$\boxed{O}$:

$\boxed{E}$

MACC Exercise 02
SS 2022

Lambert Theisen
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$\boxed{O}$: Orga : → Everything okay ?

$\boxed{E1}$ Heisenberg's Uncertainty Principle:

$$\overline{a+ib} = a-ib$$

Space $L^2(\mathbb{R},\mathbb{C})$: with all $f:\mathbb{R}\to\mathbb{C}$ s.t. $\|f\|_{L^2}^2 := \int_{\mathbb{R}} \overline{f(x)}\, f(x)\, dx < \infty$

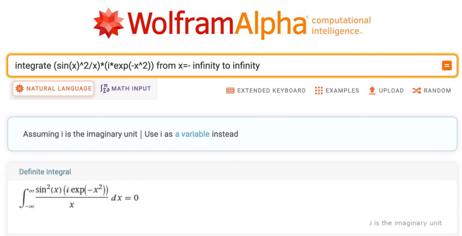
→ E.g. $f(x) := i e^{-x^2} \in L^2(\mathbb{R},\mathbb{C})$ since $\|f\|_{L^2}^2 = \int_{\mathbb{R}} (-ie^{-x^2})(ie^{-x^2})\, dx$ $\quad i^2 = -1$

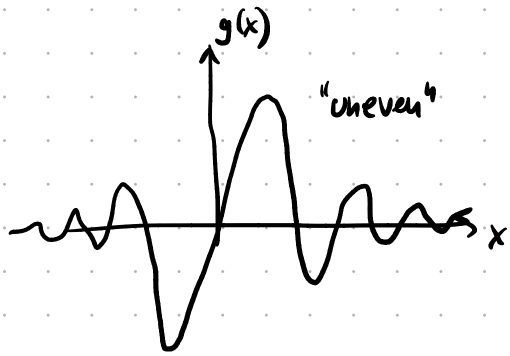
$$= \int_{\mathbb{R}} e^{-2x^2} dx = \sqrt{\frac{\pi}{2}} < \infty$$

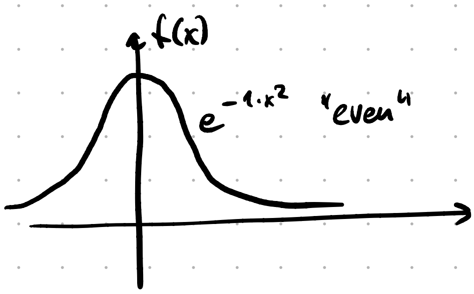
→ **Skalarprodukt:** $\langle f,g\rangle_{L^2} := \int_{\mathbb{R}} \overline{f(x)}\, g(x)\, dx \quad \forall f,g \in L^2(\mathbb{R},\mathbb{C})$

- **Orthogonality** $\Leftrightarrow \langle f,g\rangle_{L^2} = 0$, Example $g(x) := \frac{\sin(x)^2}{x}$, $f(x)$ as above

Then $\langle g,f\rangle_{L^2} = \int_{\mathbb{R}} \overline{\left(\frac{\sin(x)^2}{x}\right)} \cdot (ie^{-x^2})\, dx = 0$







Cauchy-Schwarz $|\langle f,g\rangle| \le \|f\| \cdot \|g\|$

Hat $\hat{=}$ Fourier-Transform

Fourier-Transform: $\forall f \in L^2(\mathbb{R},\mathbb{C})$, $\hat{f}(\omega) := \int_{-\infty}^{\infty} e^{-2\pi i\cdot\omega\cdot x} f(x)\, dx$

→ Plancherel: $\langle f,g\rangle = \langle \hat{f},\hat{g}\rangle$, $\|f\| = \|\hat{f}\|$ $\quad (\Rightarrow \hat{f} \in L^2)$

②

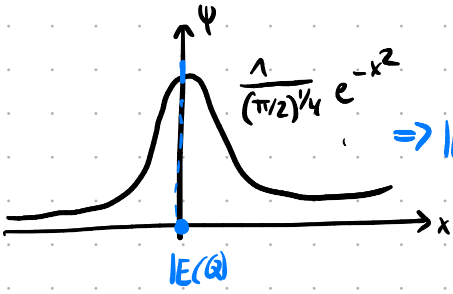
Exercise Framework: ψ wave function $\int_{\mathbb{R}} |\psi(x)|^2 dx = 1$

pos. op. : $Qf(x) = x f(x)$

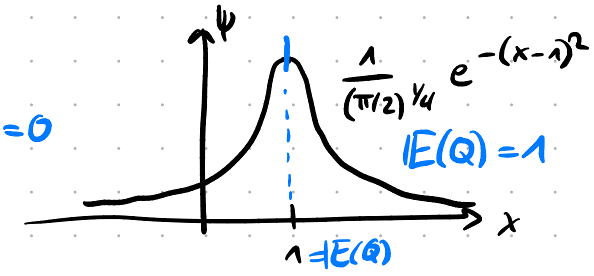
mom. op. : $Pf(x) = \frac{1}{2\pi i} \frac{\partial}{\partial x} f(x)$

Exp. average pos.:

$$\mathbb{E}(Q) := \langle \psi, Q\psi \rangle_{L^2} = \int_{\mathbb{R}} \bar{\psi}\,(x\psi)\,dx = \int_{\mathbb{R}} x\,\bar{\psi}\psi\,dx = \boxed{\int_{\mathbb{R}} x\,|\psi|^2\,dx}$$



$\Rightarrow \mathbb{E}(Q) = 0$



$\mathbb{E}(Q) = 1$

integrate x*(exp(-(x-1)^2)/(pi/2)^(1/4))^2 from x=- infinity to infinity

NATURAL LANGUAGE MATH INPUT EXTENDED KEYBOARD EXAMPLES

Definite integral

$$\int_{-\infty}^{\infty} x \left(\frac{\exp(-(x-1)^2)}{\sqrt[4]{\frac{\pi}{2}}} \right)^2 dx = 1$$

$\boxed{\xi \,\hat{=}\, \omega}$ for us.

	Function	Fourier transform unitary, ordinary frequency
	$f(x)$	$\hat{f}(\xi) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i x \xi}\, dx$
101	$a \cdot f(x) + b \cdot g(x)$	$a \cdot \hat{f}(\xi) + b \cdot \hat{g}(\xi)$
102	$f(x-a)$	$e^{-2\pi i a \xi} \hat{f}(\xi)$
103	$f(x) e^{iax}$	$\hat{f}\left(\xi - \frac{a}{2\pi}\right)$
104	$f(ax)$	$\frac{1}{\|a\|} \hat{f}\left(\frac{\xi}{a}\right)$
105	$\hat{f}(x)$	$f(-\xi)$
106	$\frac{d^n f(x)}{dx^n}$	$(2\pi i \xi)^n \hat{f}(\xi)$
107	$x^n f(x)$	$\left(\frac{i}{2\pi}\right)^n \frac{d^n \hat{f}(\xi)}{d\xi^n}$
108	$(f * g)(x)$	$\hat{f}(\xi)\hat{g}(\xi)$
109	$f(x)g(x)$	$\left(\hat{f} * \hat{g}\right)(\xi)$
110	For $f(x)$ purely real	$\hat{f}(-\xi) = \overline{\hat{f}(\xi)}$
111	For $f(x)$ purely real and even	$\hat{f}(\xi), \hat{f}($
112	For $f(x)$ purely real and odd	$\hat{f}(\xi), \hat{f}(\omega)$
113	For $f(x)$ purely imaginary	$\hat{f}(-\xi) = -\overline{\hat{f}(\xi)}$
114	$\overline{f(x)}$	$\overline{\hat{f}(-\xi)}$
115	$f(x)\cos(ax)$	$\frac{\hat{f}\left(\xi - \frac{a}{2\pi}\right) + \hat{f}\left(\xi + \frac{a}{2\pi}\right)}{2}$
116	$f(x)\sin(ax)$	$\frac{\hat{f}\left(\xi - \frac{a}{2\pi}\right) - \hat{f}\left(\xi + \frac{a}{2\pi}\right)}{2i}$

a) Derive $\mathbb{E}(P) = \int_{\mathbb{R}} \omega\, |\hat{\psi}(\omega)|^2 d\omega$ Notice smthg.?

$\rightsquigarrow$ Use Plancherel: $\mathbb{E}(P) = \langle \psi, P\psi \rangle_{L^2}$

$$= \langle \hat{\psi}, \widehat{P\psi} \rangle_{L^2}$$

$$= \int_{\mathbb{R}} \bar{\hat{\psi}}(\omega)\, \frac{1}{\cancel{2\pi i}}\, \underbrace{\hat{\psi'}(\omega)}_{(\cancel{2\pi i}\cdot\omega)^1\, \hat{\psi}(\omega)}\, d\omega = \int_{\mathbb{R}} \omega\, \underbrace{\bar{\hat{\psi}}\hat{\psi}}_{|\hat{\psi}|^2}$$

$$= \ldots$$

b) $\mathrm{Var}(Q) := \mathbb{E}\left((Q - \mathbb{E}(Q))^2\right) = \int_{\mathbb{R}} (x - \mathbb{E}(Q))^2 |\psi(x)|^2 dx$

To show: $\mathrm{Var}(P) := \mathbb{E}((P - \mathbb{E}(P))^2) \overset{!}{=} \int_{\mathbb{R}} (\omega - \mathbb{E}(P))^2 |\hat{\psi}(\omega)|^2 d\omega$

$$\langle \psi, [P - \mathbb{E}(P)]\psi \rangle$$

$$\mathrm{Var}(P) = \int \bar{\psi}\, (P - \mathbb{E}(P))^2 \psi$$

$$= \int \bar{\psi}\, [P\cdot P + 2P\,\mathbb{E}(P) + (\mathbb{E}(P))^2]\, \psi$$

$$= \underbrace{\int \bar{\psi}\,(P\cdot P)\psi}_{\substack{\text{Plancherel+} \\ \text{2-Derivative Fourier}}} + \underbrace{\int \bar{\psi}\cdot 2P\,\mathbb{E}(P)\,\psi}_{\substack{\text{Plancherel+} \\ \text{First Deriv. Fourier}}} + \underbrace{\int \bar{\psi}\, \mathbb{E}(P)^2 \psi}_{\text{Plancherel}}$$

$\overset{!}{=} \int \omega^2 |\hat{\psi}(\omega)|^2$ $\quad \overset{!}{=} \int (2\omega\,\mathbb{E}(P))\, |\hat{\psi}(\omega)|^2$ $\quad \overset{!}{=} (\mathbb{E}(P))^2 \int_{\mathbb{R}} |\hat{\psi}|^2 d\omega$

To show: Thm: $\mathrm{Var}(Q) \cdot \mathrm{Var}(P) \geq C > 0 \quad \forall \psi$

c) Change of Vars. $\tilde{x} := x - \mathbb{E}(Q) \rightarrow \mathrm{Var}(Q) = \int_{\mathbb{R}} \tilde{x}^2 \, |\psi_1(\tilde{x})|^2 \, d\tilde{x}$ ③

d) Again change of vars. $(\ldots) \Rightarrow \mathrm{Var}(P) = \int_{\mathbb{R}} \omega^2 \, |\hat{\psi}_2(\omega)|^2 d\omega \;,\; \hat{\psi}_2(\omega) = \hat{\psi}(\omega + \mathbb{E}(P))$

e) Show $|\psi_1(x)| = |\psi_2(x)|$ $\rightsquigarrow$ Use Definition of Fourier

f) Show $|x \overline{f(x)} \, f'(x)| \geq \frac{x}{2} \frac{d}{dx} |f(x)|^2$ $\rightsquigarrow$ Use e.g. $|x \overline{f(x)} \, f'(x)| \geq x \cdot \mathrm{Re}(\overline{f(x)} \, f'(x))$

g) / h) ....

E2 Hartree Fock Theory

Problem:

$$E_0 = \inf_{\substack{\Psi \in L^2_{as}(\mathbb{R}^{3N}, \mathbb{C}) \\ \|\Psi\|_{L^2} = 1}} \underbrace{E(\Psi)}_{:= \langle \Psi, \mathcal{H}\Psi \rangle}$$

is too high dimensional

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

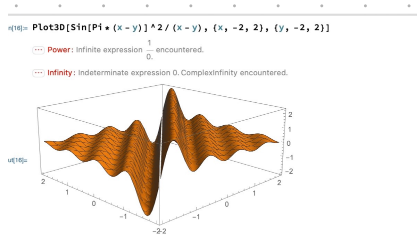
Solution: Replace $L^2_{as}(\mathbb{R}^{3N}, \mathbb{C})$ by simpler Hartree Fock space.

1·N

$$V_{HF} := \left\{ \Psi = |\psi_1, \ldots, \psi_N\rangle : \psi_i \in H^1(\mathbb{R}^3, \mathbb{C}) \;,\; \langle \psi_i, \psi_j \rangle = \delta_{ij} \right\}$$

(just a shorthand)

Slater-Determinant: $|\psi_1, \ldots, \psi_N\rangle := \frac{1}{\sqrt{N!}} \sum_{\sigma} \varepsilon(\sigma) \, \psi_{\sigma(1)}(x_1) \cdot \ldots \cdot \psi_{\sigma(N)}(x_N)$



Determinant

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \cdots & \psi_N(x_1) \\ \vdots & & \vdots \\ \psi_1(x_N) & \cdots & \psi_N(x_N) \end{vmatrix} \in L^2_{as}(\mathbb{R}^{3N}; \mathbb{C})$$

Thus, variationally "conforming" $E_{HF} \geq E_0$

σ is permutation, e.g. $\tilde{\sigma} = (1, 3, 2)$, $\varepsilon(\tilde{\sigma}) = (-1)^1$ since 1 swap needed to go from $(1, 2, 3)$ to $(1, 3, 2)$.

1 3 2

Example simplified: $f(x_1, x_2) := \frac{\sin(\pi(x_1 - x_2))}{\sqrt{2}}$, $f(x_2, x_1) = \frac{\sin(\pi(x_2 - x_1))}{\sqrt{2}} = -\frac{\sin(-\pi(x_2 - x_1))}{\sqrt{2}}$

sin is uneven $\sin(x) = -\sin(-x)$

$$= -\frac{\sin(\pi(x_1 - x_2))}{\sqrt{2}} = -f(x_1, x_2)$$

$\Rightarrow f$ is anti-symmetric

→ Can we write f using SDs? Yes, since:

$$f = \frac{1}{\sqrt{2}} \begin{vmatrix} \sin(x) & \sin(y) \\ \cos(x) & \cos(y) \end{vmatrix} = \frac{1}{\sqrt{2}} \left(\sin(x)\cos(y) - \sin(y)\cos(x) \right) = f(x) \checkmark$$

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In[15]:= Simplify[Sin[x - y]] == Simplify[Cos[y] Sin[x] - Cos[x] Sin[y]]
Out[15]= True
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Advantage:

- Using Slater - Determinant simplifies the optimization problem.

  ⇝ This is the exercise task.

a) Show that for $\Psi := |\psi_1, \dots, \psi_N\rangle$, $\rho_\Psi(x) = \sum_{i=1}^{N} |\psi_i(x)|^2$

⇝ Insert Definition...

$$\rho_\Psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(x, x_2, \dots, x_N)|^2 dx_2 \dots dx_N$$

$$= \frac{N}{N!} \int_{\mathbb{R}^{3(N-1)}} \left[\sum_\pi \left(\operatorname{sgn}(\pi)\, \psi^*_{\pi(1)}(x)\, \psi^*_{\pi(2)}(x_2) \cdots \psi^*_{\pi(N)}(x_N) \right) \right] \cdot \left[\sum_\mu \left(\operatorname{sgn}(\mu)\, \psi_{\mu(1)}(x) \cdots \psi_{\mu(N)}(x_N) \right] dx_2 \dots dx_N$$

$$= \frac{1}{(N-1)!} \int_{\mathbb{R}^{3(N-1)}} \sum_\pi \sum_\mu \left[\operatorname{sgn}(\pi) \operatorname{sgn}(\mu)\, \psi^*_{\pi(1)}(x)\, \psi_{\mu(1)}(x) \cdot \psi^*_{\pi(2)}(x_2)\, \psi_{\mu(2)}(x_2) \cdot \dots \cdot \psi^*_{\pi(N)}(x_N)\, \psi_{\mu(N)}(x_N) \right] dx_2 \dots dx_N$$

$$= \frac{1}{(N-1)!} \sum_\pi \sum_\mu \operatorname{sgn}(\pi) \operatorname{sgn}(\mu)\, \psi^*_{\pi(1)}(x)\, \psi_{\mu(1)}(x) \cdot \int_{\mathbb{R}^3} \psi^*_{\pi(2)}(x_2)\, \psi_{\mu(2)}(x_2) dx_2 \cdot \dots \cdot \underbrace{\int_{\mathbb{R}^3} \psi^*_{\pi(N)}(x_N)\, \psi_{\mu(N)}(x_N)\, dx_N}_{\text{Use orthonormality } \doteq\ \delta_{\pi(N),\mu(N)}}$$

orthon.

$= (\dots)$

b) Also insert, use orthonormality, ...

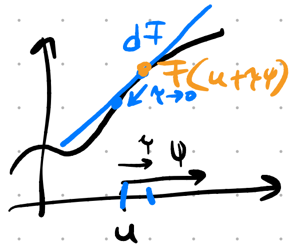
c) **Gâteaux-Derivatives** (for $\mathcal{F}: V \to \mathbb{R}$ instead of $f: \mathbb{R} \to \mathbb{R}$) (5)

⇝ Just the normal difference quotient.

Let X, Y Banach, let $\mathcal{U} \subset X$ be open, let $u \in \mathcal{U}$, $\varphi \in X$, $\mathcal{F}: X \to Y$.

The Gâteaux-Differential $d\mathcal{F}(u;\varphi)$ of $\mathcal{F}$ at x in direction φ is def.

$$d\mathcal{F}(u;\varphi) = \lim_{\tau \to 0} \frac{\mathcal{F}(u+\tau\varphi) - \mathcal{F}(u)}{\tau} = \frac{d}{d\tau} \mathcal{F}(u+\tau\varphi)\Big|_{\tau=0}$$



Example: Define $R: H^1((0,1)) \to \mathbb{R}$ as

$$R(f) = \frac{\int_0^1 f'(x) f'(x)\, dx}{\int_0^1 f(x) f(x)\, dx}$$

$$\mathcal{H} = \frac{1}{2} - \Delta \mapsto \int (f')^2$$

⇝ We want, e.g. $\min_{f \in H^1((0,1))} R(f)$. Use $dR(f;g) \overset{!}{=} 0 \quad \forall g$

$$dR(f;g) = \lim_{\tau \to 0} \frac{R(f+\tau g) - R(f)}{\tau} = \frac{\frac{\langle (f+\tau g)', (f+\tau g)' \rangle_{L^2(0,1)}}{\langle f+\tau g, f+\tau g \rangle_{L^2(0,1)}} - \frac{\langle f', f' \rangle_{L^2(0,1)}}{\langle f, f \rangle_{L^2(0,1)}}}{\tau}$$

$$\overset{(\cdot)' \text{ is lin.}}{=} \lim \frac{\frac{\langle f', f' \rangle + \tau \langle f', g' \rangle + \tau \langle f', g' \rangle + \tau^2 \langle g', g' \rangle}{\langle f, f \rangle + 2\tau \langle f, g \rangle + \tau^2 \langle g, g \rangle} - \frac{\langle f', f' \rangle}{\langle f, f \rangle}}{\tau}$$

$$= \lim \frac{1}{\tau} \Big(\underline{\langle f', f' \rangle \langle f, f \rangle} + \tau \langle f', g' \rangle \langle f, f \rangle + \tau \langle f', g' \rangle \langle f, f \rangle + \tau^2 \langle g', g' \rangle \langle f, f \rangle$$
$$\underline{- \langle f', f' \rangle \langle f, f \rangle} - 2\tau \langle f', f' \rangle \langle f, g \rangle - \tau^2 \langle f', f' \rangle \langle g, g \rangle \Big)$$

$$= \lim_{\tau \to 0} \langle f', g' \rangle \langle f, f \rangle + \langle f', g' \rangle \langle f, f \rangle + \cancel{\tau \langle g', g' \rangle} \langle f, f \rangle - 2 \langle f', f' \rangle \langle f, g \rangle$$
$$\cancel{- \tau \langle f', f' \rangle} \langle g, g \rangle$$

$$= \langle f', g' \rangle \langle f, f \rangle + \langle f', g' \rangle \langle f, f \rangle - 2 \langle f', f' \rangle \langle f, g \rangle$$

$$= 2 \big(\langle f', g' \rangle \langle f, f \rangle - \langle f', f' \rangle \langle f, g \rangle \big)$$

$d\, R(f; g) \overset{!}{=} 0 \;\forall g \quad \Rightarrow \quad \underbrace{\int_0^1 f'(x)\, g'(x) = \underbrace{\left(\frac{\int f'(x) f'(x)}{\int f(x) f(x)} \right)}_{R(f)} \int_0^1 f(x) g(x) \;\forall g}_{\text{What does this mean? :-)}}$ ⑥

$$\min_{f \in H^1((0,1))} R(f)$$

$$H^1(\Omega) := \{ u \in L^2(\Omega) : \|\nabla u\|_{L^2} < \infty \} \qquad \|u\|_{L^2} < \infty$$

c) Exercise, just use the definition and simplify.

(...)

Final solution: $\frac{d}{d\varepsilon} E(\Phi_0 + \varepsilon \Psi)\Big|_{\varepsilon=0} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\Phi_0}(y)}{|x-y|} \sum_{i=1}^{N} \left(\psi_i^*(x) \phi_i(x) + \phi_i^*(x) \psi_i(x) \right) dx\, dy$