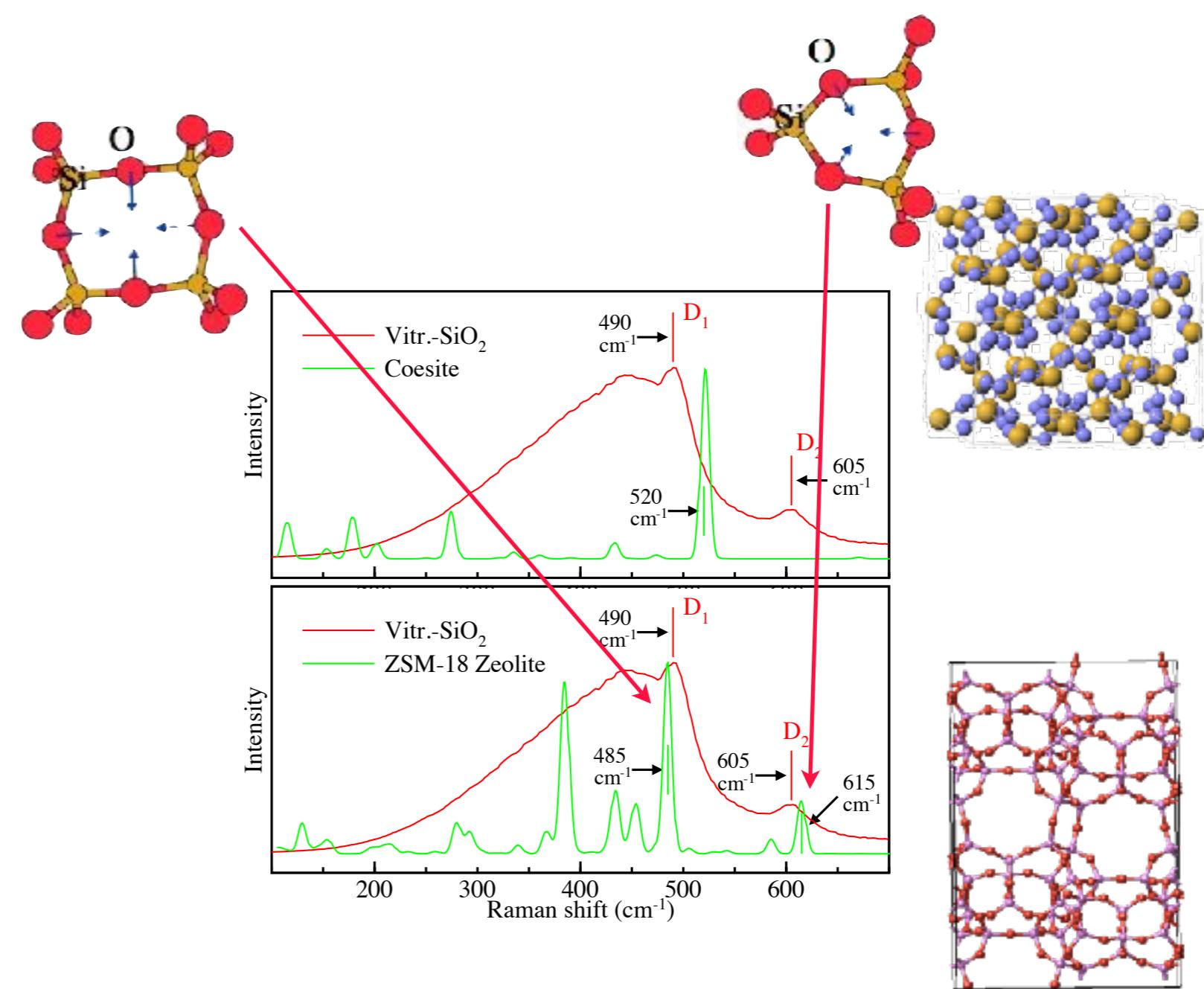
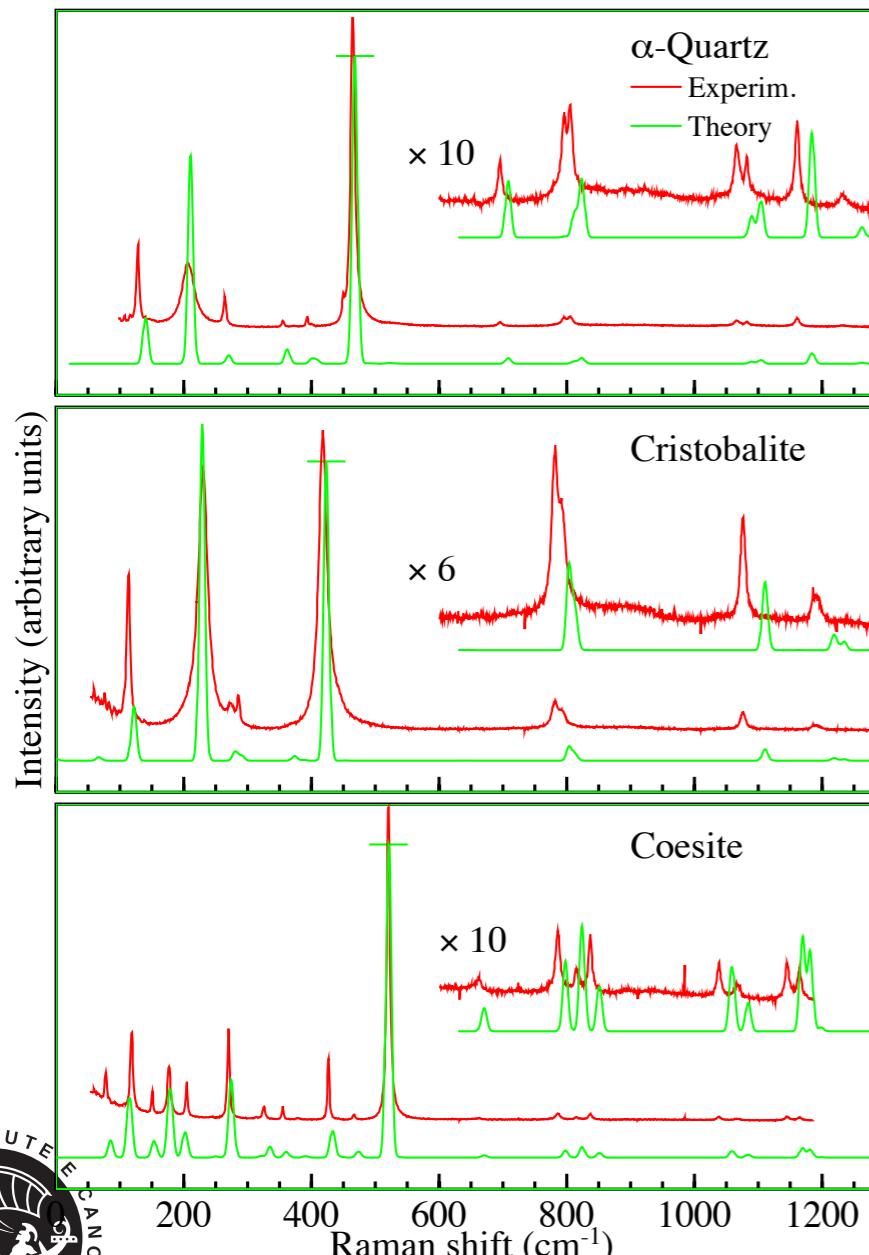
VOLUME 90, NUMBER 3

PHYSICAL REVIEW LETTERS

week ending
24 JANUARY 2003

First-Principles Calculation of Vibrational Raman Spectra in Large Systems: Signature of Small Rings in Crystalline SiO₂

Michele Lazzeri and Francesco Mauri



a sampler of recent applications

J|A|C|S

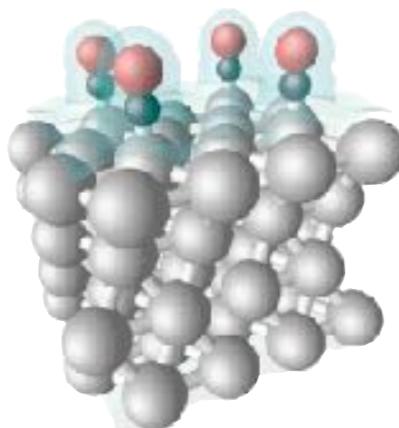
ARTICLES

Published on Web 08/17/2007

Vibrational Recognition of Adsorption Sites for CO on Platinum and Platinum–Ruthenium Surfaces

Ismaila Dabo,^{*,†} Andrzej Wieckowski,[‡] and Nicola Marzari[†]

11046 J. AM. CHEM. SOC. ■ VOL. 129, NO. 36, 2007



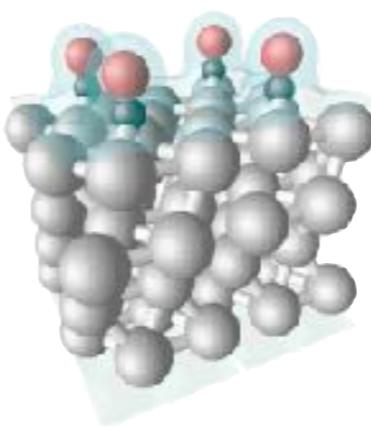
atop (CO@Pt₁)

$E_{\text{DFT}} = +0.10 \text{ eV}$

$\nu_{\text{DFT}} = 2050 \text{ cm}^{-1}$

$\nu_{\text{exp}} = 2070 \text{ cm}^{-1}$

 expt

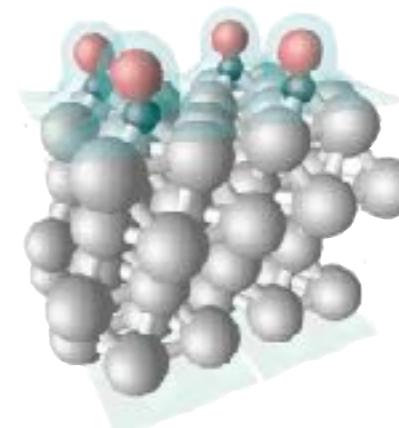


bridge (CO@Pt₂)

$E_{\text{DFT}} = +0.03 \text{ eV}$

$\nu_{\text{DFT}} = 1845 \text{ cm}^{-1}$

$\nu_{\text{exp}} = 1830 \text{ cm}^{-1}$



fcc (CO@Pt₃)

$E_{\text{DFT}} = 0 \text{ eV}$

$\nu_{\text{DFT}} = 1743 \text{ cm}^{-1}$

$\nu_{\text{exp}} = 1780 \text{ cm}^{-1}$

DFT 



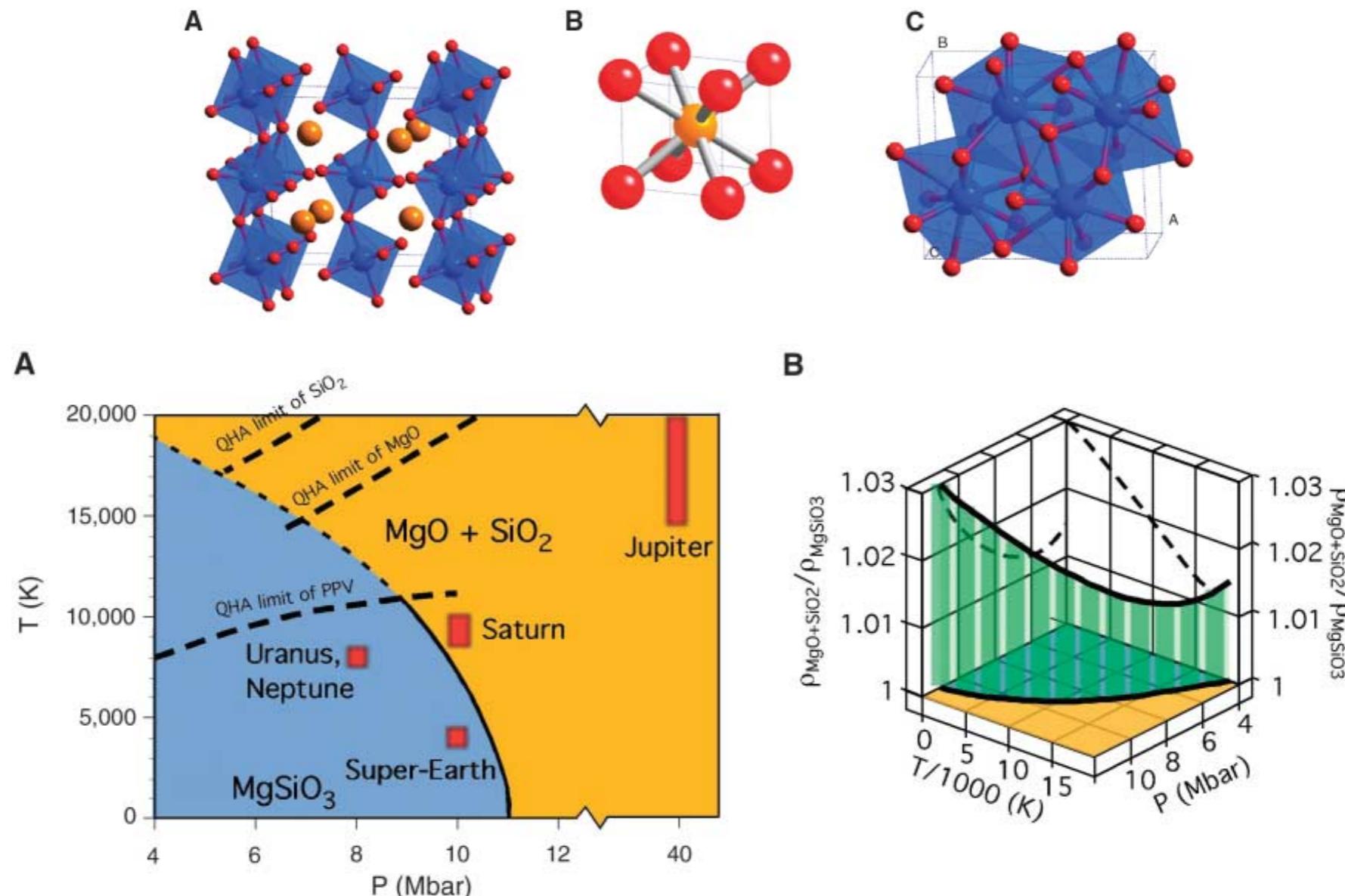
a sampler of recent applications

Dissociation of MgSiO_3 in the Cores of Gas Giants and Terrestrial Exoplanets

Koichiro Umemoto,¹ Renata M. Wentzcovitch,^{1*} Philip B. Allen²

www.sciencemag.org SCIENCE VOL 311 17 FEBRUARY 2006

983



a sampler of recent applications

PRL 100, 257001 (2008)

PHYSICAL REVIEW LETTERS

week ending
27 JUNE 2008



Ab Initio Description of High-Temperature Superconductivity in Dense Molecular Hydrogen

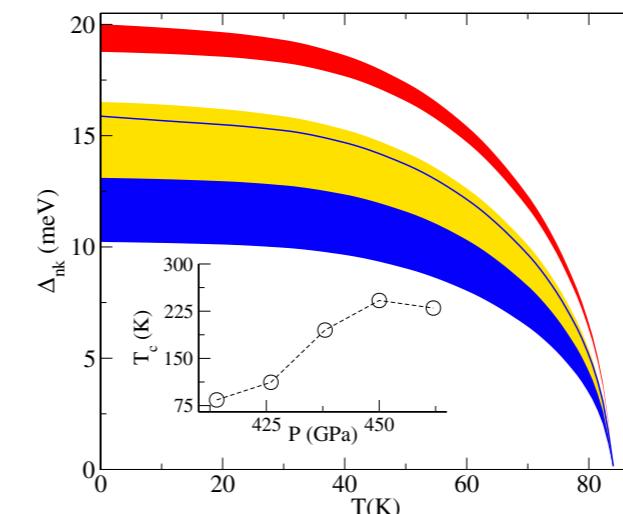
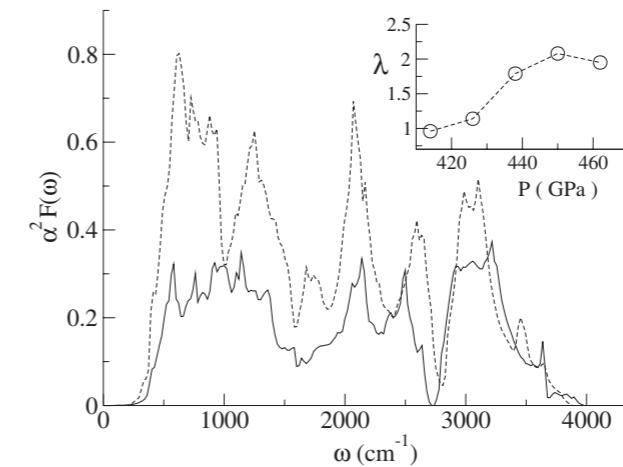
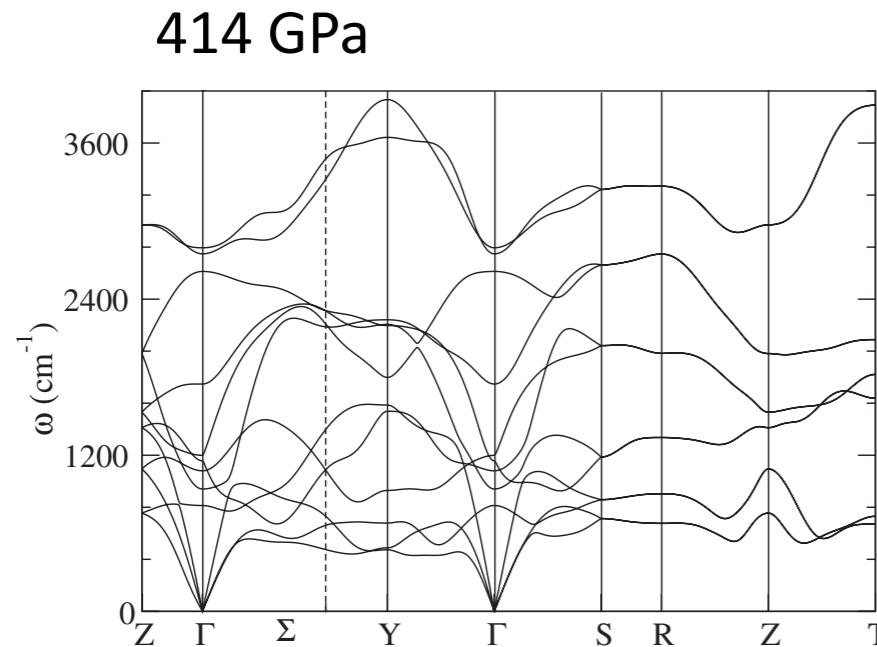
P. Cudazzo,¹ G. Profeta,¹ A. Sanna,^{2,3} A. Floris,³ A. Continenza,¹ S. Massidda,² and E. K. U. Gross³

¹CNISM - Dipartimento di Fisica, Università degli Studi dell'Aquila, Via Vetoio 10, I-67010 Coppito (L'Aquila) Italy

²SLACS-INFM/CNR—Dipartimento di Fisica, Università degli Studi di Cagliari, I-09124 Monserrato (CA), Italy

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(Received 7 December 2007; published 23 June 2008; corrected 27 June 2008)



a sampler of recent applications

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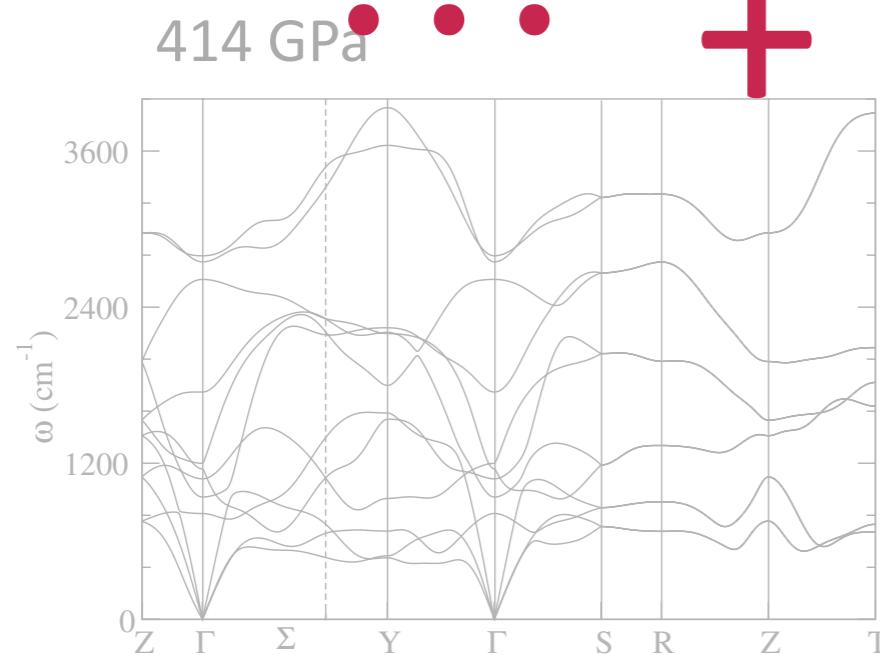
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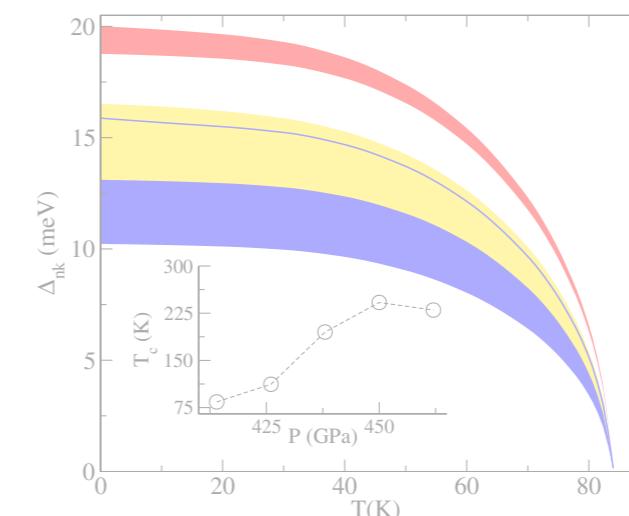
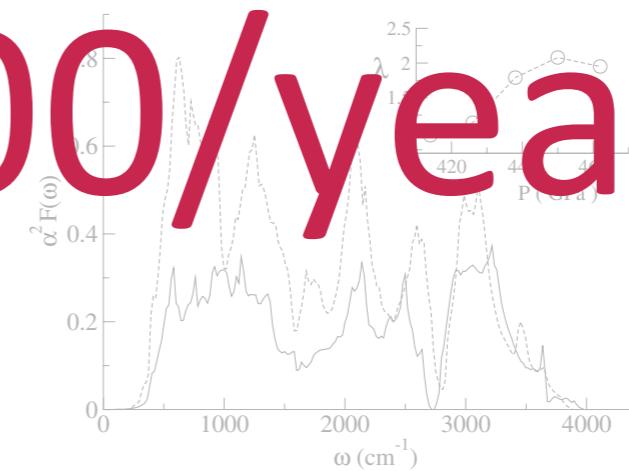
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+ $\approx 400/\text{year}$





The logo for MAX, consisting of the letters "MAX" in a large, white, sans-serif font, set against a solid red rectangular background.



That's all Folks!

these slides at
<http://talks.baroni.me>