The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2145-26

Spring College on Computational Nanoscience

17 - 28 May 2010

Response Functions and Lattice Vibrations from Density-Functional Perturbation Theory

Stefano BARONI
SISSA & CNR-IOM DEMOCRITOS Simulation Center
Trieste
Italy

density-functional perturbation theory

forces, response functions, phonons, and all that

Stefano Baroni
Scuola Internazionale Superiore di Studi Avanzati &
CNR-IOM *DEMOCRITOS* Simulation Center
Trieste - Italy

lecture given at the *Spring College on Computational Nanoscience*
The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy, May 17-28, 2010

response functions

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

- polarizability, dielectric constant $\frac{\partial \mathrm{P}_i}{\partial \mathrm{E}_j}$
- elastic constants $\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}}$
- piezoelectric constants $\frac{\partial \mathrm{P}_i}{\partial \epsilon_{kl}}$
- 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

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

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

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

$$\hat{H}_\beta = \hat{H}^\circ + \beta\hat{B}$$ (Hellmann & Feynman)

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

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

energy derivatives

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

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

- structural optimization & molecular dynamics
- (static) response functions

  elastic constants

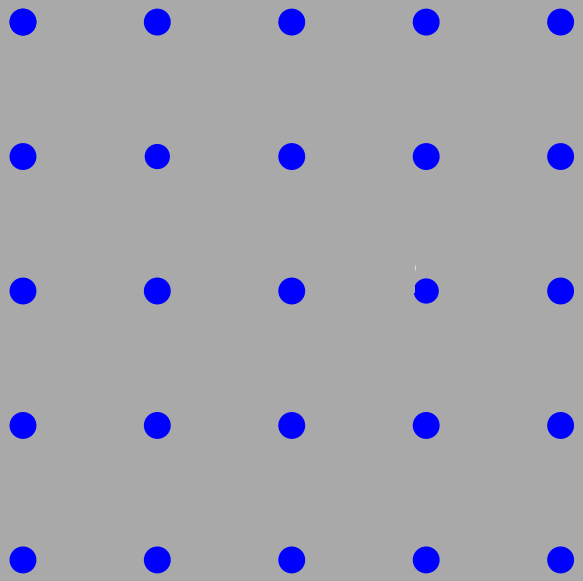
  dielectric tensor

  piezoelectric tensor

  Born effective charges

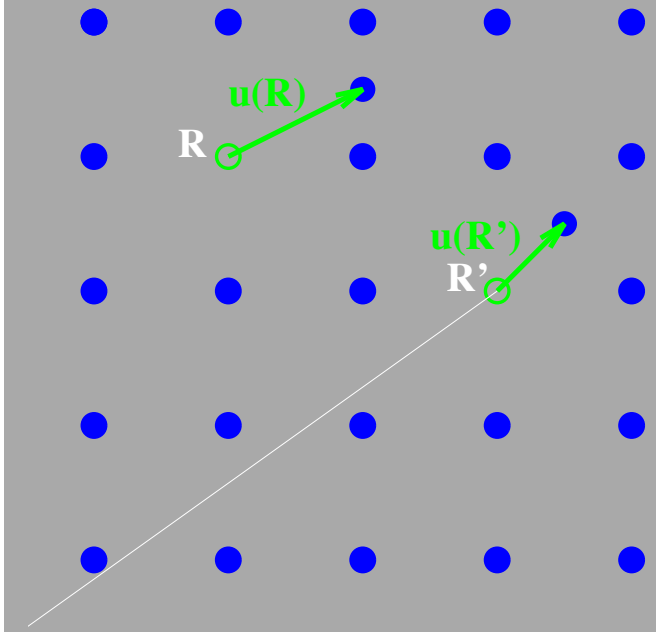
  . . .
- vibrational modes in the adiabatic approximaton

lattice dynamics



$$
\begin{aligned}
V(\mathbf{r}) &= V_0(\mathbf{r}) \\
&= \sum_{\mathbf{R}} v(\mathbf{r}-\mathbf{R}) \\
E &= E_0
\end{aligned}
$$

lattice dynamics



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

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

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

energy derivatives from perturbation theory

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

$$f_i = -\left.\frac{\partial E}{\partial \lambda_i}\right|_{\lambda=0} = -\langle \Psi_0 | v_i | \Psi_0 \rangle = \int v_i(\mathbf{r}) \rho_0(\mathbf{r}) d\mathbf{r}$$

$$\begin{aligned} h_{ij} = \left.\frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j}\right|_{\lambda=0} &= 2 \sum_n \frac{\langle \Psi_0 | v_i | \Psi_n \rangle \langle \Psi_n | v_j | \Psi_0 \rangle}{\epsilon_0 - \epsilon_n} \\ &= 2 \langle \Psi_0 | v_i | \Psi_j' \rangle = \int v_i(\mathbf{r}) \rho_j'(\mathbf{r}) d\mathbf{r} \\ &= 2 \langle \Psi_i' | v_j | \Psi_0 \rangle = \int v_j(\mathbf{r}) \rho_i'(\mathbf{r}) d\mathbf{r} \end{aligned}$$

the “2n+1” theorem

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

$$\Phi = \Phi_0 + \sum_{l=1}^{n} \lambda^l \Phi^{(l)} + \mathcal{O}(\lambda^{n+1}) \Rightarrow$$

$$E = E_0 + \sum_{l=1}^{2n+1} \lambda^l E^{(l)} + \mathcal{O}(\lambda^{2n+2})$$

$$E = \frac{\langle \Phi_0 + \Phi' | (H_0 + V') | \Phi_0 + \Phi' \rangle}{\langle \Phi_0 + \Phi' | \Phi_0 + \Phi' \rangle} + \mathcal{O}(V'^4)$$

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

density-functional perturbation theory

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i \lambda_i V_i'(\mathbf{r})$$

$$E(\lambda) = \min_n \left(F[n] + \int V_\lambda(\mathbf{r}) n(\mathbf{r}) \right) \quad \int n(\mathbf{r}) d\mathbf{r} = N \qquad \text{DFT}$$

$$\frac{\partial E(\lambda)}{\partial \lambda_i} = \int n_\lambda(\mathbf{r}) V_i'(\mathbf{r}) d\mathbf{r} \qquad \text{HF}$$

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

DFPT: the equations

DFT

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

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

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

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

DFPT

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

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

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

$$\phi'_v(\mathbf{r}) = \sum_{n \neq v} \phi_n(\mathbf{r}) \frac{\langle \phi_n | V'_{SCF} | \phi_v \rangle}{\epsilon_n - \epsilon_v}$$

DFPT: the equations

DFT

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

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

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

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

DFPT

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

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

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

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

$$\phi'_v(\mathbf{r}) = \sum_{n \neq v} \phi_n(\mathbf{r}) \frac{\langle \phi_n | V'_{SCF} | \phi_v \rangle}{\epsilon_n - \epsilon_v}$$

more about perturbation theory

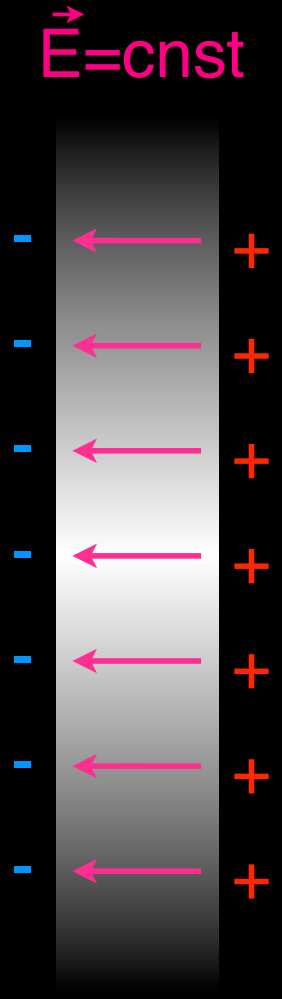
$$H = H_0 + V' \qquad \begin{cases} \phi_v^0 \to \phi_v^0 + \phi_v' \\ \epsilon_v^0 \to \epsilon_v^0 + \epsilon_v' \end{cases}$$

$$\phi_v' = \sum_{u \neq v} \phi_u^0 \frac{\langle \phi_u^0 | V' | \phi_v^0 \rangle}{\epsilon_v^0 - \epsilon_u^0} \qquad \epsilon_v' = \langle \phi_v^0 | V' | \phi_v^0 \rangle$$

$$\begin{aligned} (H_0 - \epsilon_v^0)\phi_v' &= -\sum_{u \neq v} \phi_u^0 \langle \phi_u^0 | V' | \phi_v^0 \rangle \\ &= -(1 - P_v) V' | \phi_v^0 \rangle \\ (H_0 - \epsilon_v^0) P_c \phi_v' &= -P_c V' | \phi_v^0 \rangle \end{aligned}$$

$$(H_0 - \epsilon_v^0 + \alpha P_v)\bar{\phi}_v' = -P_c V' | \phi_v^0 \rangle$$

macroscopic electric fields



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

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

$$\begin{aligned} -P_c V' \phi_v^0 &= -E \sum_c \phi_c^0 \langle \phi_c^0 | x | \phi_v^0 \rangle \\ &= -E \sum_c \phi_c^0 \frac{\langle \phi_c^0 | [H_0, x] | \phi_v^0 \rangle}{\epsilon_c^0 - \epsilon_v^0} \equiv \psi_v' \end{aligned}$$

$$(H_0 - \epsilon_v^0)\psi_v' = -E P_c [H_0, x] \phi_v^0$$

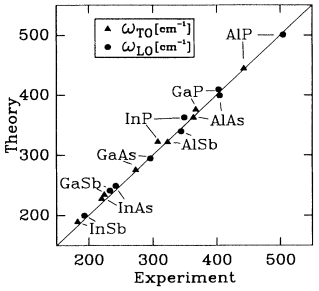
DFPT rhs

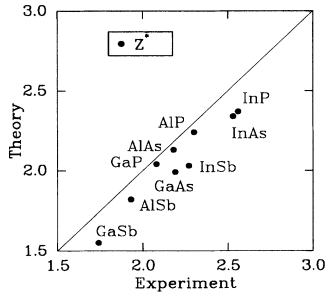
Piezoelectric Properties of III-V Semiconductors from First-Principles Linear-Response Theory

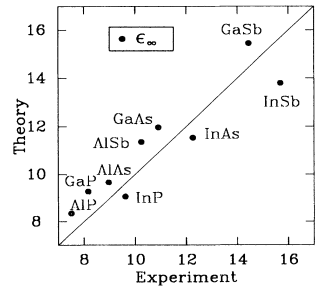
Stefano de Gironcoli[a]
Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I-34014 Trieste, Italy

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)

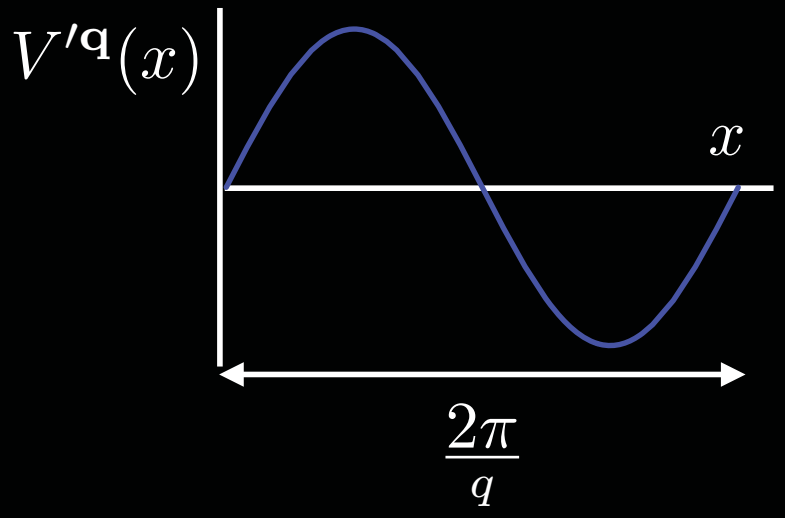






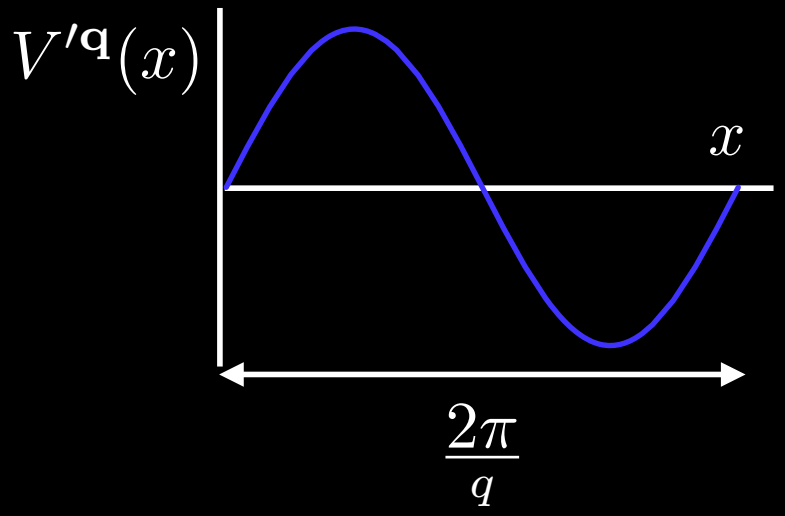
$\bar{\gamma}_{14}$	P	As	Sb
Al	0.11 (· · ·)	−0.03 (· · ·)	−0.13 (−0.16)
Ga	−0.18 (−0.18)	−0.35 (−0.32)	−0.40 (−0.39)
In	0.12 (|0.09|)	−0.08 (−0.10)	−0.20 (−0.18)

monochromatic perturbations



DFPT rhs: $-P_c V'^{\mathbf{q}} \phi_v^{\mathbf{k}}(\mathbf{r})$

monochromatic perturbations



$$\left(H_0 + \alpha P_v^{\mathbf{k}+\mathbf{q}} - \epsilon_v^{\mathbf{k}}\right)\phi_v'^{\mathbf{k}+\mathbf{q}}(\mathbf{r}) = -P_c V'^{\mathbf{q}}\phi_v^{\mathbf{k}}(\mathbf{r})$$

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

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

DFPT: the main features

- response functions calculated in terms of response orbitals, $\{\phi'_v\}$
- solve the linear system: $\phi_v \mapsto H_{KS}\phi_v$; do not calculate empty (conduction) states
- calculate the response to the perturbation you want, only
- non-local perturbations: OK
- non-periodic perturbations: OK
- macroscopic electric fields: OK

phonons in polar materials

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

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

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

$\mathrm{rot}\ \mathsf{E} \sim i\mathbf{q}\times\mathsf{E} = 0$ $\qquad$ $\mathbf{u}\perp\mathbf{q} \Rightarrow \mathsf{E} = 0$ $\qquad$ (T)

$\mathrm{div}\ \mathsf{D} \sim i\mathbf{q}\cdot\mathsf{D} = 0$ $\qquad$ $\mathbf{u}\parallel\mathbf{q} \Rightarrow \mathsf{D} = 0$ $\qquad$ (L)

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

interatomic force constants

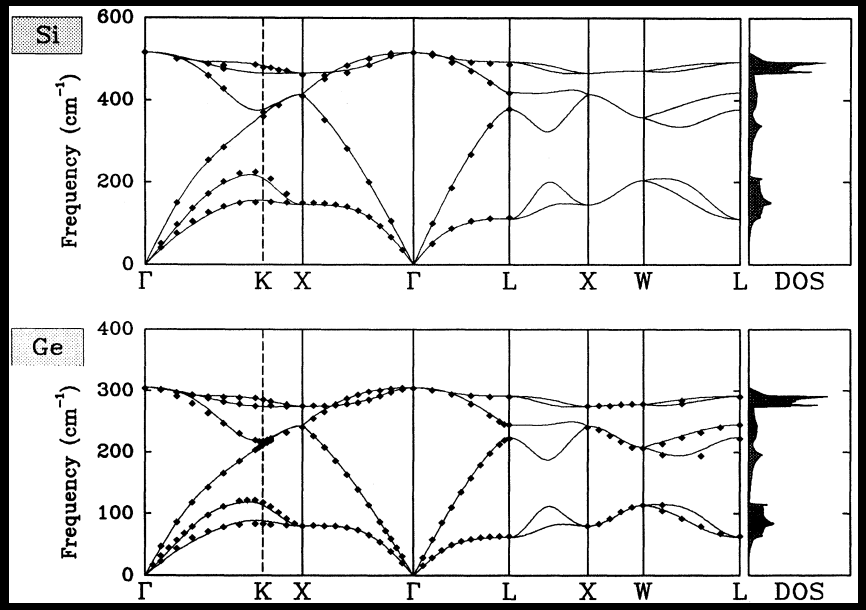
$$\Phi(\mathbf{R}-\mathbf{R}') = -\frac{\partial^2 E}{\partial \mathbf{u}_{\mathbf{R}} \partial \mathbf{u}_{\mathbf{R}'}}$$

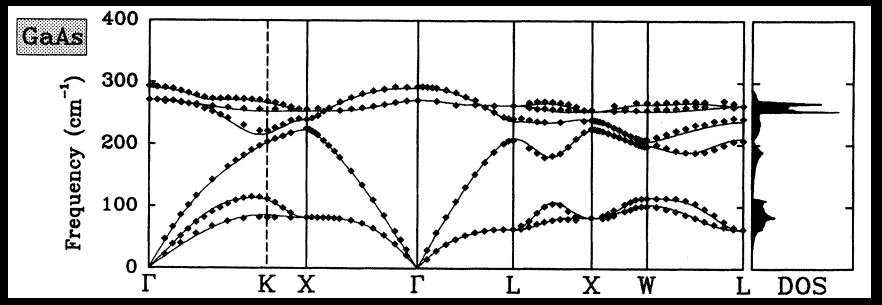
short ranged + dipole-dipole

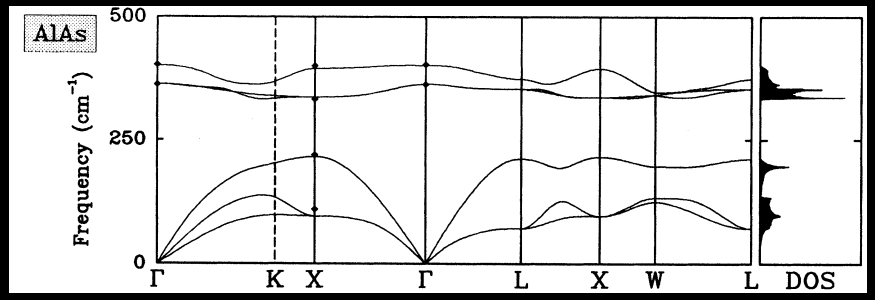
$$= \frac{\Omega}{(2\pi)^3} \int \mathrm{e}^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} D(\mathbf{q}) d\mathbf{q}$$

- do FFT's
  - # **q**'s = # **R**'s
  - remove singularities in D(q)
- store information
- interpolate phonon bands

phonons from DFPT

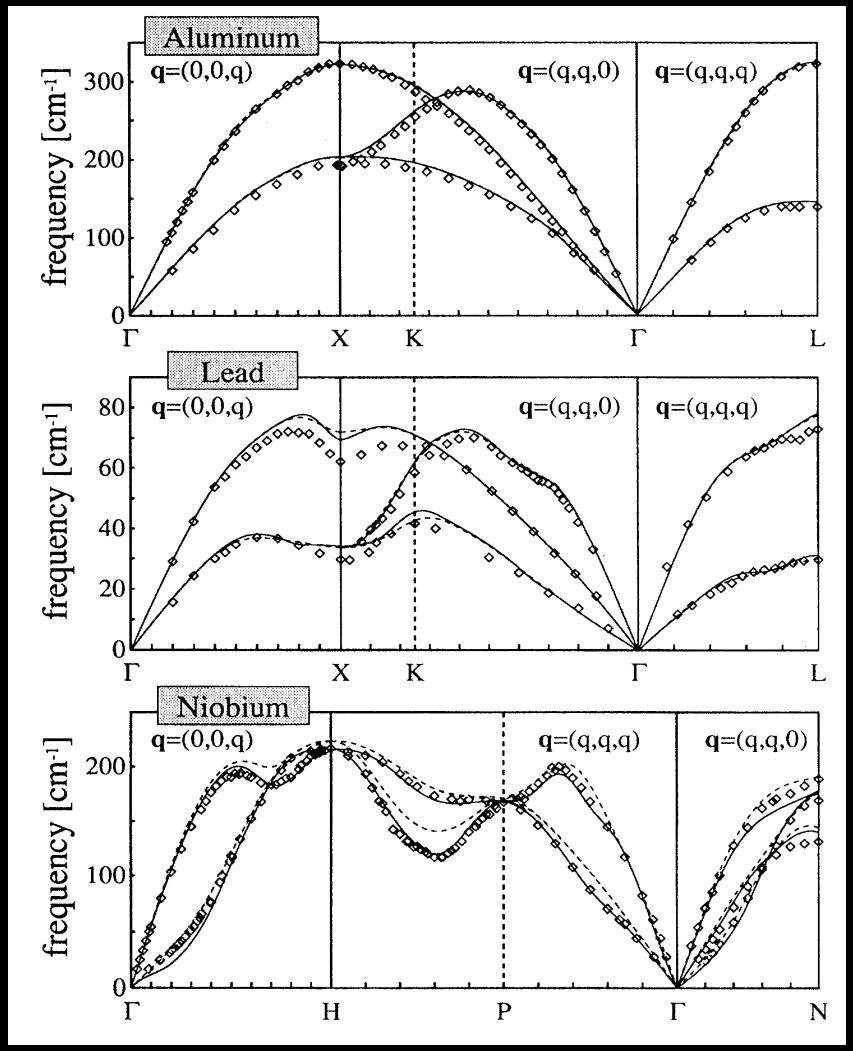






P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991)

phonons from DFPT



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

applications done so far

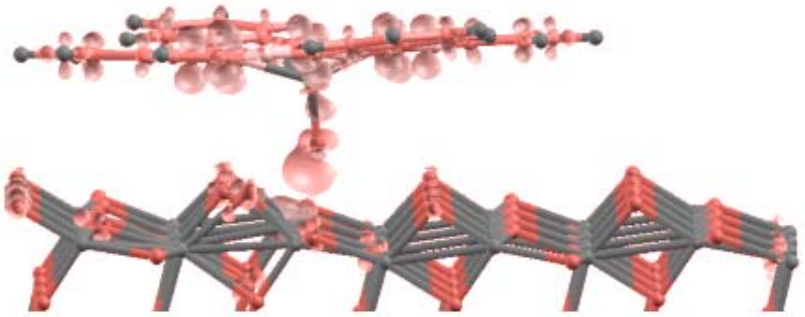
- Dielectric properties
- Piezoelectric properties
- Elastic properties
- Phonon in crystals and alloys
- Phonon at surfaces, interfaces, super-lattices, and nano-structures
- Raman and infrared activities
- Anharmonic couplings and vibrational line widths
- Mode softening and structural transitions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

S. Baroni, 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)

QUANTUMESPRESSO

16 October 2009 The new release of the Quantum ESPRESSO distribution is available for download (version 4.1.1)

Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials (both norm-conserving and ultrasoft).



20 July 2009
The new release of the Quantum-Espresso distribution is available for download (version 4.1)

21 April 2009
Snapshots of the development (CVS) tree of Quantum ESPRESSO can be downloaded from qe-forge.org

21 April 2009
The final bugfix release, v.4.0.5, of the Quantum ESPRESSO distribution, is available for download. This supersedes all previous 4.0.x releases.

15 May 2008
Version 4.0 of the Quantum-Espresso distribution is available for download

www.quantum-espresso.org

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **21** (2009) 395502 (19pp) doi:10.1088/0953-8984/21/39/395502

QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials

Paolo Giannozzi[1,2], Stefano Baroni[1,3], Nicola Bonini[4], Matteo Calandra[5], Roberto Car[6], Carlo Cavazzoni[7,8], Davide Ceresoli[4], Guido L Chiarotti[9], Matteo Cococcioni[10], Ismaila Dabo[11], Andrea Dal Corso[1,3], Stefano de Gironcoli[1,3], Stefano Fabris[1,3], Guido Fratesi[12], Ralph Gebauer[1,13], Uwe Gerstmann[14], Christos Gougoussis[5], Anton Kokalj[1,15], Michele Lazzeri[5], Layla Martin-Samos[1], Nicola Marzari[4], Francesco Mauri[5], Riccardo Mazzarello[16], Stefano Paolini[3,9], Alfredo Pasquarello[17,18], Lorenzo Paulatto[1,3], Carlo Sbraccia[1,†], Sandro Scandolo[1,13], Gabriele Sclauzero[1,3], Ari P Seitsonen[5], Alexander Smogunov[13], Paolo Umari[1] and Renata M Wentzcovitch[10,19]


That's all Folks!
these slides at
http://talks.baroni.me