MATHERIALS seminar

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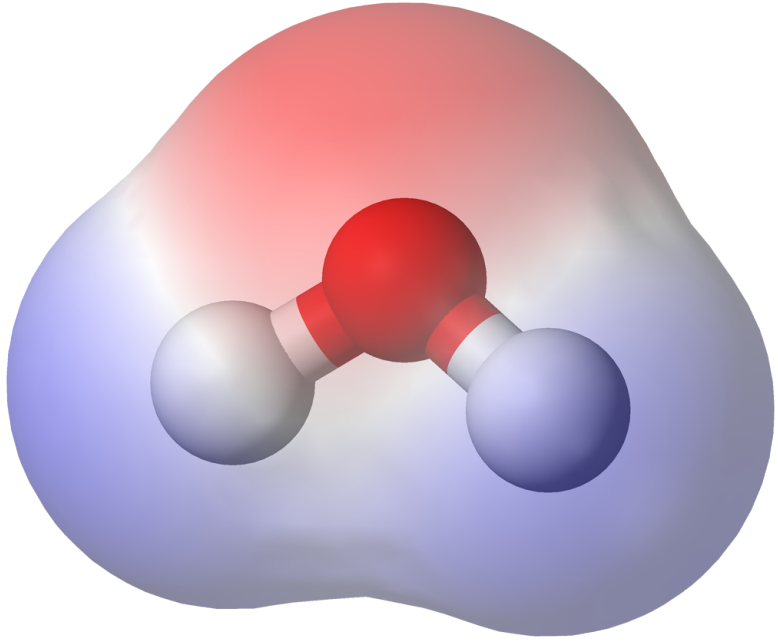
Summary

Electronic structure theory

- The behavior of "ordinary" matter is driven by the behavior of nuclei and electrons
- Nuclei can be considered classical point particles, but electrons must be modeled with quantum mechanics



Water is a good solvent because its electron distribution gives it a dipole moment

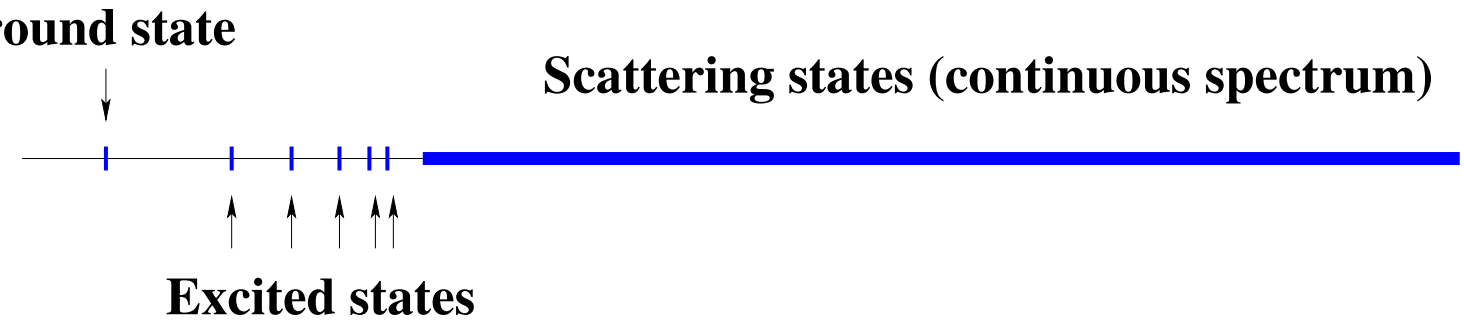
Quantum mechanics of a single electron

In atomic units, no spin, $\psi(t,\cdot) \in L^2(\mathbb{R}^3,\mathbb{C})$

$$i\partial_t \psi = H\psi$$

$$(H\psi)(x) = \underbrace{\left(-\frac{1}{2}\Delta\psi(x)\right)}_{\text{kinetic}} + \underbrace{V(x)\psi(x)}_{\text{potential}}$$

- $|\psi(x)|^2$ is the probability density of finding the particle at position x
- Stationary states: $\psi(t) = e^{-i\lambda t}\psi$, $H\psi = \lambda\psi$
- When V is "nice", H self-adjoint on $L^2(\mathbb{R}^3)$
- $V = 0 \Rightarrow$ continuous spectrum (generalized eigenvectors), wave propagation
- $V \neq 0 \Rightarrow$ possible bound states (eigenvectors in $L^2(\mathbb{R}^3)$)
- Ex: Hydrogen atom $V(x) = -\frac{1}{|x|}$



Quantum mechanics of **non-interacting** electrons

$$H\psi_n = \lambda_n \psi_n \qquad \lambda_1 \leq \lambda_2 \leq \dots$$

- Pauli exclusion principle: two electrons cannot be in the same quantum state
- Ground state: electrons fill first N energy states (*Aufbau* principle)
- Total energy:

$$E = \sum_{n=1}^{N} \lambda_n$$

- Total electronic density:

$$\rho(x) = \sum_{n=1}^{N} |\psi_n|^2(x)$$

Quantum mechanics of a molecule

Nuclei with charges z_k at positions R_k:

$$V_{\mathrm{at}}(x) = -\sum_{k=1}^{M} \frac{z_k}{|x - R_k|}$$

- Electrons at positions x and y interact through the Coulomb interaction $\frac{1}{|x-y|}$
- True laws of (many-body) quantum mechanics described by functions of $3N$ variables: much too complicated, need **approximations**
- One reasonable-looking approximation, the mean-field reduced Hartree-Fock (rHF) model: independent electrons under the mean-field

$$V_{\mathrm{H}}[\rho](x) = \int_{\mathbb{R}^3} \frac{\rho(y)}{|x - y|} dy$$

rHF and DFT

Mean-field Hamiltonian

$$H_\rho = -\frac{1}{2}\Delta + V_{\mathrm{at}}(x) + \int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|}\,dy$$

self-adjoint on $L^2(\mathbb{R}^3)$.
rHF model:

$$H_\rho \psi_n = \lambda_n \psi_n$$

$$\rho(x) = \sum_{n=1}^{N} |\psi_n|^2(x)$$

- Eigenvector-dependent eigenvalue problem ($A[x_1, \ldots, x_N]x_n = \lambda_n x_n$)
- Contains both the Pauli exclusion principle and electron-electron interaction, but mean-field approximation badly wrong (eg $N = 1$!)
- Good starting point for corrections

rHF and DFT

Mean-field Hamiltonian

$$H_\rho = -\frac{1}{2}\Delta + V_{\mathrm{at}}(x) + \int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|} dy + V_{\mathrm{xc}}[\rho](x)$$

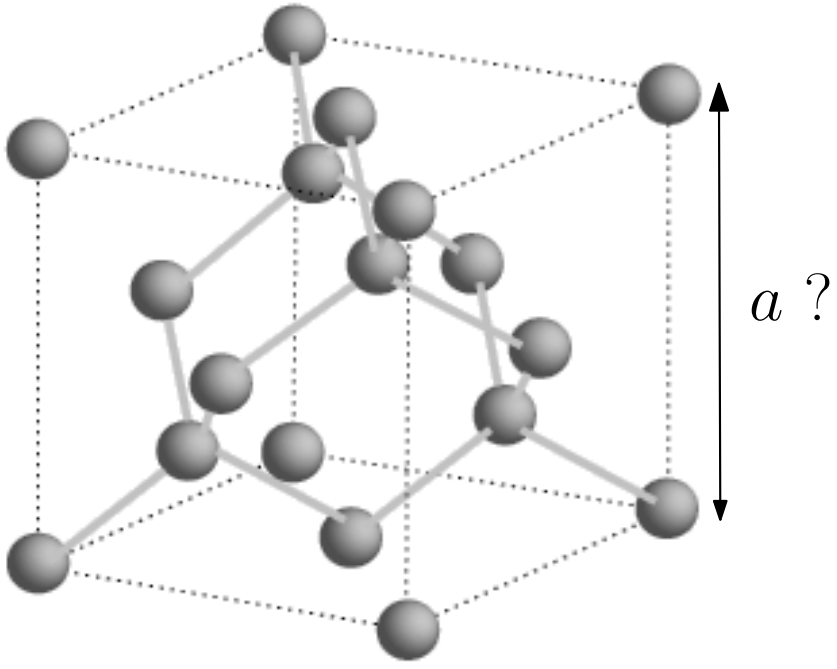
self-adjoint on $L^2(\mathbb{R}^3)$.
DFT model:

$$H_\rho \psi_n = \lambda_n \psi_n$$
$$\rho(x) = \sum_{n=1}^{N} |\psi_n|^2(x)$$

- Eigenvector-dependent eigenvalue problem ($A[x_1, \ldots, x_N]x_n = \lambda_n x_n$)
- Contains both the Pauli exclusion principle and electron-electron interaction, but mean-field approximation badly wrong (eg $N = 1$!)
- Good starting point for corrections: Density Functional Theory

Crystal properties

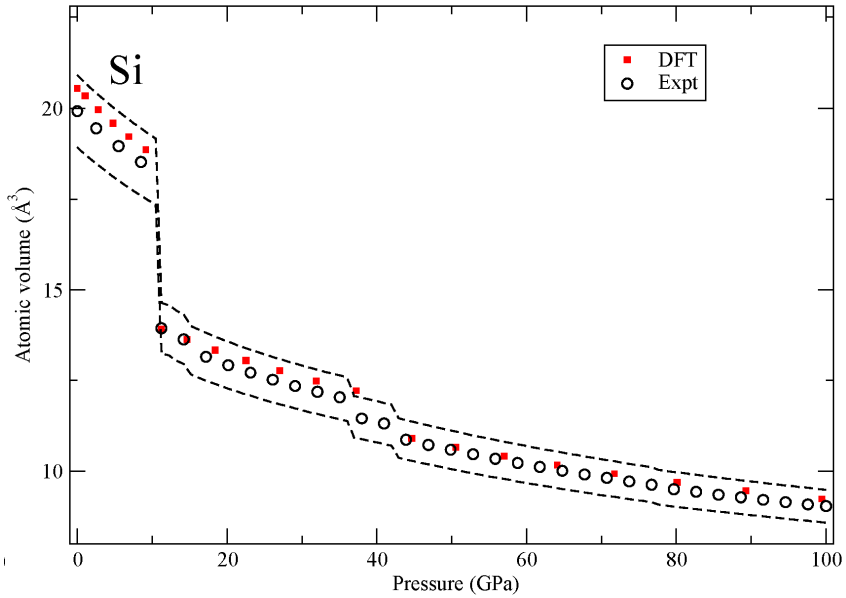
DFT gives access to $E(a)$, energy per unit volume



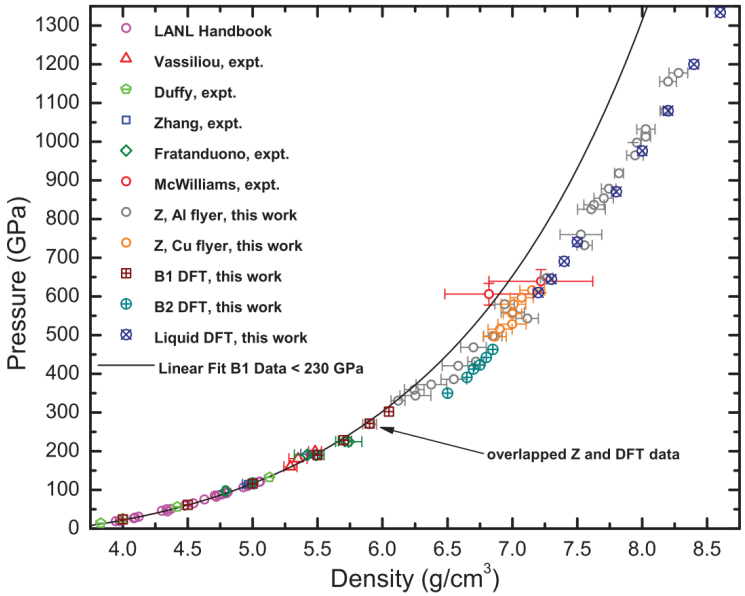
- Lattice constant: $\arg\min E(a)$
- Pressure: related to $\frac{dE}{da}$
- Young's modulus (speed of sound): related to $\frac{d^2E}{da^2}$
- Anharmonic effects: $\frac{d^3E}{da^3}$
- Many other static and dynamic properties, purely ab initio

DFT in practice

- Methodological developments since the '90s (pseudopotentials, numerical methods, HPC...): routinely solved for hundreds of atoms
- Workhorse of condensed matter physics and quantum chemistry



Equation of state of Si, Söderlind, Per, and David A. Young, Computation 6.1 (2018).

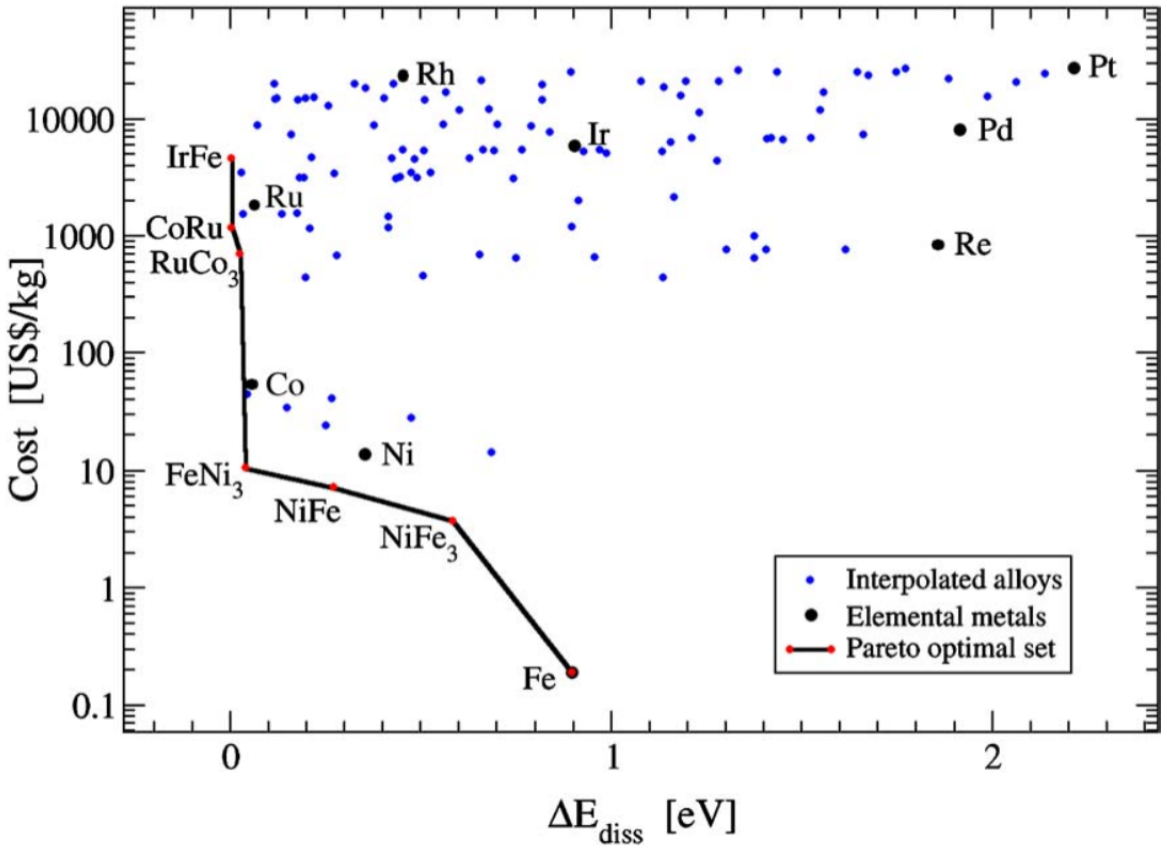


Equation of state of MgO, Root, Seth, et al., Physical Review Letters 115.19 (2015).

... but severe deficiencies (excited states, strongly correlated materials)

Applications

From fundamental physics to practical applications



Dissociation energy of adsorbed CO, Andersson, Martin P., et al. Journal of Catalysis 239.2 (2006)

Electronic structure for mathematicians

- Complex equations
- Need for reliable, automatic, accurate and fast methods
- Involves many branches of mathematics

Analysis	Computing	"Pure" math
PDEs	Linear algebra	Probability
Spectral theory	Optimization	Group theory
Complex analysis	Numerical analysis	Topology
Nonlinear analysis	HPC	Differential geometry

- Underexplored mathematically

Keyword	Web of Science	MathSciNet	Ratio
Maxwell equations	19,459	2,055	10%
Boltzmann equation	24,519	2,268	10%
Navier Stokes	47,341	9,436	20%
Density Functional Theory	142,374	171	0.1%

This talk

Mathematical theory of periodic quantum systems

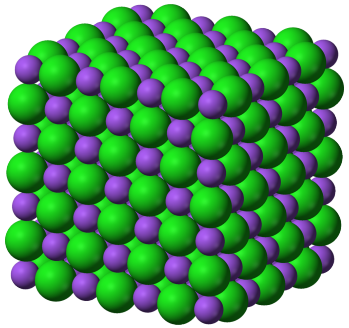
- Insulators and metals
- The supercell method

Response properties

- Time-dependent response: electrical conductivity
- Time-independent response: electric screening

Summary

DFT for crystals



A perfect crystal is defined by

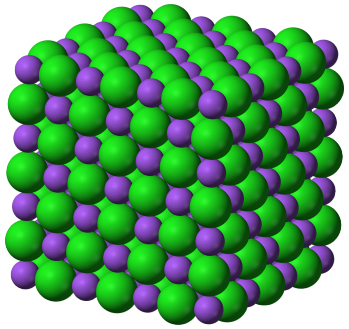
- Lattice $\mathcal{R} \subset \mathbb{R}^3$ (say $2\pi\mathbb{Z}^3$ wlog)
- $\mathcal{R}$-periodic atomic potential V_{at}
- N_{cell} electrons per unit cell

Mathematically: define a finite-size system, and let the size tend to infinity (thermodynamic limit). Subtleties [Catto/Le Bris/Lions '01]:

- Infinite number of electrons
- Symmetry breaking (non-uniqueness)
- Coulomb non-summability
- Surface effects

This talk: thermodynamic limit of non-interacting electrons with the supercell method

DFT for crystals



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- Infinite number of electrons
- ~~Symmetry breaking (non-uniqueness)~~
- ~~Coulomb non-summability~~
- ~~Surface effects~~

This talk: thermodynamic limit of non-interacting electrons with the supercell method

Translational invariance and (generalized) eigenvectors

Forget about electron-electron interaction:

$$H = -\frac{1}{2}\Delta + V_{\mathrm{at}}$$

with V_{at} periodic, self-adjoint on $L^2(\mathbb{R}^3)$. Symmetries

$$\tau_R H = H\tau_R \text{ for } R \in 2\pi\mathbb{Z}^3,$$

τ_R translation operator by R.

Commuting operators preserve each other's eigenspaces (if $AB = BA$ and $Ax = \lambda x$, then $A(Bx) = BAx = \lambda(Bx)$). A family of commuting self-adjoint operators can all be diagonalized in a basis of common (generalized) eigenvectors.

Example: fully translation-invariant operators and the Fourier transform

$$\tau_R H_{\mathrm{TI}} = H_{\mathrm{TI}}\tau_R \text{ for all } R \in \mathbb{R}^3$$

Common eigenvectors of $\{\tau_R\}_{R\in\mathbb{R}^3}$? Plane waves e^{iqx}.
H_{TI} is fully diagonal in Fourier domain

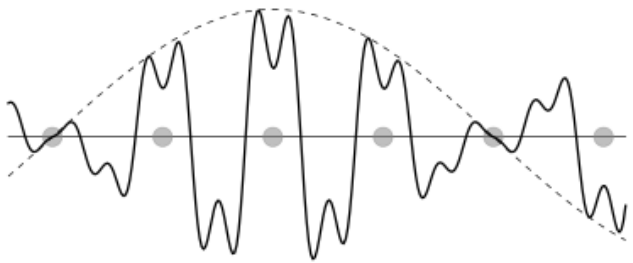
$$H_{\mathrm{TI}} e^{iqx} = H_{\mathrm{TI}}(q) e^{iqx}$$

Lattice translational invariance and Bloch waves

$$\tau_R H = H \tau_R \text{ for } R \in 2\pi\mathbb{Z}^3$$

What are the common eigenvectors of $\{\tau_R\}_{R \in 2\pi\mathbb{Z}^3}$? Bloch waves

$$\psi(x) = e^{ikx} u(x), \qquad u \text{ periodic}, \quad k \in [0,1]^3$$



H is partially diagonalized by Bloch waves

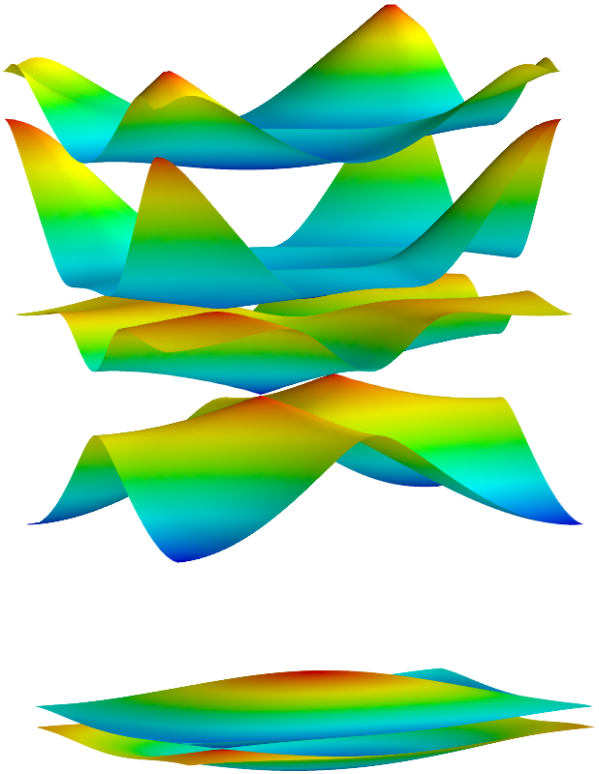
$$(H\psi)(x) = e^{ikx} \underbrace{\left[\left(\frac{1}{2}(-i\nabla + k)^2 + V_{\text{at}} \right) u \right]}_{:= H_k u,\ H_k \text{ acts on } L^2([0,2\pi]^3)} (x)$$

Reduce to a (parametrized) unit cell problem (much simpler !)

$$\psi_{nk}(x) = e^{ikx} u_{nk}(x)$$

Band structure

$$\psi_{nk}(x) = e^{ikx} u_{nk}(x)$$
$$H_k u_{nk}(x) = \varepsilon_{nk} u_{nk}(x)$$
$$\sigma(H) = \{\varepsilon_{nk}, n \in \mathbb{N}, k \in [0,1]^3\}$$



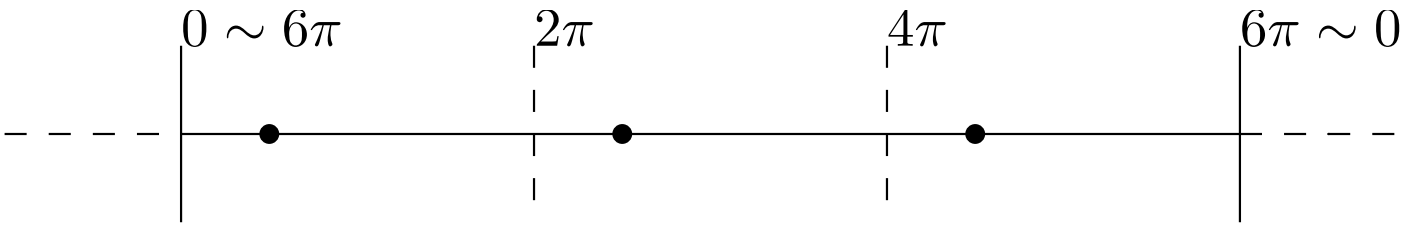
Possible gaps in the spectrum

The supercell method

Supercell method: take $L \times L \times L$ copies of the unit cell

$$\Gamma_L = [0, 2\pi L]^3$$

with periodic boundary conditions ($\simeq$ torus).



- Need to solve the Schrödinger equation $H_L\psi = \lambda\psi$ for $L^3 N_{\text{cell}}$ electrons in Γ_L
- (usual) diagonalization scales cubically: $O(L^9)$!
- The supercell method preserves periodicity: $H_L\tau_R = \tau_R H_L$ for $R \in 2\pi\mathbb{Z}^3$.
- Seek eigenvectors as $\psi_{nk}(x) = e^{ikx}u_{nk}(x)$, but supercell boundary conditions impose

$$k \in \left\{0, \frac{1}{L}, \ldots, \frac{L-1}{L}\right\}^3$$

- Uncoupled problems in the discretized Brillouin zone with step $1/L$. $O(L^3)$!

Electrons in a supercell

Recall that in the ground state, N non-interacting electrons will occupy the first N energy levels of the Hamiltonian.
Total energy of the supercell:

$$\begin{aligned} E_L &= \sum_{i=1}^{L^3 N_{\text{cell}}} \lambda_i \\ &= \sum_{k \in \{0, \frac{1}{L}, \ldots, \frac{L-1}{L}\}^3, n \in \mathbb{N}} \varepsilon_{nk} \mathbb{1}(\varepsilon_{nk} \leq \varepsilon_F) \end{aligned}$$

where the Fermi level ε_F is determined by

$$L^3 N_{\text{cell}} = \sum_{k \in \{0, \frac{1}{L}, \ldots, \frac{L-1}{L}\}^3, n \in \mathbb{N}} \mathbb{1}(\varepsilon_{nk} \leq \varepsilon_F)$$

Thermodynamic limit:

$$\lim_{L \to \infty} \frac{E_L}{L^3} = \int_{[0,1]^3} \sum_{n \in \mathbb{N}} \varepsilon_{nk} \mathbb{1}(\varepsilon_{nk} \leq \varepsilon_F) dk, \text{ with}$$

$$\int_{[0,1]^3} \sum_{n \in \mathbb{N}} \varepsilon_{nk} \mathbb{1}(\varepsilon_{nk} \leq \varepsilon_F) dk = N_{\text{cell}}$$

Insulators, semiconductors and metals

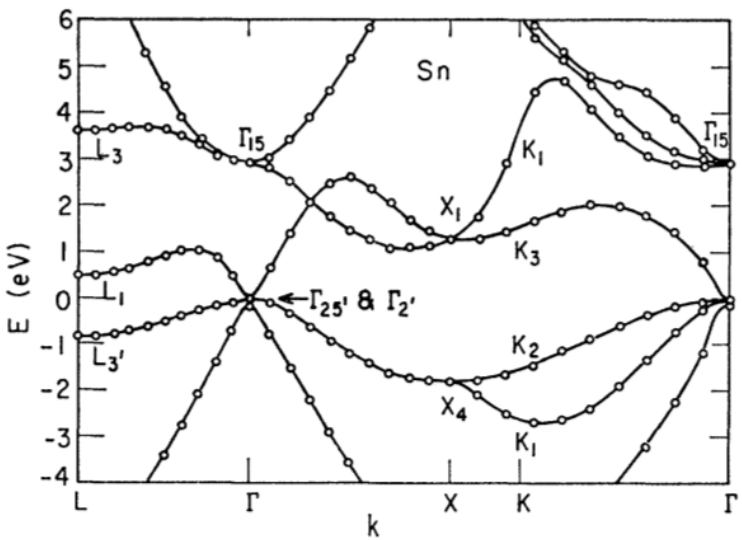
If

$$\sup_{k\in[0,1]^3} \varepsilon_{N_{\mathrm{cell}}k} < \inf_{k\in[0,1]^3} \varepsilon_{N_{\mathrm{cell}}+1,k},$$

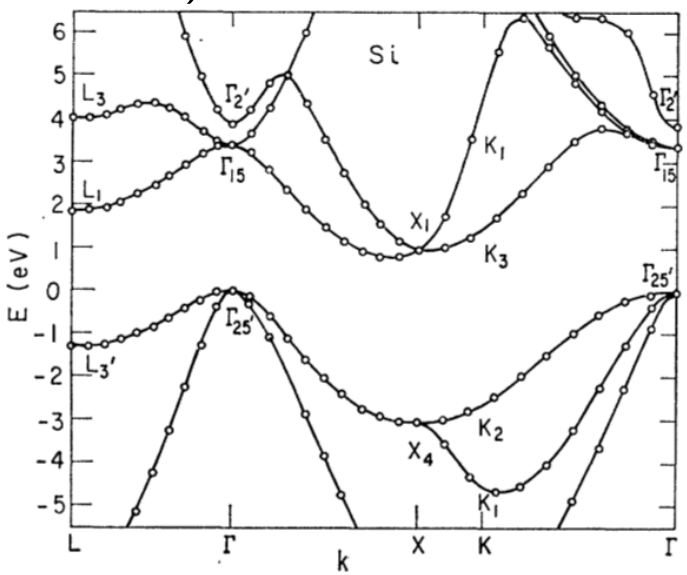
we have

$$\lim_{L\to\infty} \frac{E_L}{L^3} = \int_{[0,1]^3} \sum_{n=1}^{N_{\mathrm{cell}}} \varepsilon_{nk}\, dk$$

and the system is an insulator (or semiconductor); otherwise it is a metal.



Tin (metal)



Silicon (semiconductor)

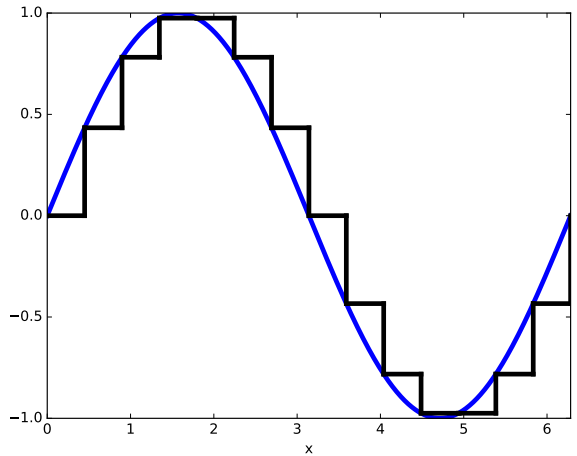
Summary

Speed of convergence with respect to L: insulators

Insulators:

$$\frac{1}{L^3} \sum_{k \in \{0, \frac{1}{L}, \ldots, \frac{L-1}{L}\}^3} \sum_{n=1}^{N_{\text{cell}}} \varepsilon_{nk} \to \int_{[0,1]^3} \left(\sum_{n=1}^{N_{\text{cell}}} \varepsilon_{nk} \right) dk$$

Usual estimates: $O(1/L)$, but massive error cancellation: quadrature exact for $e^{i2\pi nx}$, $|n| < L$



Speed of convergence related to decay of the Fourier coefficients of $\sum_{n=1}^{N_{\text{cell}}} \varepsilon_{nk}$: exponential convergence (proof by analytic eigenvalue perturbation theory + Paley-Wiener) [Gontier-Lahbabi '16]

Speed of convergence with respect to L: metals

$$\frac{E_L}{L^3} = \frac{1}{L^3} \sum_{k \in \{0, \frac{1}{L}, \dots, \frac{L-1}{L}\}^3, n \in \mathbb{N}} \varepsilon_{nk} \mathbb{1}(\varepsilon_{nk} \leq \varepsilon_F)$$

$$N_{\text{cell}} = \frac{1}{L^3} \sum_{k \in \{0, \frac{1}{L}, \dots, \frac{L-1}{L}\}^3, n \in \mathbb{N}} \mathbb{1}(\varepsilon_{nk} \leq \varepsilon_F)$$

Slow $1/L$ (in good cases...) convergence
In practice, often regularized by finite (artificial) temperature:

$$\mathbb{1}(\varepsilon_{nk} \leq \varepsilon_F) \rightsquigarrow \frac{1}{1 + e^{\frac{\varepsilon_{nk} - \varepsilon_F}{k_B T}}}$$

Theorem (Cancès, Ehrlacher, Gontier, Levitt, Lombardi '19)

Under regularity assumptions on the Fermi surface, there are $C > 0, \eta > 0$ such that

$$|E^{L,T} - E| \leq C(T^2 + T^{-4} e^{-\eta TL})$$

Huge challenge in practice!

Summary

Response properties

In practice materials are characterized by their **response properties**: mechanical, electrical, magnetic, optical, thermal, chemical...

Mathematically: **perturbation theory** for $F(X, \epsilon)$ around equilibrium

$$F(X_*, 0) = 0$$

- Time-independent:

  $$F(X, \epsilon) = 0.$$

  Implicit function theorem:

  $$X(\epsilon) = X_* - \epsilon(\partial_X F)^{-1}\partial_\epsilon F + O(\epsilon^2)$$

- Time-dependent:

  $$\dot{X} = F(X, \epsilon I(t)), X(0) = X_*.$$

  Duhamel formula:

  $$X(\epsilon, t) = X_0 + \epsilon \int_0^t e^{(t-t')\partial_X F}(\partial_\epsilon F) I(t') dt' + O(\epsilon^2)$$

  ("fluctuation-dissipation")

Response and numerical analysis

The same objects appear in **numerical analysis** at $\epsilon = 0$

- Error control

$$\underbrace{X - X_*}_{\text{error}} \approx (\partial_X F)^{-1} \underbrace{F(X)}_{\text{residual}}$$

- Iterative algorithms

$$X_{n+1} = X_n + \alpha F(X_n) \quad \Rightarrow \quad X_n - X_* \approx (1 + \alpha \partial_X F)^n (X_0 - X_*)$$

Need to understand $\partial_X F$ and its divergences (= function spaces)

Application to DFT:

- Need to formulate problem of interest as a well-posed perturbation ($\partial_X F$ invertible)
- $H_\rho \psi_n = \lambda_n \psi_n$ has invariances $\Rightarrow$ density matrices $\gamma = \sum_n |\psi_n\rangle\langle\psi_n|$
- Constraints: $\gamma^2 = \gamma^* = \gamma, \operatorname{Tr}\gamma = N$: $\Rightarrow$ differential geometry
- $\partial_X F$ is a complicated object
- Contains a huge amount of physics

Electrical conductivity

Minimal quantum model for the conductivity of a crystal [Cancès Fermanian Levitt Siraj-Dine '20]

$$i\partial_t \gamma^\epsilon = \left[\left(\frac{1}{2}\Delta + V_{\mathrm{at}} - \epsilon x_\beta \right), \gamma^\epsilon \right]$$
$$\gamma^\epsilon(0) = \mathbb{1}\left(\frac{1}{2}\Delta + V_{\mathrm{at}} \leq \varepsilon_F \right)$$

Neglect electron-electron, electron-lattice interaction: no dissipation mechanism, expect infinite conductivity for metals.
Current per unit cell:

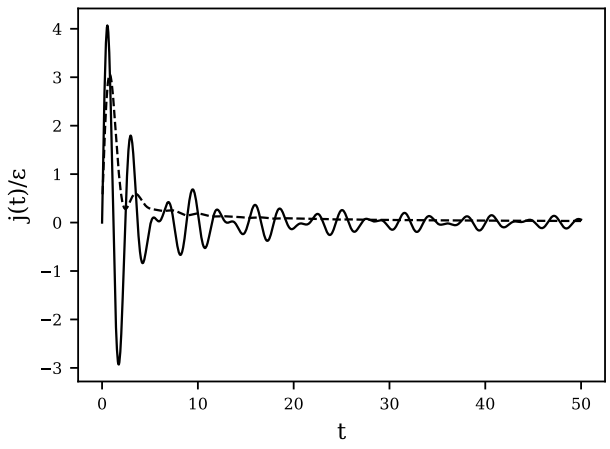
$$j^\epsilon(t) = \underline{\mathrm{Tr}}(-i\partial_\alpha \gamma^\epsilon(t))$$

where the trace per unit cell is (when well-defined)

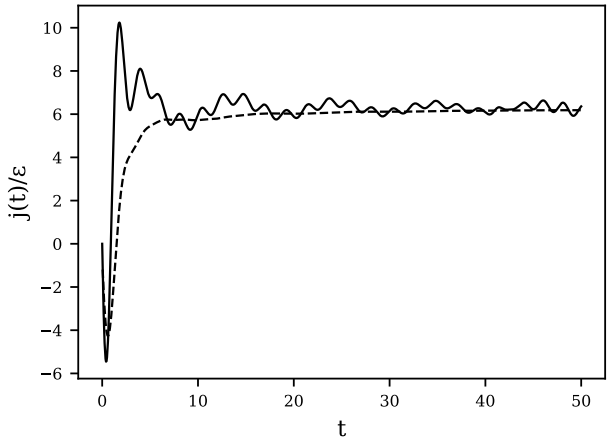
$$\underline{\mathrm{Tr}} A = \lim_{L\to\infty} \frac{1}{L^3} \mathrm{Tr}(\mathbb{1}_{\Gamma_L} A \mathbb{1}_{\Gamma_L})$$

Behavior of $j^\epsilon(t)$?

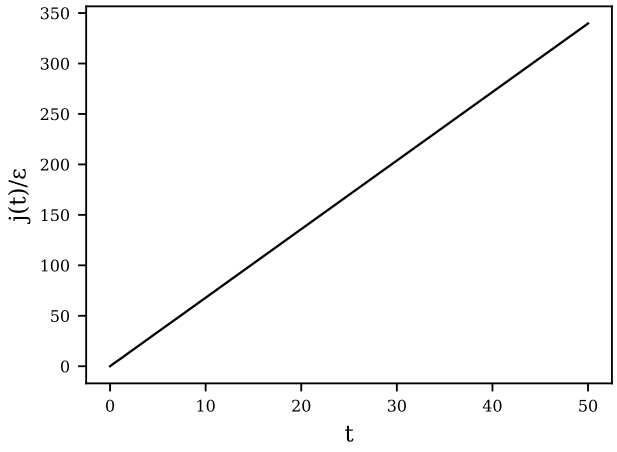
Electrical conductivity



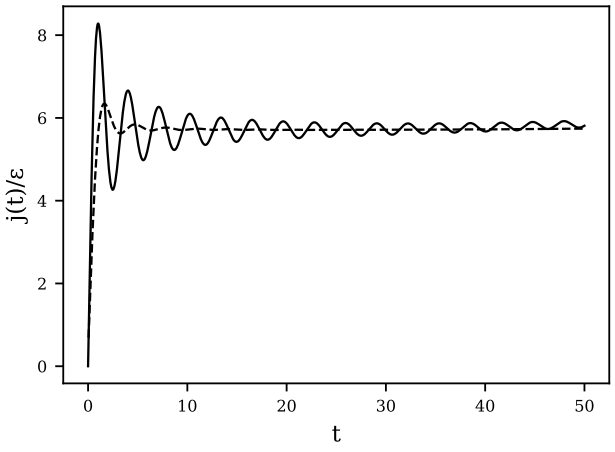
Normal insulator phase.



Chern insulator phase, transverse current.



Metallic phase.



Graphene.

Proof technique: reduction to a unit cell problem

$$i\partial_t \gamma^\epsilon = \left[\left(\frac{1}{2}\Delta + V_{\mathrm{at}} - \epsilon x_\beta \right), \gamma^\epsilon \right]$$
$$\gamma^\epsilon(0) = \mathbb{1}\left(\frac{1}{2}\Delta + V_{\mathrm{at}} \leq \varepsilon_F \right)$$

- If the operator A is periodic (commutes with lattice translation), use Bloch theory to block-diagonalize A into its fibers A_k: operators on $L^2([0,2\pi]^3)$ for $k \in [0,1]^3$.
- $\gamma^\epsilon(0)$ is periodic but $\frac{1}{2}\Delta + V_{\mathrm{at}} - \epsilon x_\beta$ is not: cannot use Bloch theory?
- But $[x_\beta, A]$ is periodic with fibers $i\partial_\beta A_k$ (the potential not periodic, but the field is)

$$i\partial_t \gamma_k + i\partial_\beta \gamma_k = [H_k, \gamma_k]$$

  Method of characteristics $\widetilde{\gamma}_k^\epsilon(t) = \gamma^\epsilon_{k+\epsilon e_\beta t}(t)$ (change of gauge)
- Turn time-independent space-dependent scalar potential into time-dependent space-independent vector potential ($E = -\nabla V - \partial A/\partial t$)

Proof technique: time-dependent perturbation theory

$$\begin{aligned} i\partial_t \widetilde{\gamma}_k^\epsilon &= [H_{k+\epsilon e_\beta t}, \widetilde{\gamma}_k^\epsilon] \\ &\approx [H_k + \epsilon t \partial_\beta H_k, \widetilde{\gamma}_k^\epsilon] \end{aligned}$$

Use time-dependent perturbation theory to compute $\widetilde{\gamma}_k^\epsilon$ then

$$j^\epsilon(t) = \int_{[0,1]^3} \mathrm{Tr}(\partial_\alpha H_{k+\epsilon e_\beta t} \widetilde{\gamma}_k^\epsilon(t)) dk$$

to first order (regularization needed to smooth out oscillations).

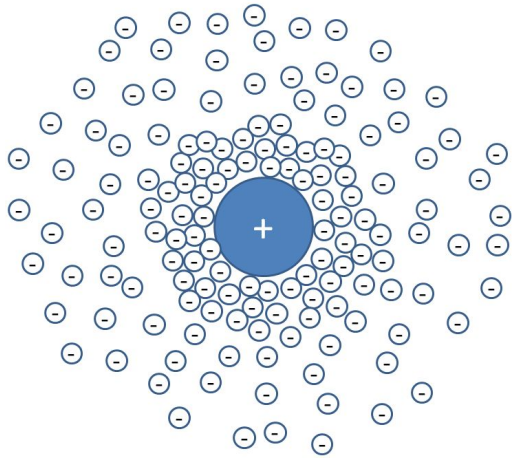
Interpretation: in response theory, an external perturbation δV coupling occupied state i and empty state j creates a response $\propto e^{i(\varepsilon_i - \varepsilon_j)t} \langle i|\delta V|j\rangle$

- In insulators, gap between occupied and empty states: purely oscillatory response, no net current
- In metals, x_β couples neighboring k points: static response on the Fermi surface

Towards more realistic models: electron-electron, electron-impurity, electron-phonon.

Summary

Screening: phenomenology



Phenomenologically, response to a point charge $V_{\text{pert}} = \frac{Q}{|x|}$:

System	V_{eff}	Features
Vacuum	$\frac{Q}{\lvert x\rvert}$	No screening
Insulator/semiconductor	$\frac{Q}{\varepsilon_r \lvert x\rvert}$	Partial screening
Uniform electron gas (Thomas-Fermi)	$\propto \frac{Q e^{-k_{\text{TF}}\lvert x\rvert}}{\lvert x\rvert}$	Full screening
Uniform electron gas (Lindhard)	$\propto \frac{Q\cos(2k_{\text{F}}\lvert x\rvert)}{\lvert x\rvert^3}$	Friedel oscillations

Screening: the dielectric operator

Consider a finite system in the reduced Hartree-Fock approximation with perturbation:

$$H_{\gamma,\epsilon} = -\frac{1}{2}\Delta + V_{\mathrm{at}} + \epsilon V_{\mathrm{pert}} + \rho_\gamma * \frac{1}{|x|}$$

Assume an Aufbau equilibrium property: γ_* is the projector on the first N eigenstates of $H_{\gamma_*,0}$.
Let $F : V \to \rho_{\gamma(V)}$ where $\gamma(V)$ is the ground state density matrix of $-\frac{1}{2}\Delta + V$. Then

$$V = V_{\mathrm{at}} + \epsilon V_{\mathrm{pert}} + F(V) * \frac{1}{|x|}$$

$$V \approx V_* + \epsilon \underbrace{\left(1 - F'(V_*)\left(\cdot * \frac{1}{|x|}\right)\right)^{-1}}_{\text{dielectric operator}} V_{\mathrm{pert}} + O(\epsilon^2)$$

Large-scale behavior of F' related to density of free electrons: zero for insulators, non-zero for metals

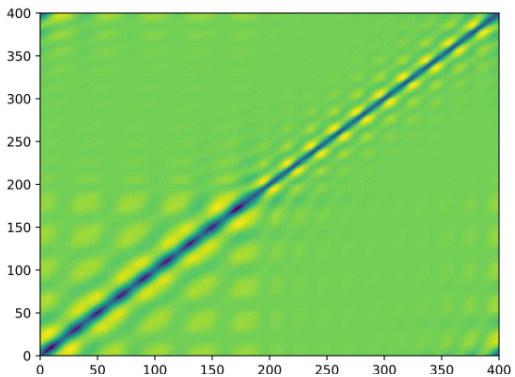
Dielectric operator and SCF convergence

$$V = V_{\mathrm{at}} + \epsilon V_{\mathrm{pert}} + F(V) * \frac{1}{|x|}$$

- The convergence of fixed-point schemes (SCF) depend on the properties of the dielectric operator
- Need good approximations to design cheap preconditioners for heterogeneous systems

"Homogenization" [Herbst, Levitt '20]

$$\int F'(V_*)(x,y)V(y)dy \approx V(x)\int F'(V_*)(x,y)dy$$
$$= V(x)\,\mathrm{LDOS}(x)$$



Preconditioners for SCF

DFTK