[0]: Schedule

[E]:

Exercise 04
MACC - SS22

30.05.22 ⓐ
Lambert Theisen

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[0]

Orga: → Note changed lecture/exercise dates

→ HW4 has 3 weeks to complete

→ Any other questions?

Lectures

- Mo 23 May 14:30 - 16:00
- Tu 31 May 16:30 - 18:00
- Mo 13 June 14:30 - 16:00
- Tu 14 June 16:30 - 18:00
- Tu 28 June 16:30 - 18:00
- Mo 11 July 14:30 - 16:00

Exercises

- Tu 17 May 16:30 - 18:00
- Mo 30 May 14:30 - 16:00
- Mo 20 June 14:30 - 16:00
- Mo 04 July 14:30 - 16:00

[E1]: **DFT Operator Minimization**

Hamiltonian: $\mathcal{H}: H^2(\Omega) \cap H_0^1(\Omega) \subset L^2(\Omega) \to L^2(\Omega)$

- $\Omega \subset \mathbb{R}^3$
- $N \in \mathbb{R}$
- $V \in L^2(\Omega)$

$$\forall u \in H^2(\Omega) : \mathcal{H}u := -\frac{1}{2}\Delta u + Vu$$

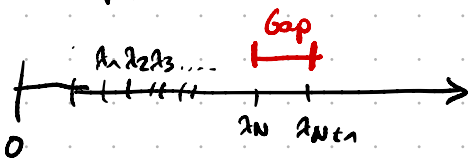
→ Space: $H^2 \cap H_0^1$ has L^2-integrable second derivatives and first derivative integrates to zero on $\partial\Omega$.

→ $\mathcal{H}$ is self-adjoint, bounded below & has compact resolvent

Thus $\exists$ non-decreasing $\{\lambda_i\}_{i\geq 0}$, $\lambda_i \in \mathbb{R}$ and ONB $\{\phi_i\}_{i\geq 0} \in L^2(\Omega)$ s.t.

$$\mathcal{H}\phi_i = \lambda_i \phi_i \qquad \checkmark > 0$$

→ Assume "gap condition": $\lambda_{N+1} - \lambda_N > 0$



Bounded linear Operators: $\mathcal{L}(L^2(\Omega))$ is set of bounded, linear operators $A: L^2(\Omega) \to L^2(\Omega)$

Linearity: $A(\alpha u + \beta v) = \alpha A(u) + \beta A(v)$

Boundedness: $\|Au\|_{L^2} \leq M \|u\|_{L^2} \quad \forall u \in L^2, \; M > 0$

Positivity: $\forall u \in L^2(\Omega): \quad \langle u, Au \rangle_{L^2} \geq 0$

→ e.g. Let $B: L^2 \to L^2$, $Bu = 2 \cdot u$. Then $\|Bu\|_{L^2} = \sqrt{\int_\Omega (2u)^2} \leq \underbrace{\sqrt{4}}_{M \text{ Boundedness}} \sqrt{\int_\Omega u^2} = 2\|u\|_{L^2}$ ✓

And $B(\alpha u + \beta v) = 2(\alpha u + \beta v) = \alpha 2u + \beta 2v = \alpha B(u) + \beta B(v)$ ✓ Linear

And $\underbrace{\langle u, Bu \rangle_{L^2}}_{\langle u, u \rangle_{L^2}} = \sqrt{\int_\Omega u(2u)} = \sqrt{2}\sqrt{\int_\Omega u^2} = \sqrt{2}\|u\|_{L^2} \geq 0$ Since norm is semi-positive ✓ positivity

Trace of matrix: For $A = \begin{bmatrix} a_{11} & \cdots & \\ a_{21} & & \\ \vdots & & \\ & & a_{NN} \end{bmatrix}$ $\quad tr(A) = \sum_{i=1}^{N} a_{ii}$

$$tr\begin{pmatrix} 1 & 100 \\ 500 & 2 \end{pmatrix} = 1+2 = 3$$

Trace of operator:

For positive $A \in \mathcal{L}(L^2(\Omega))$: $\quad Tr(A) := \sum_{n \in \mathbb{N}} \underbrace{\langle e_n | A e_n \rangle}_{= \langle \phi_n | A \phi_n \rangle} \in \mathbb{R}_+ \cup \{+\infty\}$

with $\{e_n\}_{n \in \mathbb{N}}$ is ONB of $L^2(\Omega)$. Trace is indep. of choice of $\{e_n\}$

Wave-Function Minimization

→ **energy functional:** $\mathcal{E}: [H^1(\Omega)]^N \to \mathbb{R}$, $\quad \Psi = (\psi_1, \psi_2, \dots)^T \in [H^1(\Omega)]^N$

$$\mathcal{E}(\Psi) = \sum_{i=1}^{N} \langle \psi_i | \mathcal{H} | \psi_i \rangle = \sum_{i=1}^{N} \left(\int_\Omega |\nabla \psi_i(x)|^2 dx + \int_\Omega v(x) |\psi_i(x)|^2 dx \right)$$

→ **admissible wave-functions:** $\mathcal{M} := \left\{ \Psi = (\psi_1, \psi_2, \dots)^T \in [H^1(\Omega)]^N : \int_\Omega \psi_i \psi_j = \delta_{ij} \right\}$

→ **ground-state energy:** $\quad \mathcal{E}_0 = \inf\{ \mathcal{E}(\Psi) : \Psi \in \mathcal{M} \} \quad (1)$

Density operator Minimization

$\gamma \in \mathcal{L}(L^2(\Omega))$, $\quad \gamma = \gamma^* \quad$ (self-adjoint)

$\gamma = \gamma^2 \quad$ (idempotent) "same" "power"

→ **Adm. Set of DOs:** $\mathcal{P} := \{ \gamma \in \mathcal{L}(L^2(\Omega)) \mid \gamma^* = \gamma,\ \gamma^2 = \gamma,\ Tr(\gamma) = N,\ Tr(-\Delta\gamma) < \infty \}$

with definition $Tr(-\Delta\gamma) := Tr(\underbrace{|\nabla| \gamma |\nabla|}_{\text{bounded + positive}})$ $\qquad |\nabla| \hat{=} \sqrt{-\Delta}$

Like $\pm \partial_{xx} \hat{=} \underbrace{\begin{bmatrix} 2 & -1 & \\ -1 & 2 & -1 \\ & \ddots & \ddots \end{bmatrix}}_{=:A,\ A>0} = \sqrt{A} \cdot \sqrt{A}$ (Finite Differences)

Eigen

Energy Functional $\quad E(\gamma) := \frac{1}{2} Tr(-\Delta\gamma) + Tr(\gamma V)$

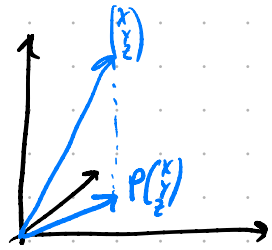
$$E_0 := \inf\{ E(\gamma) : \gamma \in \mathcal{P} \} \quad (2)$$

Equivalence: (1) is equiv. to (2) $\Rightarrow \mathcal{E}_0 = E_0$

E1a) Show that $\forall \gamma \in \mathcal{T}$, γ is $\underbrace{\text{orthogonal projection}}_{\text{OP}}$ $\qquad \gamma^2 = \gamma$

$\rightarrow$ OP: $\forall u,v \in L^2(\Omega)$ $\quad (u, \gamma v)_{L^2} = (\gamma u, \gamma v)_{L^2} = (\gamma u, v)_{L^2}$, $\gamma = \gamma^*$ $\quad$ (if this doesn't hold, then it would be oblique projection)

Example in finite dims: $P = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$, $P\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ 0 \end{pmatrix}$ $\quad \langle Ax, y \rangle = \langle x, A^T y \rangle$



$$\left\langle P\begin{pmatrix} x \\ y \\ z \end{pmatrix}, \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \right\rangle = \left\langle \begin{pmatrix} x \\ y \\ 0 \end{pmatrix}, \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \right\rangle = x\alpha + y\beta = \left\langle \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \begin{pmatrix} \alpha \\ \beta \\ 0 \end{pmatrix} \right\rangle = \left\langle \begin{pmatrix} x \\ y \\ z \end{pmatrix}, P\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \right\rangle$$

E1b): To show: GS density operator $\gamma_0 \in \mathcal{T}$, $\gamma_0 := \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i|$ $\quad$ eigenfunctions of $\mathcal{H}$

is orthogonal projection onto $\operatorname{span}\{\phi_i\} \subset L^2(\Omega)$.

$\rightarrow$ Show that $(\gamma_0 u, v)_{L^2} = (u, \gamma_0 v)_{L^2}$ $\quad \forall u,v \in L^2(\Omega)$

$\rightarrow$ Write u, v in Eigen basis: $\quad u = \sum_{j=1}^{\infty} u_j |\phi_j\rangle$ $\quad$ basis coeff

$$v = \sum_{j=1}^{\infty} v_j |\phi_j\rangle$$

and insert. E.g. $\gamma_0 u \overset{\text{Def.}}{=} \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i| \left(\sum_{j=1}^{\infty} u_j |\phi_j\rangle \right) = \sum_{i=1}^{N} \sum_{j=1}^{\infty} |\phi_i\rangle\, u_j \langle\phi_i|\phi_j\rangle = \ldots$

E1c): Show that $\operatorname{Tr}(-\Delta\gamma_0) = \sum_{i=1}^{N} \int_\Omega |\nabla\phi_i|^2 dx$, which requirement for ϕ_i s.t. $\operatorname{Tr}(-\Delta\gamma_0) < \infty$?

$\rightarrow$ Use Definition $\operatorname{Tr}(\Delta\gamma_0) = \operatorname{Tr}\left(|\nabla| \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i| \, |\nabla| \right)$

$$= \sum_{n \in \mathbb{N}} \langle e_n | \, |\nabla| \sum_{i=1}^{N} |\phi_i\rangle\langle\phi_i| \, |\nabla| \, | e_n \rangle$$

$$= \ldots$$

$\rightarrow$ Pick $\{e_n\}$ to be Fourier basis such that, e.g., $\langle \phi_i | |\nabla| e_n \rangle = \langle \phi_i | n e_n \rangle$

Also expand ϕ_i in Fourier basis to get, e.g. $\langle e_n | |\nabla| \phi_i \rangle = \langle e_n | \sum_{k=1}^{\infty} k \hat{\phi}_{ik} e_k \rangle = n \hat{\phi}_{in}$

E1d): Also use Fourier basis and the definition

E2 **Pair-Density** Kohn-Sham DFT $\hat{=}$ minimization over wave functions can be equivalent to minimization over suitable class of electronic densities.

not the same as in Hartree-Fock $\Rightarrow$ just artificial

→ Electronic Density of the Kohn-Sham orbitals: $\rho_\Psi = \sum_{j=1}^{N} |\psi_j|^2$ with $\Psi = \{\psi_1, \psi_2, \dots, \psi_N\}$

→ Assumption was that electrons are non-interacting and corresp. wave function can be expressed as Slater determinant.

→ Thus, kinetic operator T has $\langle \Psi | T | \Psi \rangle = \sum_{j=1}^{N} \int_{\mathbb{R}^3} |\nabla \psi_j|^2$

→ Coloumb energy: $J(\rho_\Psi) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_\Psi(x)\rho_\Psi(y)}{|x-y|} dx dy$

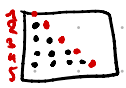
→ All many-body effects go into exchange-correlation functional E_{xc}

Pair Density Probability to find an electron at x and y simultaneously.

$\frac{n!}{k!(n-k)!} \approx \frac{N!}{2(N-2)!} = \frac{N(N-1)}{2}$

$$\gamma(x,y) = \binom{N}{2} \int_{\mathbb{R}^{3(N-2)}} |\Psi(x, y, x_3, \dots, x_N)|^2 dx_3 \dots dx_N$$

$\sum_{i=1}^{N-1} i$ kleines Gauß, lower diag



$\frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}} \frac{1}{|x_i - x_j|}$ Coulomb-Op.

E2a) Show that $\langle \Psi | V_{ee} | \Psi \rangle = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\gamma_\Psi(x,y)}{|x-y|} dx dy$

→ Insert V_{ee}, use Definition of expectation value $\langle \Psi | V_{ee} | \Psi \rangle$, split $3N = 3(N-2) + 6$ integrals recognize expression for $\gamma(x,y)$

E2b) easy, just insert. Hartree Functional $J(\rho) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy \approx \langle \Psi | V_{ee} | \Psi \rangle$

E2c) Use similar strategy as in HW2

E2d) Insert and use c)