Density Functional Theory (DFT):

Hohenberg-Kohn (1960's): $E = E[n]$, where $n \equiv |\Psi|^2$

- exact but **density functional** not known ("$E_X + E_C$")
- $E[n]$ may be parameterized from *exact* numerical electron-gas solns.

  (Quantum Monte Carlo, etc.)

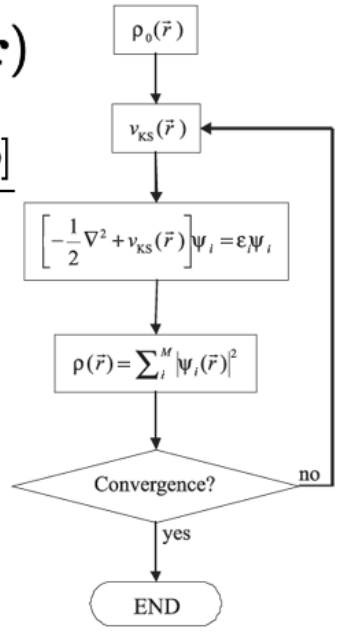
Kohn-Sham: variational minimization -> single-particle KS eqns.

- not unlike HF eqns we have seen
- energies ("bandstructures") *related* to excitation/ ionization energies

Convenient basis set for constructing n

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + e^2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})}$$

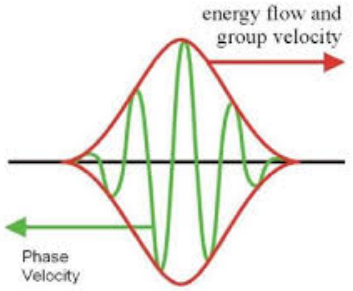


- Many packages; "ab initio" calculations
- LDA: Local density approx.; GGA popular, gradients of n
- Can predict properties successfully (but *excitations* & *correlated systems* difficult ; other methods hybrids, DMF, Greens Functions …)

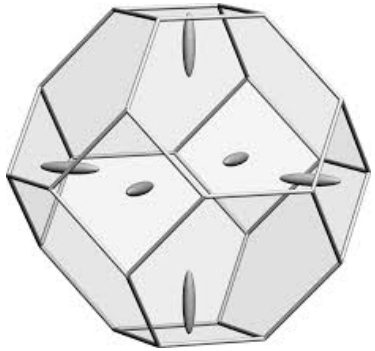
(VB-CB band-gap)

Semiclassical Electron Dynamics: (ch. 12)

- Group velocity $$\vec{v}_g = \frac{1}{\hbar}\vec{\nabla}_k \varepsilon$$



- Effective mass: $$\left[M^{-1}\right]_{\alpha\beta} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k_\alpha \partial k_\beta}$$



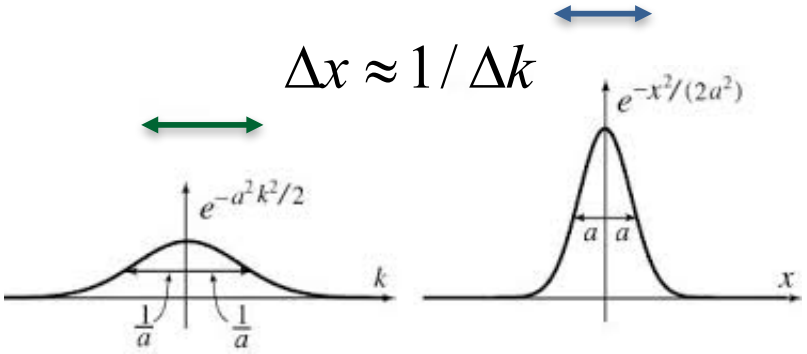
Silicon conduction-band pockets (M. Marder)

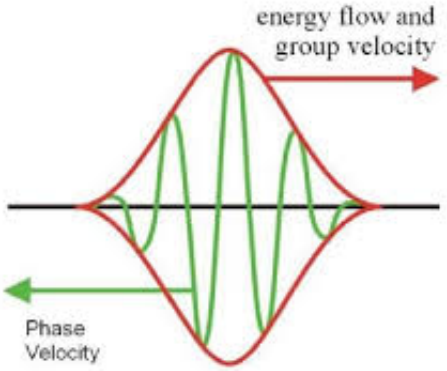
- Lorentz force equation: $$\hbar\dot{\vec{k}} = -e\left[\vec{E} + \frac{1}{\hbar c}\vec{\nabla}_k \varepsilon \times \vec{B}\right]$$

Progression to *adjacent states* in *same band.*

  - correct for sufficiently small fields.
  - electric transport properties; also Bloch oscillations (perfect conductor); magnetic quantization effects.

Group velocity & wavepackets:





$v_{phase} = \omega / k$

$\Delta k <<$ size of B. Zone
(packet construct from continuum).
requires macroscopic crystal.

$$u(\vec{r}) = \int u(\vec{k}) e^{i(\vec{k}\cdot\vec{r}-\omega t)} d^3k$$

$$\approx \int u(\vec{k}) e^{i(\vec{k}_o\cdot\vec{r}-\omega_o t)} e^{i(\delta\vec{k}\cdot\vec{r}-[\vec{\nabla}_k\omega\cdot\delta\vec{k}]t)} d^3k$$

k independent

Determines packet motion:

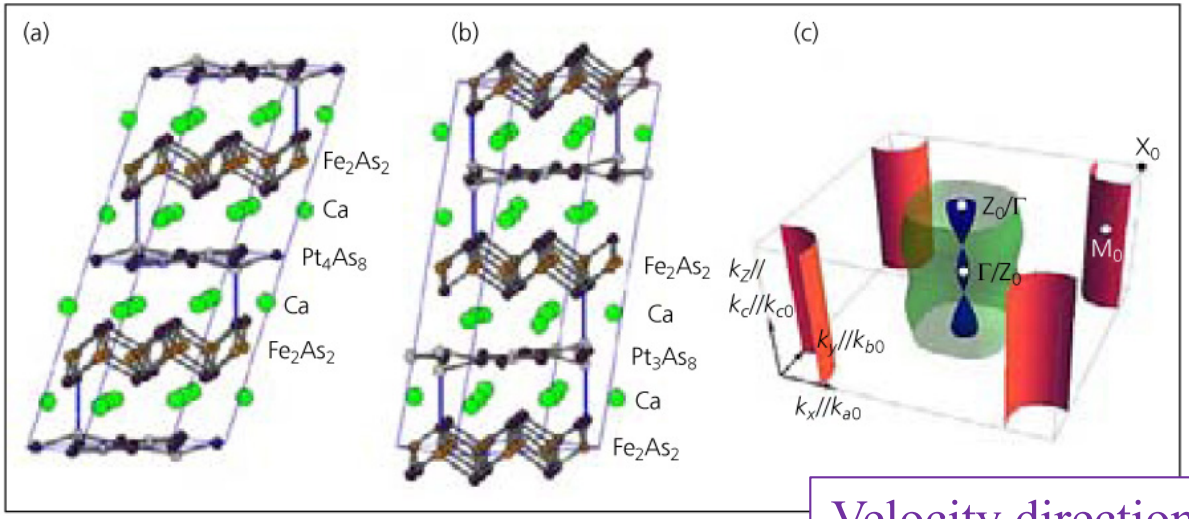
$$(\vec{r} - \vec{\nabla}_k \omega t) = const. \Rightarrow$$
$$\vec{\nabla}_k \omega \equiv \vec{\nabla}_k \varepsilon / \hbar = \vec{v}_{group}$$

- group velocity; 1D:
$$\frac{\partial \omega}{\partial k} = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k}$$
- generally zero at high symmetry points on B.Z. ("standing waves")
- also works for other excitations (e.g. phonons…)

Pnictide Superconductor Fermi surface images: ($BaFe_2As_2$ – related system)

Ivanovskii, Platinum Metals Rev. 57, 87 (2013)

$Ca_{10}(Pt_3As_8)\ (Fe_{2-x}Pt_xAs_2)_5$



Velocity directions?

Semiclassical Electron Dynamics

- Lorentz force equation:

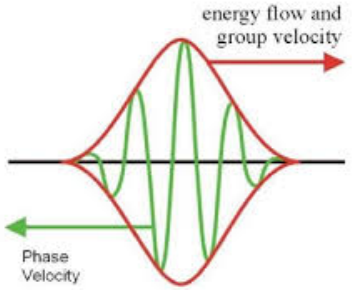
$$\hbar\dot{\vec{k}} = -e\left[\vec{E} + \frac{1}{\hbar c}\vec{\nabla}_k \varepsilon \times \vec{B}\right]$$

  - Requires fields sufficiently small for wavepacket to remain within single band.
  - *E* fields: normally difficult to exceed this criterion (Zener breakdown); *B* fields: "magnetic breakdown" sometimes important (several-T fields)

- One consequence: Bloch Oscillations; "no electrical conductivity in perfect crystal"

Semiclassical Electron Dynamics

- Group velocity $$\vec{v}_g = \frac{1}{\hbar}\vec{\nabla}_k \varepsilon$$



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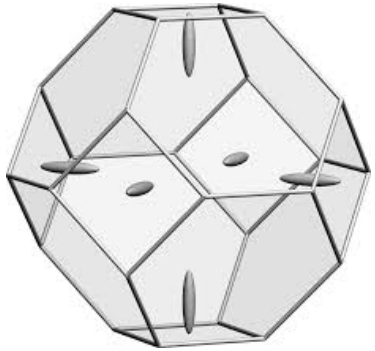

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