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MACC Exercise 03
SS 2022

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O: → Dates changed → See Moodle email

→ Everything ok?

→ Request samples solutions

weak solution

E1 Hartree - Fock Discretization

Electronic Schrödinger Eq.

anti-symmetric see last ex.

weil kinetischer Term braucht Gradient

→ Define space of wave-functions $W_N := \left\{ u \in L^2_{as}(\mathbb{R}^{3N}) \cap H^1(\mathbb{R}^{3N}) \;\middle|\; \|u\|_{L^2} = 1 \right\}$

Diag cancels out

→ Hamiltonian Op: $\mathcal{H} := \sum_{i=1}^N \left(-\frac{1}{2} \Delta_{x_j} - \sum_{\alpha=1}^M \frac{Z_\alpha}{|R_\alpha - x_j|} \right) + \frac{1}{2} \sum_{i,j=1}^N \frac{1}{|x_i - x_j|}$

→ Ground state: $E_0 = \inf_{\Psi \in W_N} \langle \Psi, \mathcal{H}\Psi \rangle = \inf_{\Psi \in L^2_{as} \cap H^1} \frac{\langle \Psi, \mathcal{H}\Psi \rangle}{\langle \Psi, \Psi \rangle}$

c.f. Rayleigh-Quotient

→ HF space $V_{HF} := \left\{ \Psi = \{\varphi_1, \dots, \varphi_N\} : \langle \varphi_i, \varphi_j \rangle_{L^2} = \delta_{ij} \right\}$

↳ Simplifies equations:

$$\forall j = 1\dots N,\ \forall \psi \in H^1(\mathbb{R}^3): \ \frac{1}{2} \int_{\mathbb{R}^3} \nabla\varphi_j(x) \cdot \nabla\psi(x) + \int_{\mathbb{R}^3} \left[V(x)\, \varphi_j(x) + \sum_{i=1}^N \int_{\mathbb{R}^3} \frac{|\varphi_i(y)|^2}{|x-y|} dy\, \varphi_j(x) \right.$$

$$\left. - \sum_{i=1}^N \int_{\mathbb{R}^3} \frac{\varphi_i(y)\, \varphi_j(y)}{|x-y|} dy\, \varphi_i(x) \right] \psi(x)\, dx =$$

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

1a) → Use $V(x) = \sum_{\alpha=1}^M \frac{Z_\alpha}{|R_\alpha - x|}$

→ Use $i=1$ and insert into HF eqs.

→ Derive 1st order optimality cond. of Euler-Lagrange of ES eq.

E1) b) → $N_\delta = 1$

Discretization: $\varphi_i^\delta = \sum_{\mu=1}^{N_\delta} C_{\mu j}\chi_\mu$ ← Basis fct.

Coefficient matrix: $C \in \mathbb{R}^{N_\delta \times N}$, $C_{\mu j} \hat{=}$ coeff of j-th orbital and μ-th Basis

Overlap (Mass) Matrix: $S \in \mathbb{R}^{N_\delta \times N_\delta}$, $S_{\mu,\nu} = \langle \chi_\mu, \chi_\nu \rangle$

Density matrix $D \in \mathbb{R}^{\nu \times \mu}$, $D_{\mu\nu} = \sum_{i=1}^{N} C_{\mu i} C_{\nu i}$

Fock-Matrix: $F(D) = h_{\mu\nu} + \sum_{\nu'=1}^{N_\delta} \sum_{\mu'=1}^{N_\delta} \left[(\mu\nu|\mu'\nu') - (\mu\nu'|\mu'\nu)\right] D_{\nu',\mu'}$

$$\langle \mu\nu, \mu'\nu' \rangle = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\chi_\mu(x)\chi_\nu(x)\chi_{\mu'}(y)\chi_{\nu'}(y)}{|x-y|}\,dx\,dy$$

E.g. for $N_\delta = 2$:
$$F(D) = \begin{bmatrix} \frac{1}{2}\langle \nabla\chi_1, \nabla\chi_2\rangle + V\langle \chi_1, \chi_1\rangle & \dots \\ \frac{1}{2}\langle \nabla\chi_1, \nabla\chi_2\rangle + V\langle \chi_1, \chi_2\rangle & \dots \end{bmatrix}$$
$$+ \begin{bmatrix} \langle 11|22\rangle - \langle 12|21\rangle & \langle 12|21\rangle - \langle 11|22\rangle \\ \langle 12|21\rangle - \langle 11|22\rangle & \langle 11|22\rangle - \langle 12|21\rangle \end{bmatrix} \circ \underbrace{\begin{bmatrix} C_1^2 & C_1C_2 \\ C_1C_2 & C_2^2 \end{bmatrix}}_{D}$$

1b): Calc all matrices and then compare HF to ES

E2 **Regularity Coloumb:**

$f: \mathbb{R}^3 \setminus \{0\} \to \mathbb{R}$

to show: $V_{\text{nuclei-electron}} \in L^{3/2} + L^\infty$ wit $V_{ne} := f(x) = \frac{1}{|x|}$

→ I.e. find $u \in L^{3/2}(\mathbb{R}^3)$, $v \in L^\infty(\mathbb{R}^3)$ s.t. $f(x) = u(x) + v(x)$

$p=2$, $p=1.5$

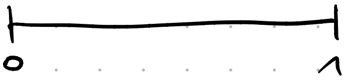
Spaces: $L^{3/2}(\mathbb{R}^3) := \left\{ f \;\middle|\; \|f\|_{L^{3/2}}^{2/3} := \int_{\mathbb{R}^3} |f(x)|^{3/2}\,dx < \infty \right\}$

$L^\infty(\mathbb{R}^3) := \{ f \mid \|f\|_\infty < \infty \}$, $\|f\|_\infty := \inf\{ C \geq 0 \mid |f(x)| \leq C \text{ a.e.} \}$

E2

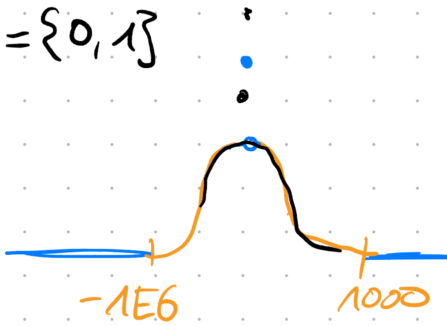
- Try Yukawa potential $u(x) = \underbrace{\frac{e^{-|x|}}{|x|}}_{\in L^{3/2}} + \underbrace{\frac{-e^{-|x|}+1}{|x|}}_{L^\infty}$ $\;=0$
- Use spherical coords for the integrations...

Weak Solutions:



$$(S)\begin{cases} -\underbrace{\Delta \varphi(x)}_{\varphi''(x)} + V(x)\varphi(x) = \overset{\in \mathbb{R}}{\lambda}\varphi(x) & \forall x \in \Omega := (0,1) \\ \varphi(x) = 0 & \text{on } \partial\Omega = \{0,1\} \end{cases}$$

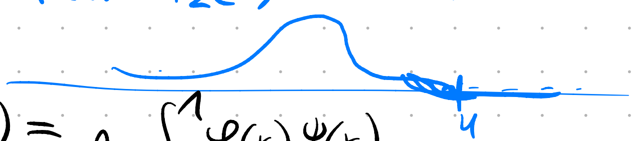
- Multiply (S) with $\psi \in C_0^\infty$ & integrate



$$(\omega)\quad \int_0^1 -\Delta\varphi(x)\cdot\psi(x) + V(x)\varphi(x)\psi(x) = \lambda\int_0^1 \varphi(x)\psi(x) \quad \forall \psi \in C_0^\infty(\Omega)$$

$f \neq 0$ on $(-C, 0)$

$[\psi_1' \psi_2]_{-\infty}^{\infty} = 0$ since $\psi \in C_0^\infty$ means that $\psi_2(x) = 0 \quad x > U$



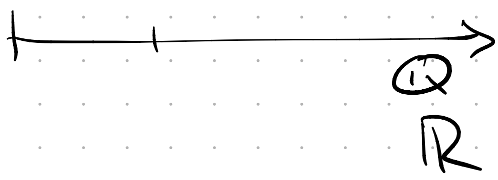
IP

$$\underbrace{\int_0^1 \nabla\varphi(x)\cdot\nabla\psi(x) + \int_0^1 V(x)\varphi(x)\psi(x)}_{a(\varphi,\psi)} = \lambda\int_0^1 \varphi(x)\psi(x)$$

If RHS $\ell(\psi) = \int_0^1 f(x)\cdot\psi(x)$

$a : H^1(\Omega)\times H^1(\Omega) \longrightarrow \mathbb{R}$

Find $\varphi \in H_0^1(\Omega)$ s.t. $\forall \psi \in H_0^1$



$H_0^1 = H^1(\Omega) \cap \{ u \in H^1 \mid u = 0 \}$

I) $a(\varphi,\varphi) = \int_0^1 \nabla\varphi \cdot \nabla\varphi + \int_0^1 V \varphi^2 \geq \int_0^1 \nabla\varphi \cdot \nabla\varphi \; (*)$

Assume $V \geq 0$, $V \in L^\infty$

Friedrichs inequ : $\forall \varphi \in H_0^1(\Omega)$: $\|\nabla\varphi\|_{L^2} \geq C \cdot \|\varphi\|_{L^2}$

$$(*) = \frac{1}{2}\|\nabla\varphi\|_{L^2}^2 + \frac{1}{2}\|\nabla\varphi\|_{L^2}$$

$$\geq \frac{1}{2} \cdot C \|\varphi\|_{L^2}^2 + \frac{1}{2}\|\nabla\varphi\|_{L^2}$$

$$\geq \frac{1}{2} \min\{C, 1\} \underbrace{\|\varphi\|_{L^2}^2 + \|\nabla\varphi\|_{L^2}^2}_{=: \|\varphi\|_{H^1}^2}$$

$$= D \cdot \|\varphi\|_{H^1(\Omega)}^2 \quad \forall \varphi \in V := H_0^1(\Omega)$$

(Coercivity)

$a(\varphi,\varphi)$

$\geq \quad \varphi \mathrel{\hat{=}} x$

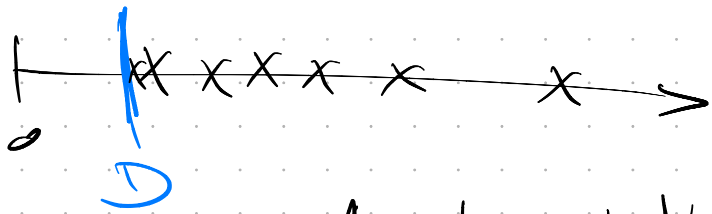
$x^T A x \geq D \, x^T x$

$\Longleftrightarrow \quad \frac{x^T A x}{x^T x} = R_A(x) \geq D$

$\Rightarrow \lambda_1 \geq D$

$\min_x R_A(x) = \lambda_1$

$A^T = A$



$Ax = b$ solvable?

$\det(A) \neq 0$

A regular

$\det A = \lambda_1 \cdot \lambda_2 \cdot \lambda_3 \cdot \ldots$

Iff $\lambda_i \geq D \Rightarrow \det(A) \neq 0$

$\Rightarrow Ax = b$ has a solution

$V \in L^\infty$

II) $a(\varphi,\psi) \leq C \cdot \|\varphi\|_{H^1} \cdot \|\psi\|_{H^1}$ Continuity

$$a(\varphi,\psi) = \int_0^1 \nabla\varphi \cdot \nabla\psi + \int_0^1 \underbrace{V(x)}_{\leq C} \varphi(x)\, \psi(x)$$

$$\leq \langle \nabla\varphi, \nabla\psi \rangle_{L^2((0,1))} + C \langle \varphi, \psi \rangle_{L^2(\Omega)}$$

Cauchy Schwarz Ineq.

$$\leq 1 \cdot \|\nabla\varphi\|_{L^2} \cdot \|\nabla\psi\|_{L^2} + C \cdot \|\varphi\|_{L^2} \cdot \|\psi\|_{L^2}$$

$$\leq \underbrace{\max\{1, C\}}_{= D} \left(\|\nabla\varphi\| \|\nabla\psi\|_{L^2} + \|\varphi\|_{L^2} \cdot \|\psi\|_{L^2} \right)$$

$\mathbb{R}^3$ x y z

$\|\nabla\varphi\|^2 \|\nabla\psi\|_L^2 +$ $(x^2+y^2+z^2)^{1/2}$

$<$ Add crossterms $\|\varphi\|_{L^2} \|\nabla\psi\|_{L^2} \geq 0$

$$\leq \|\varphi\|_{H^1} \cdot \|\psi\|_{H^1}$$

$$= \big(\underbrace{\|\varphi\|^2_{L^2}}_{a} + \underbrace{\|\nabla\varphi\|^2_{L^2}}_{b} \big)^{1/2} \cdot \big(\underbrace{\|\psi\|^2_{L^2}}_{c} + \underbrace{\|\nabla\varphi\|^2_{L^2}}_{d} \big)^{1/2} \leftarrow \sqrt{(a+b)(c+d)}$$

$\sqrt{ac+ad+bc+bd}$

$V \in L^\infty \iff \|V\|_{L^\infty(\Omega)} < \infty$

$\in C^0$ $\quad \|V\|_{L^\infty(\Omega)} := \{ C \in \mathbb{R} \mid |V(x)| \leq C \ \underbrace{\forall x \in \Omega \text{ a.e.}}_{\forall x \in \Omega \setminus N} \}$

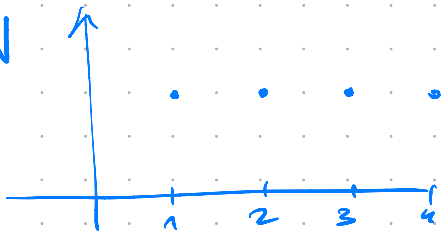
$\text{meas}(N) = 0$

L^2

e.g $N = \{1\}$

$N = \mathbb{N}$

$\text{meas}_{\mathbb{R}}(\mathbb{N})$



$\text{meas}(N) = 0$

$$\iff \int_\Omega f\,dx = \int_\Omega \begin{cases} 10 & \text{if } x \in N \\ f & \text{else} \end{cases} dx$$

III) $a(\varphi,\psi) = \ell(\psi)$

$\ell(\psi) = \int_0^1 f \cdot \psi \overset{C.S.}{\leq} C \cdot \|\psi\|$ if f is regular enough

$\Rightarrow$ Lax-Milgram tells us that there exists a unique $\underline{\varphi \in H_0^1(\Omega)}$ st. weak form is fulfilled.

Weak form