Sketch of Proof:

Define the current density

$$j(x,t) := f \int_{\mathbb{R}^{3(f-1)}} \operatorname{Im}\left(\Psi(x,x_2,\ldots,x_f,t)\nabla\bar{\Psi}(x,x_2,\ldots,x_f,t)\right) \cdot dx_2 \cdots dx_f$$

We first prove the Heisenberg equation:

For an observable A, consider the so-called Heisenberg picture of its evolution,

$$A(t) = e^{itH} A e^{-itH}.$$

We compute (noting $\frac{d}{dt} e^{-itH} = \frac{1}{i} H e^{-itH} = e^{-itH} \frac{1}{i} H$)

$$\frac{dA(t)}{dt} = \frac{1}{i} e^{itH}(-HA + AH)e^{-itH} = \frac{1}{i}[A(t), H].$$

Now consider the expectation value of the operator $A(t)$:

$$\frac{d}{dt}\langle \Psi(t)| A(t) | \Psi(t)\rangle = \langle \dot{\Psi} | A | \Psi \rangle + \langle \Psi | \dot{A} | \Psi \rangle + \langle \Psi | A | \dot{\Psi} \rangle =$$

$$= \langle -iH\Psi | A\Psi \rangle + \langle \Psi | \dot{A} | \Psi \rangle + \langle \Psi | A | -iH\Psi \rangle =$$

$$= \langle \Psi | iHA\Psi \rangle + \langle \Psi | \dot{A} | \Psi \rangle + \langle \Psi | A(-iH\Psi) \rangle =$$

$$= \langle \Psi | \dot{A} - i[A,H] | \Psi \rangle.$$

Assume the potentials differ by more than a constant. Recall that the corresponding Hamiltonians differ only in the exterior potentials v_{ext}. Compute (with j^* the operator associated with $j(x,t)$)

$$\frac{d}{dt}\left(j(x,t)-\tilde{j}(x,t)\right)\Big|_{t=0} = -i\left\langle \Psi(x,0)\left|\left[j^*(x,t), H(0)-\tilde{H}(0)\right]\right|\Psi(x,0)\right\rangle\Big|_{t=0}$$

$$= -i\left\langle \Psi(x,0)\left|\left[j^*(x,0), H(0)-\tilde{H}(0)\right]\right|\Psi(x,0)\right\rangle =$$

$$= -i\left\langle \Psi(x,0)\left|\left[j^*(x,0), v_{ext}(x,0)-\tilde{v}_{ext}(x,0)\right]\right|\Psi(x,0)\right\rangle$$

$$= -\rho(x,0)\nabla\left(v_{ext}(x,0)-\tilde{v}_{ext}(x,0)\right).$$

Repeatedly using this argument, it is found that

$$\frac{d^{k+1}}{dt^{k+1}}\left(j(x,t)-\tilde{j}(x,t)\right)\Big|_{t=0} = -\rho(x,0)\nabla\frac{d^k}{dt^k}\left(v_{ext}(x,t)-\tilde{v}_{ext}(x,t)\right)\Big|_{t=0}$$

From $v_{ext}-\tilde{v}_{ext}\neq c(t)$, there must be $k\in\mathbb{N}$ s.t. $-\rho(x,0)\nabla\frac{d^k}{dt^k}\left(v_{ext}(x,t)-\tilde{v}_{ext}(x,t)\right)\Big|_{t=0}$ does not vanish $\Rightarrow$ by Taylor expansion of the potential (which we tacitly assume possible) it follows that

$$j(x,t)\neq\tilde{j}(x,t)$$

This establishes one-to-one correspondence between current densities and external potentials.

One can prove the continuity equation

$$\frac{d\rho(x,t)}{dt} = -\nabla \cdot j(x,t).$$

Thus, one finds

$$\frac{d^{k+2}}{dt^{k+2}} \left(\rho(x,t) - \tilde{\rho}(x,t) \right) \Big|_{t=0} =$$

$$= \nabla \cdot \left[\rho(x,0) \nabla \frac{d^k}{dt^k} \left(v_{ext}(x,t) - \tilde{v}_{ext}(x,t) \right) \Big|_{t=0} \right]$$

To complete the proof, we look at the rhs.

We show that if $f(x) = \frac{d^k}{dt^k} \left(v_{ext}(x,t) - \tilde{v}_{ext}(x,t) \right) \Big|_{t=0}$

is non-constant for some k, then $\rho - \tilde{\rho} \neq 0$.

Write

$$\int f(x) \nabla \cdot \left[\rho(x,0) \nabla f(x) \right] dx =$$

$$= \int \Big\{ \underbrace{\nabla \cdot \left[f(x) \rho(x,0) \nabla f(x) \right]}_{\substack{\int \text{ vanishes for all potentials} \\ \text{decaying faster than } \frac{1}{|x|}}} \underbrace{- \rho(x,0) |\nabla f(x)|^2}_{\substack{< 0 \text{ if } \nabla f \neq 0 \\ \text{somewhere.}}} dx$$

Thus, the integral on the left cannot vanish, and its integrand must be non-zero somewhere.

$\Rightarrow$ The density determines the potential up to a time-dependent constant $\Rightarrow$ wave function determined up to a time-dep. phase, which cancels out of the expectation value of any observable.

Thus, the expectation value of any operator is a functional of the time-dependent density and initial state. //

Time-Dependent Kohn-Sham Equations:

Define a ficticious system of non-interacting electrons that satisfy "time-dependent Kohn-Sham equations"

$$i \dot{\phi}_j(x_j,t) = -\frac{1}{2}\Delta \phi_j(x_j,t) + V_{KS}(\rho)(x,t)\,\phi_j(x,t) \quad (1)$$

whose density,

$$\rho(x,t) = \sum_{j=1}^{f} |\phi_j(x,t)|^2$$

is defined to be the same as that of the real system.

By the Runge-Gross Theorem, V_{KS} yielding this density is unique.

Now define the "exchange-correlation potential"

$V_{XC} := V_{KS} - v_{ext} - V_H$, with the "Hartree potential"

$$V_H(x,t) := \int_{\mathbb{R}^3} \frac{\rho(y,t)}{|x-y|}\,dy$$

In the time-dependent Kohn-Sham equations (1) on 74, only V_{KS} is unknown, but known to depend on ρ. Thus, fixed point iteration is employed to determine $\rho \Leftrightarrow V_{KS}$ in each time-step.
(referred to in the physics and chemistry literature as "self-consistent solution")

4. Space Discretization – Pseudospectral Methods

4.1 Recall: Hermite functions,

$$\varphi_k(x) = \frac{1}{\sqrt[4]{\pi}} \frac{1}{\sqrt{2^k k!}} H_k(x) e^{-x^2/2}, \quad k = 0, 1, 2, \dots$$

H_k … "k-th Hermite polynomial" (orthogonal polynomial w.r.t. the weight function $e^{-x^2/2}$ on $\mathbb{R}$.

Harmonic oscillator eigenfunctions $\phi_k(x)$:

$$H = \tfrac{1}{2}(p^2 + q^2), \quad p: \phi \mapsto -i\phi', \; q: \phi \mapsto x\phi$$

$A := \frac{1}{\sqrt{2}}(q + ip)$, $A^+ := \frac{1}{\sqrt{2}}(q - ip)$ "ladder operators"

$A^+A = \frac{1}{2}(p^2 + q^2) - \frac{1}{2}$, $AA^+ = \frac{1}{2}(p^2 + q^2) + \frac{1}{2}$

A^+ … "raising operator", A … "lowering operator"

$$\phi_0(x) := \frac{1}{\sqrt[4]{\pi}} e^{-x^2/2}$$

$$\phi_{k+1}(x) := \frac{1}{\sqrt{k+1}} A^+ \phi_k, \quad \phi_{k-1} := \frac{1}{\sqrt{k}} A\phi_k.$$

Theorem: The functions φ_k and ϕ_k defined above coincide. They form a complete orthonormal set in $L^2(\mathbb{R})$ and are the eigenfunctions of the quantum harmonic oscillator.

Approximation Properties:

Denote by P_K the orthogonal projector onto $V_K = \mathrm{span}(\varphi_0, \dots, \varphi_{K-1})$, given by

$$P_K f = \sum_{k<K} \langle \varphi_k | f \rangle \varphi_k$$

This is the best approximation of f in V_K w.r.t the L^2-norm. It satisfies the bound (recall $A = \frac{1}{\sqrt{2}}(x + \frac{d}{dx})$):

Theorem: For every integer $s \leq K$ and every function f in the Schwartz space S

(Recall: S = arbitrarily differentiable functions, which together with all their partial derivatives decay faster than the inverse of any polynomial as $x \to \infty$)

$$\| f - P_K f \| \leq \frac{1}{[K(K-1)\cdots(K-s+1)]^{1/2}} \| A^s f \| = O(K^{-s/2})$$

Proof: We use the relations

$$\langle A^+ \varphi | \psi \rangle = \langle \varphi | A \psi \rangle \qquad \forall \varphi, \psi \in S$$

$$\varphi_{k+1} = \frac{1}{\sqrt{k+1}} A^+ \varphi_k \ , \ k \geq 0$$

$$f = \sum_{k=0}^{\infty} \langle \varphi_k | f \rangle \varphi_k .$$

We obtain for any $s \le K$

$$f - P_K f = \sum_{k \ge K} \langle \varphi_k | f \rangle \varphi_k =$$

$$= \sum_{k \ge K} \frac{1}{\sqrt{k(k-1)\cdots(k-s+1)}} \langle (A^+)^s \varphi_{k-s} | f \rangle \varphi_k$$

$$= \sum_{k \ge K} \frac{1}{\sqrt{k(k-1)\cdots(k-s+1)}} \langle \varphi_{k-s} | A^s f \rangle \varphi_k .$$

By orthonormality, this yields

$$\|f - P_K f\|^2 = \langle f - P_K f | f - P_K f \rangle$$

$$\le \frac{1}{K(K-1)\cdots(K-s+1)} \sum_{j \ge 0} |\langle \varphi_j | A^s f \rangle|^2$$

$$= \frac{1}{K(K-1)\cdots(K-s+1)} \|A^s f\|^2 \quad \text{(by Parseval's equality)}$$

4.7 Galerkin Method

Variational approximation on a fixed approximation space $\mathcal{V}_K \subseteq L^2$, $\mathcal{V}_K = \operatorname{span}\{\varphi_0, \dots, \varphi_{K-1}\}$:

Determine $\mathcal{V}_K \ni \psi_K(t) \approx \psi$ s.t.

$$\dot\psi_K \in \mathcal{V}_K \quad \text{s.t.} \quad \langle \varphi | i\dot\psi_K - H\psi_K \rangle = 0 \quad \forall \varphi \in \mathcal{V}_K .$$

With $\psi_K(t) = \sum_{k=0}^{K-1} c_k(t) \varphi_k$ and $i\dot\psi = H\psi$, this yields

$$i M_K \dot c = H_K c ,$$

$$M_K := (\langle \varphi_j | \varphi_k \rangle)_{j,k=0}^{K-1} , \quad H_K := (\langle \varphi_j | H | \varphi_k \rangle)_{j,k=0}^{K-1} .$$

<u>Theorem</u>: Consider the Galerkin method with the 1D Hermite basis $(\varphi_0, \dots, \varphi_{K-1})$ applied to a 1D Schrödinger equation with a potential $V(x) = (1+x^2)B(x)$ with bounded B, with initial value $\psi_K(0) = P_K \psi(0)$. Then, if the exact solution is in $D(A^{s+2})$ for some integer $s \leq \frac{K}{2}$, the error is bounded by

$$\|\psi_K(t) - \psi(t)\| \leq C K^{-s/2} (1+t) \max_{0 \leq \tau \leq t} \|A^{s+2}\psi(\tau)\|,$$

where C is independent of K and t, is bounded by $C \leq c 2^{s/2}$ in dependence of s, and depends linearly on the bound of B.

<u>Proof</u>: [14]

4.3 Higher Dimensions: Hyperbolic Cross

Full tensor-product basis: The approximation results immediately imply analogous results for a full tensor-product basis of Hermite functions

$$\varphi_{k_1 \dots k_d}(x_1, \dots, x_d) = \varphi_{k_1}(x_1) \cdots \varphi_{k_d}(x_d)$$

<u>But</u>: Exponential scaling $\sim K^d \Rightarrow$ infeasible for d large

Solution: Hyperbolic Reduced Tensor-Product Basis

Hyperbolic multi-index set $\mathcal{K}$,

$$\mathcal{K} = \mathcal{K}(d, K) := \{(k_1, \dots, k_d) : k_n \geq 0, \prod_{n=1}^{d} (1+k_n) \leq K \}$$

Illustration: [14], p. 70

Lemma: The number $N = N(K, d) = \# \mathcal{K}$ satisfies

$$N \leq K (\log K)^{d-1}$$

Theorem: For every fixed integer s and every function f in the Schwartz space over $\mathbb{R}^d$,

$$\| f - P_{\mathcal{K}} f \| \leq C(s, d) K^{-s/2} \max_{|\sigma|_\infty \leq s} \| A^\sigma f \|,$$

with the maximum taken over all $\sigma = (\sigma_1, \dots, \sigma_d)$, $\sigma_k \leq s \; \forall k$.

Proof: [14]

Theorem: Consider the Galerkin method with a hyperbolically reduced tensor Hermite basis applied to a d-dimensional Schrödinger equation with a potential $V = (1 + |x|^2) B(x)$ with bounded B, with initial value $\psi_{\mathcal{K}}(0) = P_{\mathcal{K}} \psi(0)$.

Then, for any fixed integer s the error is bounded by

$$\| \psi_{\mathcal{K}}(t) - \psi(t) \| \leq C(s, d) K^{-s/2} (1+t) \max_{0 \leq \tau \leq t} \max_{|\sigma|_\infty \leq s+2} \| A^\sigma \psi(\tau) \|.$$