Title: Explorations in Condensed Matter-3

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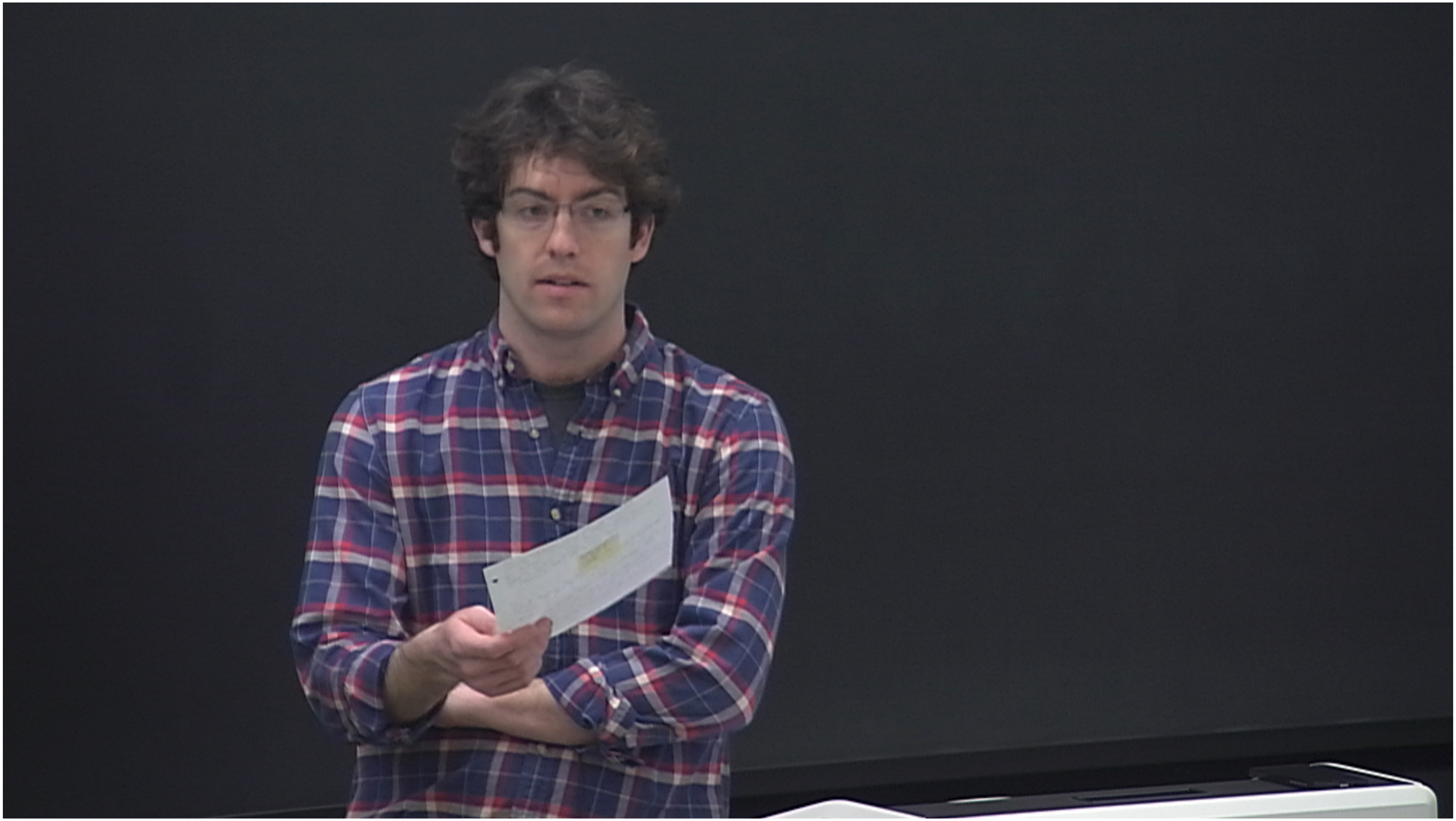
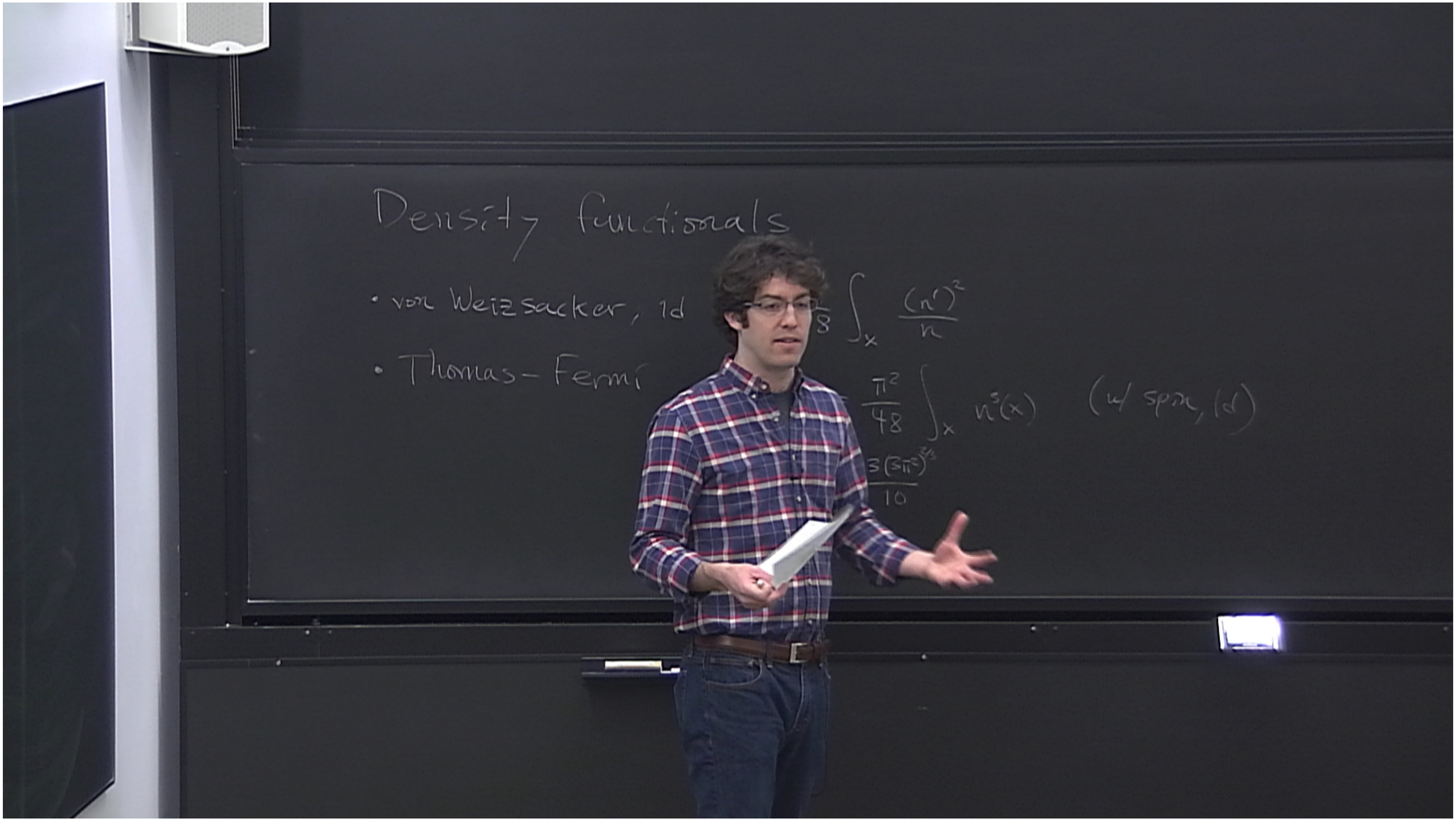
Abstract:




Density functionals
• von Weizsacker, 1d
• Thomas-Fermi
(w/ spin, 1d)

# Density functionals

- von Weizsacker, 1d $\quad T^{vW}(n) = \frac{1}{8}\int_x \frac{(n')^2}{n}$
- Thomas-Fermi $\quad T^{TF}(n) = \frac{\pi^2}{48}\int_x n^3(x)$ (w/ spin, 1d)

$$= \frac{3(3\pi^2)^{2/3}}{10}\int_{\vec{r}} n^{5/3}(x) \quad \text{(w/ spin, 3d)}$$

Thomas-Fermi $T^{TF}(n) = \frac{\pi^2}{48}\int_x n^3(x)$ (w/ spin, 1d)

$$= \frac{3(3\pi^2)^{2/3}}{10}\int_{\vec r} n^{5/3}(x) \quad \text{(w/ spin, 3d)}$$

$$\hat H_v = \underbrace{\hat T + \hat V_{ee}}_{\text{given, fixed}} + \int_r v(\vec r)\,\hat n(\vec r)$$

externally varied

Hohenberg, Kohn showed: two H's, $\hat H = \hat H_v$, $\hat H' = \hat H_{v'}$, both non-degen g.s. ($\psi$, $\psi'$ resp.)

assume $\psi, \psi' \longrightarrow$ same density $n(\vec r) = \langle\psi|\hat n(\vec r)|\psi\rangle = \langle\psi'|\hat n(\vec r)|\psi'\rangle$

$\Longrightarrow$ $v(\vec r)$ and $v'(\vec r)$ only differ by a constant $v(\vec r) = v'(\vec r) + C$

Proof variational principle $\langle\psi|\hat H|\psi\rangle \le \langle\psi'|\hat H|\psi'\rangle$

$$\Rightarrow \langle\psi|\hat T + \hat V_{ee}|\psi\rangle + \int_r v(\vec r)n(\vec r) \le \ldots|\hat T + \ldots$$

assume $\psi, \psi'$ ... both non-degen g.s. ($\psi, \psi'$ resp.)

$\longrightarrow$ same density $n(\vec r) = \langle \psi | \hat n(\vec r) | \psi \rangle = \langle \psi' | \hat n(\vec r) | \psi' \rangle$

$\Longrightarrow$ $v(\vec r)$ and $v'(\vec r)$ only differ by a constant $v(\vec r) = v'(\vec r) + C$

Proof  variational principle $\langle \psi | \hat H | \psi \rangle \leq \langle \psi' | \hat H | \psi' \rangle$

$\Rightarrow \langle \psi | \hat T + \hat V_{ee} | \psi \rangle + \int_{\vec r} v(\vec r) n(\vec r) \leq \langle \psi' | \hat T + \hat V_{ee} | \psi' \rangle + \int_{\vec r} v(\vec r) n(\vec r)$

$\Rightarrow \langle \psi | \hat T + \hat V_{ee} | \psi \rangle \leq \langle \psi' | \hat T + \hat V_{ee} | \psi' \rangle$

Likewise, $\langle \psi' | \hat H' | \psi' \rangle \leq \langle \psi | \hat H' | \psi \rangle \Rightarrow \langle \psi' | \hat T + \hat V_{ee} | \psi' \rangle \leq \langle \psi | \hat T + \hat V_{ee} | \psi \rangle$

$\Rightarrow \langle \psi | T + V_{ee} | \psi \rangle = \langle \psi' | T + V_{ee} | \psi' \rangle$  equality

$\Rightarrow$ same density $n(\vec{r}) = \langle\Psi|\hat{n}(\vec{r})|\Psi\rangle = \langle\Psi'|\hat{n}(\vec{r})|\Psi'\rangle$

$\Rightarrow$ $v(\vec{r})$ and $v'(\vec{r})$ only differ by a constant $v(\vec{r}) = v'(\vec{r}) + C$

Proof variational principle $\langle\Psi|\hat{H}|\Psi\rangle \leq \langle\Psi'|\hat{H}|\Psi'\rangle$

$$\Rightarrow \langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle + \cancel{\int_{\vec{r}} v(\vec{r})n(\vec{r})} \leq \langle\Psi'|\hat{T}+\hat{V}_{ee}|\Psi'\rangle + \cancel{\int_{\vec{r}} v(\vec{r})n(\vec{r})}$$

$$\Rightarrow \langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle \leq \langle\Psi'|\hat{T}+\hat{V}_{ee}|\Psi'\rangle$$

Likewise, $\langle\Psi'|\hat{H}'|\Psi'\rangle \leq \langle\Psi|\hat{H}'|\Psi\rangle \Rightarrow \langle\Psi'|\hat{T}+\hat{V}_{ee}|\Psi'\rangle \leq \langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle$

$$\Rightarrow \langle\Psi|T+V_{ee}|\Psi\rangle = \langle\Psi'|T+V_{ee}|\Psi'\rangle$$

equality

Hohenberg, Kohn showed: <u>two</u> H's, $\hat{H} = \hat{H}_v$, $\hat{H}' = \hat{H}_{v'}$, both <u>non-degen</u> g.s. ($\psi$, $\psi'$ resp.)

assume $\psi, \psi' \longrightarrow$ same density $n(\vec{r}) = \langle\psi|\hat{n}(\vec{r})|\psi\rangle = \langle\psi'|\hat{n}(\vec{r})|\psi'\rangle$

$\Longrightarrow$ $v(\vec{r})$ and $v'(\vec{r})$ only differ by a constant $v(\vec{r}) = v'(\vec{r}) + C$

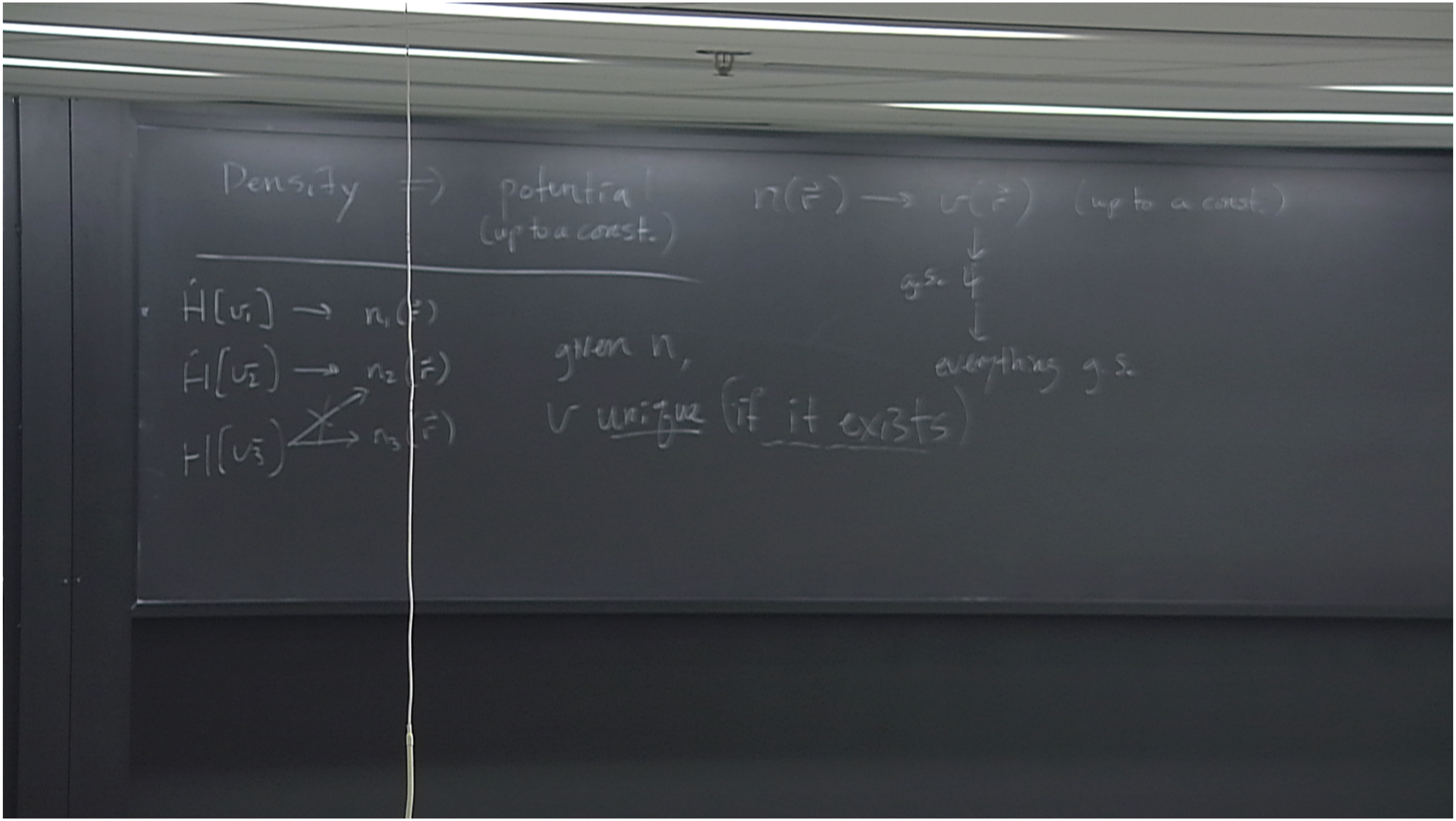
<u>Proof</u> variational principle $\langle\psi|\hat{H}|\psi\rangle \le \langle\psi'|\hat{H}|\psi'\rangle$

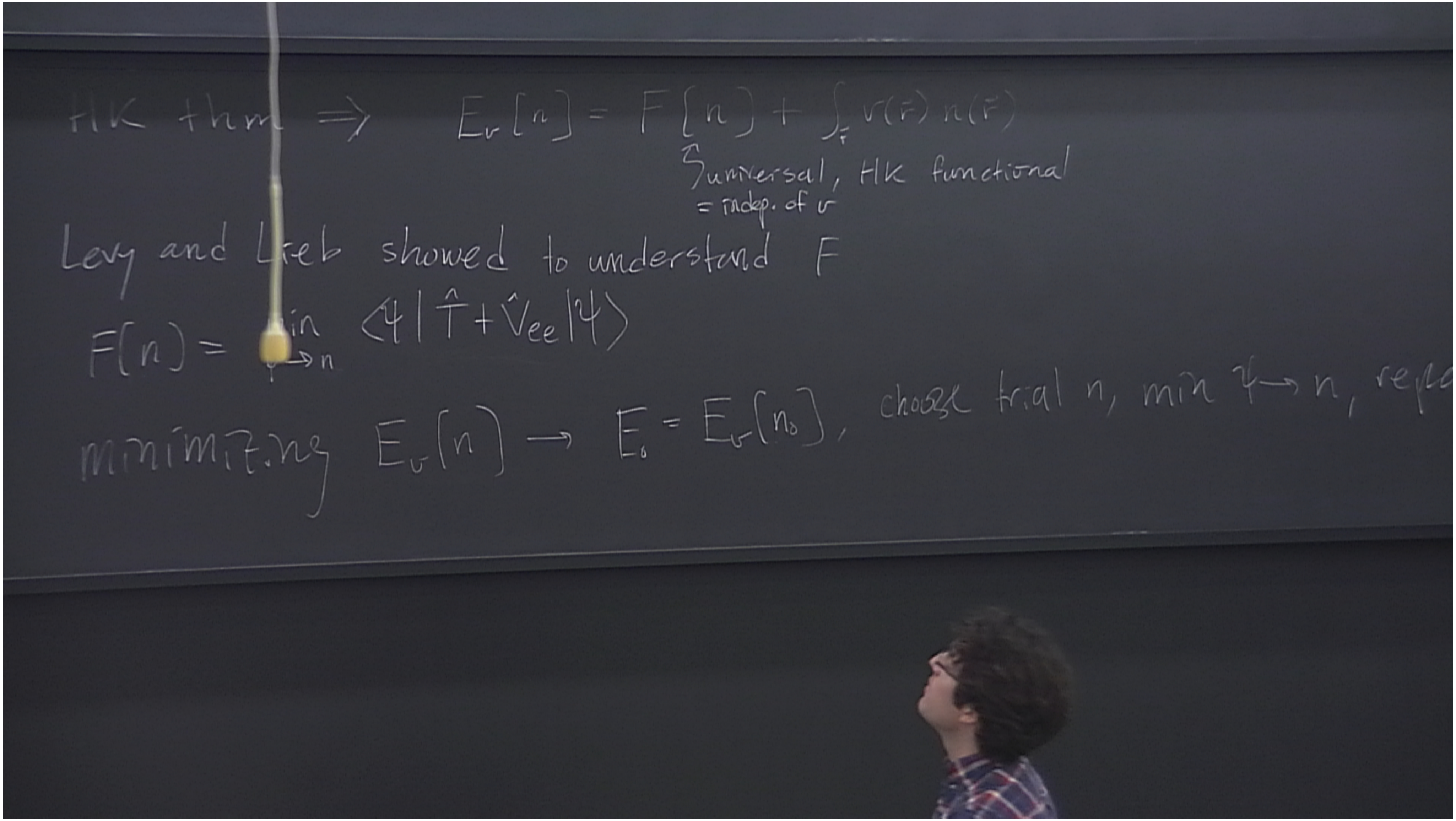
$$\Rightarrow \langle\psi|\hat{T}+\hat{V}_{ee}|\psi\rangle + \int_{\vec{r}} \cancel{v(\vec{r})n(\vec{r})} \le \langle\psi'|\hat{T}+\hat{V}_{ee}|\psi'\rangle + \int_{\vec{r}} \cancel{v(\vec{r})n(\vec{r})}$$

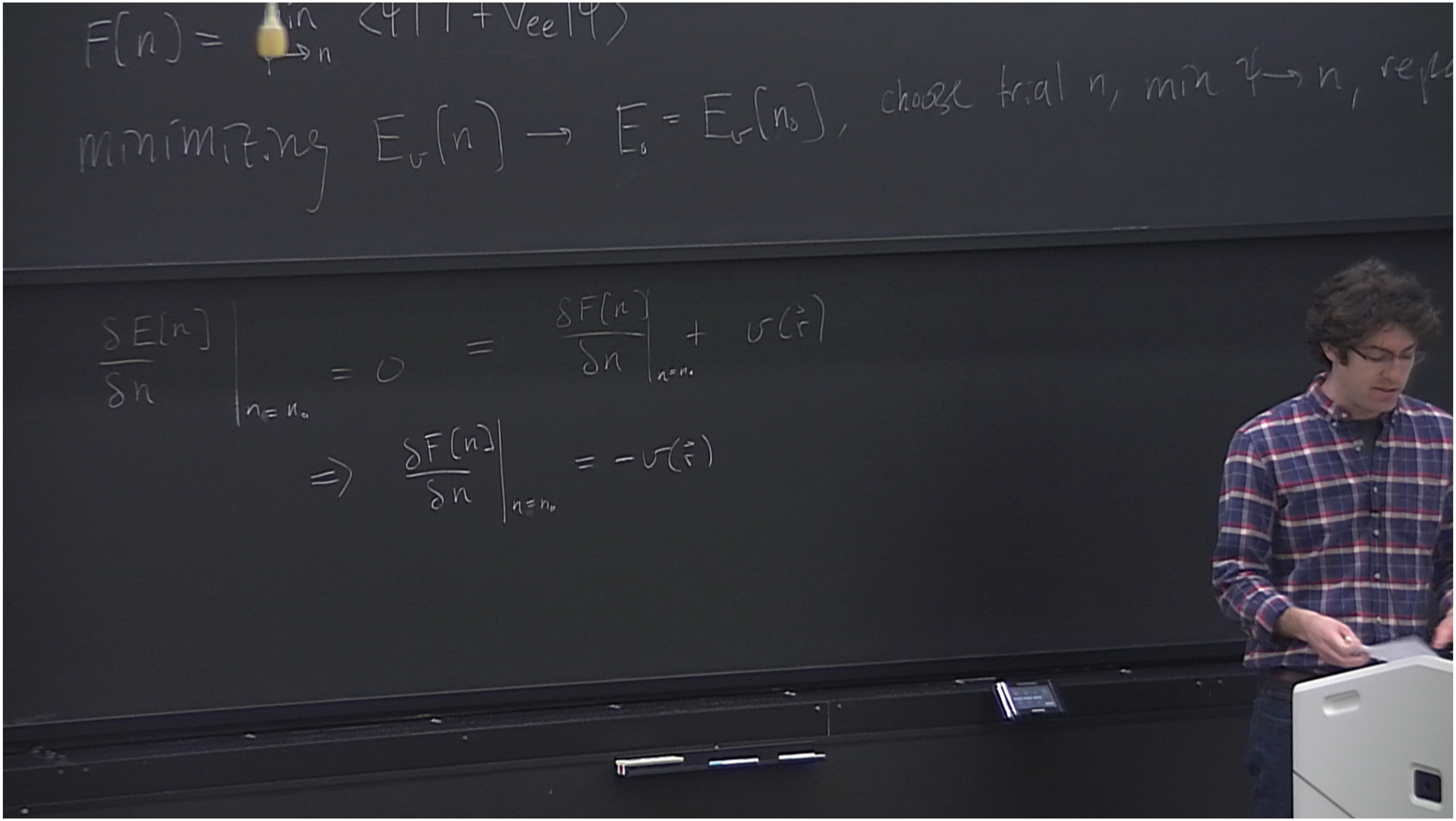
$$\Rightarrow \langle\psi|\hat{T}+\hat{V}_{ee}|\psi\rangle \le \langle\psi'|\hat{T}+\hat{V}_{ee}|\psi'\rangle$$

Likewise, $\langle\psi'|\hat{H}'|\psi'\rangle \le \langle\psi|\hat{H}'|\psi\rangle \Rightarrow \langle\psi'|\hat{T}+\hat{V}_{ee}|\psi'\rangle \le \langle\psi|\hat{T}+\hat{V}_{ee}|\psi\rangle$

$$\Rightarrow \langle\psi|T+V_{ee}|\psi\rangle = \langle\psi'|T+V_{ee}|\psi'\rangle \Rightarrow \langle\psi|\hat{T}+\hat{V}_{ee}|\psi\rangle + \int v'(\vec{r})n(\vec{r}) = \langle\psi'|\hat{T}+\hat{V}_{ee}|\psi'\rangle + \int_{\vec{r}} v'(\vec{r})n(\vec{r})$$


Density ⇒ potential
(up to a const.)
$n(\vec{r}) \longrightarrow v(\vec{r})$ (up to a const.)
g.s. $\psi$
everything g.s.
$\hat{H}[v_1] \rightarrow n_1(\vec{r})$
$\hat{H}[v_2] \rightarrow n_2(\vec{r})$
$\hat{H}[v_3] \rightarrow n_3(\vec{r})$
given n,
v unique (if it exists)


HK thm ⇒ E_v[n] = F[n] + ∫_r v(r) n(r)
universal, HK functional
= indep. of v
Levy and Lieb showed to understand F
F(n) = min_{ψ→n} ⟨ψ| T̂ + V̂_ee |ψ⟩
minimizing E_v(n) → E_0 = E_v(n_0), choose trial n, min ψ→n,

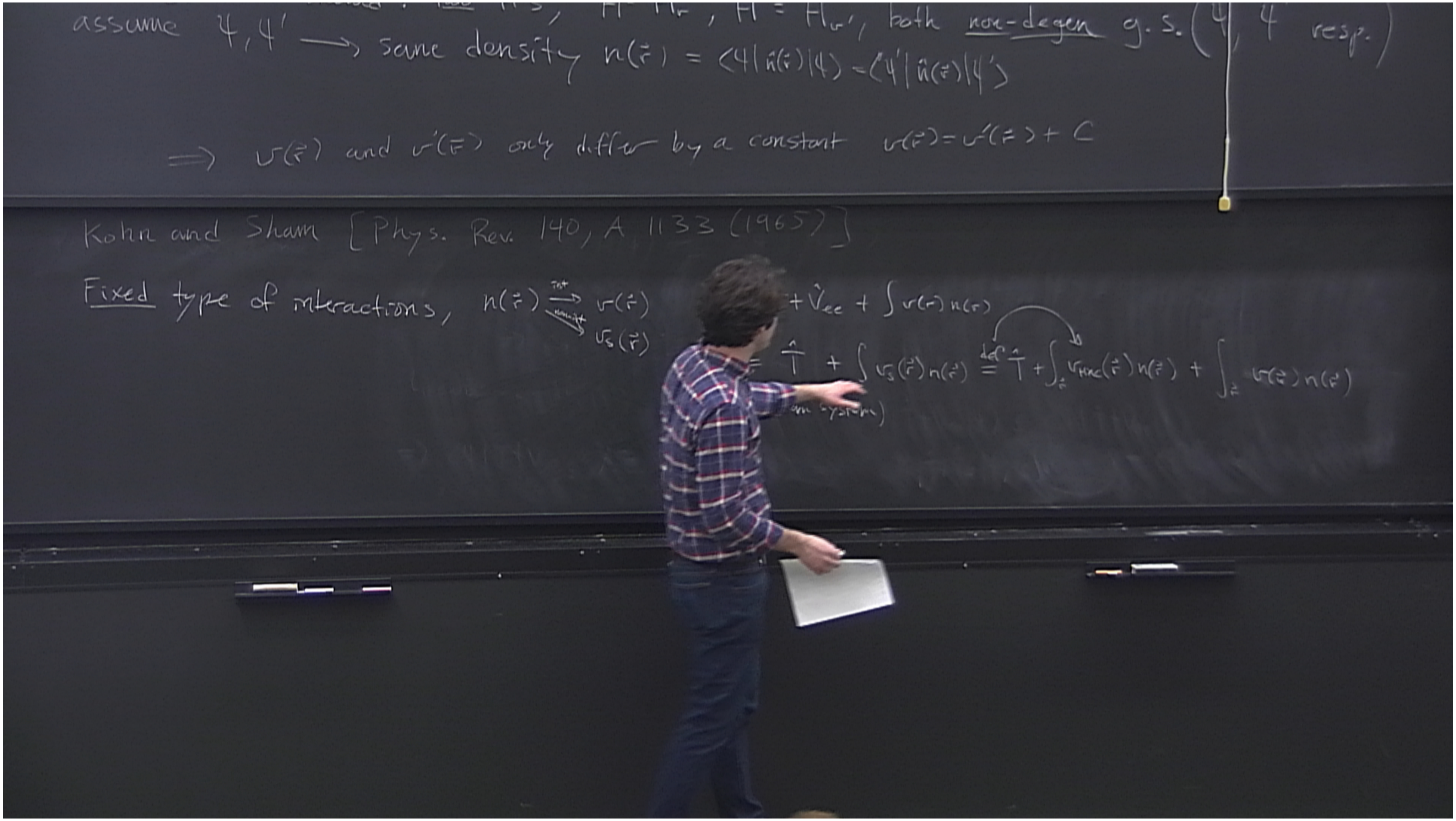

F(n) = min ⟨Ψ| T + Vee |Ψ⟩
minimizing Ev(n) → E0 = Ev(n0), choose trial n, min Ψ → n, rep
δE[n]/δn |n=n0 = 0 = δF(n)/δn |n=n0 + v(r)
⇒ δF(n)/δn |n=n0 = −v(r)

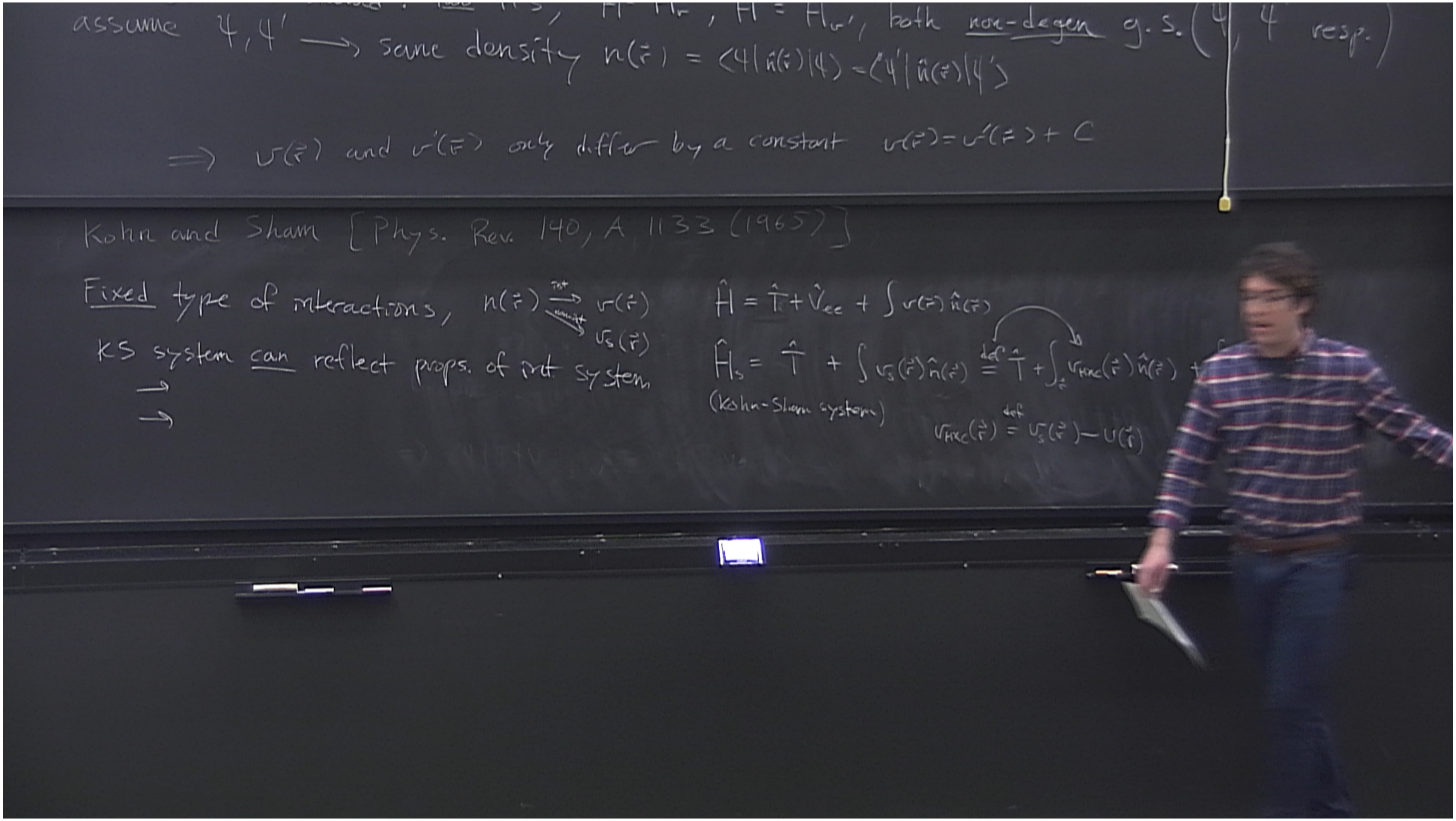
$$F[n] = \min_{\Psi \to n} \langle \Psi | T + V_{ee} | \Psi \rangle$$

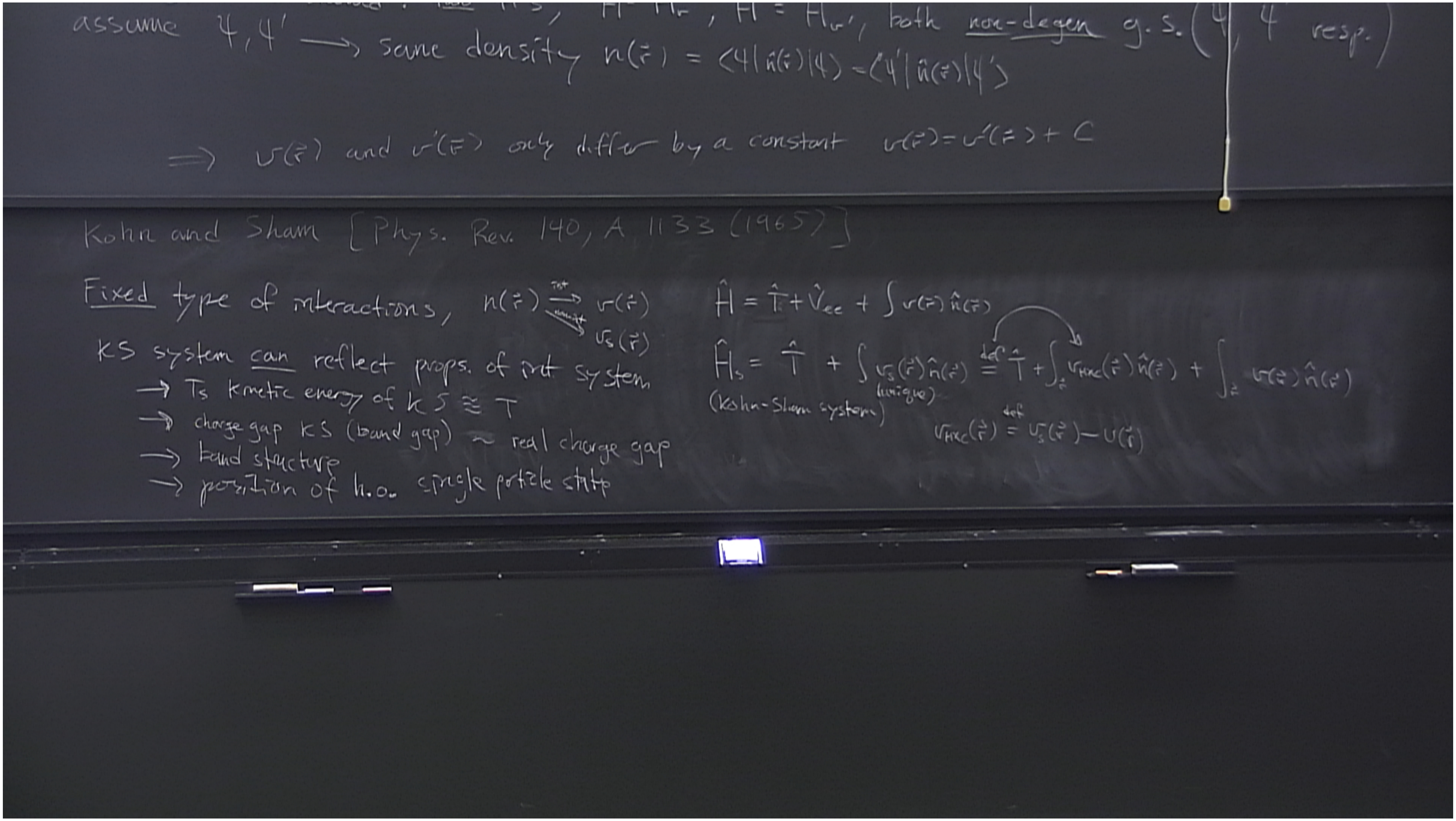
minimizing $E_v[n] \longrightarrow E_0 = E_v[n_0]$, choose trial $n$, min $\Psi \to n$, repl

$$\left.\frac{\delta E[n]}{\delta n}\right|_{n=n_0} = 0 = \left.\frac{\delta F[n]}{\delta n}\right|_{n=n_0} + v(\vec{r})$$

$$\Rightarrow \left.\frac{\delta F[n]}{\delta n}\right|_{n=n_0} = -v(\vec{r})$$


both non-degen g.s. (Ψ, Ψ' resp.)
assume Ψ, Ψ' ⟶ same density n(r) = ⟨Ψ|n̂(r)|Ψ⟩ = ⟨Ψ'|n̂(r)|Ψ'⟩
⟹ v(r) and v'(r) only differ by a constant v(r) = v'(r) + C
Kohn and Sham [Phys. Rev. 140, A 1133 (1965)]
Fixed type of interactions, n(r) → v(r)
v_s(r)
+ V̂_ee + ∫ v(r) n(r)
T̂ + ∫ v_s(r) n(r) =def T̂ + ∫ v_Hxc(r) n(r) + ∫ v(r) n(r)


assume Ψ, Ψ' → same density n(r) = ⟨Ψ|n̂(r)|Ψ⟩ = ⟨Ψ'|n̂(r)|Ψ'⟩
both non-degen g.s. (Ψ, Ψ' resp.)
⟹ v(r) and v'(r) only differ by a constant v(r) = v'(r) + C
Kohn and Sham [Phys. Rev. 140, A 1133 (1965)]
Fixed type of interactions, n(r) → v(r), v_s(r)
KS system can reflect props. of int. system
Ĥ = T̂ + V̂_ee + ∫ v(r) n̂(r)
Ĥ_s = T̂ + ∫ v_s(r) n̂(r) =def T̂ + ∫ v_Hxc(r) n̂(r) +
(Kohn-Sham system)
v_Hxc(r) =def v_s(r) − v(r)


assume Ψ, Ψ' → same density n(r) = ⟨Ψ|n̂(r)|Ψ⟩ = ⟨Ψ'|n̂(r)|Ψ'⟩
H = H_v, H' = H_v', both non-degen g.s. (Ψ, Ψ' resp.)
⟹ v(r) and v'(r) only differ by a constant v(r) = v'(r) + C
Kohn and Sham [Phys. Rev. 140, A 1133 (1965)]
Fixed type of interactions, n(r) → v(r)
v_S(r)
KS system can reflect props. of int system
→ T_S kinetic energy of KS ≈ T
→ charge gap KS (band gap) ~ real charge gap
→ band structure
→ position of h.o. single particle state
Ĥ = T̂ + V̂_ee + ∫ v(r) n̂(r)
Ĥ_S = T̂ + ∫ v_S(r) n̂(r) =def T̂ + ∫ v_HXC(r) n̂(r) + ∫ v(r) n̂(r)
(unique)
(Kohn-Sham system)
v_HXC(r) =def v_S(r) − v(r)