Quantum Mechanical Calculation of Polarization in Condensed Matter

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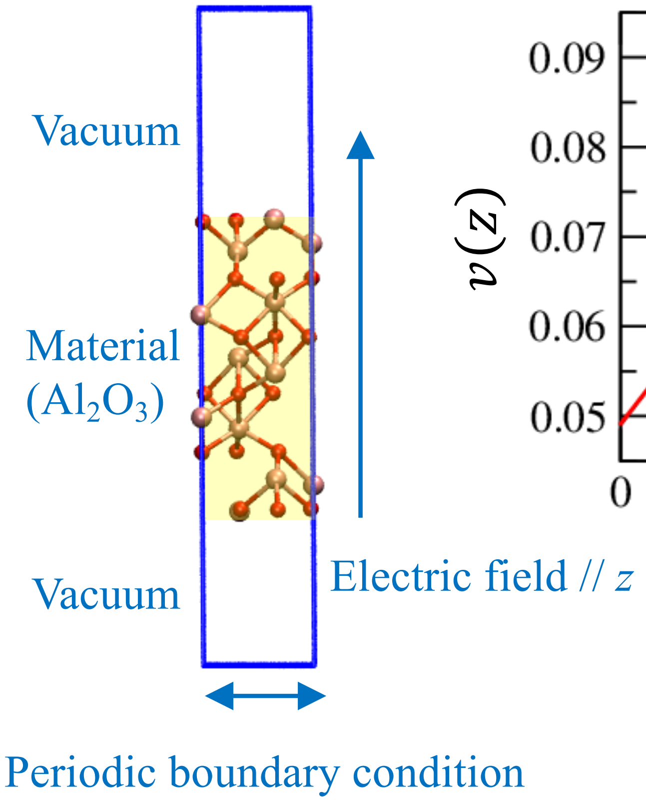
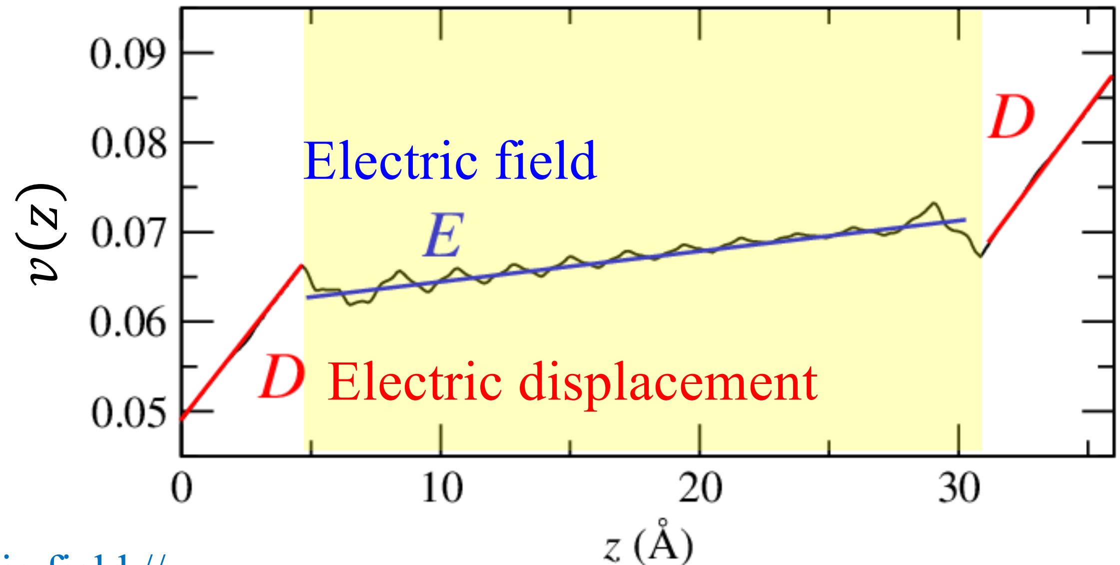
Finite Slab Method

- **Simulate a finite slab normal to the electric field**

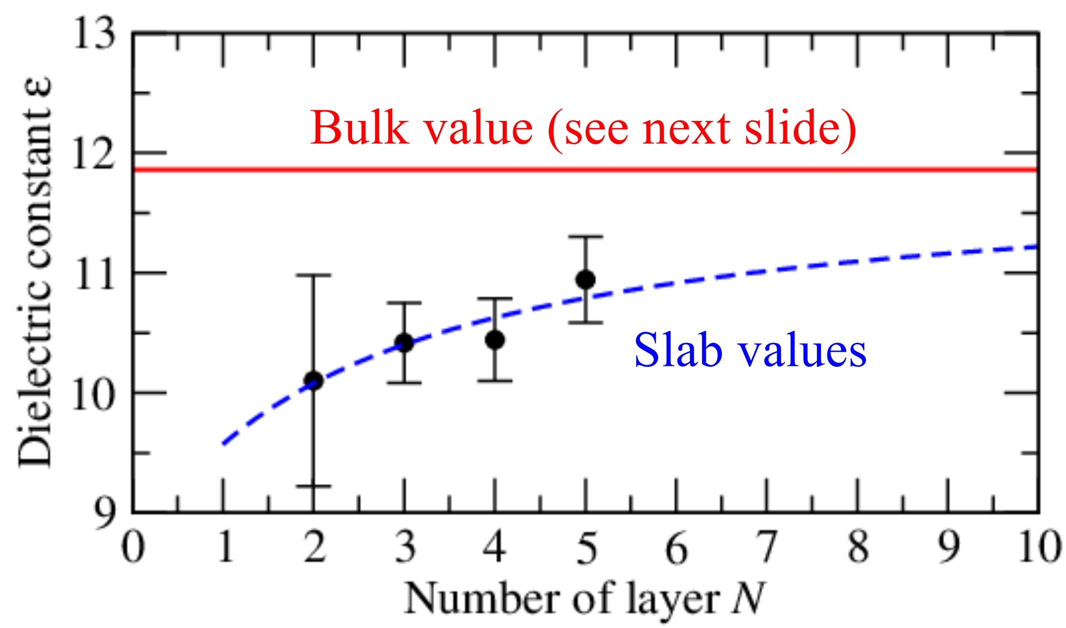




$$\varepsilon = \frac{D}{E}$$

Dielectric constant

- **Require very thick slab to reach bulk limit (computationally expensive)**



Modern Quantum Theory of Polarization

- **Change of polarization upon adiabatic switching of finite electric field $\mathcal{E}$ with periodic boundary condition**
  R. Resta, *Phys. Rev. Lett*. **80**, 1800 ('98); P. Umari & A. Pasquarello, *ibid*. **89**, 157602 ('02)

$$\Delta P_{\mathrm{el},x} = -\frac{L}{\pi}\mathrm{Im}(\ln\det[\langle\psi_m|\exp(i2\pi x/L)|\psi_n\rangle]) \quad (m,n \in \{\mathrm{occupied}\})$$

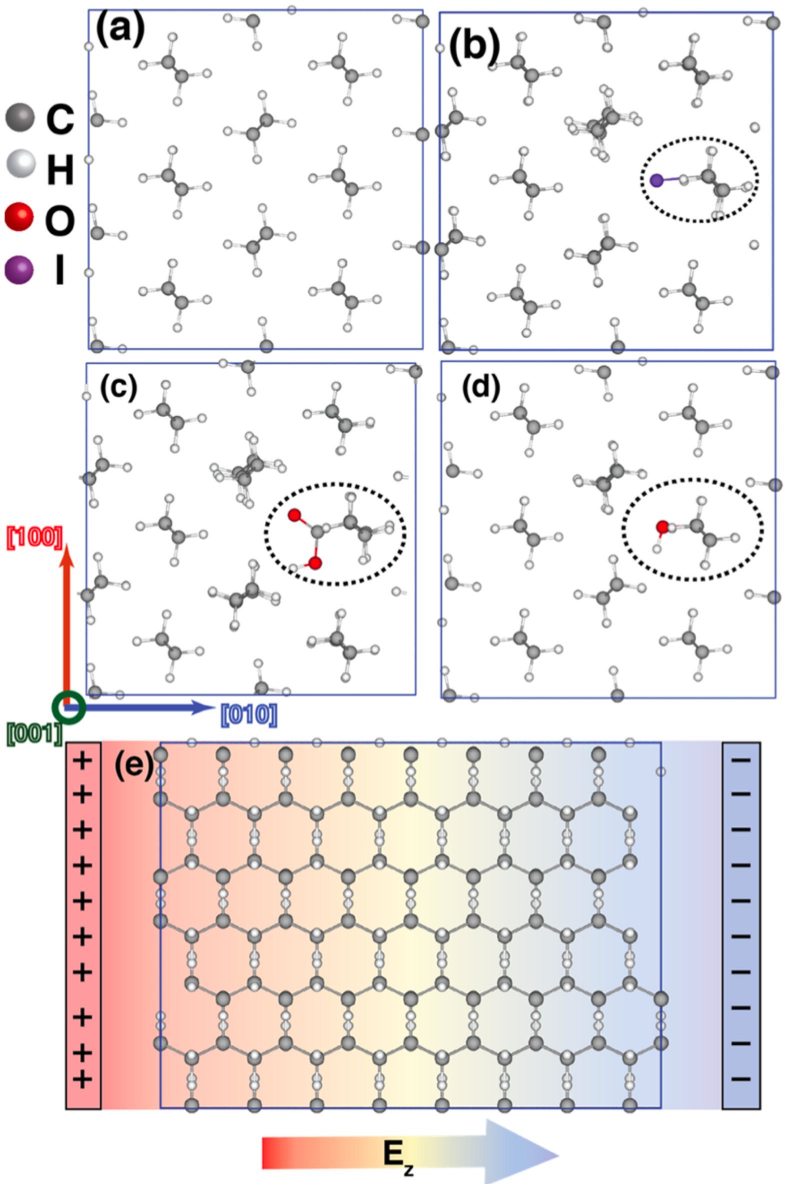
$$\{\psi_m\} = \mathrm{argmin}\left(E_{\mathrm{Kohn-Sham}}[\{\psi_m\}] - \mathcal{E}\Delta P_{\mathrm{el},x}[\{\psi_m\}]\right)$$

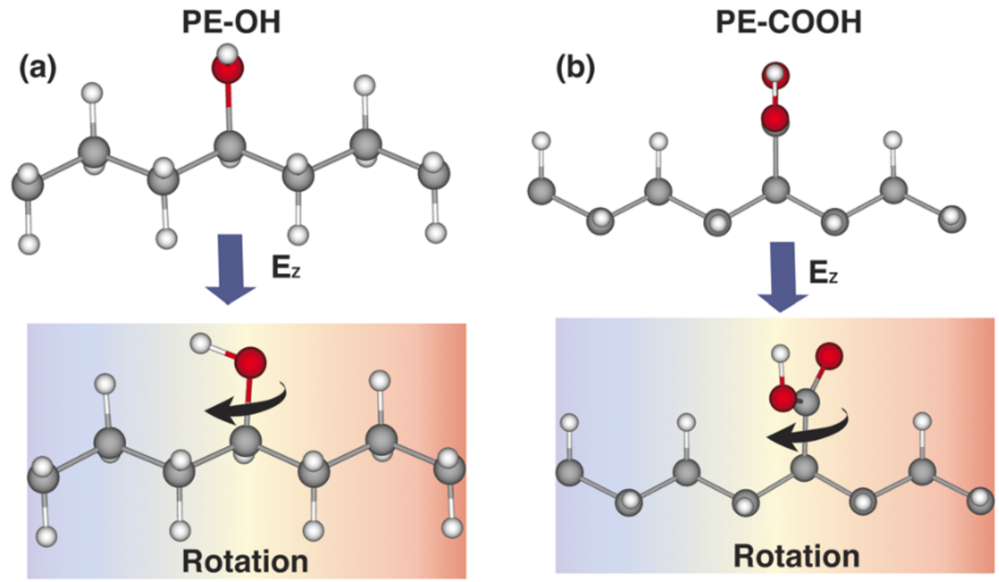
- **The above formula is equivalent to a sum of valence-band Berry phases**
  R. D. King-Smith & D. Vanderbilt, *Phys. Rev. B* **47**, 1651('93);
  I. Souza, J. Iniguez & D. Vanderbilt, *Phys. Rev. Lett*. **89**, 117602 ('02)

$$\Delta\mathbf{P}_{\mathrm{el}} = \int_0^{\mathcal{E}} d\lambda \frac{\partial\mathbf{P}_{\mathrm{el}}}{\partial\lambda} = -\frac{ie}{(2\pi)^3}\sum_{n\in\{\mathrm{occupied}\}}\int_{\mathrm{Brillouin\ zone}} d\mathbf{k}\left\langle\psi_{n\mathbf{k}}\middle|\frac{\partial}{\partial\mathbf{k}}\middle|\psi_{n\mathbf{k}}\right\rangle$$

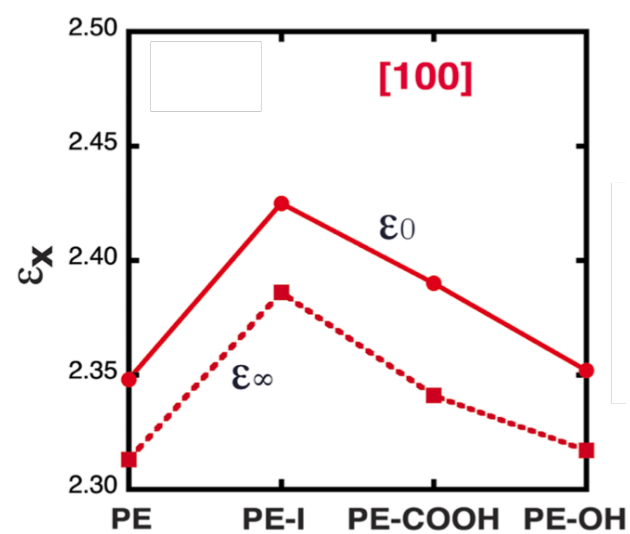
- **Above a critical field $\mathcal{E}_c$, the energy functional has no minimum, indicating Zener breakdown (*i.e.* tunneling from valence to conduction bands)**

Example: Polyethylene Crystal





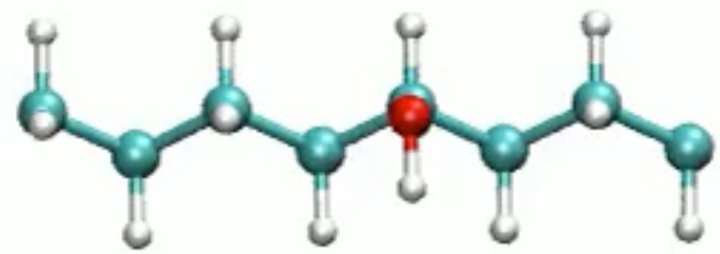
Chemical-defect-sensitive dielectric constant (–OH, –COOH, –I)



S. Fukushima *et al.*, *AIP Adv.* **9**, 045022('19)

Polyethylene Under Electric Field

With –OH defect



Electric field

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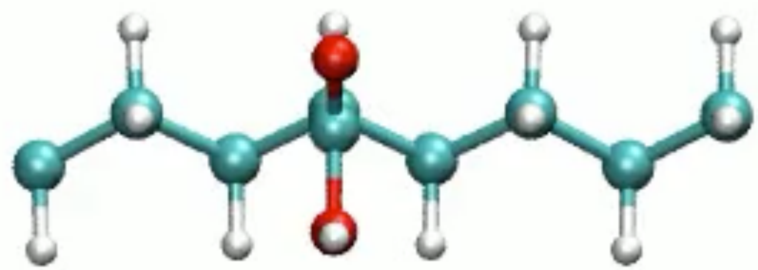
Polyethylene Under Under Electric Field

With –COOH defect



Electric field

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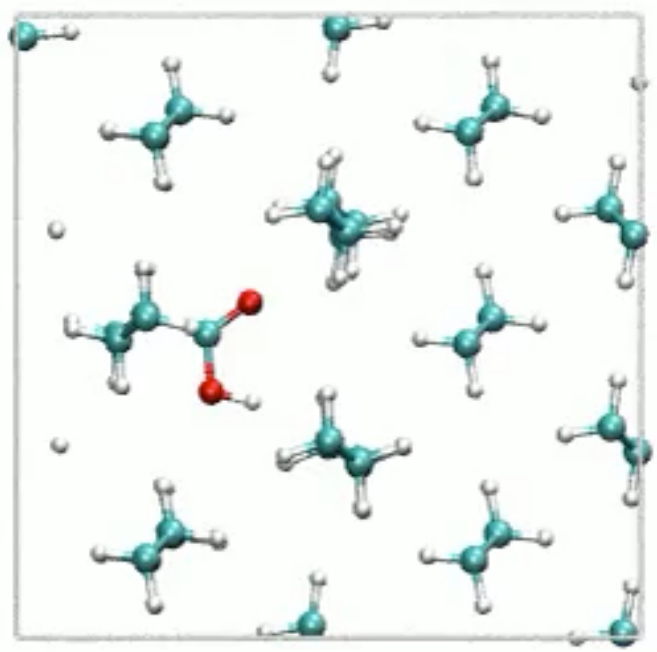
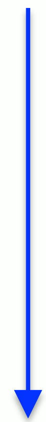
Polyethylene Under Electric Field

With –COOH defect (different field direction)





Electric field

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