First-Principles Calculation of Electric Polarization

Fumiyuki Ishii
Kanazawa University

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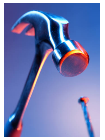
Electric polarization

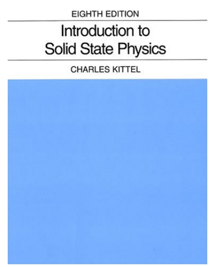
- Fundamental physical quantity of insulators
- Characterize dielectric properties of insulators
- Piezoelectricity, Ferroelectricity, Magnetoelectric effect
- Many applications
  - Capacitor, Piezoelectric device, Ferroelectric memory
- Momentum dependence: Characterize topological insulators

Perturbations and Responses

Perturbations / Responses	1. Mecanical 	2. Thermal 	3. Electric 	4. Magnetic 	5. Chemical 
1. Mecanical	Elasticity	Thermal expansion	Electromechanical	Magnetostriction	Osmotic pressure
2. Thermal	Thermal insulating	Thermal conductivity	Pyroelectric/ Thermoelectric (Peltier)	Thermomagnetic	Heat diffusion
3. Electric	Piezoelectric	Pyroelectric/ Thermoelectric (Seebeck)	Electric Polarization Electric Conductivity	Magnetoelectric	Battery
4. Magnetic	Magnetostriction	Thermomagnetic	Magnetoelectric	Magnetization	?
5. Chemical	Osmotic pressure	Heat diffusion	Battery	?	diffusion

Based on the table of Hidetoshi Takahashi

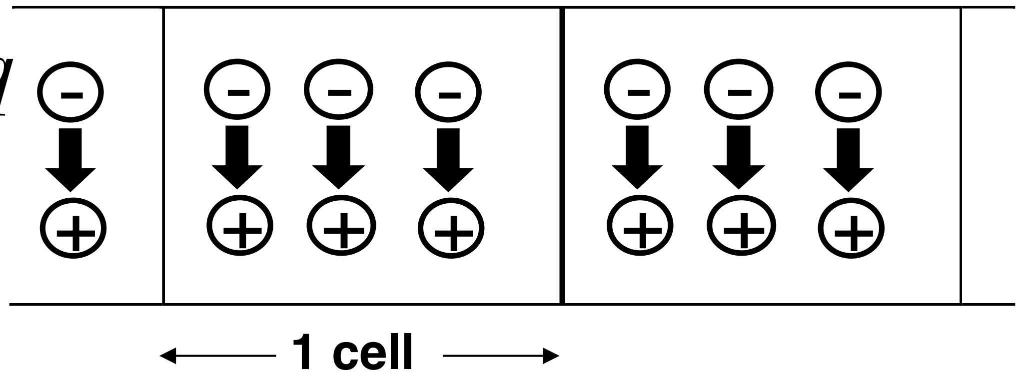
In the textbook …



The polarization P is defined as the dipole moment per unit volume, averaged over the volume of a cell.

$$\mathbf{P} = \frac{1}{V_s}\sum_{i}^{s}\mathbf{p}_i = \frac{1}{V_s}\sum_{n}^{s}\mathbf{r}_n q$$

$$= \frac{1}{V_c}\sum_{n}^{c}\mathbf{r}_n q_n$$



Periodic boundary condition

S:sample ,C:cell

Dipole sum of discrete charges

Problems in electric polarization

- **Resta (1992):**

  Contrary to common textbook statements, the dipole of a periodic charge distribution is ill defined, except the case in which the total charge is unambiguously decomposed into an assembly of localized and neutral charge distributions.

  P is not a bulk property, while the variations of P are indeed measurable.

Can we compute *P* from charge density ?

Charge distribution is continuous in real materials.

R. M. Martin, PRB 9, 1998(1974).

Local polarization field $\mathbf{P}_{el}(\mathbf{r})$

$$\nabla \cdot \mathbf{P}_{el}(\mathbf{r}) = -\rho(\mathbf{r})$$

$$\mathbf{P}_{el} = \frac{1}{\Omega}\int_{cell} \mathbf{P}(\mathbf{r}) d\mathbf{r}$$

$$= \frac{1}{\Omega}\int_{cell} d\mathbf{r}\,\rho(\mathbf{r})\mathbf{r} + \underline{\frac{1}{\Omega}\int_{surface} \mathbf{r}[\mathbf{n}\cdot\mathbf{P}(\mathbf{r})] ds}$$

cell to cell term (current)

Conclusion :

•Absolute value of polarization is not bulk property

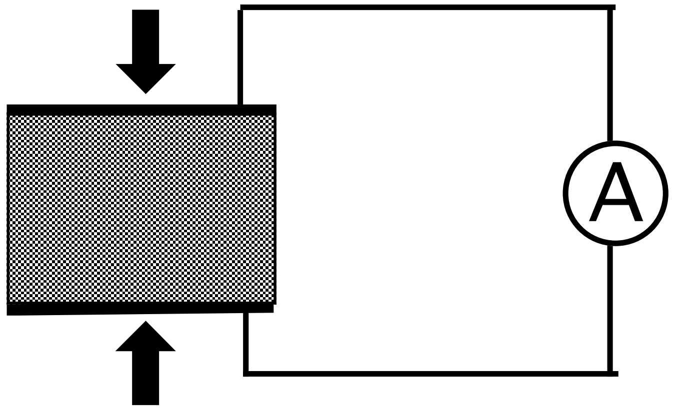
•Dipole moment divided by unit cell volume ≠ Polarization

Observation of electric polarization

- Current induced by perturbation

$$\mathbf{J}(\lambda) = \frac{\partial \mathbf{P}}{\partial \lambda}$$

- Change in polarization by perturbation



$$\Delta \mathbf{P} = \int \mathbf{J}(\lambda) d\lambda = \int \frac{\partial \mathbf{P}}{\partial \lambda} d\lambda$$

In classical way:

$$\mathbf{j} = -ne\mathbf{v}$$

$$\Delta \mathbf{P} = \int_0^{\Delta t} -ne\mathbf{v}dt = [-ne\mathbf{r}(\Delta t)] - [-ne\mathbf{r}(0)]$$

$$= \mathbf{P}(\Delta t) - \mathbf{P}(0)$$

Electric polarization expressed by wave function

$$\boldsymbol{P} = \frac{e}{V}\sum_{\boldsymbol{k}}\sum_{n=1}^{occ}\langle\psi_n^{\boldsymbol{k}}|\boldsymbol{r}|\psi_n^{\boldsymbol{k}}\rangle$$

$$H|\psi_n^{\boldsymbol{k}}\rangle = E_n^{\boldsymbol{k}}|\psi_n^{\boldsymbol{k}}\rangle$$

$$\begin{aligned}
\frac{d\boldsymbol{P}}{dt} &= \frac{e}{V}\sum_{\boldsymbol{k}}\sum_{n=1}^{occ}\frac{d}{dt}\langle\psi_n^{\boldsymbol{k}}|\boldsymbol{r}|\psi_n^{\boldsymbol{k}}\rangle \\
&= \frac{e}{V}\sum_{\boldsymbol{k}}\sum_{n=1}^{occ}\left(\langle\partial_t\psi_n^{\boldsymbol{k}}|\boldsymbol{r}|\psi_n^{\boldsymbol{k}}\rangle + \langle\psi_n^{\boldsymbol{k}}|\boldsymbol{r}|\partial_t\psi_n^{\boldsymbol{k}}\rangle\right) \\
&= \frac{e}{V}\sum_{\boldsymbol{k}}\sum_{n=1}^{occ}\sum_{m=1}^{\infty}(\langle\partial_t\psi_n^{\boldsymbol{k}}|\psi_m^{\boldsymbol{k}}\rangle\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{r}|\psi_n^{\boldsymbol{k}}\rangle \\
&+ \langle\psi_n^{\boldsymbol{k}}|\boldsymbol{r}|\psi_m^{\boldsymbol{k}}\rangle\langle\psi_m^{\boldsymbol{k}}|\partial_t\psi_n^{\boldsymbol{k}}\rangle)
\end{aligned}$$

Electric polarization expressed by wave function

$$\frac{d\boldsymbol{P}}{dt} = \frac{e}{V}\sum_{\boldsymbol{k}}\sum_{n=1}^{occ}\sum_{m=1}^{\infty}\left(\langle\partial_t\psi_n^{\boldsymbol{k}}|\psi_m^{\boldsymbol{k}}\rangle\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{r}|\psi_n^{\boldsymbol{k}}\rangle + \langle\psi_n^{\boldsymbol{k}}|\boldsymbol{r}|\psi_m^{\boldsymbol{k}}\rangle\langle\psi_m^{\boldsymbol{k}}|\partial_t\psi_n^{\boldsymbol{k}}\rangle\right)$$

Velocity operator

$$\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{v}|\psi_n^{\boldsymbol{k}}\rangle = i\hbar\langle\psi_m^{\boldsymbol{k}}|[\boldsymbol{r},H]|\psi_n^{\boldsymbol{k}}\rangle = i\hbar(E_n^{\boldsymbol{k}} - E_m^{\boldsymbol{k}})\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{r}|\psi_n^{\boldsymbol{k}}\rangle$$

$$\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{r}|\psi_n^{\boldsymbol{k}}\rangle = \frac{\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{v}|\psi_n^{\boldsymbol{k}}\rangle}{i\hbar(E_n^{\boldsymbol{k}} - E_m^{\boldsymbol{k}})}$$

$$\langle\psi_n^{\boldsymbol{k}}|\boldsymbol{r}|\psi_m^{\boldsymbol{k}}\rangle = (\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{r}|\psi_n^{\boldsymbol{k}}\rangle)^*$$

Electric polarization expressed by wave function

$$\frac{d\boldsymbol{P}}{dt} = \frac{-ie}{V\hbar}\sum_{\boldsymbol{k}}\sum_{n=1}^{occ}\sum_{m\neq n}\left(\frac{\langle\partial_t\psi_n^{\boldsymbol{k}}|\psi_m^{\boldsymbol{k}}\rangle\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{v}|\psi_n^{\boldsymbol{k}}\rangle}{(E_n^{\boldsymbol{k}}-E_m^{\boldsymbol{k}})} - c.c\right)$$

Bloch wavefunction and its periodic part

$$\begin{aligned}
|\psi_n^{\boldsymbol{k}}\rangle &= e^{i\boldsymbol{k}\cdot\boldsymbol{r}}|u_n^{\boldsymbol{k}}\rangle \\
H|\psi_n^{\boldsymbol{k}}\rangle &= E_n^{\boldsymbol{k}}|\psi_n^{\boldsymbol{k}}\rangle \\
e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}He^{i\boldsymbol{k}\cdot\boldsymbol{r}}|u_n^{\boldsymbol{k}}\rangle &= E_n^{\boldsymbol{k}}|u_n^{\boldsymbol{k}}\rangle \\
\tilde{H}|u_n^{\boldsymbol{k}}\rangle &= E_n^{\boldsymbol{k}}|u_n^{\boldsymbol{k}}\rangle \\
\langle\psi_m^{\boldsymbol{k}}|\boldsymbol{v}|\psi_n^{\boldsymbol{k}}\rangle &= \langle u_m^{\boldsymbol{k}}|\tilde{\boldsymbol{v}}|u_n^{\boldsymbol{k}}\rangle
\end{aligned}$$

Heisenberg Equation of Motion

$$
\begin{aligned}
i\hbar \frac{d\boldsymbol{r}}{dt} &= [\boldsymbol{r}, H] \\
i\hbar \boldsymbol{v} &= [\boldsymbol{r}, H]
\end{aligned}
$$

Bloch wavefunction and its periodic part

$$
\begin{aligned}
\tilde{H} &= e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} H e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \\
e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}[\boldsymbol{r}, H]e^{i\boldsymbol{k}\cdot\boldsymbol{r}} &= e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \left(i\hbar \frac{d\boldsymbol{r}}{dt} \right) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = i\hbar \tilde{\boldsymbol{v}} \\
\text{if } [\nabla_{\boldsymbol{k}}, H] = 0, & \\
\nabla_{\boldsymbol{k}} \tilde{H} &= -i\boldsymbol{r} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} H e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} H e^{i\boldsymbol{k}\cdot\boldsymbol{r}} i\boldsymbol{r} \\
\nabla_{\boldsymbol{k}} \tilde{H} &= -i[\boldsymbol{r}, \tilde{H}] = \hbar \tilde{\boldsymbol{v}} \\
\langle \psi_m^{\boldsymbol{k}} | \boldsymbol{v} | \psi_n^{\boldsymbol{k}} \rangle &= \langle u_m^{\boldsymbol{k}} | \tilde{\boldsymbol{v}} | u_n^{\boldsymbol{k}} \rangle = \langle u_m^{\boldsymbol{k}} | \frac{\nabla_{\boldsymbol{k}} \tilde{H}}{\hbar} | u_n^{\boldsymbol{k}} \rangle
\end{aligned}
$$

Electric polarization expressed by wave function

$$\begin{aligned}
\frac{d\boldsymbol{P}}{dt} &= \frac{-ie}{8\pi^3\hbar}\int_{BZ} d\boldsymbol{k} \sum_{n=1}^{occ}\sum_{m\neq n}\left(\frac{\langle \partial_t \psi_n^{\boldsymbol{k}}|\psi_m^{\boldsymbol{k}}\rangle\langle \psi_m^{\boldsymbol{k}}|\boldsymbol{v}|\psi_n^{\boldsymbol{k}}\rangle}{(E_n^{\boldsymbol{k}}-E_m^{\boldsymbol{k}})} - c.c\right)\\
&= \frac{-ie}{8\pi^3\hbar}\int_{BZ} d\boldsymbol{k} \sum_{n=1}^{occ}\sum_{m\neq n}\left(\frac{\langle \partial_t u_n^{\boldsymbol{k}}|u_m^{\boldsymbol{k}}\rangle\langle u_m^{\boldsymbol{k}}|\tilde{\boldsymbol{v}}|u_n^{\boldsymbol{k}}\rangle}{(E_n^{\boldsymbol{k}}-E_m^{\boldsymbol{k}})} - c.c\right)\\
&= \frac{-ie}{8\pi^3}\int_{BZ} d\boldsymbol{k} \sum_{n=1}^{occ}\sum_{m\neq n}\left(\frac{\langle \partial_t u_n^{\boldsymbol{k}}|u_m^{\boldsymbol{k}}\rangle\langle u_m^{\boldsymbol{k}}|\nabla_{\boldsymbol{k}}\tilde{H}|u_n^{\boldsymbol{k}}\rangle}{(E_n^{\boldsymbol{k}}-E_m^{\boldsymbol{k}})} - c.c\right)\\
&= \frac{-ie}{8\pi^3}\int_{BZ} d\boldsymbol{k} \sum_{n=1}^{occ}\left(\langle \partial_t u_n^{\boldsymbol{k}}|\nabla_{\boldsymbol{k}} u_n^{\boldsymbol{k}}\rangle - \langle \nabla_{\boldsymbol{k}} u_n^{\boldsymbol{k}}|\partial_t u_n^{\boldsymbol{k}}\rangle\right)
\end{aligned}$$

First-order perturbation theory

$$
\begin{aligned}
\delta\tilde{H} &= \tilde{H}(k+\Delta k) - \tilde{H}(k) \\
|u_n^{\boldsymbol{k}+\boldsymbol{\Delta k}}\rangle &= |u_n^{\boldsymbol{k}}\rangle \\
&+ \sum_{m\neq n} |u_m^{\boldsymbol{k}}\rangle \frac{\langle u_m^{\boldsymbol{k}}|\delta\tilde{H}|u_n^{\boldsymbol{k}}\rangle}{E_n^{\boldsymbol{k}} - E_m^{\boldsymbol{k}}} + O(\delta\tilde{H}^2) \\
|\nabla_{\boldsymbol{k}} u_n^{\boldsymbol{k}}\rangle &\simeq \sum_{m\neq n} |u_m^{\boldsymbol{k}}\rangle \frac{\langle u_m^{\boldsymbol{k}}|\nabla_{\boldsymbol{k}}\tilde{H}|u_n^{\boldsymbol{k}}\rangle}{E_n^{\boldsymbol{k}} - E_m^{\boldsymbol{k}}}
\end{aligned}
$$

Ordinary derivative to partial derivative

$$
\frac{d}{dt}|u_{k_\alpha,t}\rangle = \partial_{k_\alpha}|u_{k_\alpha,t}\rangle\frac{dk_\alpha}{dt} + \partial_t|u_{k_\alpha,t}\rangle = \partial_t|u_{k_\alpha,t}\rangle
$$

Electric polarization expressed by wave function

$$\int_0^{\Delta t} dt \frac{d\boldsymbol{P}}{dt} = \boldsymbol{P}(\Delta t) - \boldsymbol{P}(0)$$

$$= \frac{-ie}{8\pi^3} \int_0^{\Delta t} dt \int_{BZ} d\boldsymbol{k} \sum_{n=1}^{occ} \left(\langle \partial_t u_n^{\boldsymbol{k}} | \nabla_{\boldsymbol{k}} u_n^{\boldsymbol{k}} \rangle - \langle \nabla_{\boldsymbol{k}} u_n^{\boldsymbol{k}} | \partial_t u_n^{\boldsymbol{k}} \rangle \right)$$

$$= \frac{-ie}{8\pi^3} \int_0^{\Delta t} dt \int_{BZ} d\boldsymbol{k} \sum_{n=1}^{occ} \left(\partial_t \langle u_n^{\boldsymbol{k}} | \nabla_{\boldsymbol{k}} u_n^{\boldsymbol{k}} \rangle - \nabla_{\boldsymbol{k}} \langle u_n^{\boldsymbol{k}} | \partial_t u_n^{\boldsymbol{k}} \rangle \right)$$

For k_α direction,

$$P_\alpha(\Delta t) - P_\alpha(0)$$

$$= \frac{ie}{8\pi^3} \int dk_\beta dk_\gamma \times$$

$$\int_0^{\Delta t} dt \int_0^{G_\alpha} dk_\alpha \sum_{n=1}^{occ} \left(\partial_{k_\alpha} \langle u_n^{\boldsymbol{k}} | \partial_t u_n^{\boldsymbol{k}} \rangle - \partial_t \langle u_n^{\boldsymbol{k}} | \partial_{k_\alpha} u_n^{\boldsymbol{k}} \rangle \right)$$

Electric polarization expressed by Berry phase
(King-Smith & Vanderbilt 1993)

$$P_\alpha(t) = \frac{-ie}{8\pi^3}\int dk_\beta dk_\gamma \sum_{n=1}^{occ}\int_0^{G_\alpha} dk_\alpha \langle u_n^{\boldsymbol{k}}(t)|\partial_{k_\alpha}|u_n^{\boldsymbol{k}}(t)\rangle$$

$$= \quad \frac{e}{8\pi^3}\int dk_\beta dk_\gamma \sum_{n=1}^{occ} \mathrm{Im}\int_0^{G_\alpha} dk_\alpha \langle u_n^{\boldsymbol{k}}(t)|\partial_{k_\alpha}|u_n^{\boldsymbol{k}}(t)\rangle$$

Example: Orthorhombic unitcell

Case: $(k_\beta, k_\gamma) = (0,0)$ sampling , $G_\beta = \frac{2\pi}{b}$, $G_\gamma = \frac{2\pi}{c}$

$$
\begin{aligned}
P_\alpha(t) &= \frac{e}{8\pi^3} \int dk_\beta dk_\gamma \sum_{n=1}^{occ} \mathrm{Im} \int_0^{G_\alpha} dk_\alpha \langle u_n^{\boldsymbol{k}}(t) | \partial_{k_\alpha} | u_n^{\boldsymbol{k}}(t) \rangle \\
&= \frac{e}{8\pi^3} \int dk_\beta dk_\gamma \phi(t) \\
&= \frac{e}{8\pi^3} \frac{2\pi}{b} \frac{2\pi}{c} \phi(t) = \frac{e}{2\pi bc} \phi(t) = \frac{ea}{2\pi abc} \phi(t) \\
&= \frac{ea}{2\pi \Omega_{cell}} \phi(t) = \frac{ea}{\Omega_{cell}} \left(\frac{\phi(t)}{2\pi} \right)
\end{aligned}
$$

Numerical calculation of Berry Phase

$$\phi(t) = \sum_{n=1}^{occ} \mathrm{Im} \int_0^{G_\alpha} dk_\alpha \langle u_n^{\boldsymbol{k}}(t) | \partial_{k_\alpha} | u_n^{\boldsymbol{k}}(t) \rangle$$

We difine overlap matrix $S(\boldsymbol{k}, \boldsymbol{k}', t)$, where
$S_{nm}(\boldsymbol{k}, \boldsymbol{k}', t) \equiv \langle u_n^{\boldsymbol{k}}(t) | \partial_{k_\alpha} | u_n^{\boldsymbol{k}}(t) \rangle$.
We use well-known matrix identity, $\det \exp A = \exp \operatorname{tr} A$,
when $A = \log S \leftrightarrow \exp A = S$. $\log \det S = \operatorname{tr} \log S$.

$$\begin{aligned} \phi(t) &= \mathrm{Im} \int_0^{G_\alpha} dk_\alpha \mathrm{tr} \partial_{k'_\alpha} \langle u_n^{\boldsymbol{k}}(t) | u_m^{\boldsymbol{k}'}(t) \rangle |_{\boldsymbol{k}'=\boldsymbol{k}} \\ &= \mathrm{Im} \int_0^{G_\alpha} dk_\alpha \mathrm{tr} \partial_{k'_\alpha} S(\boldsymbol{k}, \boldsymbol{k}', t) |_{\boldsymbol{k}=\boldsymbol{k}'} \end{aligned}$$

Numerical calculation of Berry Phase

- $A = \log S \leftrightarrow \exp A = S$
- $\det \exp A = \exp \mathrm{tr}\, A$, $\log \det S = \mathrm{tr} \log S$
- $S_{nm}(\boldsymbol{k}, \boldsymbol{k}', t)|_{\boldsymbol{k}=\boldsymbol{k}'} = \delta_{mn}$

$$
\begin{aligned}
\phi(t) &= \mathrm{Im} \int_0^{G_\alpha} dk_\alpha \mathrm{tr} \partial_{k'_\alpha} S(\boldsymbol{k}, \boldsymbol{k}', t)|_{\boldsymbol{k}=\boldsymbol{k}'} \\
&= \mathrm{Im} \int_0^{G_\alpha} dk_\alpha \mathrm{tr} \left[\frac{\partial_{k'_\alpha} S(\boldsymbol{k}, \boldsymbol{k}', t)}{S(\boldsymbol{k}, \boldsymbol{k}', t)} \right]_{|_{\boldsymbol{k}=\boldsymbol{k}'}} \\
&= \mathrm{Im} \int_0^{G_\alpha} dk_\alpha \mathrm{tr} \partial_{k'_\alpha} \log\ S(\boldsymbol{k}, \boldsymbol{k}', t)|_{\boldsymbol{k}=\boldsymbol{k}'} \\
&= \mathrm{Im} \int_0^{G_\alpha} dk_\alpha \partial_{k'_\alpha} \log\ \det S(\boldsymbol{k}, \boldsymbol{k}', t)|_{\boldsymbol{k}=\boldsymbol{k}'}
\end{aligned}
$$

Numerical calculation of Berry Phase

$$\phi(t) \;=\; \mathrm{Im}\int_0^{G_\alpha} dk_\alpha \partial_{k'_\alpha} \log\ \det S(\boldsymbol{k}, \boldsymbol{k}', t)|_{\boldsymbol{k}=\boldsymbol{k}'}$$

If we use k-point sampling mesh J along k_α direction, $k_{\alpha,s} = sG_\alpha/J$ and $\Delta k_\alpha = G_\alpha/\mathrm{J}$.

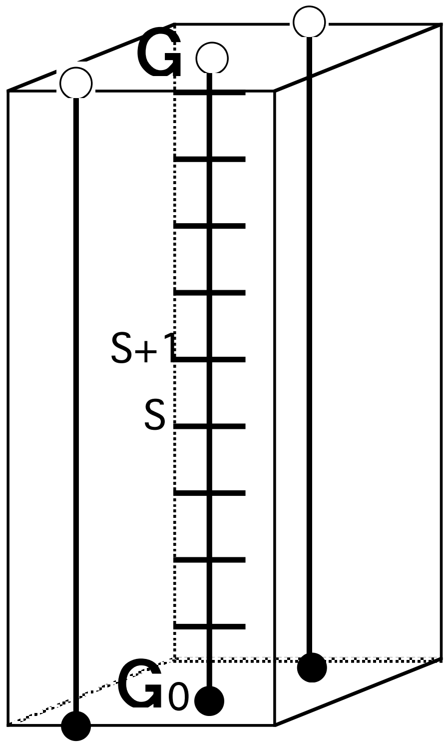
$$\phi(t) = \mathrm{Im} \lim_{\Delta k_\alpha \to 0} \sum_{s=0}^{J-1} \Delta k_\alpha \times$$

$$\frac{\log\det S_{nm}(k_{\alpha,s}, k_{\alpha,s} + \Delta k_\alpha, t) - \log\det S_{nm}(k_{\alpha,s}, k_{\alpha,s}, t)}{\Delta k_\alpha}$$

$$\phi(t) = \mathrm{Im} \lim_{\Delta k_\alpha \to 0} \sum_{s=0}^{J-1} \log\det S_{nm}(k_{\alpha,s} k_{\alpha,s} + \Delta k_\alpha, t)$$

Numerical calculation of Berry Phase

$$
\begin{aligned}
\phi(t) &= \operatorname{Im} \lim_{\Delta k_\alpha \to 0} \sum_{s=0}^{J-1} \log \det S_{nm}(k_{\alpha,s} k_{\alpha,s} + \Delta k_\alpha, t) \\
&= \operatorname{Im} \lim_{\Delta k_\alpha \to 0} \log \prod_{s=0}^{J-1} \det S_{nm}(k_{\alpha,s} k_{\alpha,s} + \Delta k_\alpha, t)
\end{aligned}
$$



Overlap matrix S in OpenMX

$$
\begin{aligned}
\psi_{\sigma\mu}^{(\mathbf{k})}(\mathbf{r}) &= \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} u_{\sigma\mu}^{(\mathbf{k})}(\mathbf{r}), \\
&= \frac{1}{\sqrt{N}} \sum_{\mathrm{n}}^{N} \mathrm{e}^{\mathrm{i}\mathbf{R}_{\mathrm{n}}\cdot\mathbf{k}} \sum_{i\alpha} c_{\sigma\mu,i\alpha}^{(\mathbf{k})} \phi_{i\alpha}(\mathbf{r} - \tau_i - \mathbf{R}_{\mathrm{n}}),
\end{aligned}
$$

$$
\begin{aligned}
\langle u_{\sigma\mu}^{(\mathbf{k})} | u_{\sigma\nu}^{(\mathbf{k}+\Delta\mathbf{k})} \rangle &= \langle \psi_{\sigma\mu}^{(\mathbf{k})} | \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \mathrm{e}^{-\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}} | \psi_{\sigma\nu}^{(\mathbf{k}+\boldsymbol{\Delta}\mathbf{k})} \rangle, \\
&= \langle \psi_{\sigma\mu}^{(\mathbf{k})} | \mathrm{e}^{-\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}} | \psi_{\sigma\nu}^{(\mathbf{k}+\boldsymbol{\Delta}\mathbf{k})} \rangle, \\
&= \frac{1}{N} \sum_{\mathrm{n},\mathrm{n}'} \sum_{i\alpha,j\beta} c_{\sigma\mu,i\alpha}^{(\mathbf{k})*} c_{\sigma\nu,j\beta}^{(\mathbf{k}+\boldsymbol{\Delta}\mathbf{k})} \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot(\mathbf{R}_{\mathrm{n}} - \mathbf{R}_{\mathrm{n}'})} \times \\
&\quad \langle \phi_{i\alpha}(\mathbf{r} - \tau_i - \mathbf{R}_{\mathrm{n}}) | \mathrm{e}^{-\mathrm{i}\Delta\mathbf{k}\cdot(\mathbf{r} - \mathbf{R}_{\mathrm{n}'})} | \phi_{j\beta}(\mathbf{r} - \tau_j - \mathbf{R}_{\mathrm{n}'}) \rangle.
\end{aligned}
$$

$$
\mathbf{r}' = \mathbf{r} - \tau_i - \mathbf{R}_{\mathrm{n}},
$$

Overlap matrix *S* in OpenMX

$$
\begin{aligned}
\langle u_{\sigma\mu}^{(\mathbf{k})} | u_{\sigma\nu}^{(\mathbf{k}+\Delta\mathbf{k})} \rangle &= \frac{1}{N} \sum_{\mathrm{n},\mathrm{n}'} \sum_{i\alpha,j\beta} c_{\sigma\mu,i\alpha}^{(\mathbf{k})*} c_{\sigma\nu,j\beta}^{(\mathbf{k}+\boldsymbol{\Delta}\mathbf{k})} \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot(\mathbf{R}_{\mathrm{n}}-\mathbf{R}_{\mathrm{n}'})} \times \\
&\quad \langle \phi_{i\alpha}(\mathbf{r}') | \mathrm{e}^{-\mathrm{i}\Delta\mathbf{k}\cdot(\mathbf{r}'+\tau_i+\mathbf{R}_{\mathrm{n}}-\mathbf{R}_{\mathrm{n}'})} | \phi_{j\beta}(\mathbf{r}'+\tau_i-\tau_j+\mathbf{R}_{\mathrm{n}}-\mathbf{R}_{\mathrm{n}'}) \rangle .
\end{aligned}
$$

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

$$
\mathrm{e}^{-\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}'} \approx 1 - i\Delta\mathbf{k}\cdot\mathbf{r}'.
$$

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

Application

Electric polarization and water dipole moment in ferroelectric ice

Molecular Simulation
Vol. 38, No. 5, April 2012, 369–372

Taylor & Francis
Taylor & Francis Group

First-principles study of spontaneous polarisation and water dipole moment in ferroelectric ice XI

Fumiyuki Ishii[a]*, Kei Terada[b] and Shinichi Miura[a]

[a]*Faculty of Mathematics and Physics, Institute of Science and Engineering, Kanazawa University, Kanazawa 920-1192, Japan;* [b]*Department of Computational Science, Faculty of Science, Kanazawa University, Kanazawa 920-1192, Japan*

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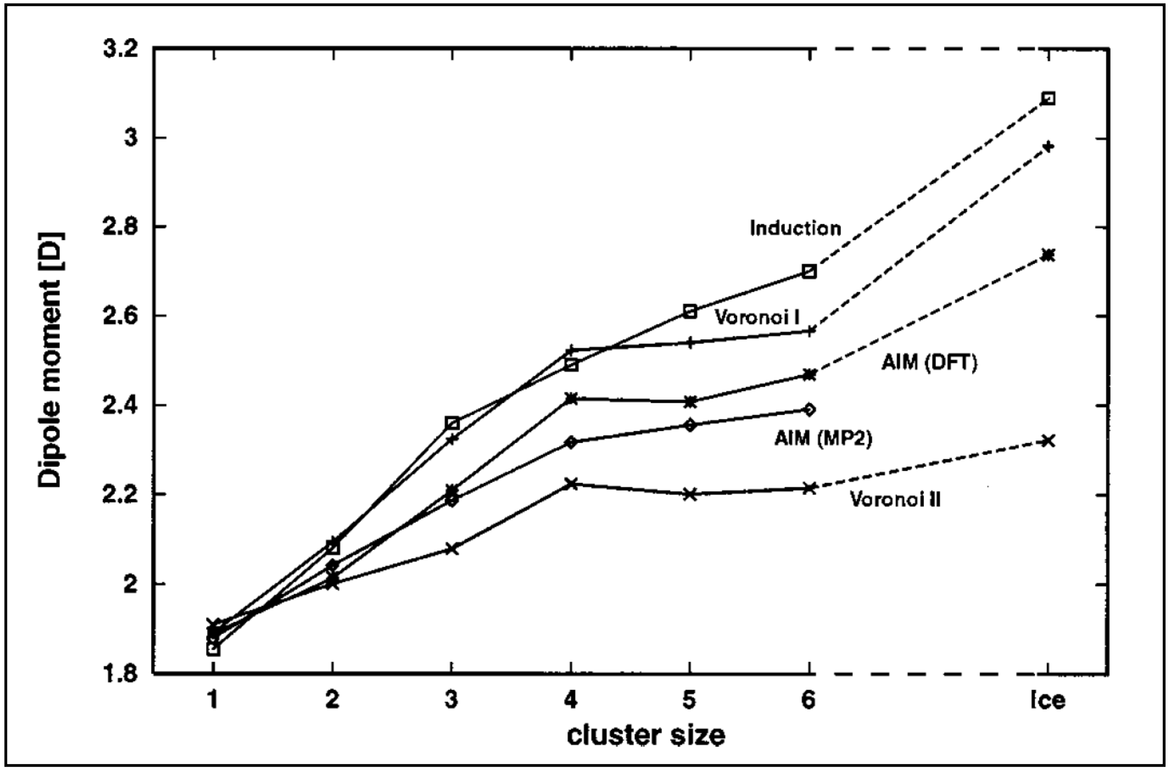
Using density functional calculations, spontaneous polarisation of proton-ordered *ferroelectric* ice XI phase is calculated for the first time. Spontaneous polarisation along the *c*-axis of orthorhombic $Cmc2_1$ structure is calculated to be 21 $\mu C/cm^2$, which corresponds to water dipole moment 3.3 D. We have performed systematic calculation of the water dipole moment in proton-ordered ice without ambiguity.

Keywords: water molecule; ice; density functional theory; electric polarisation; electric dipole moment, electronic structure

Problem: definition of dipole moment in periodic system

- R. Martin (1974)
- *Knowledge of the charge density in a unitcell is not sufficient to determine the polarization.*



E.R. Batista, S.S. Xantheas, H. Jonsson (J. Chem. Phys. **111**, 6011(1999))

$$\mathbf{P} = \Omega^{-1} \int_{cell} \mathbf{P}(\mathbf{r}) d^3\mathbf{r} \qquad \nabla \cdot \mathbf{P}(\mathbf{r}) = -n(\mathbf{r})$$

$$\mathbf{P} = \Omega^{-1} \int_{cell} \mathbf{r} n(\mathbf{r}) d^3\mathbf{r} + \underline{\Omega^{-1} \int_{surface} \mathbf{r}[\mathbf{P}(\mathbf{r}) \cdot d\mathbf{S}]}$$

Charge density partition

E.R. Batista, S.S. Xantheas, H. Jonsson
(J. Chem. Phys. **111**, 6011(1999))

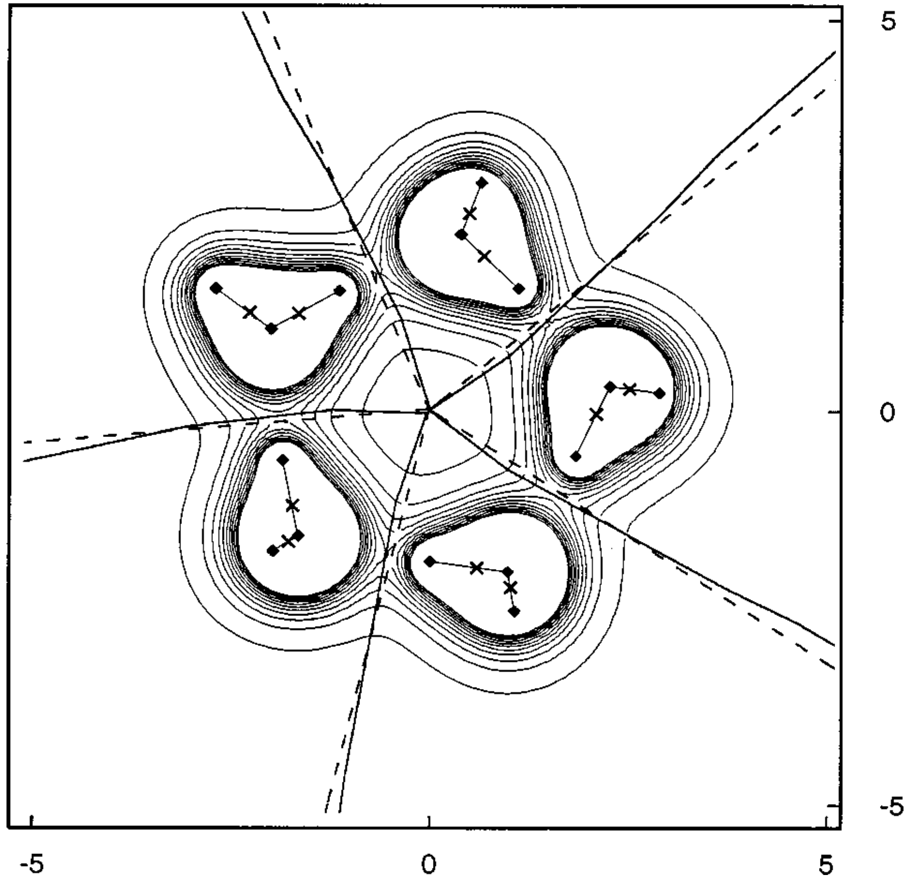


FIG. 1. Contour plot of the charge density of the water pentamer in the plane of the cluster. The figure displays the charge density partitioned according to the Voronoi I (dotted line) and Voronoi II (solid line) schemes (see text). In the Voronoi I scheme, the Voronoi cell is constructed around one center per molecule, placed at the center of nuclear charge. In Voronoi II, the Voronoi cells are around three ''atomic'' centers per molecule: one at the oxygen atom and the other two (shown with crosses) on the O–H bonds, at 40% of the displacement from the oxygen atom to the hydrogen nucleus. Although both surfaces are very similar, the latter passes closer through the minimum of the charge density between the molecules.

F. Ishii, K. Terada, S. Miura, Mol. Siml. **38** 369 (2012).

Charge distribution in ferroelectric ice

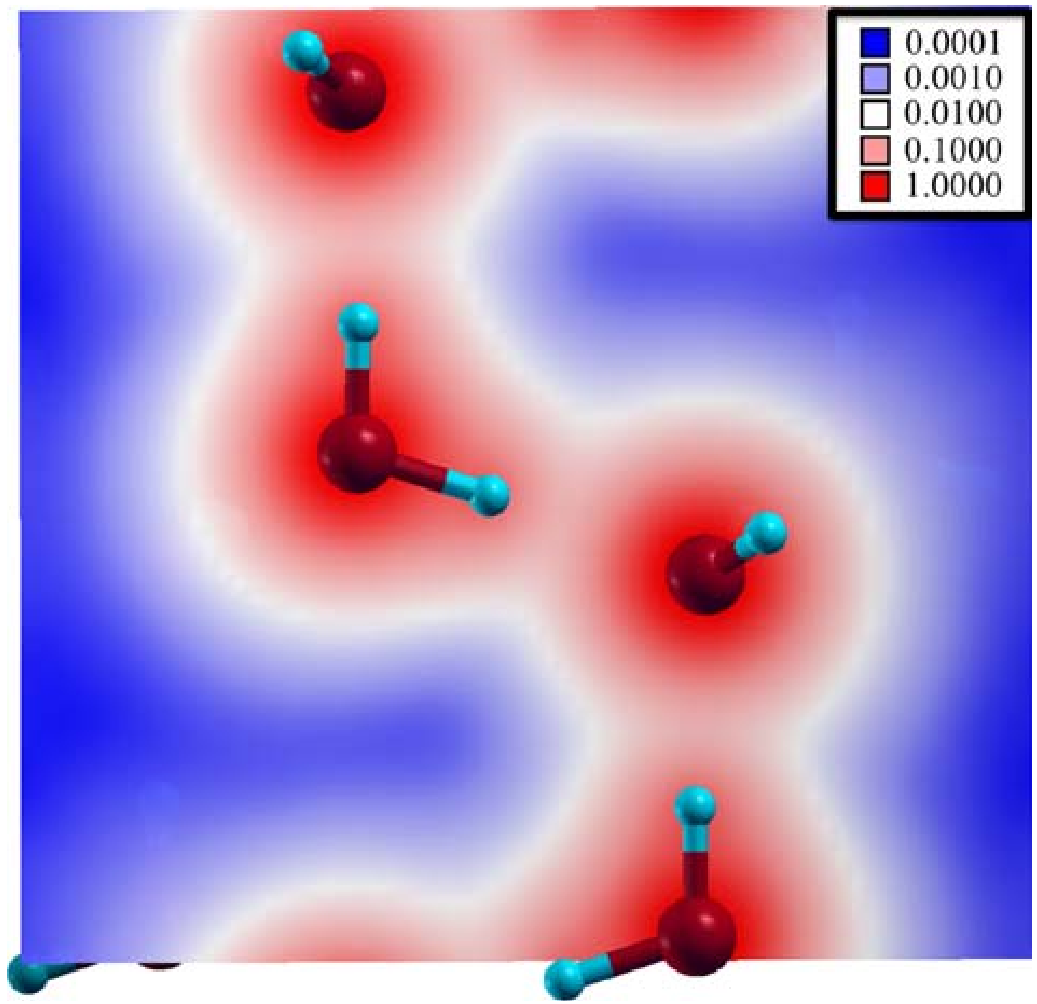


Figure 2. The charge density of ice XI phase viewed from a-axis perpendicular to the polarisation direction. Contours are drawn on a logarithmic scale (from 1.0e-4 to 1.0 e/bohr^3).

F. Ishii, K. Terada, S. Miura, Mol. Siml. **38** 369 (2012).

Water dipole moment in hypothetical crystal

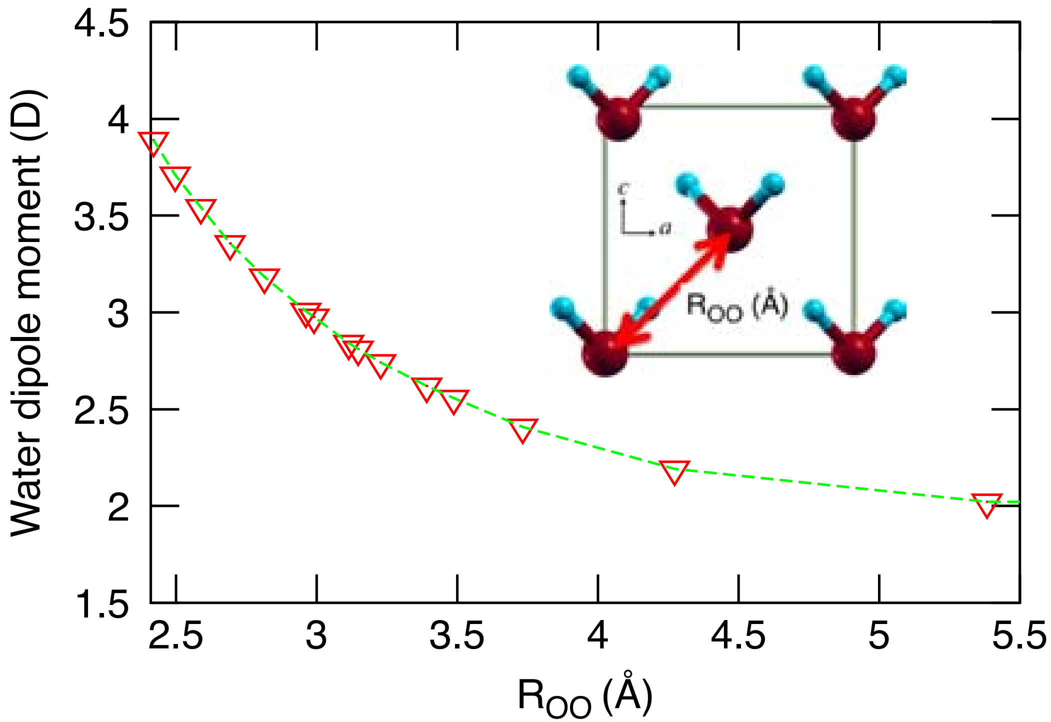


Figure 4. Water dipole moment of model ice with a perspective view of the structure. The triangle indicates water dipole moment versus oxygen–oxygen distance R_{OO}. The lines are a guide to the eye.