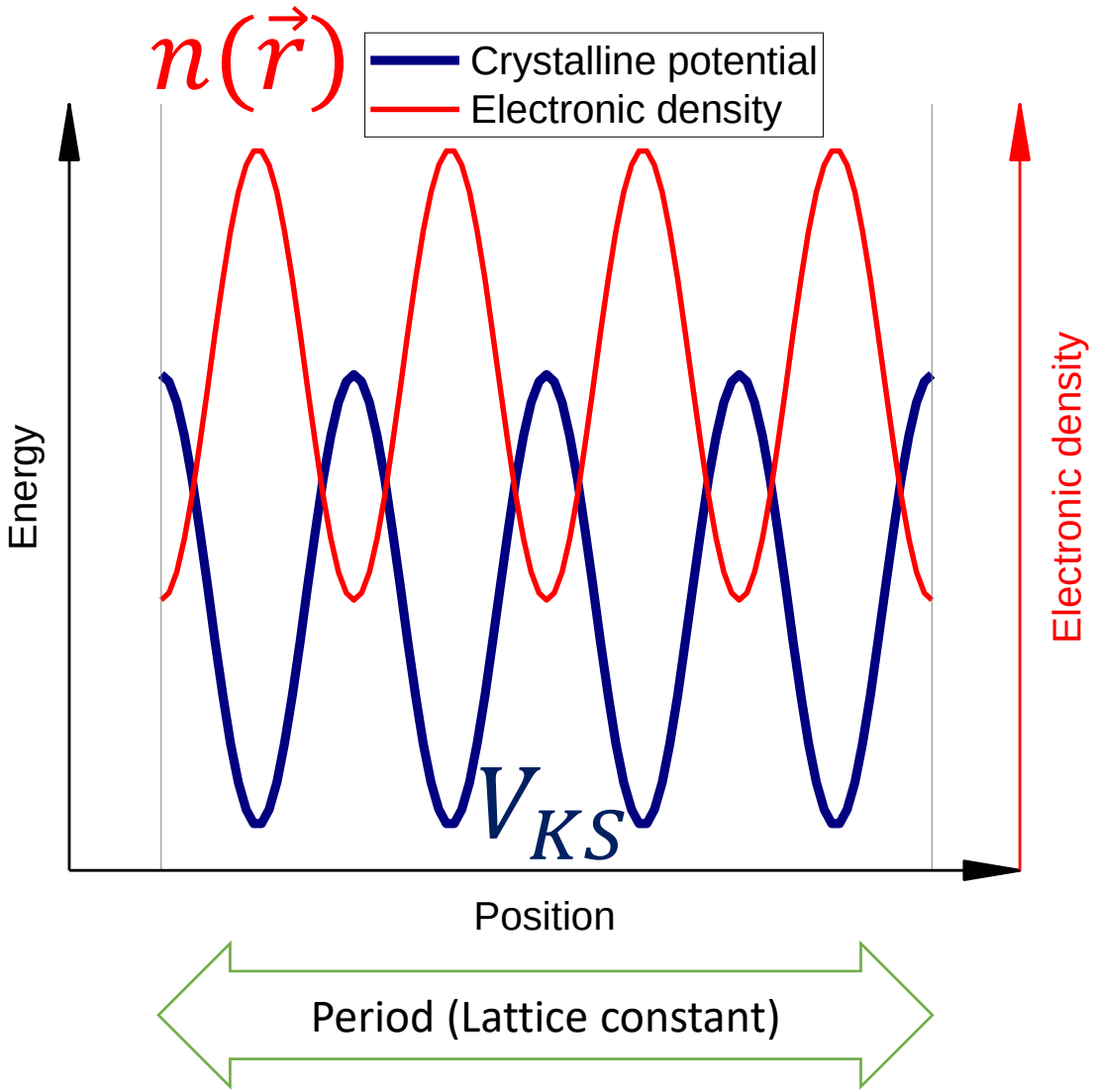
Finite Electric Field Calculations based on the Berry Phase Method in OpenMX

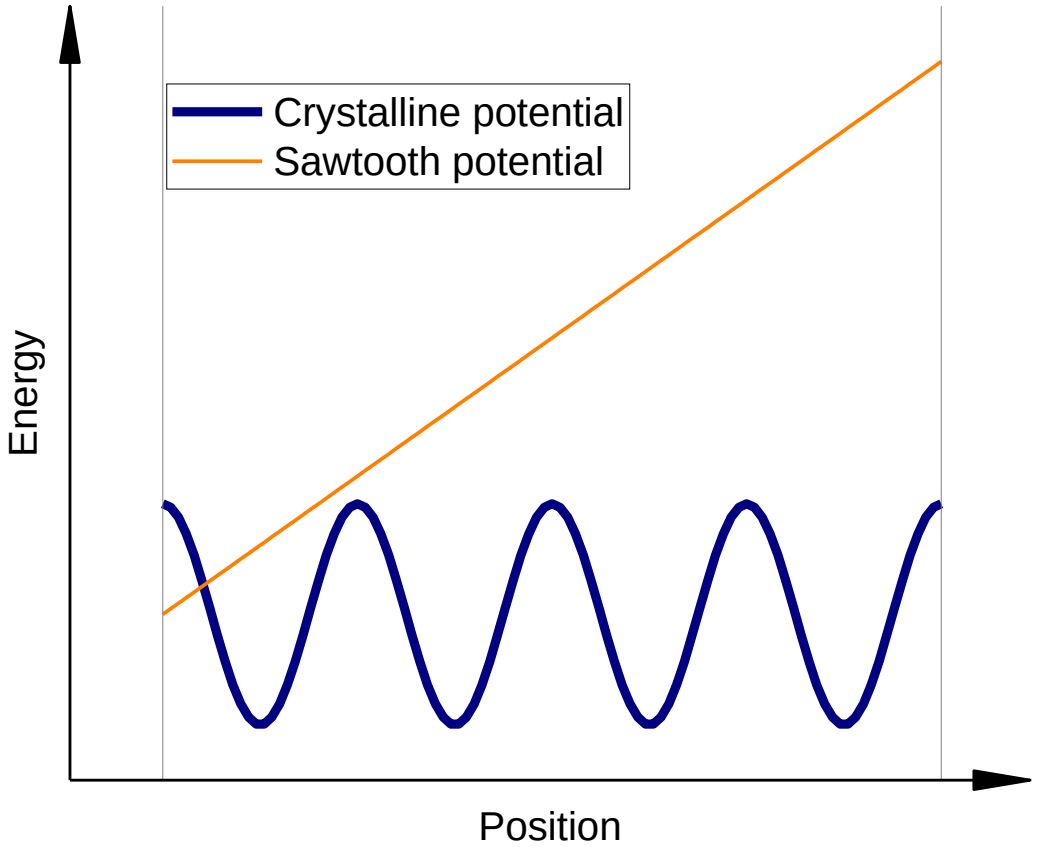
Naoya Yamaguchi
Nanomaterials Research Institute (NanoMaRi), Kanazawa University

First-principles LCPAO approach for insulators under finite electric fields with forces

Comput. Phys. Commun. **280**, 108487 (2022). (arXiv:2203.10441)



In a crystal, the electronic density is distributed.

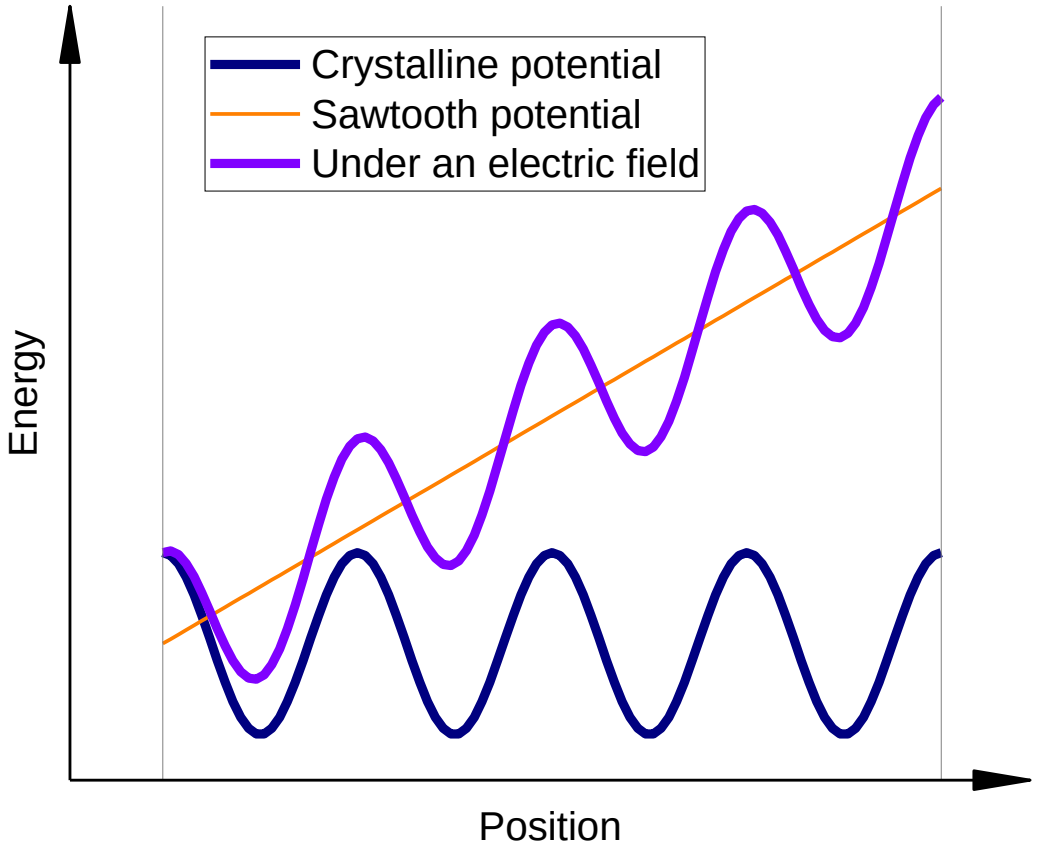


Sawtooth potential is added to apply an electric field ***E***.

$$V = e\boldsymbol{E} \cdot \boldsymbol{r}$$

Elementary charge

Position



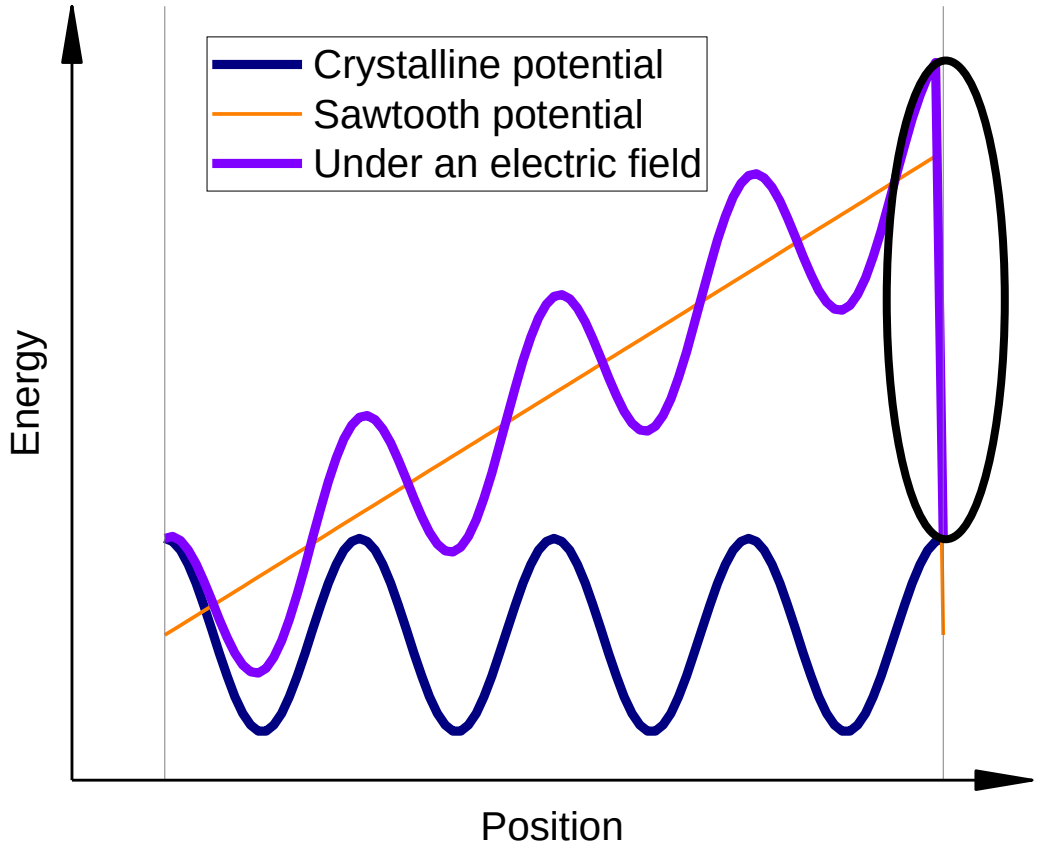
Potential under a uniform electric field ***E***

$$V = e\boldsymbol{E} \cdot \boldsymbol{r}$$

Elementary charge

Position

$$V_{KS}^{\boldsymbol{E}} = V_{KS} + e\boldsymbol{E} \cdot \boldsymbol{r}$$

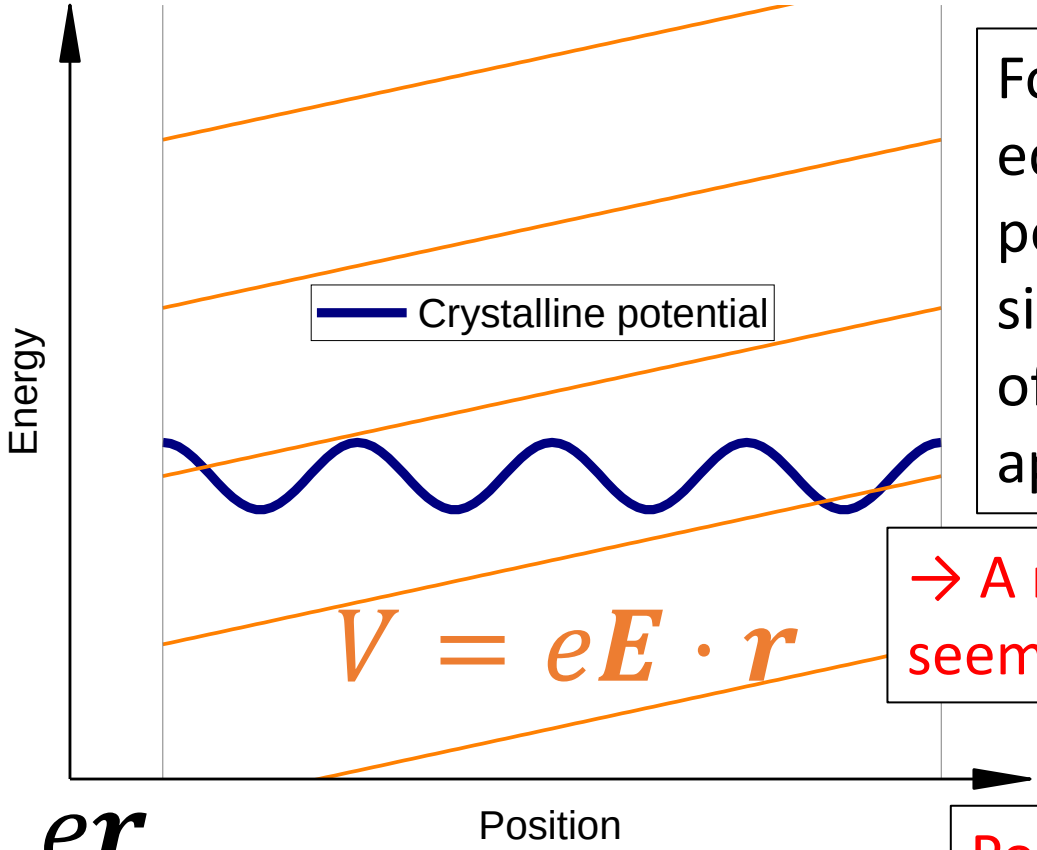


Periodic boundary condition gives unphysical potential.

In systems with boundaries and no unphysical regions in the vacuum region, the use of a sawtooth potential is not applicable.

$$V = e\boldsymbol{E} \cdot \boldsymbol{r}$$

$$V_{KS}^{\boldsymbol{E}} = V_{KS} + e\boldsymbol{E} \cdot \boldsymbol{r}$$



For systems without edges such as crystals, potential that is a single-valued function of the position is not appropriate.

→ A multivalued function seems to be appropriate?

$$\frac{e\boldsymbol{r}}{\Omega} \rightarrow \boldsymbol{P}, V = \Omega \boldsymbol{E} \cdot \boldsymbol{P}$$

Ω Cell volume

Polarization $\boldsymbol{P}$ can be expressed by a multivalued function.

Homogeneous electric fields in insulating solids based on MTP

$$\mathcal{F}[\boldsymbol{E}] = \mathcal{E}_{\mathrm{KS}} - \Omega \boldsymbol{E} \cdot \boldsymbol{P}$$

R.W. Nunes, D. Vanderbilt, Phys. Rev. Lett. **73**, 712 (1994).

Electric fields in first-principles calculations using a plane-wave basis

$$\delta \mathcal{F} / \delta \left\langle u_{\mu}^{(\sigma \boldsymbol{k})} \right|$$ Periodic part of Bloch orbitals

I. Souza, J. Íñiguez, D. Vanderbilt, Phys. Rev. Lett. **89**, 117602 (2002).

P. Umari, A. Pasquarello, Phys. Rev. Lett. **89**, 157602 (2002). (Car-Parrinello method)
J.W. Zwanziger, J. Galbraith, Y. Kipouros, M. Torrent, M. Giantomassi, X. Gonze, Comput. Mater. Sci. **58**, 113 (2012). (projector augmented wave framework)

The implementation for finite electric fields with forces in the localized basis set, particularly in the pseudo-atomic orbital linear combination (LCPAO) method, which is ideal for nanoscale simulations, have not been developed until then.

Electric polarization in solids (modern theory of polarization (MTP))

(cf. R. D. King-Smith, and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).)

Electronic contribution of polarization

Spin degeneracy

$$\boldsymbol{G}_a \cdot \boldsymbol{P}_e = \frac{ef}{\Omega N_b N_c} \sum_{\sigma} \sum_{I_b=0}^{N_b-1} \sum_{I_c=0}^{N_c-1} \mathrm{Im} \ln \det \prod_{I_a=0}^{N_a-1} M_a^{(\sigma, I_a, I_b, I_c)}$$

Reciprocal lattice vectors

Spin

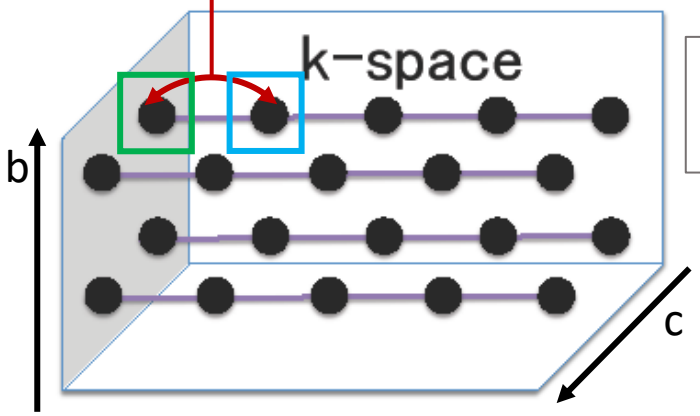
Berry phases

$$M_{a\mu\nu}^{(\sigma, I_a, I_b, I_c)} = \left\langle u_\mu^{(\sigma \boldsymbol{k}(I_a, I_b, I_c))} \middle| u_\nu^{(\sigma \boldsymbol{k}(I_a+1, I_b, I_c))} \right\rangle$$

Overlap matrices between two successive k-points

Periodic part of Bloch orbitals

$$\boldsymbol{k}(I_a, I_b, I_c) = (I_a/N_a)\boldsymbol{G}_a + (I_b/N_b)\boldsymbol{G}_b + (I_c/N_c)\boldsymbol{G}_c.$$



e.g. $N_b = N_c = 2$, i.e. , $I_b, I_c = (0,0), (0,1), (1,0), (1,1)$;
$N_a = 5$, i.e. , $I_a = 0, 1, 2, 3, 4$

Solving the eigenvalue problem at each wave number (k-point) to obtain eigenvectors, from which *M* can be calculated.

Linear combination of pseudo atomic orbitals (LCPAO)

The Bloch function of band μ can be expressed as follows:

$$\langle \boldsymbol{r} | \psi_{\mu}^{(\sigma \boldsymbol{k})} \rangle = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n} \sum_{i\alpha} c_{i\alpha,\mu}^{(\sigma \boldsymbol{k})} \langle \boldsymbol{r} | \phi_{i\alpha}^{\boldsymbol{R}_n} \rangle ,$$

N: the number of cells considered in the calculation
$\boldsymbol{R}_n$: lattice vector of cell n. c: LCPAO expansion coefficients.
ϕ: PAO. i: index of the atom. α: index of the orbital.

The previous implementation of $\boldsymbol{M}_{\mu\nu}$ calculations in polB (cf. the technical note).

$$\begin{aligned}\langle u_{\sigma\mu}^{(\mathbf{k})} | u_{\sigma\nu}^{(\mathbf{k}+\Delta\mathbf{k})} \rangle &= \sum_{\mathrm{n}} \sum_{i\alpha,j\beta} c_{\sigma\mu,i\alpha}^{(\mathbf{k})*} c_{\sigma\nu,j\beta}^{(\mathbf{k}+\Delta\mathbf{k})} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}_{\mathrm{n}}} \mathrm{e}^{-\mathrm{i}\Delta\mathbf{k}\cdot(\tau_i - \mathbf{R}_{\mathrm{n}})} \times \\ & \{ \langle \phi_{i\alpha}(\mathbf{r}') | \phi_{j\beta}(\mathbf{r}' + \tau_i - \tau_j - \mathbf{R}_{\mathrm{n}}) \rangle - i\Delta\mathbf{k} \cdot \langle \phi_{i\alpha}(\mathbf{r}') | \mathbf{r}' | \phi_{j\beta}(\mathbf{r}' + \tau_i - \tau_j - \mathbf{R}_{\mathrm{n}}) \rangle \}\end{aligned}$$

Efficient LCPAO approach for MTP

N. Yamaguchi, F. Ishii, Comput. Phys. Commun. **280**, 108487 (2022).

$$\boldsymbol{G}_a \cdot \boldsymbol{P}_e = \frac{ef}{\Omega N_b N_c} \sum_{\sigma} \sum_{I_b=0}^{N_b-1} \sum_{I_c=0}^{N_c-1} \mathrm{Im} \ln \det \prod_{I_a=0}^{N_a-1} M_a^{(\sigma, I_a, I_b, I_c)}$$

$$M_{a\mu\nu}^{(\sigma, I_a, I_b, I_c)} = \left(C^{(\sigma \boldsymbol{k}(I_a, I_b, I_c))\dagger} \mathrm{T}_a^{(\boldsymbol{k}(I_a+1, I_b, I_c))} C^{(\sigma \boldsymbol{k}(I_a+1, I_b, I_c))} \right)_{\mu\nu}$$

The matrix form is optimal in terms of efficiency and simplicity in calculations, and it is particularly effective for iterative calculations like SCF calculations.

$$\mathrm{T}_{ai\alpha, j\beta}^{(\boldsymbol{k})} = \sum_{n=0}^{N-1} e^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_n} \left\langle \phi_{i\alpha}^{\boldsymbol{0}} \middle| e^{-\mathrm{i}\frac{\boldsymbol{G}_a}{N_a}\cdot\boldsymbol{r}} \middle| \phi_{j\beta}^{\boldsymbol{R}_n} \right\rangle$$

T(***k***) need preparing **only once**
at the beginning of each SCF calculation.

LCPAO approach for finite electric field in insulating solids

N. Yamaguchi, F. Ishii, Comput. Phys. Commun. **280**, 108487 (2022).

from the relation $V = \sum_{\sigma \boldsymbol{k}} \mathrm{tr}(c^{(\sigma \boldsymbol{k})\dagger} A^{(\sigma \boldsymbol{k})} c^{(\sigma \boldsymbol{k})})$. Considering the derivative of V with respect to the LCPAO coefficients, we get

$$\frac{\partial V}{\partial c^{(\sigma \boldsymbol{k})*}_{i\alpha,\mu}} = (A^{(\sigma \boldsymbol{k})} c^{(\sigma \boldsymbol{k})})_{i\alpha,\mu}. \quad (5)$$

Extract the matrix elements *A* of the electric field potential *V*

Moreover, we expand Eq. 5 with the cell vectors $\mathbf{v}_a$, $\mathbf{v}_b$, and $\mathbf{v}_c$, and obtain

$$\frac{\partial V}{\partial c^{(\sigma \boldsymbol{k})*}_{i\alpha,\mu}} = -\Omega \boldsymbol{E} \cdot \frac{\partial \boldsymbol{P}}{\partial c^{(\sigma \boldsymbol{k})*}_{i\alpha,\mu}} = -\Omega \boldsymbol{E} \cdot \frac{\partial \boldsymbol{P}_e}{\partial c^{(\sigma \boldsymbol{k})*}_{i\alpha,\mu}} = -\frac{\Omega}{2\pi} \sum_{\lambda=a,b,c} (\boldsymbol{E} \cdot \mathbf{v}_\lambda) \frac{\partial}{\partial c^{(\sigma \boldsymbol{k})*}_{i\alpha,\mu}} (\boldsymbol{G}_\lambda \cdot \boldsymbol{P}_e). \quad (6)$$

Here,

$$\frac{\partial}{\partial c^{(\sigma \boldsymbol{k})*}_{i\alpha,\mu}} (\boldsymbol{G}_{\boldsymbol{a}} \cdot \boldsymbol{P}_e) = \frac{ef}{\Omega} \left(\left(\frac{O_a^{(\sigma \boldsymbol{k})} - O_a^{(\sigma \boldsymbol{k})\dagger}}{2i} \right) c^{(\sigma \boldsymbol{k})} \right)_{i\alpha,\mu}, \quad (7)$$

where $O_a^{(\sigma \boldsymbol{k}(I_a,I_b,I_c))} =$

$$\frac{1}{N_b N_c} \mathrm{T}_a^{\boldsymbol{k}(I_a+1,I_b,I_c)} c^{(\sigma \boldsymbol{k}(I_a+1,I_b,I_c))} \left(M_a^{(\sigma,I_a,I_b,I_c)} \right)^{-1} \left(M_a^{(\sigma,I_a-1,I_b,I_c)} \right)^{-1} c^{(\sigma \boldsymbol{k}(I_a-1,I_b,I_c))\dagger} \mathrm{T}_a^{\boldsymbol{k}(I_a,I_b,I_c)}$$

LCPAO approach for finite electric field in insulating solids

N. Yamaguchi, F. Ishii, Comput. Phys. Commun. **280**, 108487 (2022).

Then, we get

$$\frac{\partial V}{\partial c^{(\sigma \boldsymbol{k})*}_{i\alpha,\mu}} = \left(\left(\frac{efi}{2\pi} \sum_{\lambda=a,b,c} (\boldsymbol{E}\cdot\mathbf{v}_\lambda) \frac{O^{(\sigma\boldsymbol{k})}_\lambda - O^{(\sigma\boldsymbol{k})\dagger}_\lambda}{2} \right) c^{(\sigma\boldsymbol{k})} \right)_{i\alpha,\mu},$$

lattice vector

Therefore, the matrix elements of A are given as

$$A^{(\sigma\boldsymbol{k})}_{i\alpha,j\beta} = \left(\frac{efi}{2\pi} \sum_{\lambda=a,b,c} (\boldsymbol{E}\cdot\mathbf{v}_\lambda) \frac{O^{(\sigma\boldsymbol{k})}_\lambda - O^{(\sigma\boldsymbol{k})\dagger}_\lambda}{2} \right)_{i\alpha,j\beta}.$$

where $O^{(\sigma\boldsymbol{k}(I_a,I_b,I_c))}_a =$

$$\frac{1}{N_b N_c} \mathrm{T}^{\boldsymbol{k}(I_a+1,I_b,I_c)}_a c^{(\sigma\boldsymbol{k}(I_a+1,I_b,I_c))} \left(M^{(\sigma,I_a,I_b,I_c)}_a\right)^{-1} \left(M^{(\sigma,I_a-1,I_b,I_c)}_a\right)^{-1} c^{(\sigma\boldsymbol{k}(I_a-1,I_b,I_c))\dagger} \mathrm{T}^{\boldsymbol{k}(I_a,I_b,I_c)}_a$$

Constructed from information at the three k-points including the points before and after

Adding *A* to the Hamiltonian results in a Hamiltonian under a uniform electric field.

→We implemented it in OpenMX

Force acting on an atom under an electric field

N. Yamaguchi, F. Ishii, Comput. Phys. Commun. **280**, 108487 (2022).

Ionic contribution to the electric polarization

Ionic $$\Omega \boldsymbol{E} \cdot \frac{\partial \boldsymbol{P}_I}{\partial \boldsymbol{\tau}_i} = Z_i e \boldsymbol{E}$$

Position of atom i — Ionic charge

Electronic

$$\Omega \boldsymbol{E} \cdot \frac{\partial \mathbf{P}_e}{\partial \boldsymbol{\tau}_i} = \frac{ef}{2\pi} \sum_{\sigma \boldsymbol{k}} \sum_{\lambda=a,b,c} (\boldsymbol{E} \cdot \mathbf{v}_\lambda) \mathrm{Im tr} \left(\left(\frac{\partial c^\dagger}{\partial \boldsymbol{\tau}_i} \mathrm{T} c + c^\dagger \frac{\partial \mathrm{T}}{\partial \boldsymbol{\tau}_i} c + c^\dagger \mathrm{T} \frac{\partial c}{\partial \boldsymbol{\tau}_i} \right) M^{-1} \right)$$

In LCPAO, unlike a complete basis set like plane waves, the electronic part remains as a Pulay force.

→ **Only $c^\dagger \frac{\partial \mathrm{T}}{\partial \boldsymbol{\tau}_i} c$ needs to be explicitly computed.**

Hamiltonian

(Other terms are included in $\frac{\partial c^\dagger}{\partial \boldsymbol{\tau}_i} \mathrm{H} c + c^\dagger \mathrm{H} \frac{\partial c}{\partial \boldsymbol{\tau}_i}$)

Evaluation of Forces → **effective charges & static dielectric constant.**

Electronic dielectric constants

N. Yamaguchi, F. Ishii, Comput. Phys. Commun. **280**, 108487 (2022).

System	LDA;*standard*	LDA;*precise*	GGA;*precise*	Ref. (theor.)	Ref. (expt.)
C	5.61	5.67	5.67	5.9 [20]	5.7 [21]
Si	12.17	12.74	12.36	12.9 [20]	11.6 [21]
AlP	8.05	8.16	7.89	8.1 [5,20], 7.84 [9]	7.4 [21]
AlAs	8.84	9.05	8.85	9.6 [5], 8.80 [9], 9.3 [20]	8.16 [21]
GaP	10.33	10.45	9.94	9.4 [5], 10.4 [20]	8.8 [21]
GaAs	13.84	14.42	13.16	11.9 [5], 13.7 [20]	10.86 [21]
AlSb	10.84	11.14	10.90	11.45 [9], 11.5 [20]	9.88 [21]
InP	11.07	10.91	10.08	11 [20]	9.9 [21]
ZnS	5.93	6.12	5.77	5.9 [20]	5.1 [21]
ZnSe	7.15	7.41	6.90	7.2 [20]	5.9 [21]
ZnTe	8.35	8.86	8.24	8.9 [20]	6.9 [21]
CdSe	7.64	8.21	7.21	7.6 [20]	6.2 [21]
CdTe	8.09	8.75	7.89	8.6 [20]	7.1 [21]
MgO	3.09	3.18	3.14	3.1 [20]	3.1 [21]

This work

$$\varepsilon_{xx} = 1 + \frac{1}{\varepsilon_0}\frac{\partial P_x}{\partial E_x}$$

Dielectric constant

Electric constant

LDA: [5] Phys. Rev. Lett. **89**, 117602 (2002).
GGA: [9] Comput. Mater. Sci. **58**, 113 (2012);
[20] Phys. Rev. B **95**, 075302 (2017).
expt.: [21] Properties of Group-IV, III-V and II-VI Semiconductors, John Wiley & Sons, Ltd, 2005, pp.211–281.

Born effective charges

N. Yamaguchi, F. Ishii, Comput. Phys. Commun. **280**, 108487 (2022).

System	LDA;*precise*	GGA;*precise*	Ref. (theor.)	Ref. (expt.)
AlP	2.19	2.20	2.24 [5], 2.23 [9], 2.20 [22]	2.15 [25]
AlAs	2.12	2.09	2.14 [5], 2.110 [23], 2.17 [9], 2.12 [22]	2.20 [26]
GaP	2.05	2.11	2.10 [5], 2.06 [22]	2.16 [27]
GaAs	2.09	2.10	2.00 [5], 2.18 [23], 2.08 [22]	2.18 [26]
AlSb	1.81	1.75	1.83 [9], 1.81 [22]	1.93 [28]
InP	2.44	2.48	2.50 [22]	2.55 [29]
ZnS	1.87	1.89	-1.99 [24]	2.15 [29]
ZnSe	1.95	1.95	2.12 [30]	2.03 [29]
ZnTe	1.87	1.86	**This work**	2.00 [29]
CdSe	2.19	2.17		2.25 [29]
CdTe	2.09	2.08		2.35 [29]
MgO	1.98	1.98	1.96 [8]	1.77 [29]

[8] Phys. Rev. Lett. **89**, 157602 (2002); [22] J. Appl. Phys. **121**, 125701 (2017).
[23] Phys. Rev. B **75**, 115116 (2007); [24] Phys. Rev. B **50**, 10715 (1994).
[25] AIP Conf. Proc. **1653**, 020065 (2015).; [26] Phys. Rev. B **50**, 14125 (1994).
[27] J. Vac. Sci. Technol. B **39**, 052201 (2021);
[28] Solid State Commun. **57**, 483 (1986).
[29] Phys. Rev. B **4**, 1367 (1971).
[30] AIP Adv. B **4**, 067138 (2014).

The values in [9] and [30] were those in GGA,
and the other reference values were those in LDA.

Born effective charge $Z^*_{xx} = \frac{1}{e}\frac{\partial F_x}{\partial E_x}$ **Force**

Static dielectric constants

N. Yamaguchi, F. Ishii, Comput. Phys. Commun. **280**, 108487 (2022).

System	LDA	GGA	Ref.(theor.)	Ref.(expt.)
AlP	10.26	9.94	10.2(LDA[5]), 10.26(GGA[9])	9.6[21]
AlAs	10.90	10.56	11.5(LDA[5]), 11.05(GGA[9])	10.6[21]
GaP	11.96	11.69	11.2(LDA[5])	11.0[21]
MgO	7.92	8.79 9.56 **This work** (for expt. lattice constant)	7.93(LDA[8])	9.8[21]

The static dielectric constants were accurately determined.
→ the electronic states and forces acting on atoms under an electric field were calculated with sufficient accuracy.
→ First-principles molecular dynamics under an applied electric field **in LCPAO** can be achieved at a sufficient level.

Summary

- We developed a method to construct the effective potential for applying an electric field using the Berry phase method within the framework of the LCPAO method, including the forces.
- In our implemented code, the calculated values for electronic and static dielectric constants and Born effective charges match the reference values.
- This method enables large-scale first-principles calculations under an electric field, making it possible to study the behavior of electronic states under electric fields even in complex systems.

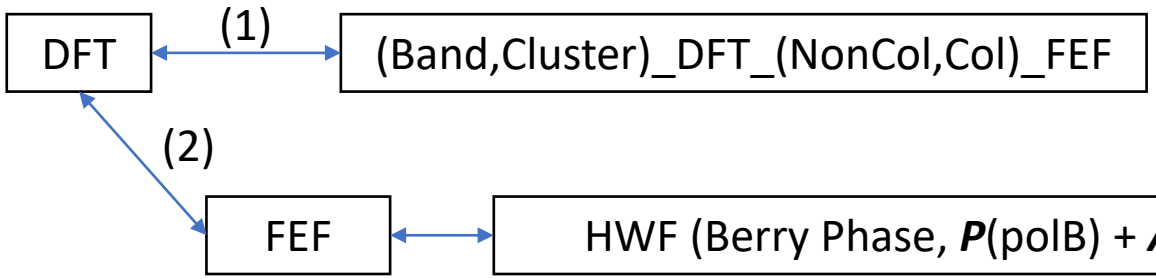
This section is based on
Comput. Phys. Commun. **280**, 108487 (2022). (arXiv:2203.10441)

New Functions for Finite Electric Fields in OpenMX

Implementation

- Output_CompTime.c
- Force.c
- Make_InputFile_with_FinalCoord.c
- Total_Energy.c
- Set_XC_Grid.c
- DFT.c
- Input_std.c
- FEF.c
- Band_DFT_Col_FEF.c
- Band_DFT_NonCol_FEF.c

- HWC.c
- HWCfunc.c
- Cluster_DFT_Col_FEF.c
- Hamiltonian_Cluster_Hs_FEF.c
- Cluster_DFT_NonCol_FEF.c
- Hamiltonian_Cluster_NC_Hs2_FEF.c
- mimic_read_scfout.h
- HWCfunc.h
- openmx_common.h



In 1 SCF step
(1) Eigen value problem
(2) Effective potential ***A***(**k**)

Input keywords

- scf.Electric.Field.Type BerryP # sawtooth|BerryP

- scf.Electric.Field 0.1 0.0 0.0 # in GV/m
  # x, y, z in BerryP, while a, b, c in sawtooth

- FEF.Polarization.Switch On # Off|On
  # To evaluate electric polarization P
- FEF.Continue.Mode Update # Off|Zero|Update
  # Too strong an electric field is
  (not acceptable|not applied|reduced and applied).
- FEF.Born.Effective.Charges.Switch On # Off|On
  # To evaluate F_(x,y,z)/E

Calculation process

1. Get the SCF convergence w/o electric field
2. Break the convergence flag
3. Calculate the k-independent part of $\boldsymbol{T}$
4. Calculate $\boldsymbol{A}(\mathbf{k})$
5. Start the next SCF step:
   In setting the Hamiltonian, $\boldsymbol{A}(\mathbf{k})$ is added to the global form of the Hamiltonian (k-dependent).
6. Check the SCF convergence
7. Convergence → finish; otherwise → 4

Example: Diamond