Finite electric field

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(Part of the material based on a talk by David Vanderbilt and review article by Vanderbilt & Resta)

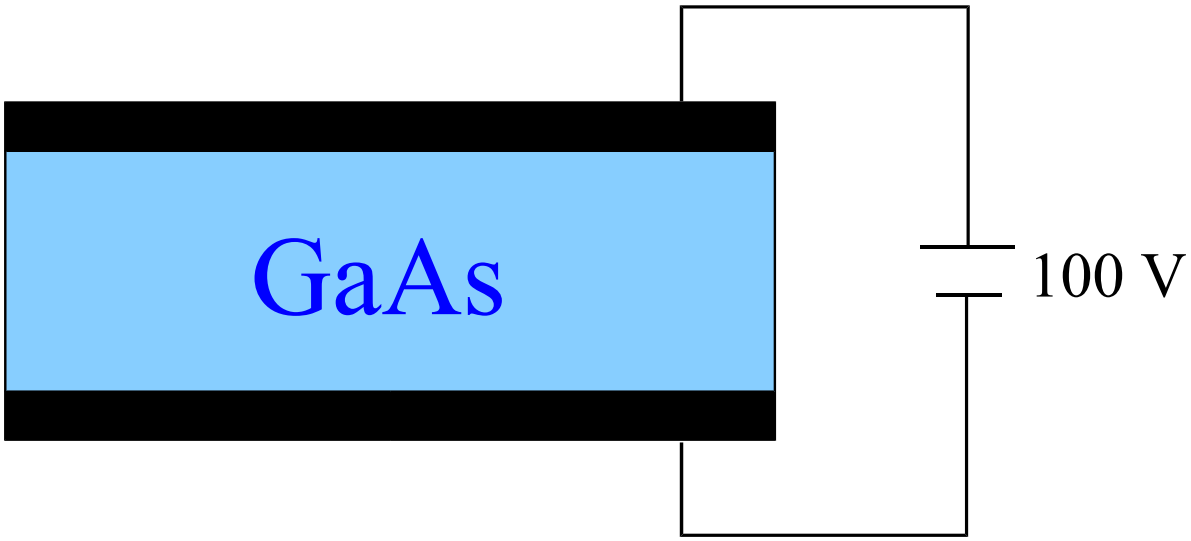
Finite electric fields: Motivation

Applications:

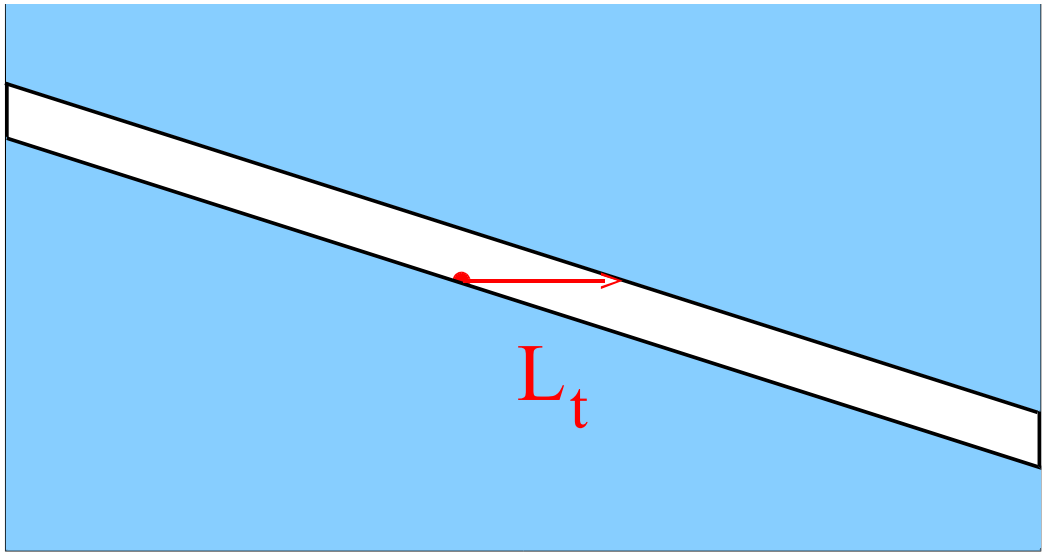
- Finite difference calculation of field derivatives @ E=0 (alternative to density-functional perturbation theory)
- Truly finite-field effects
  - ➔ Field-induced structural phase transitons
  - ➔ Bloch oscillations
  - ➔ Electro-absorption (Franz-Keldysh effect)

Insulators in electric fields: The problem

Easy to do in practice:



But ill-defined in principle:



Zener tunneling

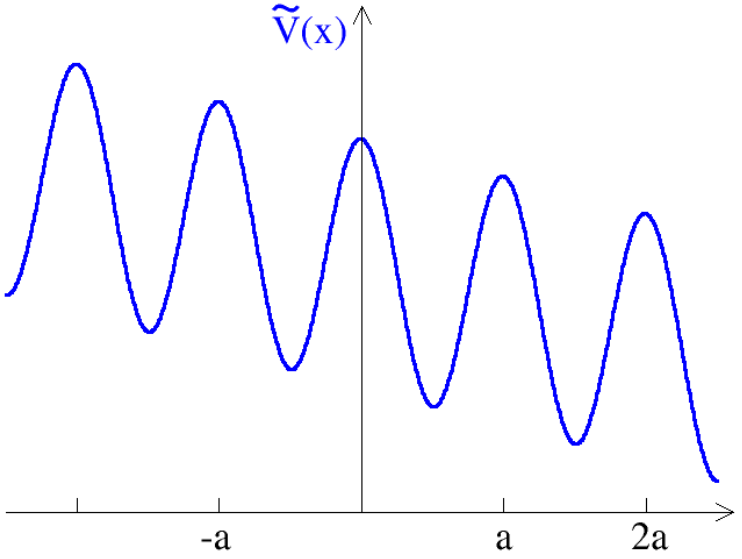
$L_t = E_g / \mathcal{E}$

For small E-field, $\tau_{Zener} \gg \tau_{Universe}$; is it OK?

Electric fields: The problem

$$H = H_0 - e\mathcal{E}x = \frac{p^2}{2m} + \tilde{V}(x),$$

$$\tilde{V}(x) = V_{per}(x) - e\mathcal{E}x$$



Problems specific to crystals

- $\tilde{V}(x)$ is not periodic
- Bloch's theorem does not apply

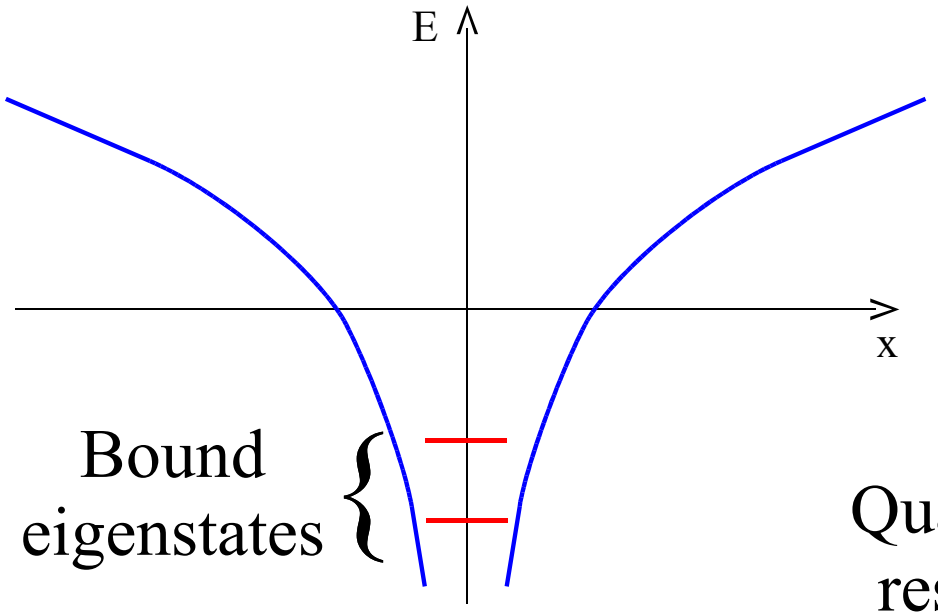
- $\mathcal{E}$ acts as a singular perturbation on eigenfunctions
- $\tilde{V}(x)$ not bounded from below
- There is no ground state

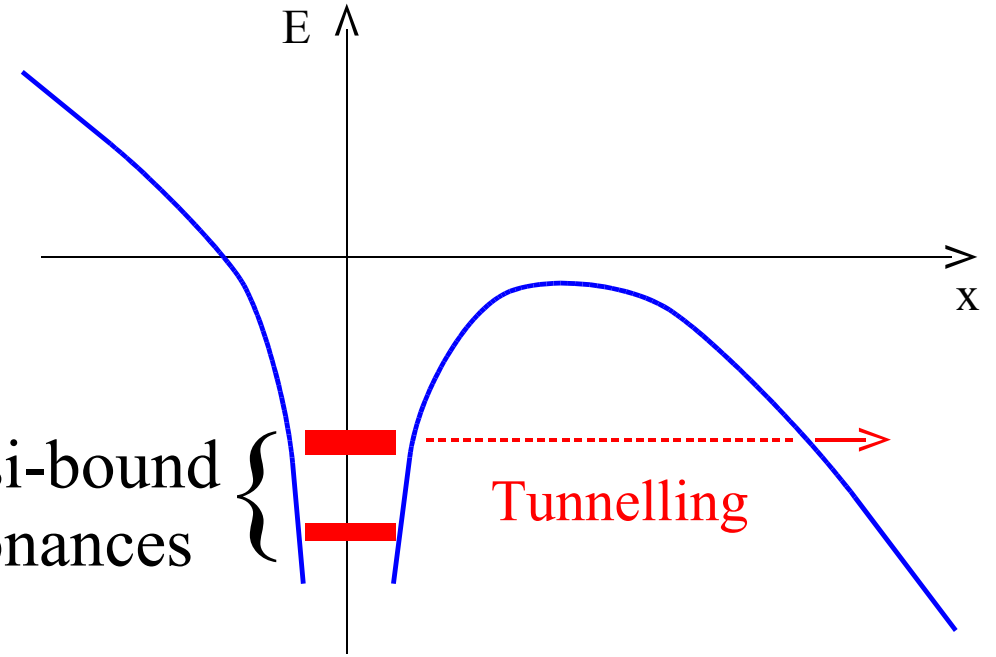
Common to both crystals and finite systems

Finite systems in electric fields: The problem

Auto-ionization:

- Sharp eigenstates turn into resonances with finite width
- Finite lifetime: electrons eventually escape to the right (quasi-bound resonance decays into an unbound runaway solution)



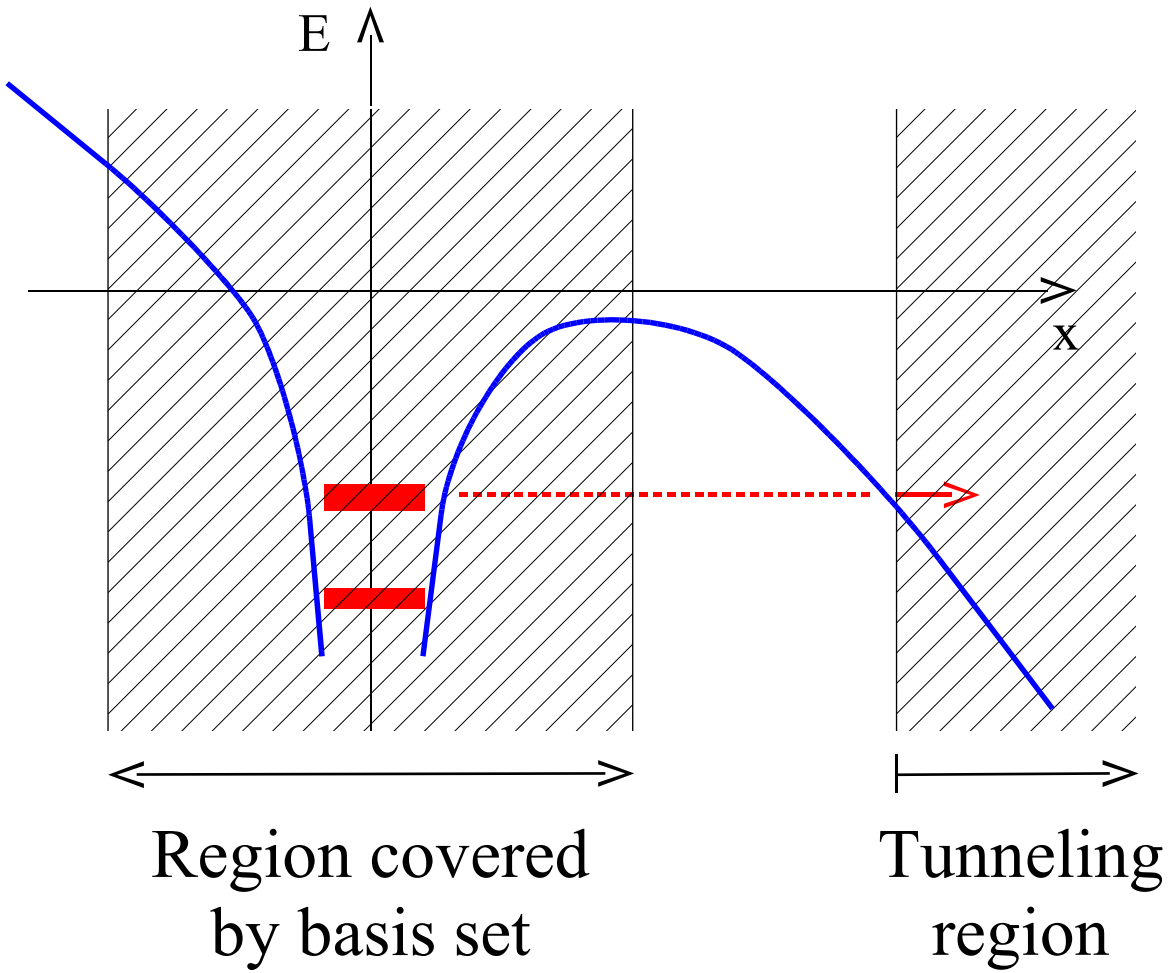


$$V(x) = V_{atom}(x)$$

$$\tilde{V}(x) = V_{atom}(x) - e\mathcal{E}x$$

The solution (finite systems)

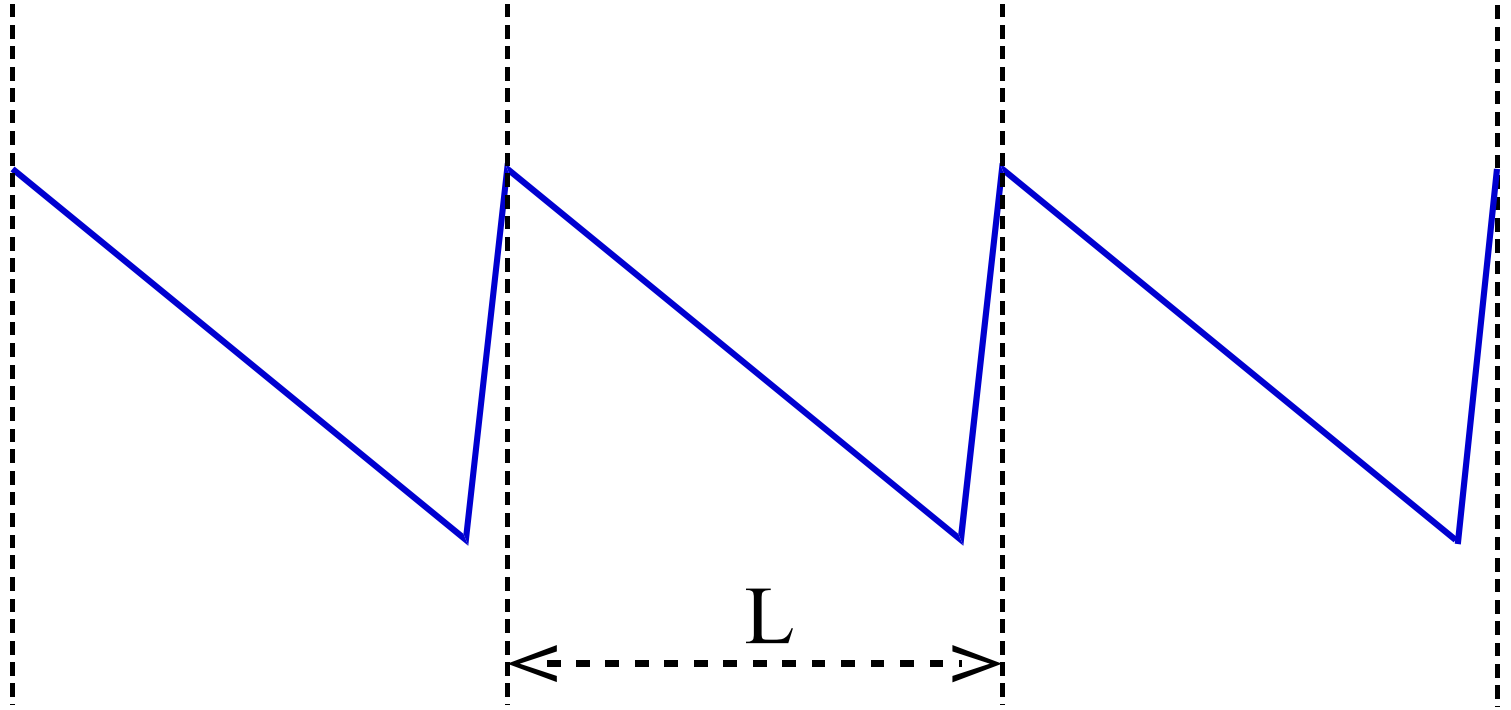
Use a localized-orbital basis that does not extend into the vaccum



Does not work for crystals, since sample (and hence the basis) covers entire space, when using periodic boundary conditions

Another solution (finite systems)

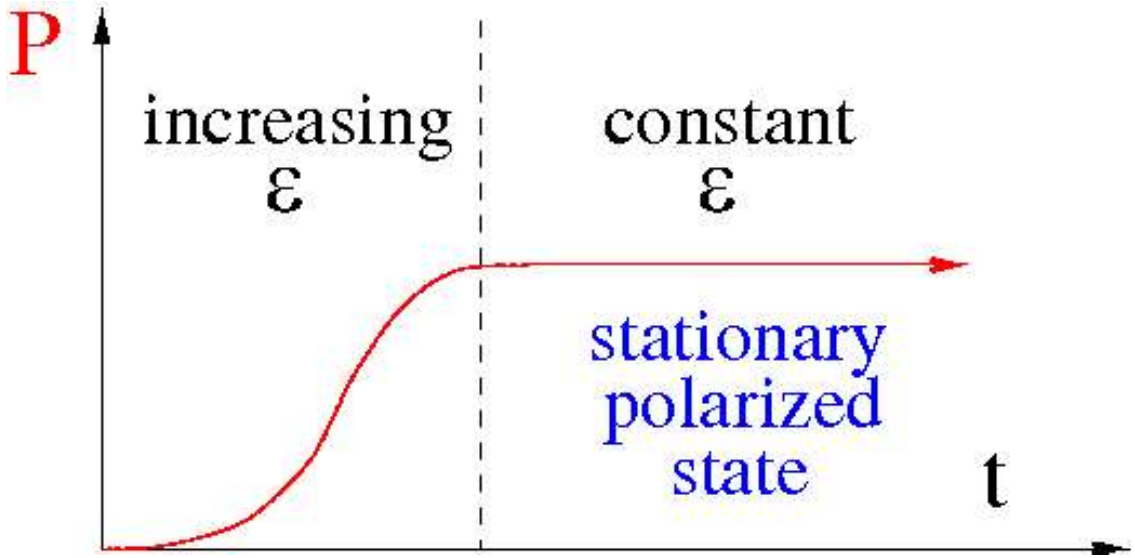
Sawtooth potential over a large supercell; place molecule at the center, far from the sharp edges of V(r) close to boundaries:



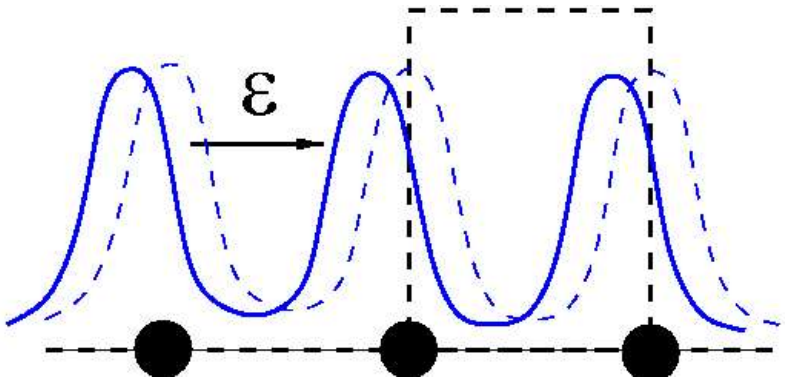
- Does not work for crystals, since sharp edges would necessarily occur inside the sample
- Even for molecules, if L is large there is a critical field above which electrons escape from molecule to right side of box

A possible strategy for insulating crystals

- Start from the insulating ground state
- Slowly turn on a small E-field (tunneling is negligible)



$\rho(\boldsymbol{r})$ remains periodic under homogeneous E-field



Problem: need to solve a time-dependent Schrodinger eqn. (expensive, result depends on the time-history of switching on E-field)

Can we solve for the field-polarized state directly, as for finite systems?

Practical solution for insulating crystals

- Seek long-lived resonance
- Described by polarized Bloch functions $\{\psi_{n\boldsymbol{k}}\}$
- Minimize the "electric enthalpy" functional w.r.t. $\{\psi_{n\boldsymbol{k}}\}$

$$F = E_{KS} - \Omega \mathcal{E} \cdot \boldsymbol{P}$$

$$E_{KS} = \frac{1}{N} \sum_{n\boldsymbol{k}} \langle \psi_{n\boldsymbol{k}} | T + V_{per} | \psi_{n\boldsymbol{k}} \rangle \longleftarrow \text{Usual Kohn-Sham}$$

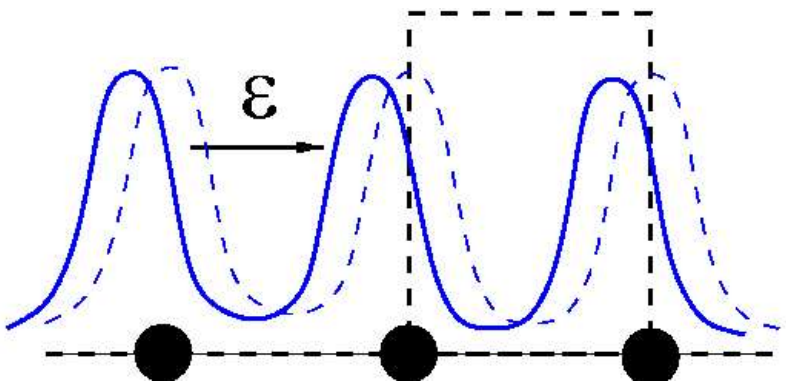
$$\boldsymbol{P} = \boldsymbol{P}[\hat{n}] = \boldsymbol{P}[\{\psi_{n\boldsymbol{k}}\}] \longleftarrow \text{Berry-phase polarization}$$

$$F[\{\psi_{n\boldsymbol{k}}\}] = \langle H \rangle, \qquad H = T + V_{per} - e\mathcal{E} \cdot \boldsymbol{r}$$

$$\langle -e\mathcal{E} \cdot \boldsymbol{r} \rangle = -\mathcal{E} \cdot \boldsymbol{d} \qquad \boldsymbol{P} = \frac{\boldsymbol{d}}{\Omega} = \frac{-e\langle \boldsymbol{r} \rangle}{\Omega} : \text{ dipole per unit volume}$$

Berry-phase formula $\Rightarrow$ how to evaluate $\langle \boldsymbol{r} \rangle$ within PBCs!

Justification



Seek long-lived metastable periodic solution

- Want periodic charge density:

$$\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}+\boldsymbol{R})$$

- Want periodic one-particle density matrix:

$$n(\boldsymbol{r},\boldsymbol{r}') = n(\boldsymbol{r}+\boldsymbol{R},\boldsymbol{r}'+\boldsymbol{R})$$

- Use Bloch representation of density matrix:

$$n(\boldsymbol{r},\boldsymbol{r}') = \langle \boldsymbol{r}|\hat{n}|\boldsymbol{r}'\rangle = \sum_{n\boldsymbol{k}} \psi_{n\boldsymbol{k}}(\boldsymbol{r})\psi^*_{n\boldsymbol{k}}(\boldsymbol{r}')$$

even though $\{\psi_{n\boldsymbol{k}}\}$ are not eigenstates!

Derivation of Berry-phase P: Wannier functions

Bloch functions $\psi_{n\boldsymbol{k}}$:

- Labeled by band n and crystal momentum $\boldsymbol{k}$
- Localized in $\boldsymbol{k}$, extended in $\boldsymbol{r}$

Wannier functions $w_{n\boldsymbol{R}}$:

- Labeled by band n and unit cell $\boldsymbol{R}$
- Localized in $\boldsymbol{r}$, extended in $\boldsymbol{k}$

Related by a unitary transformation (Fourier transform):

$$|w_{n\boldsymbol{R}}\rangle = \frac{\Omega}{(2\pi)^3}\int_{BZ} d\boldsymbol{k}\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}}|\psi_{n\boldsymbol{k}}\rangle$$

For insulators only (*M* filled bands), can use a Wannier representation of the density matrix:

$$n(\boldsymbol{r},\boldsymbol{r}') = \sum_{n=1}^{M}\sum_{\boldsymbol{k}} w_{n\boldsymbol{R}}(\boldsymbol{r})\, w^{*}_{n\boldsymbol{R}}(\boldsymbol{r}')$$

Advantage: WFs are localized in $\boldsymbol{r}$ $\Rightarrow$ evaluation of $\langle \boldsymbol{r} \rangle$ becomes simple

$$\boldsymbol{P}=\boldsymbol{P}[\hat{n}]=\boldsymbol{P}[\{w_{n\boldsymbol{R}}\}] \qquad \boldsymbol{P}=\frac{\boldsymbol{d}}{\Omega}=\frac{-e\langle \boldsymbol{r}\rangle}{\Omega} \qquad \langle \boldsymbol{r}\rangle = Tr_c(\hat{n}\hat{\boldsymbol{r}})$$

Trace per unit cell ($\boldsymbol{r}$ representation):

$$Tr_c\hat{O}=\frac{1}{N}\int_{all\ space}\langle \boldsymbol{r}|\hat{O}|\boldsymbol{r}\rangle d\boldsymbol{r} \qquad (N=\#\text{ cells})$$

$$\langle \boldsymbol{r}|\hat{n}\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle=\langle \boldsymbol{r}|\hat{n}\underbrace{\int d\boldsymbol{r}'|\boldsymbol{r}'\rangle\langle \boldsymbol{r}'|}_{\equiv\hat{\mathbf{1}}}\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle \qquad \langle \boldsymbol{r}'|\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle=\boldsymbol{r}\,\delta(\boldsymbol{r}'-\boldsymbol{r})$$

$$\Rightarrow\langle \boldsymbol{r}|\hat{n}\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle=n(\boldsymbol{r},\boldsymbol{r})\boldsymbol{r} \qquad \langle \boldsymbol{r}\rangle=\frac{1}{N}\int d\boldsymbol{r}\,n(\boldsymbol{r},\boldsymbol{r})\boldsymbol{r}$$

$$\langle \boldsymbol{r}\rangle=\frac{1}{N}\sum_n\sum_{\boldsymbol{R}}\int d\boldsymbol{r}\,w^*_{n\boldsymbol{R}}(\boldsymbol{r})\boldsymbol{r}\,w_{n\boldsymbol{R}}(\boldsymbol{r})$$

$$\boldsymbol{r}=\boldsymbol{r}'-\boldsymbol{R}$$

$$\langle \boldsymbol{r}\rangle=\frac{1}{N}\sum_n\sum_{\boldsymbol{R}}\int d\boldsymbol{r}'\,w^*_{n\boldsymbol{R}}(\boldsymbol{r}'-\boldsymbol{R})\boldsymbol{r}\,w_{n\boldsymbol{R}}(\boldsymbol{r}'-\boldsymbol{R})$$

$$\langle \boldsymbol{r} \rangle = \frac{1}{N} \sum_n \sum_{\boldsymbol{R}} \int d\boldsymbol{r}\, w^*_{n\boldsymbol{R}}(\boldsymbol{r}-\boldsymbol{R})\, \boldsymbol{r}\, w_{n\boldsymbol{R}}(\boldsymbol{r}-\boldsymbol{R})$$

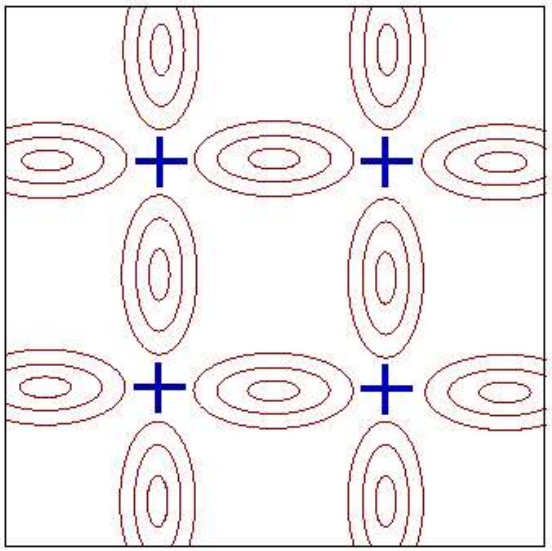
$$w_{n\boldsymbol{R}}(\boldsymbol{r}-\boldsymbol{R}) = w_{n\boldsymbol{0}}(\boldsymbol{r})$$

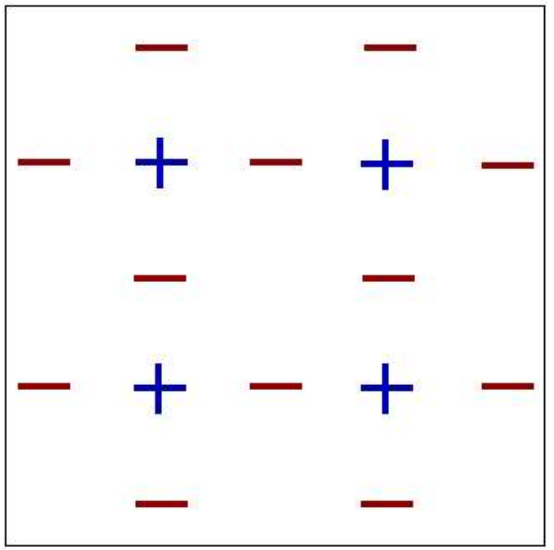
Center of charge of Wannier fct.

$$\langle \boldsymbol{r} \rangle = \sum_n \langle w_{n\boldsymbol{0}} | \hat{\boldsymbol{r}} | \boldsymbol{r}\, w_{n\boldsymbol{0}} \rangle = \sum_n \boldsymbol{r}_{n\boldsymbol{0}}$$

$$\boldsymbol{P}_{el} = \frac{-e\langle \boldsymbol{r} \rangle}{\Omega} = \frac{-e}{\Omega} \sum_n \boldsymbol{r}_{n\boldsymbol{0}}$$

- Point ions
- Diffuse e^-_s





- Point ions
- Point e^-_s located at Wannier centers

$$\boldsymbol{P}_{total} = \boldsymbol{P}_{el} + \boldsymbol{P}_{ion}$$

Derivation of Berry-phase P: Bloch functions

In practice want to compute ***P*** from Bloch functions, not WFs

1-dim, 1 band: $P = \frac{-e\,x_0}{a}$ $\qquad x_0 = \langle w_0 | \hat{x} | w_0 \rangle$

$$|w_0\rangle = \frac{a}{2\pi}\int_0^{2\pi/a} d\,k\, e^{i\,kx}|u_k\rangle \qquad |\psi_k\rangle = e^{ikx}|u_k\rangle$$

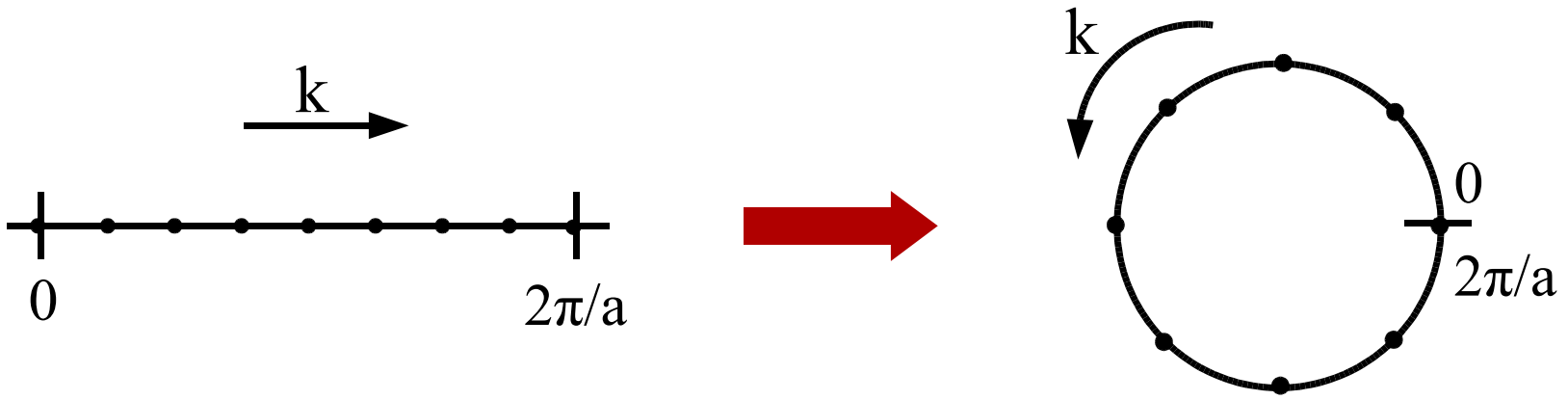
$$x|w_0\rangle = \frac{a}{2\pi}\int dk\,(-i\,\partial_k e^{ikx})|u_k\rangle = \frac{a}{2\pi}\int dk\, e^{ikx}\, i|\partial_k u_k\rangle$$

Integration by parts

$$x_0 = (\ldots) = \frac{a}{2\pi}\int_0^{2\pi/a} dk\,\langle u_k | i\,\partial_k | u_k\rangle$$ Heuristically: $\hat{x} \to i\,\partial_k$

$$x_0 = \frac{a\phi}{2\pi} \qquad \phi = -\Im \int_0^{2\pi/a} dk \langle u_k | \partial_k u_k \rangle \quad \text{Berry phase}$$

Periodic gauge: $|\psi_{2\pi/a}\rangle = |\psi_0\rangle \quad \Rightarrow \quad$ BZ is a closed ring



Berry phase ϕ is a global phase property
of the Bloch band as k is carried around BZ

Practical calculations on a discrete k-mesh:

$$\phi \simeq -\Im \ln \prod_{j=0}^{M-1} \langle u_{k_j} | u_{k_{j+1}} \rangle$$

Overall phase factor of each Bloch state is arbitrary and not smooth as a function of $\boldsymbol{k}$:

"Gauge phase"

$$|u_{\boldsymbol{k}_j}\rangle \to e^{i\theta_{\boldsymbol{k}_j}}|u_{\boldsymbol{k}_j}\rangle$$

$$\langle u_{\boldsymbol{k}_j}| \to e^{-i\theta_{\boldsymbol{k}_j}}\langle u_{\boldsymbol{k}_j}|$$

Each state appears twice: once as a bra and once as a ket:

$$\langle u_{\boldsymbol{k}_0}|u_{\boldsymbol{k}_1}\rangle\langle u_{\boldsymbol{k}_1}|u_{\boldsymbol{k}_2}\rangle \ldots \langle u_{\boldsymbol{k}_{j-1}}|e^{i\theta_{\boldsymbol{k}_j}}u_{\boldsymbol{k}_j}\rangle\langle e^{-i\theta_{\boldsymbol{k}_j}}u_{\boldsymbol{k}_j}|u_{\boldsymbol{k}_{j+1}}\rangle \ldots \langle u_{\boldsymbol{k}_{J-1}}|u_{\boldsymbol{k}_J}\rangle$$

$\Rightarrow$ Gauge phases drop out! (Clever discretization)

Important: set $|\psi_{\boldsymbol{k}_J}\rangle = |\psi_{\boldsymbol{k}_0}\rangle \Leftrightarrow |u_{\boldsymbol{k}_J}\rangle = e^{-i\boldsymbol{G}\cdot\boldsymbol{r}}|u_{\boldsymbol{k}_0}\rangle$ "periodic gauge"

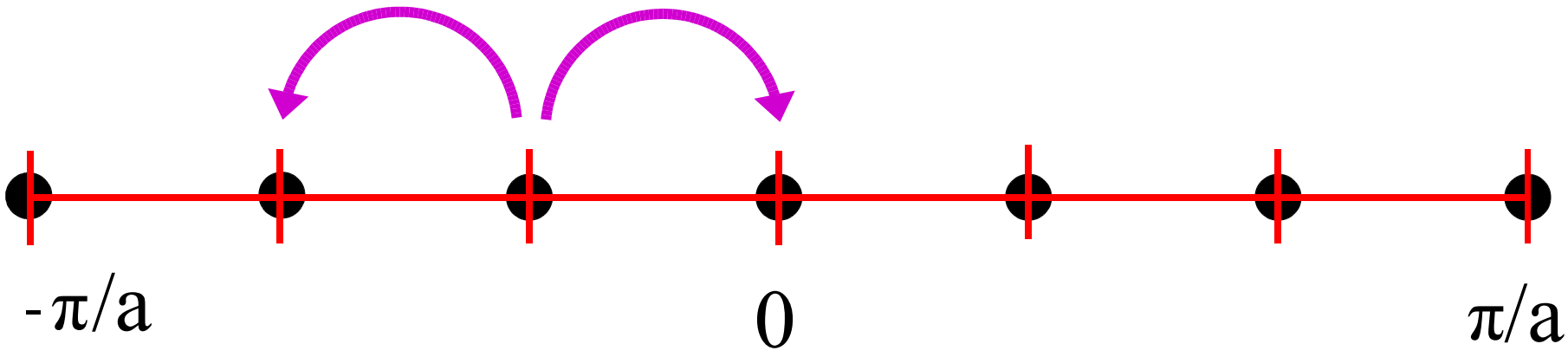
Electric fields: Implementation

Minimize the electric enthalpy functional

$$F = E_{KS} - a\,\mathcal{E}\,P$$

$$= \frac{1}{N}\sum_{nk}\langle\psi_{nk}|T+V_{per}|\psi_{nk}\rangle - \frac{ea\mathcal{E}}{2\pi}\Im\ln\prod_{j=0}^{M-1}\langle u_{k_j}|u_{k_{j+1}}\rangle$$

The $\mathcal{E}\cdot\boldsymbol{P}$ term introduces coupling between k-points



Can use standard methods to find the minimum

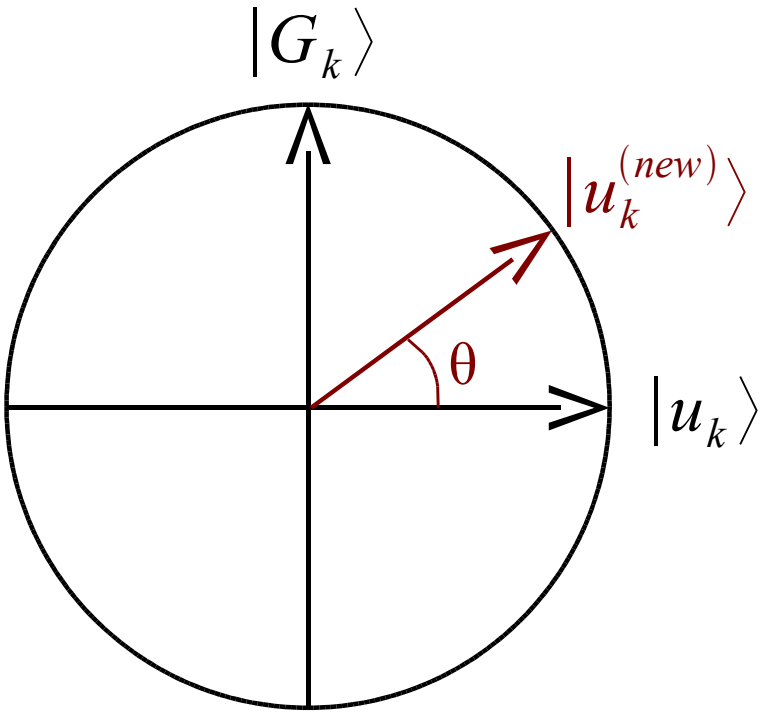
- Conjugate-gradients [Souza, Íñiguez and Vanderbilt '02]
- Car-Parrinello [Umari and Pasquarello '02]

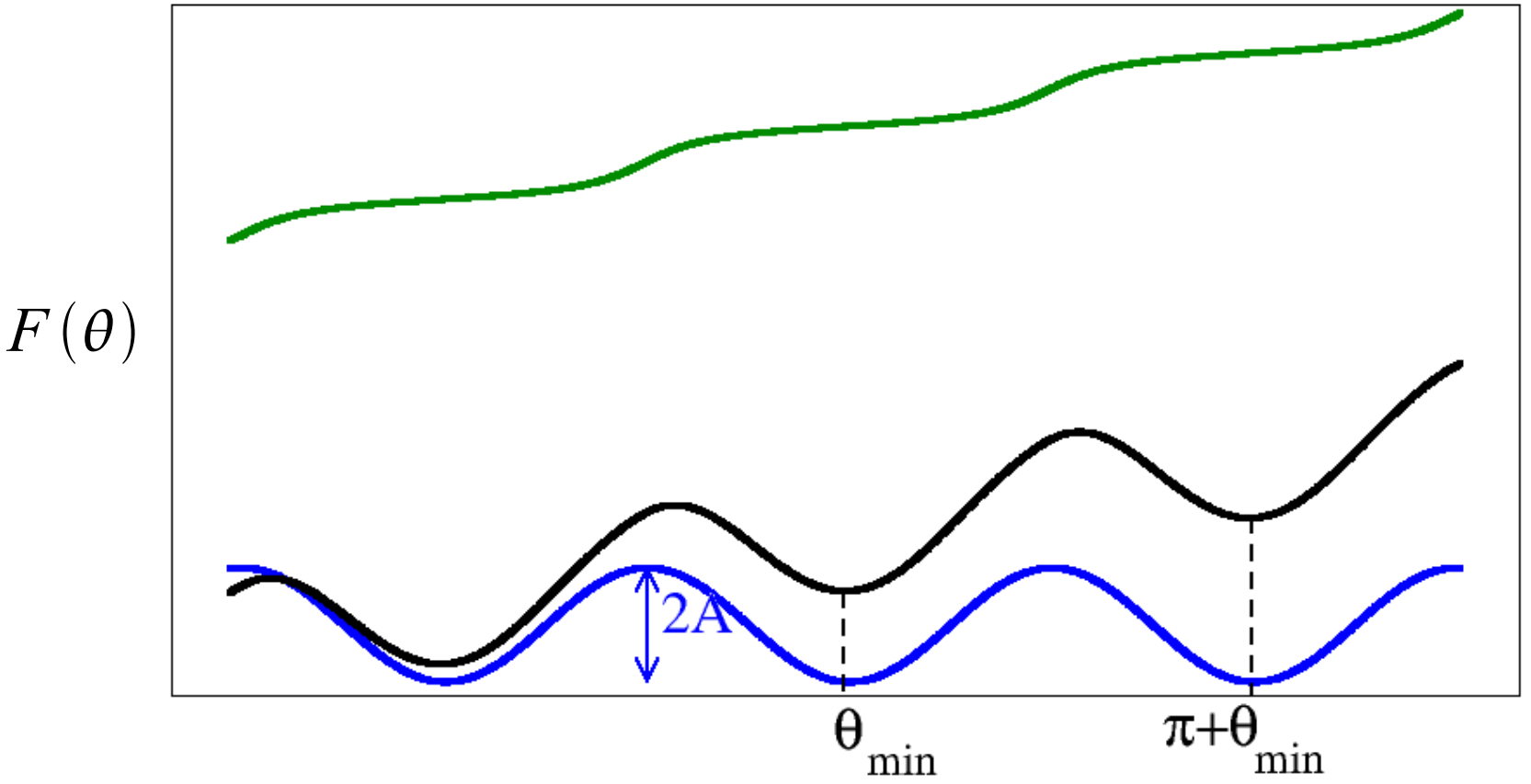
Example: update each $|u_k\rangle$ by steepest-descent:

- Find the gradient vector $|G_k\rangle = \dfrac{\delta F}{\langle \delta u_k|}$
- Trial updated state:

$$|u_k^{(new)}\rangle(\theta) = \cos\theta\,|u_k\rangle + \sin\theta\,|G_k\rangle$$

- Minimize *F(θ)*
- Proceed to next band or *k*-point





— $E_{KS}(\theta)$ $[A \propto E_{gap}/N]$

— $a\mathcal{E}\,P(\theta)$ [avg. slope $\propto \mathcal{E}$]

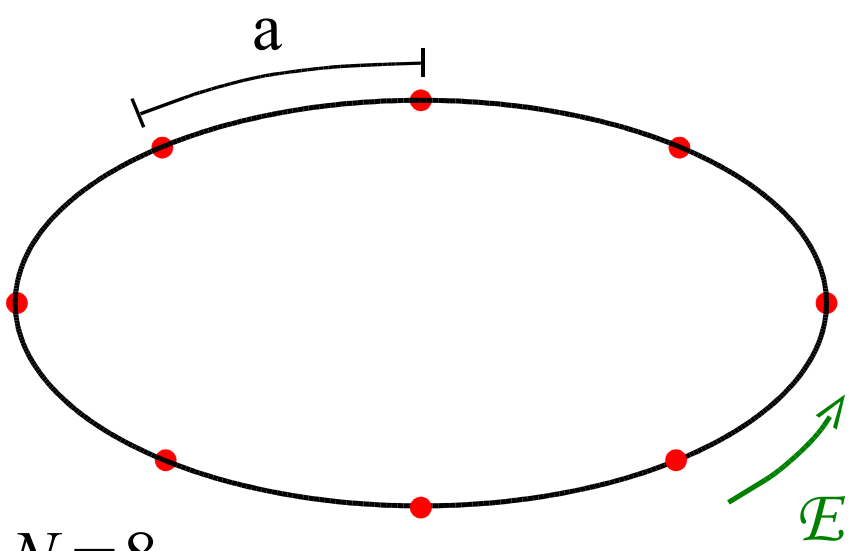
— $F(\theta)$

- $F(\theta)$ has local minima only!
- They disappear when

$$ea\mathcal{E} > E_{gap}/N$$

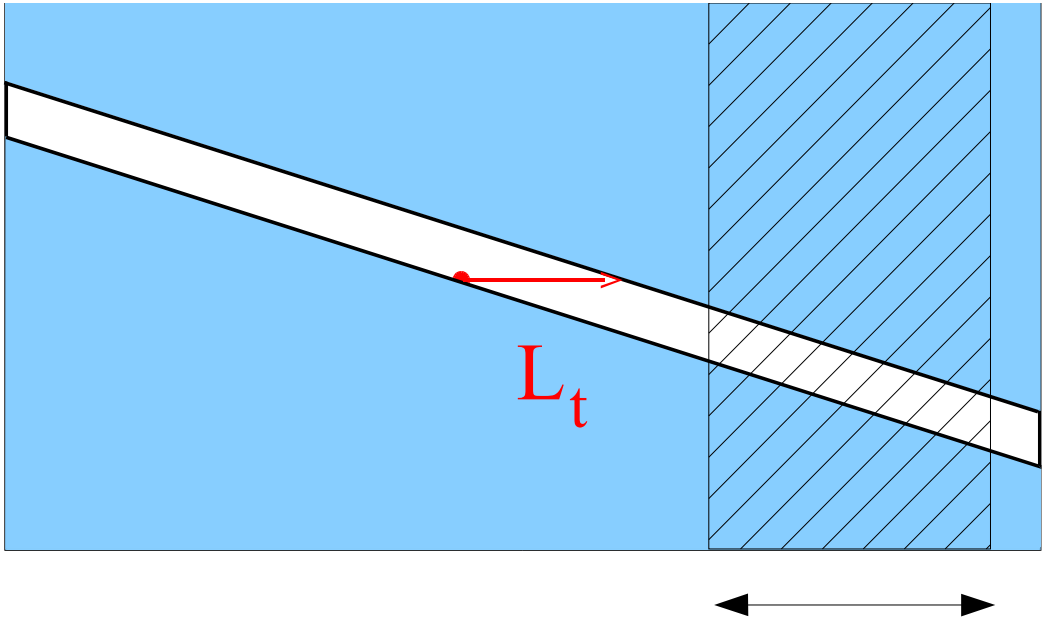
$\Rightarrow$ onset of Zener tunneling!

- For given E-field, there is a limit on *k*-point sampling (and vice-versa)
- Length scale $L_c = 1/\Delta k$
- Meaning: L_c = supercell dimension



$N = 8$

$L_c = 8a$



Solution: Keep $L_c = \dfrac{N}{2\pi/a} < L_t = \dfrac{E_g}{e\mathcal{E}}$

Forces and stress

$$\boldsymbol{F}_i = -\frac{d\,F}{d\,\boldsymbol{r}_i} = -\frac{\partial\,F}{\partial\,\boldsymbol{r}_i} - \sum_{\boldsymbol{k},n} \frac{|\delta\,u_{\boldsymbol{k}n}\rangle}{\partial\,\boldsymbol{r}_i} \frac{\delta\,F}{\langle \delta\,u_{\boldsymbol{k}n}|}$$

At solution $\dfrac{\delta\,F}{\langle \delta\,u_{\boldsymbol{k}n}|} = 0 \quad \Rightarrow \quad \boldsymbol{F}_i = -\dfrac{\partial\,F}{\partial\,\boldsymbol{r}_i}$

(Implicit dependence via wavefunctions can be dropped: Hellmann-Feynmann)

$$\boldsymbol{F}_i = -\frac{\partial\,F}{\partial\,\boldsymbol{r}_i} = -\frac{\partial\left[E_{KS} - \Omega\mathcal{E}\cdot\left(\boldsymbol{P}_{el} + \boldsymbol{P}_{ion}\right)\right]}{\partial\,\boldsymbol{r}_i} = -\frac{\partial\,E_{KS}}{\partial\,\boldsymbol{r}_i} + e\,Z_i^{(ion)}\mathcal{E}$$

Standard $\mathcal{E}=0$ expression already coded

$\dfrac{\partial\,\boldsymbol{P}_{el}}{\partial\,\boldsymbol{r}_i} = 0$ (Berry phase only depends explicitly on wavefunctions)

(Similar arguments for stress)