Perturbation treatment of response properties of insulators in finite electric fields

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Outline

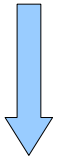
- A short introduction of density functional perturbation theory (DFPT) in zero electric field
- DFPT in finite electric field
- Perturbation expansion of energy functional in finite electric fields

  atomic displacement (phonon),
  electric field (born effective charges and dielectric constant)
- Implementation details
- Test calculations

DFPT in zero electric field

- Density Functional Perturbation Theory

(Density functional theory + Perturbation theory)



Compute the derivatives of total energy

Applications:

- Phonon properties
- Born effective charges
- Dielectric constants

Advantages:

- Avoid supercell calculation
- Incommensurate perturbation

S. Baroni *et. al.*, RMP (2001)
X. Gonze and C. Lee, PRB (1997)

DFPT in zero electric field

Consider small perturbation parameter λ such as

- Atomic displacements
- Electric fields

Physical quantities Q (energy, wave functions) can be expanded in series

$$Q(\lambda)=Q(0)+Q^{(1)}\lambda+Q^{(2)}\lambda^2+...$$

Expansion of total energy (2n+1 theorem)

minimize $E^{(2)}=\frac{\partial^2 E}{2\partial\lambda^2}=E^{(2)}[\psi^{(0)},\psi^{(1)}]$

Unperturbed wavefunction

First-order wavefunction (variational function)

Motivations and goals

It is interesting to understand

- Electric field effect on phonon frequencies
- Field-dependence of Born effective charge and dielectric constant

Our goal

- Extend the formalism of DFPT to be applied in finite electric field
- Calculate response properties of insulators in finite electric field

DFPT in the presence of electric fields

Response of solids to electric field

- Lattice response (approximate)
  Sai, Rabe and Vanderbilt (2002);Fu and Bellaiche (2003)

$$f = f_{HF}^{\varepsilon=0} + Z^* e \cdot \varepsilon \quad \Rightarrow \quad \Delta R_{appr}$$

- Lattice + Electronic response (exact)
  Souza, Ìñiguez, and Vanderbilt (2002)
  Umari and Pasquarello (2002)

Field-dependent energy functional $\Rightarrow$ ΔR_{exact} & Electronic response

DFPT in the presence of electric fields

Challenge from static electric field potential $\mathcal{E} \cdot r$

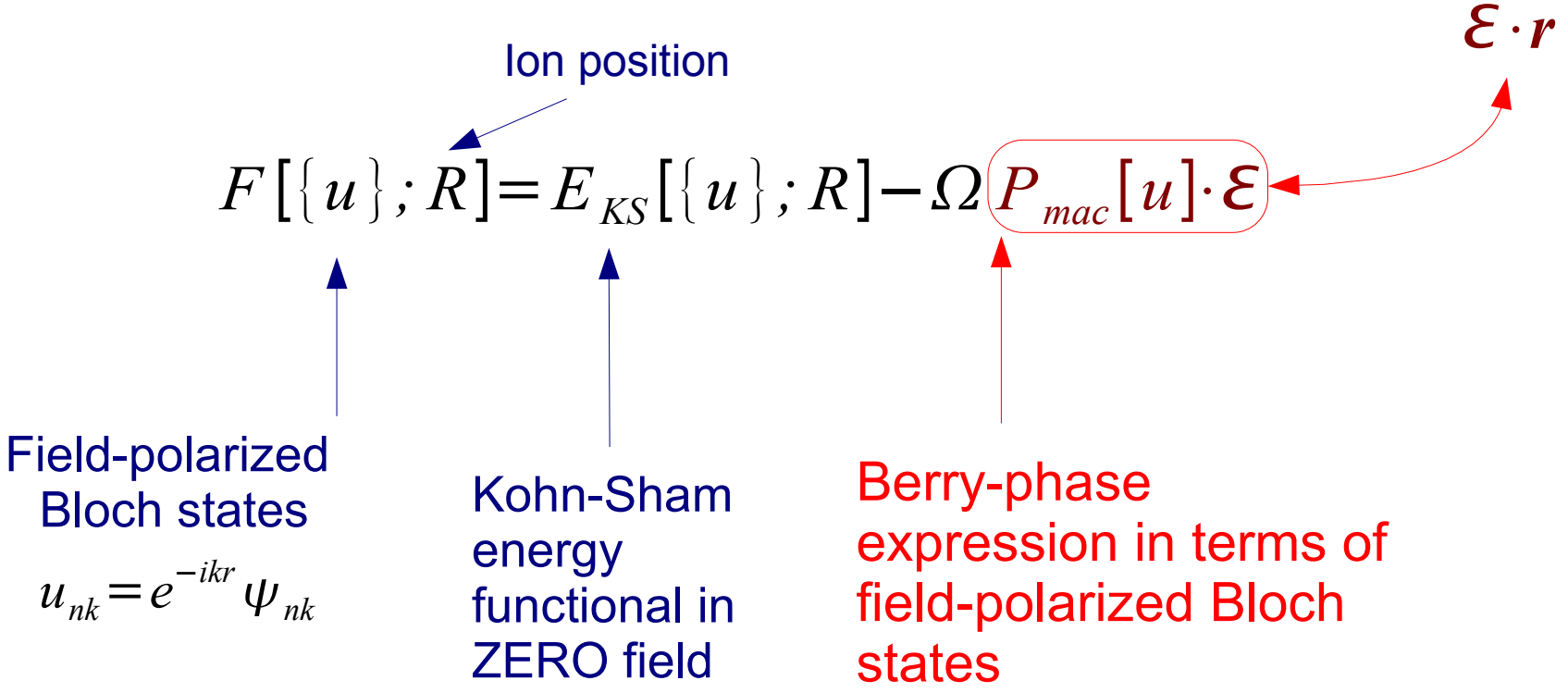
- No true ground state $H = T + v_{ext} + \mathcal{E} \cdot r$

- However, in the small electric field regime
  - Periodicity of charge density retained
  - “polarized” states exist (long-lived resonance)

R. W. Nunes and D. Vanderbilt, Phys. Rev. Lett. (1994)

DFPT in the presence of electric fields

Total energy functional including the electric field term



R.W. Nunes and X. Gonze, PRB (2001)
I. Souza, J. Ìñiguez, and D. Vanderbilt, PRL (2002)
P. Umari and A. Pasquarello, PRL (2002)

DFPT in the presence of electric fields

Berry phase expression for polarization

Derivative in k space
(Berry phase)

$$P_{mac} = \frac{ie}{4\pi^3} \sum_{n=1}^{occ} \int_{BZ} d\,\boldsymbol{k} \langle u_{nk} | \nabla_k | u_{nk} \rangle$$

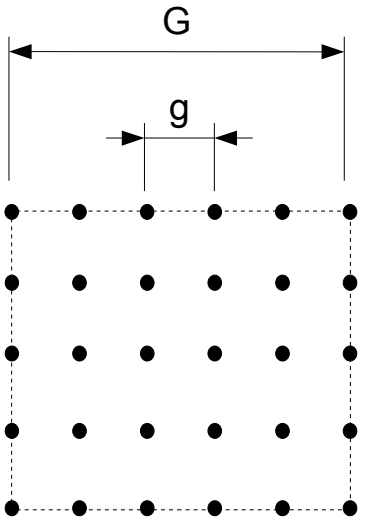
(continuous form)

$$P_{mac} = \frac{e}{\pi \Omega} \sum_{i=1}^{3} \frac{\boldsymbol{a}_i}{N^{(i)}} \sum_k \boldsymbol{Im}\, ln\, det\, S_{k,k+g_i}$$

(discrete form)

Building block - overlap matrix

$$S_{k,k+g_i,mn} = \langle u_{mk} | u_{nk+g_i} \rangle$$



Brillouin Zone

King-Smith and Vanderbilt (1993)

Perturbation expansion of total energy – atomic displacement

Expansion of total energy functional

Force constant

$$F[R]=F[R_0]+\frac{\partial F}{\partial \tau}\tau+\frac{\partial^2 F}{2\partial \tau^2}\tau^2+\ldots$$

Atomic displacement

$$R=R_0+\tau$$

functional of $u^{(0)}$, $u^{(1)}$ and variational to $u^{(1)}$

$$\frac{\partial^2 F}{\partial \tau^2}=\frac{\partial^2 E_{KS}}{\partial \tau^2}-\Omega\frac{\partial^2 P_{mac}}{\partial \tau^2}\cdot\varepsilon$$

$$\frac{\partial^2 P_{mac}}{\partial \tau^2}=\frac{e}{\pi\Omega}\sum_{i=1}^{3}\frac{\boldsymbol{a}_i}{N^{(i)}}\sum_k D_k^{(i)}$$

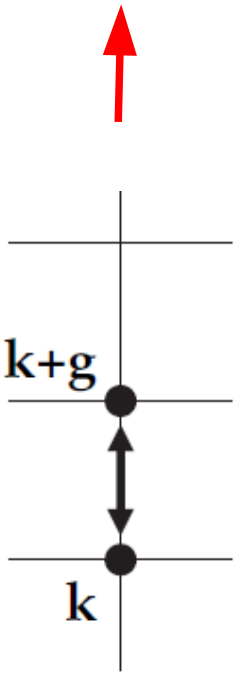
$\mathbf{a}_i$ primitive lattice vector

D_k defined in the next page

Perturbation expansion of total energy – atomic displacement

Perturbation with zero-q wave vector
(real perturbation parameter λ)

$$D_k^{(i)} = Tr\left[S^{(2)}_{k,k+g} Q_{k+g,k} - S^{(1)}_{k,k+g} Q_{k+g,k} S^{(1)}_{k,k+g} Q_{k+g,k}\right]$$



$$S_{k,k+g_i,mn} \equiv \langle u_{mk} | u_{nk+g_i} \rangle$$

$$S = S^{(0)} + S^{(1)}\lambda + S^{(2)}\lambda^2 + \ldots$$

$$Q = (S^{(0)}_{k,k+g})^{-1}$$

All S and Q are LxL matrix, L=No. of occupied bands

Perturbation expansion of total energy – atomic displacement

Non-zero-q wave vector

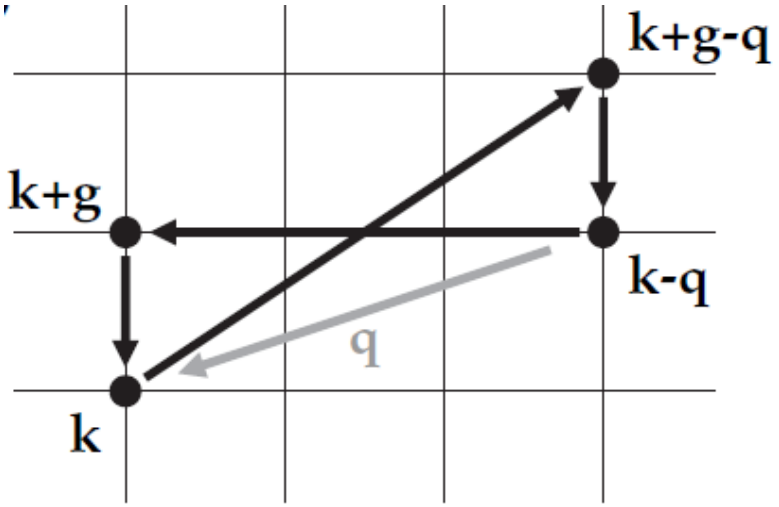
(complex perturbation parameter λe^{iqr}, $\lambda^* e^{-iqr}$)

$$D_k^{(i)} = Tr\left[S^{(1,1)}_{k,k+g} Q_{k+g,k} - S^{(1,0)}_{k,k+g-q} Q_{k+g-q,k-q} S^{(0,1)}_{k-q,k+g} Q_{k+g,k}\right]$$

1st index for λ*

2nd index for λ

$$S^{(a,b)}_{k,k'}$$



Perturbation expansion of total energy – atomic displacement

Determination of $\{u^{(1)}\}$

- by minimization of $F^{(2)}$
- Equivalent to Sternheimer Equation
- Note extra complexity: coupling between $u_k^{(1)}$ and $u_{k'}^{(1)}$

Construction of the force-constant matrix

- Diagonal elements $\dfrac{\partial^2 F}{\partial \tau_\alpha^2}$
- Off-diagonal elements $\dfrac{\partial^2 F}{\partial \tau_\alpha \partial \tau_\beta}$

Perturbation expansion of total energy – electric field

Expand total energy functional w.r.t. electric field perturbation

$$F[\varepsilon] = F[\varepsilon_0] + \frac{\partial F}{\partial \varepsilon}\delta\varepsilon + \frac{\partial^2 F}{\partial \varepsilon^2}\delta\varepsilon^2 + \ldots$$

$$\varepsilon = \varepsilon_0 + \delta\varepsilon$$

$$F = E_{KS} - \Omega P \cdot \varepsilon$$

$$\frac{\partial^2 F}{\partial \varepsilon^2} = \frac{\partial^2 E_{KS}}{\partial \varepsilon^2} - \Omega \frac{\partial^2 P_{mac}}{\partial \varepsilon^2} \cdot \varepsilon_0 - \Omega \frac{\partial P}{\partial \varepsilon}$$

Extra term for E perturbation

Is variational with respect to u^{ε}_{nk}

The same as phonon perturbation term

Perturbation expansion of total energy – electric field

From the optimized first order wave functions u^{ε}_{nk}

Born effective charge

$$\frac{\partial^2 F}{\partial \varepsilon_\alpha \partial \tau} = \sum_k \sum_{n=1}^{occ} \langle u^{(0)}_{nk} | (T + v_{ext})^{\tau} | u^{\varepsilon}_{nk} \rangle \quad \text{or} \quad \Omega \frac{\partial P_\alpha}{\partial \tau}$$

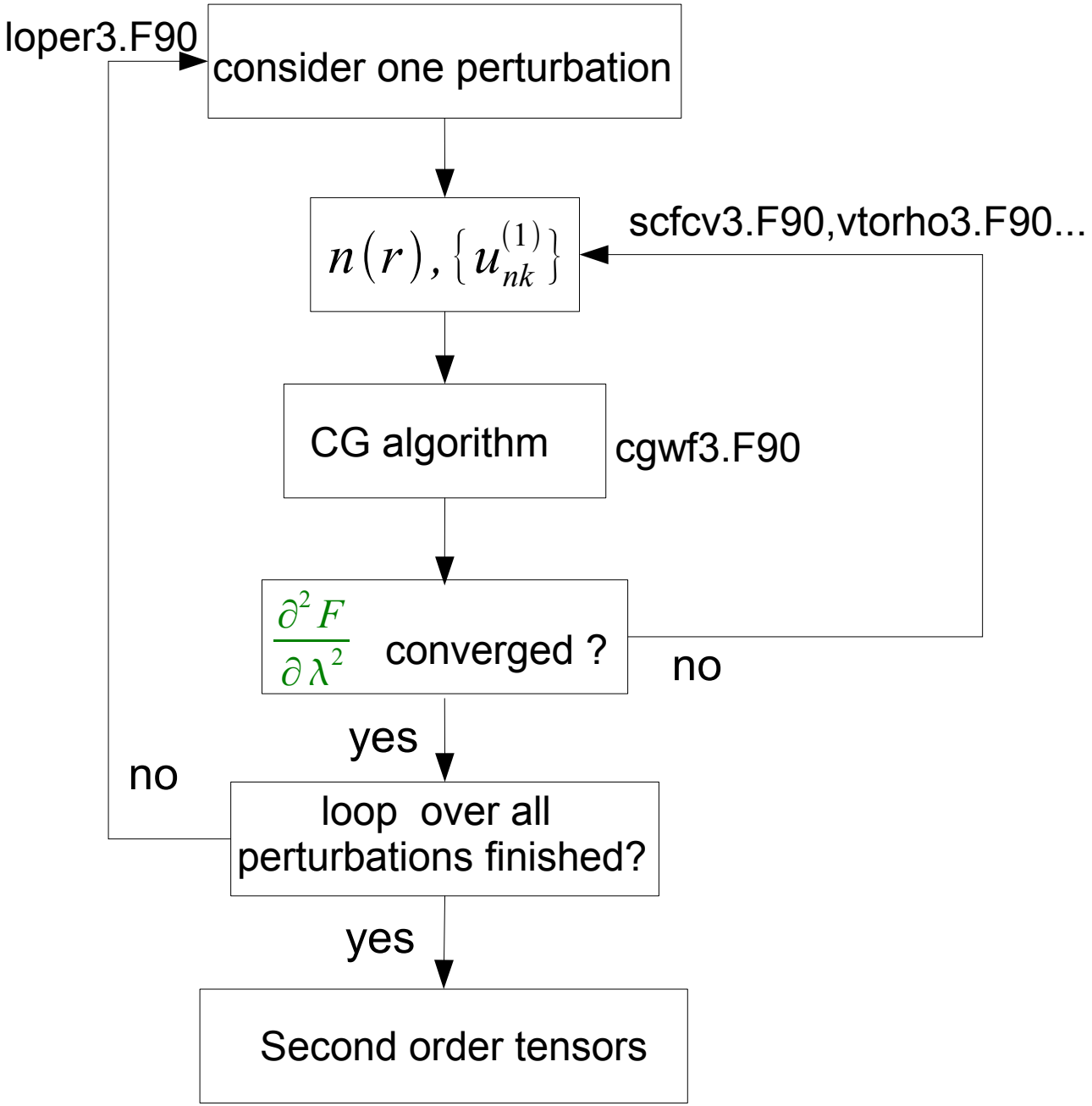
Dielectric constant

$$\frac{\partial^2 F}{\partial \varepsilon_\alpha \partial \varepsilon_\beta} = \Omega \frac{\partial P_\beta}{\partial \varepsilon_\alpha}$$

Implementation

Implementation is based on the linear response part in ABINIT code.

- Band by band minimization
- Conjugate gradient method



Implementation

Atomic displacement perturbation: (included since 5.2.2 version)

New subroutines:

qmatrix.F90	calculate Q matrix
initberry3.F90	initialization of response calculation
gradberry3.F90	calculate the gradient of the 2nd energy
ebp3.F90	calculate the field-coupling term

X. Wang and D. Vanderbilt, PRB **74**, 054304 (2006)

Electric field perturbation: (to be included in the future version)

New subroutines:

edie3.F90	calculation the field-coupling term
gbefd3.F90	calculate the gradient of the second order energy
bec3.F90	calculate the Born effective charge and dielectric constant

X. Wang and D. Vanderbilt submitted to PRB

Test calculation

Consistency check

Finite difference
vs. Linear response

E=5.14X10^8 V/m

TABLE I. Calculated frequency shifts, in cm^{-1}, induced by an electric field of 5.14×10^8 V/m applied along x in GaAs and AlAs. "FD" are the results of finite-difference (frozen-phonon) calculations in which atoms are displaced by hand and restoring forces are calculated, while "LR" refers to the use of the linear-response developed here. The L and X points are at $(2\pi/a)(1,1,1)$ and $(2\pi/a)(1,0,0)$, respectively.

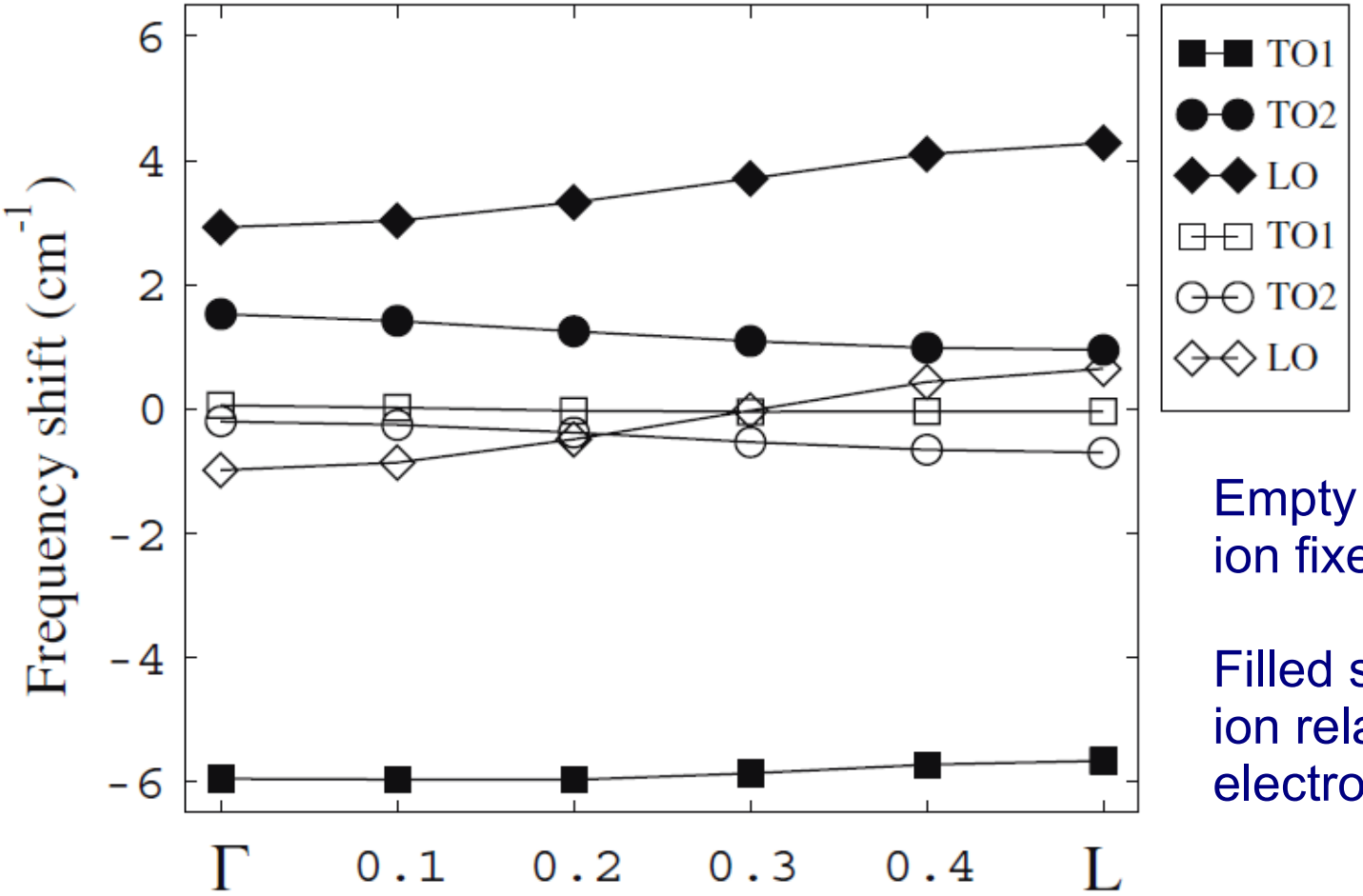
	GaAs		AlAs	
Mode	FD	LR	FD	LR
Γ O(1)[a]	−3.856	−3.856	−5.941	−5.941
Γ O(2)[a]	−0.282	−0.281	−0.300	−0.299
Γ O(3)[a]	3.548	3.548	5.647	5.647
L LO	2.701	2.703	4.282	4.282
L TO(1)	−3.749	−3.749	−5.663	−5.663
L TO(2)	0.567	0.564	0.952	0.952
X LO	0.050	0.050	−0.243	−0.243
X TO(1)	−3.953	−3.953	−6.083	−6.083
X TO(2)	3.753	3.753	5.919	5.919

[a]The nonanalytic long-range Coulomb contributions are excluded for the Γ modes.

Test calculation

The electric-field-induced shift in phonon frequencies of AlAs

Electric field: 5.14x10^8 V/m



Empty symbol:
ion fixed (electronic effect only)

Filled symbol:
ion relaxed (lattice effect + electronic effect)

Test calculation

Consistency check

Dielectric tensor

		ϵ_∞	$\Delta\epsilon_{\infty,23}$	$\Delta\epsilon_{\infty,11}$	$\Delta\epsilon_{\infty,33}$
AlAs	LR	9.681	0.039	0.027	0.013
	FD	9.681	0.040	0.027	0.013
GaAs	LR	13.315	0.202	0.211	0.104
	FD	13.319	0.203	0.207	0.098

Born effective charge

		Z^*	ΔZ^*_{23} $(\times 10^{-3})$	ΔZ^*_{11} $(\times 10^{-3})$	ΔZ^*_{33} $(\times 10^{-3})$
AlAs	LR	2.110	17.23	−0.06	−0.13
	FD	2.110	17.22	−0.05	−0.11
GaAs	LR	2.186	52.88	−3.42	−3.17
	FD	2.186	52.83	−3.36	−3.14

Test calculation

Calculation of the high order optical tensors of AlAs
(Mixed method Linear response + finite difference)

$$\chi^{(2)}_{123} = \frac{\partial \chi^{(1)}_{23}}{\partial \varepsilon}(pm/V) \qquad |\alpha_{TO}| = |\frac{\partial Z^{*}_{23}}{\partial \varepsilon}|(\mathring{A}^2)$$

(Susceptibility) (Raman polarizability)

Present work	62	8.0
Theory[1]	70	8.5

[1] Veithen, X. Gonze, and Ph. Ghosez (2005)

Summary

- Extended DFPT to finite electric field
- Tractable computational scheme
- Zone-center phonon and arbitrary phonon in finite electric field
- Born effective charge and dielectric constant