Schrödinger eqn

$$H \Psi_0 = E_0 \Psi_0$$

$$\Psi_0 \in W_N = \{ \Psi \in \bigwedge^N L^2(\mathbb{R}^3, \mathbb{C}) \cap H^1(\mathbb{R}^{3N}), \; \|\Psi\| = 1 \}$$

$$H = \underbrace{\sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i + V(x_i) \right)}_{T} + \underbrace{\sum_{\substack{i,j=1 \\ i<j}}^{N} \frac{1}{|x_i - x_j|}}_{\text{Vee}}$$

$$V \in L^\infty + L^{3/2}$$

Coercent - Fisher:

$$E_0 = \operatorname*{argmin}_{\Psi \in W_N} \mathcal{E}(\Psi) \qquad \mathcal{E}(\Psi) = \langle \Psi | H | \Psi \rangle$$

Aside: Silicon crystal $N = 28$

2 quadrature points per DoF $\simeq 2 \cdot 10^{25}$ integral evals

1 year → 7.5 as / eval !

⇒ we need to do better!

Electronic density

$$\rho_\Psi(r) = N \int_{\mathbb{R}^3} |\Psi(r, r_2, r_3, \dots, r_N)|^2 \, dr_2 \cdots dr_N$$

$$\langle \Psi | \sum_{i=1}^{N} V(r_i) | \Psi \rangle = \int \rho_\Psi V$$

Goal of DFT: Solve Schrödinger problem in density only. (more or less)

Levy-Lieb constrained search

$$R_N = \{ \rho \mid \exists \Psi \in W_N \text{ s.t. } \rho = \rho_\Psi \}$$

Lieb '79

$$= \left\{ \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int \rho = N \right\}$$

$\Rightarrow$ Idea: split up search over densities & wavefctns.

with this

$$E_0(v) = \inf_{\psi \in W_N} \left[\langle \psi | T + V_{ee} | \psi \rangle + \int \rho_\psi v \right]$$

$$= \inf_{\rho \in R_N} \inf_{\substack{\psi \in W_N \\ \rho_\psi = \rho}} \left[\langle \psi | T + V_{ee} | \psi \rangle + \int \rho v \right]$$

$$= \inf_{\rho \in R_N} \left[\inf_{\substack{\psi \in W_N \\ \rho_\psi = \rho}} \langle \psi | T + V_{ee} | \psi \rangle + \int \rho v \right]$$

$$= \inf_{\rho \in R_N} F_{LL}(\rho) + \int \rho v$$

$$F_{LL}(\rho) = \inf_{\substack{\Psi \in W_N \\ \rho_\Psi = \rho}} \langle \Psi | T + V_{ee} | \Psi \rangle$$

- Evaluating $F_{LL}(\rho)$ is not easy as W_N vast!

Assume (for a second) a non-interacting system

$$\hat{H}_N = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i + V(x_i) \right) \; ; \; \hat{E}_0 = \min_{\Psi \in W_N} \langle \Psi | \hat{H}_N | \Psi \rangle$$

$\Rightarrow$ separable problem

minimizer of form $\tilde{\Psi} = \phi_1 \wedge \phi_2 \wedge \dots \wedge \phi_N$ — Slater det.

$$\phi_i \in H^1(\mathbb{R}^3, \mathbb{C}) \; ; \; \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

For such a system $\rho_\Psi = \sum_{i=1}^{N} |\phi_i|^2$

$$\langle \Psi | T | \Psi \rangle = \frac{1}{2} \sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \varphi_i|^2$$

We define

$$T_{KS}(\rho) := \inf \left\{ \frac{1}{2} \sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \varphi_i|^2 \;\middle|\; \varphi_i \in H^1(\mathbb{R}^3), \; (\varphi_i | \varphi_j) = \delta_{ij}, \; \rho_\Psi = \rho \right\}$$

such that for a non-interacting system:

$$F_{LL}(\rho) = T_{KS}(\rho)$$

Kohn-Sham idea:

- Let exact density be replaced by non-interacting electrons:

$$F_{LL}(\rho) = T_{KS}(\rho) + J(\rho) + E_{xc}(\rho)$$

(Lieb-Oxford)

"correction term"

(Formally no approx)

where

$$J(\rho) = \frac{1}{2} \iint_{\mathbb{R}^3 \mathbb{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\,dx\,dy$$

classical approx to $\langle \Psi | V_{ee} | \Psi \rangle$

- key point:

$$T(\rho) \simeq T_{KS}(\rho)$$ i.e. not fully exact

- We reformulate

$$E_0(v) = \inf_{\rho \in R_N} \left[F_{LL}(\rho) + \int \rho v \right]$$

$$= \inf \left\{ E_{KS}(\Phi) \,\middle|\, \varphi_i \in H^1(\mathbb{R}^3),\ (\varphi_i | \varphi_j) = \delta_{ij},\ i = 1, \dots N \right\}$$

with

$$E_{KS}(\Phi) = \frac{1}{2}\sum_{i=1}^{N} |\nabla \varphi_i|^2 + \int \rho_\Phi V + \frac{1}{2}\iint \frac{\rho_\Phi(x)\,\rho_\Phi(y)}{|x-y|}\,dx\,dy + E_{xc}(\rho_\Phi)$$

E_{Hxc}

- Indeed $\forall \rho \in R_N$:

$$F_{LL}(\rho) + \int \rho V$$

$$= T_{KS}(\rho) + T_c(\rho) + E_{xc}(\rho) + \int \rho V$$

$$= \inf\left\{ \frac{1}{2}\sum_{i=1}^{N} \int |\nabla \varphi_i|^2 + E_{Hxc}(\rho_\Phi) + \int \rho_\Phi V \;\middle|\; \varphi_i \in H^1(\mathbb{R}^3),\ (\varphi_i|\varphi_j) = \delta_{ij},\ \rho_\Phi = \rho,\ i = 1 \dots N \right\}$$

$$= \inf\left\{ E_{KS}(\Phi) \;\middle|\; \dots\dots \quad \rho_\Phi = \rho \right\}$$

thus

$$\inf_{\rho \in R_N} \left(F_L(\rho) + \int \rho v \right)$$

$$= \inf_{\rho \in R_N} \inf \left\{ E_{KS}(\underline{\Phi}) \,\middle|\, \varphi_i \in H^1,\ (\varphi_i | \varphi_j) = \delta_{ij},\ \rho_{\underline{\Phi}} = \rho \right\}$$

$$= \inf \left\{ E_{KS}(\underline{\Phi}) \,\middle|\, \varphi_i \in H^1,\ (\varphi_i | \varphi_j) = \delta_{ij} \right\}$$

as desired.

This is an orthogonality-constained optimisation problem. First-order optimality conditions (proof skipped) can be written as

$$\begin{cases} \left[-\frac{1}{2}\Delta + V + V_{Hxc}(\rho) \right] \varphi_i = \varepsilon_i \varphi_i \\ (\varphi_i | \varphi_j) = \delta_{ij}\ ; \quad \varepsilon_1 \le \varepsilon_2 \le \dots \\ \rho = \sum_{i=1}^{N} |\varphi_i|^2 \end{cases}$$

where $V_{Hxc} = \nabla_\rho E_{Hxc}$.

$\Rightarrow$ Non-linear eigenvalue problem!

- Define

$$\rho(V_{Hxc}) = \sum_{i=1}^{N} |\varphi_i|^2$$

where $\left(-\frac{1}{2}\Delta + V + V_{Hxc}\right)\varphi_i = \varepsilon_i \varphi_i$

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

- equivalently

$$\rho(V_{Hxc})(x) = \sum_{i=1}^{N} \varphi_i(x)\, \varphi_i^*(x)$$

$$= \left[\sum_{i=1}^{N} \varphi_i(\cdot)\, \varphi_i^*(\cdot)\right](x, x)$$

integral kernel of an operator

$$= \text{diag}\left[\mathbb{1}_{(-\infty, \varepsilon_F]}\left(-\frac{1}{2}\Delta + V + V_{Hxc}\right)\right](x)$$

where ε_F s.t. $\int_\Omega \rho(V_{Hxc}) = N$

- With this we can denote an equivalent fixed-point problem

$$\rho(V_{Hxc}(\rho)) = \rho \quad \text{or} \quad F(\rho) = \rho$$

$$F[\rho] \equiv \rho(V_{Hxc}(\rho))$$

called the self-consistent field (SCF) problem.

We denote its sol^n as ρ^*

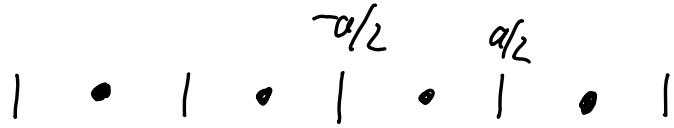
Lattices and plane-wave basis sets

Periodicity, e.g. sine:

$$\sin(x) = \sin(x + 2\pi m) \qquad m \in \mathbb{Z}$$

In general for $f: \mathbb{R} \to \mathbb{R}$ a-periodic characterizing f in $[-a/2, a/2)$ uniquely defines the full f.

Atomic systems:



unit cell $\Omega = [-a/2, a/2)$; lattice $\mathbb{L} = a\mathbb{Z}$

at each atom potential $V(x_i)$

$\Rightarrow$ $\sum_{i=1}^{N} V(x_i)$ $\mathbb{L}$-periodic

Let us **assume** φ_i are $\mathbb{L}$-periodic. (not true, we fix this later)

Then ρ is $\mathbb{L}$-periodic.

Plane-wave discretization:

- Main unknowns are $\mathbb{L}$-periodic

$$u(r) = \sum_{G \in \mathbb{L}^*} \hat{u}_G \, e_G(r)$$

dual lattice — Fourier coeff — plane wave / Fourier mode

$$\mathbb{L}^* = \frac{2\pi}{a}\mathbb{Z}$$

$$e_G(r) = \frac{e^{iG\cdot r}}{\sqrt{|\Omega|}}$$

$$\hat{u}_G = \langle e_G, u \rangle_{L^2_{per}(\Omega)} = \frac{1}{\sqrt{|\Omega|}} \int_\Omega u(r)\, e^{-iGr}\, dr$$

key relations: $\int_\Omega |u(r)|^2 dr = \sum_{G \in \mathbb{L}^*} |\hat{u}_G|^2$ Parseval

$$[-i\nabla u]_G = G\,\hat{u}_G$$

Plane-wave approximations:

$$\mathcal{X}_{cut} = \text{span}\left(e_G,\ G \in \mathbb{L}^*_{cut}\right); \quad \mathbb{L}^*_{cut} = \left\{G \in \mathbb{L}^* \;\middle|\; \frac{|G|^2}{2} \le E_{cut}\right\}$$

Assumption: V is C^∞_{per} & bounded

↳ E_{cut} can be chosen small

↳ plane-waves are a good basis set

Elliptic regularity: "elliptic bootstrapping"

Consider the (linear, 1D) Schrödinger-like problem:

$$-\frac{1}{2}\psi'' + V\psi = E\psi \quad \Rightarrow \psi'' = -2(V-E)\psi$$

where $V \in C^\infty_{per}$.

Then $\psi'' = -2(V-E)\psi$ (*)

Integrate:

$$\psi' = -2\int_0 (V-E)\psi + c$$

$\psi \in L^2_{per}$ & $(V-E)$ bounded $\Rightarrow (V-E)\psi$ integrable

$\Rightarrow \psi' \in C^0_{per}$

$\Rightarrow \psi \in C^1_{per}$ (same trick)

$\Rightarrow V\psi \in C^1_{per}$

$\Rightarrow \psi'' \in C^1_{per}$ (from (*))

$\Rightarrow \psi \in C^3_{per}$

$\vdots$

$\psi \in C^\infty_{per}$

Regularity and Fourier decay

$$u(x) = \sum_{G \in L^*} \hat{u}_G \, e_G(x)$$

$$\frac{d^m u}{dx^m}(x) = \sum_{G \in L^*} (-iG)^m \hat{u}_G \, e_G(x)$$

Parseval's thm:

$$\left\| \frac{d^m u}{dx^m} \right\|^2_{L^2_{per}} = \sum_{G \in L^*} |G|^{2m} |\hat{u}_G|^2$$

$$\Rightarrow \forall G \in L^*, \; m \in \mathbb{N}: \quad \left\| \frac{d^m u}{dx^m} \right\|_{L^2_{per}} \geq |G|^m |\hat{u}_G|$$

$$\Rightarrow |\hat{u}_G| \leq \frac{\left\| \frac{d^m u}{dx^m} \right\|_{L^2_{per}}}{|G|^m}$$

$\Rightarrow$ Fourier coeff decay faster than all polynomials

$\Rightarrow$ Expect small E_{cut} sufficient.

Pseudopotentials

- Coulomb potential $\notin C^\infty_{per}$ & not bounded!
- Do we really need to treat all electrons?
  - ↳ Silicon: $14e^-$, but only 4 valence
  - ↳ core electrons do not change much between molecule, atom, crystal, ...
- Idea of pseudopotentials:
  - ↳ effective potential that models sum of nuclear attraction & core electron repulsion
  - ↳ modifies wavefct ψ, exact only outside core region.
- For some pseudopotentials (e.g. GTH) C^∞_{per} & bounded is bounded & leads to error estimate
- With pseudos V splits into local & non-local term

$$D(V_{Hxc}) = \mathbb{1}_{(-\infty, \varepsilon_F]}\left(-\frac{1}{2}\Delta + V_e + V_{nl} + V_{Hxc}\right)$$

Periodicity, supercells & k-points

- Previously we assumed ψ_i to be $\mathbb{L}$-periodic
- It turns out this is too restrictive
  → Rationalization: Physical quantities depend on $|\psi_i|^2$ ⇒ phase degree of freedom
- Phase results from interaction of waves across cells

⇒ Ansatz: Solve problem in a supercell:

single cell	↪	M^3 copies
N electrons		NM^3 electrons
$\Omega = \left(-\frac{a}{2}, \frac{a}{2}\right)^3$		$\Omega_M = \left(-\frac{a}{2}, \frac{a}{2}\right)^3$
$\mathbb{L} = a\mathbb{Z}^3$		$\mathbb{L}_M = (aM)\mathbb{Z}^3$
$\mathbb{L}^* = \frac{2\pi}{a}\mathbb{Z}^3$		$\mathbb{L}_M^* = \frac{2\pi}{aM}\mathbb{Z}^3$

- Full solution to $\mathbb{L}$-periodic problem, i.e. problem where $V_{el} + V_{nl}$ are $\mathbb{L}$-periodic:
  — Solve SCF assuming $\mathbb{L}_M$-periodicity for ψ_i
  — Let $M \to \infty$
- In practice: $M \simeq 4$ to $M \simeq 20$ sufficient
- But: M^3 supercell around $O(M^6)$ times more expensive than single cell.
- Let's try to avoid the extra cost...

- Assume no spontaneous symmetry breaking

  $\Rightarrow$ ρ_* & $D(V_{Hxc}(\rho_*))$ are $\mathbb{L}$-periodic

  $\Rightarrow$ so $V_{Hxc}(\rho_*)$ is also $\mathbb{L}$-periodic

  $\Rightarrow$ $H_{\rho_*} = -\frac{1}{2}\Delta + V_e + V_{ne} + V_{Hxc}(\rho_*)$ $\mathbb{L}$-periodic

  i.e. invariant wrt. $\mathbb{L}$-translation group, an abelian group $\mathcal{G}$ of order M^3 on $L^2_{per}(\Omega_M)$

Group elements: For $R \in \mathbb{L}$ denote

- $T_R : L^2_{per}(\Omega) \to L^2_{per}(\Omega)$

  R-translation operator, i.e.

  $\forall \psi \in L^2_{per}(\Omega_M) \quad (T_R\psi)(r) = \psi(r-R)$

- there are M^3 of these since

  $\forall R \in \mathbb{L}, R_M \in \mathbb{L}_M : T_{R+R_M} = T_R$

- We discretize H_{ρ_*} in approx. space

  $\mathcal{X}_M = \text{span}\left(e_{G_M}, G_M \in \mathbb{L}^*_{M,cut}\right)$

  $\mathbb{L}^*_{M,cut} = \left\{ G_M \in \mathbb{L}^*_M \mid \frac{|G_M|^2}{2} \le E_{cut} \right\}$

  to get H_M.

- For all $R \in \mathbb{L}$ & $G_M \in \mathbb{L}^*_M$

$$\left(T_R\, e_{G_M}\right)(r) = \frac{e^{iG_M\cdot(r-R)}}{\sqrt{\Omega_M}} = e^{-iG_M\cdot R}\, e_{G_M}(r)$$

$\Rightarrow$ e_{G_M} are eigenfct^n of T_R with eval

- Any $G_M \in \mathbb{L}^*_M$ can be uniquely decomposed

$$G_M = G + K \quad \text{with} \quad G \in \mathbb{L}^*$$
$$\& \; K \in \left[-\tfrac{\pi}{a}, \tfrac{\pi}{a}\right)^3$$
$$\& \; e^{-iG_M\cdot R} = e^{-iK\cdot R}$$

- We denote:
  - $\Omega^* := \left[-\frac{\pi}{a}, \frac{\pi}{a}\right)^3$ is the 1st BZ
  - $K \in \mathbb{B}^*_M \equiv \Omega^* \cap \mathbb{L}^*_M$ which is a regular grid of M^3 points (Monkhorst-Pack grid)

$\Rightarrow$ $\mathcal{X}_M$ is T_R - invariant $\forall R \in \mathbb{L}$. For each $R \in \mathbb{L}$ (jointly) the eigenspaces corresponding to T_R in $\mathcal{X}_M$ are:

$$\mathcal{X}_K = \text{span}\left(e_{K+G},\, G \in \mathbb{L}^*_{K,\text{cut}}\right);$$

$$\mathbb{L}^*_{K,\text{cut}} = \left\{G \in \mathbb{L}^* \;,\; \frac{|G+K|^2}{2} \le E_{\text{cut}}\right\}$$

where

$$\forall R \in \mathbb{L},\ \forall \psi_K \in \mathcal{X}_K \qquad \left(T_R \psi_K\right)(r) = e^{-ik\cdot R} \psi_K(r)$$

$\Rightarrow$ any $\psi_K \in \mathcal{X}_K$ is of the form

$$\boxed{\psi_K(r) = e^{ikr}\, u(r)}$$

Bloch decomposition

with $u(r) \in \mathcal{X}_K^{per} = \mathrm{span}\left(e_G,\ G \in \mathbb{L}^*_{K,cut}\right)$

$\subset L^2_{per}(\Omega)$

Recall H_{g*} is $\mathbb{L}$-translation invariant

$\Rightarrow$ it commutes with T_R, $R \in \mathbb{L}$

$\Rightarrow$ its approx^n in $\mathcal{X}_M$ is block-diagonal in decomposition

$$\mathcal{X}_M = \bigoplus_{K \in \mathbb{B}^*_M} \mathcal{X}_K^{per}$$

"gather all G_M's with the same k-point"

$$H_{g*}\big|_{\mathcal{X}_M} = \begin{pmatrix} H_{K_1} & & & 0 \\ & H_{K_2} & & \\ & & H_{K_3} & \\ & & & \ddots \\ 0 & & & H_{K_{M^3}} \end{pmatrix}$$

- The entries of the H_K are

$$[H_K]_{GG'} = \langle e_{K+G} | H_{\rho^*} | e_{K+G'} \rangle \qquad G, G' \in \mathbb{L}^*_{K,\text{cut}}$$

$$= \delta_{GG'} \frac{|G+k|^2}{2} + \langle e_{K+G} | V_{ne} | e_{K+G'} \rangle$$

$$+ \underbrace{\langle e_G | V_e + V_{Hxc}(\rho_K) | e_{G'} \rangle}_{K \text{ independent}}$$

Thermodynamic limit: What happens for $M \to \infty$

the operator

$$H_{\rho^*} = -\frac{1}{2}\Delta + V_e + V_{ne} + V_{Hxc}(\rho^*)$$

is $\mathbb{L}$-periodic, self-adjoint on $L^2(\mathbb{R}^3)$ given

$$P^* = \mathbb{1}_{(-\infty, \varepsilon_F]}(H_{\rho^*}) \qquad \text{GS density matrix}$$

$$\rho^* = \text{diag } P^*, \quad \int_\Omega \rho^* = N$$

Using the Bloch transform

$$H_{\rho^*, K} = \frac{1}{2}(-\nabla + k)^2 + V_e + V_{ne,K} + V_{Hxc}(\rho^*)$$

is self-adjoint on $L^2_{per}(\Omega)$

$$H_{\rho^*, K} = \sum_{n=1}^{\infty} \varepsilon_{nK} |u_{nK}\rangle\langle u_{nK}| \qquad \delta_{mn} = \langle u_{mK} | u_{nK} \rangle_{L^2_{per}}$$

$$\rho^*(r) = \int_{\mathbb{L}^*} \sum_{n=1}^{\infty} \mathbb{1}_{\varepsilon_{nK} \le \varepsilon_F} |u_{nK}(r)|^2 \, dk,$$

$$\int_\Omega \rho^* \, dr = N$$

Temperature

- For modelling some materials the energetic gap between states near ε_F is small
- $\mathbb{1}_{(-\infty, \varepsilon_F]}(H_{g^*})$ difficult to capture numerically.

$\Rightarrow$ instead of step function use blurred step

$$f_{\varepsilon_F}(x) = \frac{1}{1 + e^{\frac{x - \varepsilon_F}{T}}}$$

with parameter T

Denser

$\Rightarrow$ modified SCF problem

$$D(V_{Hxc}(\rho)) = \rho$$

$$D(V_{Hxc}) = \operatorname{diag}\left[f_{\varepsilon_F}\left(-\tfrac{1}{2}\Delta + V_e + V_{ne} + V_{Hxc} \right) \right]$$

where ε_F s.t. $\int_\Omega D(V_{Hxc}) = N$

Exercise:
- Day 1 / Intro periodic problems
- Day 2 / Discretization & convergence
- Day 2 / Pseudopotentials

Discuss SCF convergence & preconditioning notebook

Exercise:
- Day 2 / SCF algorithms
- Day 2 / Analysis SCF convergence
- DFTK tutorials & examples