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MATHEMATICAL FOUNDATIONS OF DFT

I - The Schrödinger Equation

Consider an isolated N-electron system in the Born-Oppenheimer approximation (nonrelativistic) The system is described by a wave function $\Psi(x_1 \dots x_N)$. The states of the system are eigenf

Stationary states with definite energies are eigenfunctions of the Hamiltonian

$$H = -\frac{1}{2}\sum_{j=1}^{N} \Delta_{x_j} + \sum_{j=1}^{N} U(x_j) + \sum_{i<j} \frac{1}{|x_i - x_j|}$$

$$U(x) = -\sum_{\alpha} \frac{Z_\alpha}{|R_\alpha - x|}$$

H is defined in $\mathcal{D}(H) \subset L^2(\mathbb{R}^{3N})$

Consider $H_0 = -\frac{1}{2}\sum_{j=1}^{n} \Delta_{x_j} + \sum_{i<j} \frac{1}{|x_i - x_j|}$

Kato proved that H_0 is self-adjoint on $\mathcal{D}(H_0) = H^2 \cap$

The Kato-Rellich theorem states that if H_0 is self-adjoint on $\mathcal{D}(H_0)$ and if $\hat{V}$ is defined on a dense set, $\mathcal{D}(H_0) \subset \mathcal{D}(\hat{V})$

symmetric, and $\hat{V}$ is H_0-bounded with relative bound $a<1$, i.e. $\exists a, b \in \mathbb{R}$:

$$\|\hat{V}\psi\| \leq a\|H_0\psi\| + b\|\psi\| \qquad \forall \psi \in D(H_0)$$

then $H = H_0 + \hat{V}$ is self-adjoint on $D(H_0)$.
Thus, if $v \in L^{\infty} + L^{3/2}$, one can prove that H is self-adjoint on $D(H_0) = H^2 \cap \mathcal{A}$.

The ground state is also the minimizer

~~$E_{gs} = \inf_{\psi \in D(H)} (\psi, H\psi)$~~

$$E_{gs} = \inf_{\substack{\psi \in D(H) \\ \|\psi\| = 1}} (\psi, H\psi)$$

We can define the ~~form~~ form domain as the domain on which ~~$(\psi, H\psi) =$~~ $b(\psi, \psi) = (\psi, H\psi)$ is well defined, which is bigger than than $D(H)$. In fact, $Q(H) = H^1 \cap \mathcal{A}$.

So we can define

$$E_{gs} = \inf_{\substack{\psi \in Q(H) \\ \|\psi\| = 1}} (\psi, H\psi)$$

Given a wave function ψ, we define the electron density

$$\rho(x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, y)|^2 \, dy$$

If ψ has finite kinetic energy, then

$$T(\psi) = \sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_{x_j} \psi|^2 \, dx < +\infty.$$

Therefore, $\rho \geq 0$, $\sqrt{\rho} \in H^1$, and $\int \rho = N$.

To see this, notice that

$$\nabla \rho = N \int (\nabla_x \psi^* \cdot \psi + \psi^* \nabla_x \psi)(x, y) \, dy.$$

By Cauchy-Schwarz,

$$|\nabla \rho(x)| \leq 2N \cdot \left(\int |\nabla_x \psi^*|^2 \, dy \right)^{1/2} \cdot \left(\int |\psi(x,y)|^2 \, dy \right)^{1/2}$$

$$= 2N \sqrt{\rho(x)} \cdot \left(\int |\nabla_x \psi^*|^2 \, dy \right)^{1/2}$$

$$\rightarrow \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 \, dx \leq N \int \int |\nabla_x \psi|^2 \, dy \, dx$$

$$= T(\psi), \text{ so } \sqrt{\rho} \in H^1(\mathbb{R}^3),$$

Moreover, if $\rho \geq 0$, $\sqrt{\rho} \in H^1$, $\int \rho = N$, one can find N functions $\psi_i(x)$ $x \in \mathbb{R}^3$ such that $\psi_i \in H^1$, $(\psi_i, \psi_j)_{L^2} = \delta_{ij}$, and if we define the Slater determinant

$$\Psi(x_1 \dots x_N) = \frac{1}{\sqrt{N!}} \det\left(\psi_i(x_j)\right)_{i,j}$$

then $\Psi \in Q(H)$ and $\rho(x) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(x, y)|^2 dy$

(Lieb '83, based on a construction by March and Young '58)

Define, for $x = (x_1, x_2, x_3)$

$$f(x_1) = \frac{2\pi}{N} \int_{-\infty}^{x_1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(s, t, u)\, du\, dt\, ds$$

f is monotonic between $0, 2\pi$. Define

$$\psi_k(x) = \sqrt{\frac{\rho(x)}{N}}\, e^{ikf(x_1)}$$

Then $$(\psi_k, \psi_r) = \int_{\mathbb{R}^3} \frac{\rho(x)}{N} e^{i(k-r)f(x_1)}\, dx$$

$$= \frac{1}{2\pi} \int_{\mathbb{R}} e^{i(k-r)f(x_1)} \underbrace{\left[\frac{2\pi}{N} \int_{\mathbb{R}^2} \rho(x_1, t, u)\, dt\, du \right]}_{f'(x_1)} dx_1$$

$$= \frac{1}{2\pi} \int_{\mathbb{R}} f'(x_1)\, e^{i(k-r)f(x_1)}\, dx_1$$

So, if $k=r \longrightarrow (\psi_k, \psi_k) = 1$

and if $k \neq r \longrightarrow (\psi_k, \psi_r) = \frac{1}{2\pi i (k-r)} \left. e^{i(k-r)f(x)} \right|_{-\infty}^{+\infty} = 0$

For a Slater determinant $\Psi = \frac{1}{\sqrt{N!}} \det(\psi_i(x_j))$,

$$\tilde{\rho}(x) = N \int |\Psi(x,y)|^2 dy = \sum_j |\psi_j(x)|^2$$

and in this case $\tilde{\rho}(x) = \rho(x)$.

Now: $N \int_{\mathbb{R}^3} |\nabla \psi_k|^2 dx = \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}\, e^{ikf(x_1)} + \sqrt{\rho}\, ikf'(x_1) e^{ikf(x_1)}|^2$

$$= \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 + \int k^2 \rho(x) |f'|^2(x_1)$$

$$= \int |\nabla \sqrt{\rho}|^2 + \left(\frac{2\pi k}{N}\right)^2 \int dx_1 \left[\int_{\mathbb{R}^2} \rho(x_1, y)\, dy\right]^2 \cdot \left(\int_{\mathbb{R}^2} \rho(x_1, y)\, dy\right)$$

$$= \int |\nabla \sqrt{\rho}|^2 + \left(\frac{2\pi k}{N}\right)^2 \int dx_1 \cdot g(x_1)^3$$

$g(x) = \int_{\mathbb{R}^2} \rho(x,y)\, dy \longrightarrow \sqrt{g} \in H^1(\mathbb{R})$, since

$$\int \frac{(g')^2}{g} dx = \int \frac{1}{\int_{\mathbb{R}^2} \rho(x,y) dy} \cdot \left(\int \partial_x \rho(x,y)\, dy\right)^2 dx$$

$$\mathcal{O} = \int \frac{1}{g(x)} \cdot \left(\int \frac{\partial_x \rho(x,y)}{\sqrt{\rho(x,y)}} \cdot \sqrt{\rho(x,y)}\, dy \right)^2 dx$$

$$\leq \int \frac{1}{g} \int \frac{|\partial_x \rho|^2}{\rho}(x,y)\, dy \cdot \underbrace{\int \rho(x,y)\, dy}_{g(x)} \cdot dx$$

$$\leq \int \frac{|\nabla \rho|^2}{\rho} < +\infty$$

Remark. For a potential v, the ground state is defined to be

$$E(v) = \inf \left\{ (\psi, (H_0 + V)\psi) \;\middle|\; \psi \in H^1,\ \|\psi\| = 1,\ \psi \text{ antisymmetric} \right\}$$

Note that if $\psi \in H^1$, then

$$(\psi, (H_0 + V)\psi) = (\psi, H_0 \psi) + \int \rho \cdot v$$

Since $\sqrt{\rho} \in H^1 \to \rho \in L^1 \cap L^3$, so the second term makes sense if $v \in (L^1 \cap L^3)^* = L^\infty + L^{3/2}$.

Note also that, given $v \in L^\infty + L^{3/2}$, there may or may not be a minimizer. For example, take $v = 0$, and choose

$$\psi_\lambda(x) = \lambda^{3N/2} \psi(\lambda x) \quad \text{for } \lambda > 0.$$

$\{\psi_\lambda\}$ is a . Then $(\psi_\lambda, H_0 \psi_\lambda) \xrightarrow{\lambda \to \infty} 0$.

The functional $E(v)$ has the following properties:

Thm: (i) $E(v)$ is concave, i.e., if $v_1, v_2 \in L^\infty + L^{3/2}$, $0 \le \alpha \le 1$, then

$$E(\alpha v_1 + (1-\alpha) v_2) \ge \alpha E(v_1) + (1-\alpha) E(v_2)$$

(ii) $E(v)$ is monotonic: if $v_1 \le v_2$, then $E(v_1) \le E(v_2)$

(iii) $E(v) > -\infty \quad \forall v \in L^\infty + L^{3/2}$

Proof: (i) Let $\psi \in W_N$. Then

$$(\psi, H_v \psi) = (\psi, H_0 \psi) + \alpha \int v_1 \rho + (1-\alpha) \int v_2 \rho$$
$$= \alpha (\psi, H_{v_1} \psi) + (1-\alpha)(\psi, H_{v_2} \psi)$$

$$\ge \alpha E(v_1) + (1-\alpha) E(v_2).$$

(ii) $\forall \psi \in W_N$: $(\psi, H_{v_2} \psi) \ge (\psi, H_{v_1} \psi) \ge E(v_1)$

(iii) $\forall \psi \in W_N$: $(\psi, H_v \psi) \ge \sum_j \int |D_{x_j} \psi|^2 + \int v \rho$

Let $v = v_1 + v_2$, $v_1 \in L^{3/2}$, $v_2 \in L^\infty$

$$\to (\psi, H_v \psi) \ge \sum_j \int |D_{x_j} \psi|^2 + \left(\int v_1 \rho + \int v_2 \rho \right)$$

$$\ge \sum_j \int |D_{x_j} \psi|^2 - \|v_1\|_{3/2} \cdot \|\rho\|_3 - \|v_2\|_\infty \|\rho\|_1$$

$$\ge \sum_j \int |D_{x_j} \psi|^2 - \|v_1\|_{3/2} \, C \int \frac{|\nabla \rho|^2}{\rho} - \|v_2\|_\infty \cdot N$$

(Sobolev's ineq)

$$\ge (1 - C\|v_1\|_{3/2}) \sum_j |D_{x_j} \psi|^2 - \|v_2\|_\infty \cdot N$$

(Pick $1 - \|v_1\|_{3/2} C > 0$)

2.- Density functional Theory.

The idea of using the electron density as fundamental variable dates back to Thomas '26 and Fermi '27. They wrote a set of equations, which can be understood variationally as minimizers of

$$F_{TF}[\rho] = C_{TF}\int \rho^{5/3} + \frac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|} + \int V(x)\rho(x)$$

in $\mathcal{A} = \{\rho \in L^1 \cap L^{5/3} \mid \rho \geq 0,\ \int \rho = N\}$.

In 1964, Hohenberg and Kohn created what today is understood as Density Functional Theory (DFT).

Thm I (HK '64) Suppose that ψ_j is a ground state for V_j. If $V_1 \neq V_2 +$ constant, then $\rho_1 \neq \rho_2$

Proof: Suppose $\rho_1 = \rho_2$. Since $V_1 \neq V_2 +$ const. $\psi_1 \neq \psi_2$ (since they solve diff. equations - there is a technical difficulty here if ψ_j vanishes on a set of positive measure)

Now,

$$E_1 = (\psi_1, H_1\psi_1) < (\psi_2, H_1\psi_2) = (\psi_2, H_2\psi_2) + \int (V_1 - V_2)\rho$$

$$= E_2 + \int (V_1 - V_2)\rho.$$

Also,

$$E_2 = (\psi_2, H_2 \psi_2) < (\psi_1, H_2 \psi_1) = (\psi_1, H_1 \psi_1) + \int (V_2 - V_1)\rho$$

$$= E_1 + \int (V_2 - V_1)\rho$$

Adding both, $E_1 + E_2 < E_1 + E_2$. qed

Mathematically, this means the following:

Let $V_N = \{v \mid H_v$ has a (nondegenerate) ground state$\}$ and $\mathcal{A}_N = \{\rho \mid \rho$ comes from a ground state$\}$.

The HK Theorem I implies the existence of a ~~1-to-1 map~~ bijection

$$G : V_N/\sim \longrightarrow \mathcal{A}_N.$$

Given $\rho \in \mathcal{A}_N$, $\exists!\ v \in V_N/\sim$ and therefore $\exists!\ \psi_\rho$ s.t. ψ_ρ is a groundstate of H_v ~~and~~ with density ρ. Therefore ψ_ρ is a functional of ρ, and HK define

$$F_{HK}[\rho] = \langle \psi_\rho, (T+U)\psi_\rho \rangle = E(v) - \int v\rho$$

Therefore $E(v) = \inf \{F_{HK}[\rho] + \int v\rho \mid \rho \in \mathcal{A}_N\}$.

Proof: If $\rho \in \mathcal{A}_N \to \exists\, \tilde{v}$ s, ψ_ρ ground state.

$$E(v) \leq \langle \psi_\rho, H\psi_\rho \rangle = \langle \psi_\rho, (T+U)\psi_\rho \rangle + \int v\rho$$

$$= F_{HK}[\rho] + \int v\rho.$$

and since $v \in V_N$, $\exists!$ ground state ψ_v

so $E(v) = \langle \psi_v, H\psi_v \rangle = F[\rho_v] + \int v\rho_v$ Q.e.d

This is the second HK theorem: $\exists$ Universal functional F_{HK} of ρ s.t.

$$E(v) = \inf \{ F_{HK}[\rho] + \int v\rho \}.$$

This holds only for $v \in V_N$, which is unknown, and the variation is restricted to A_N, which is also unknown. This is the issue of v-representability, and there exist densities $\underline{\rho}$ that are not v-representable.

Mel Levy (1979) avoids the problem of non-representability by defining the following functional: Given $v \in L^{4} + L^{3/2}$

$$E(v) = \inf_{\psi} \langle \psi, (H_0 + V)\psi \rangle =$$

$$= \inf_{\rho} \inf_{\psi \mapsto \rho} \langle \psi, (H_0 + V)\psi \rangle$$

$$= \inf_{\rho} \left\{ \left[\inf_{\psi \mapsto \rho} \langle \psi, H_0 \psi \rangle \right] + \int V\rho \right\}.$$

Therefore, we define

$$F_{LL}[\rho] = \inf_{\psi \mapsto \rho} \langle \psi, (T+U)\psi \rangle$$

and it is defined only for densities ρ that come from a wave function ψ with finite kinetic energy. We proved earlier that this space is precisely

$$I_N = \{ \rho \geq 0 \mid \sqrt{\rho} \in H^1, \int \rho = N \}$$

One can prove that $\forall \rho \in I_N$, $\exists \psi \in H^1 \cap \mathcal{A}$, $\|\psi\|=1$ s.t. $F_{LL}[\rho] = \langle \psi, (T+U)\psi \rangle$ (the inf is achieved).

Clearly $E(v) = \inf \{ F_{LL}[\rho] + \int v\rho \mid \rho \in I_N \}$, and therefore $F_{LL}[\rho] = F_{HK}[\rho]$ if $\rho \in \mathcal{A}_N$.

The main difficulty with F_{LL} is that it is not convex, (F_{HK} is not either).

To overcome this, Lieb ('83) defines

$$F[\rho] = \sup \{ E(v) - \int v\rho \mid v \in L^\infty + L^{3/2} \}.$$

$\forall \rho \in R_N = \{ \rho \in L^1 \cap L^3 \mid \rho \geq 0, \int \rho = N \}$

F is the Legendre transform of E, so F is convex and weak lower semicontinuous

One can show also that

$$E(v) = \inf\{F(\rho) + \int v\rho \mid \rho \in L^1 \cap L^3\}$$

and

$$E(v) = \inf\{F[\rho] + \int v\rho \mid \rho \in I_N\}.$$

Moreover, if $\rho \in A_N$, then

$$F_{HK}[\rho] = F_{LL}[\rho] = F[\rho].$$

Note: One can prove that F is the convex envelope of F_{LL}.

3.- The Kohn-Sham Equations

Going back to the many body problem, remember that

$$E(v) = \inf_{\psi \in W_N} \{(\psi, H\psi)\}.$$

where

$$W_N = \{\psi \in H^1(\mathbb{R}^{3N}) \mid \psi \text{ antisymmetric and } \|\psi\| = 1\}.$$

We have seen that an easy way to construct an element in W_N is to construct the so-called Slater determinant of N orthonormal "single electron" wave functions. Given $\phi_1 - \phi_N \in H^1(\mathbb{R}^3)$, we define

$$\Psi(x_1 \dots x_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_1(x_1) & \cdots & \phi_N(x_1) \\ \vdots & & \vdots \\ \phi_1(x_N) & & \phi_N(x_N) \end{pmatrix}$$

Not every antisymmetric function is a Slater determinant, of course, but one can write any antisymmetric, square integrable Ψ as ~~limit in~~ L^2 (with finite kinetic energy) as the limit of linear combinations of Slater determinants.

The basic idea in Hartree-Fock theory is to find the optimal Slater determinant in the following sense: Define

$$E^{HF}(v) = \inf_{\phi_1 \dots \phi_N \in H^1(\mathbb{R}^3)} \left\{ (\Psi, H\Psi) \;\middle|\; \langle \phi_i, \phi_j \rangle = \delta_{ij} \text{ and } \Psi = \frac{1}{\sqrt{N!}} \det(\phi_i(x_j)) \right\}$$

When we substitute Ψ into $(\Psi, H\Psi)$, we get

$$\left(\Psi, -\frac{1}{2}\sum_j \Delta_{x_j} \Psi\right) = \frac{1}{2} \sum_{j=1}^{N} \int |\nabla \phi_i|^2 = \text{kinetic energy of non-interacting electron.}$$

$$(\Psi, \hat{V}\Psi) = \int \rho v \quad \text{with}$$

$$\rho(x) = \sum_{j=1}^{N} |\phi_i(x)|^2$$

and the Coulomb term

$$(\Psi, W\Psi) = \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|}\,dy\,dx$$
$$- \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \iint \frac{\phi_i^*(x_1)\phi_j(x_1)\phi_i(y)\phi_j^*(y)}{|x-y|}\,dx\,dy.$$

The first term is the usual Coulomb interaction between electrons, and the second term is called (Hartree-Fock) exchange.

The theory of Hartree-Fock is well understood (Lieb and Simon '77, Lions '87 to deal with finite systems, while Catto, LeBris and Lions '01 deal with infinite systems in the thermodynamic limit. See also Bach, Lieb, Loss, and Solovej '94, who showed that for Hartree-Fock, each energy level is either completely filled, or completely empty, that is, there are no unfilled shells (for a negative definite potential V)

Going back to the HK DFT theory, remember that F is unknown, and so it must be approximated for practical purposes.

As mentioned earlier, Thomas and Fermi independently wrote the equations that correspond to the functional

$$F_{TF}[\rho] = C_{TF}\int \rho^{5/3} + \frac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|} + \int V\rho$$

minimized ~~on~~ in $A_{TF} = \{\rho \in L^1 \cap L^{5/3} \mid \rho \geq 0, \int \rho = N\}$.

One can think of this as an approximation to the HK DFT functional, but it turns out to be too inaccurate for practical purposes. In particular it does not allow chemical bonding. (Teller '62; Lieb & Simon '77). It is, however, exact in the limit as the nuclear charges go to infinity (Lieb & Simon '77); in the same article, Lieb & Simon compute the thermodynamic limit of the Thomas-Fermi energy for the study of ~~solids~~ crystalline solids.

Von Weizsäcker added an additional term to the kinetic energy:

$$F^{TFW}[\rho] = \frac{1}{2}\int \frac{|\nabla\rho|^2}{\rho} + C_{TF}\int \rho^{5/3} + \frac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|}$$

$$+ \int V\rho$$

Note: The energy can be written in terms of $u = \sqrt{\rho}$, an minimized in

$$\mathcal{B} = \{ u \in H^1(\mathbb{R}^3) \mid \int u^2 = 1, \ \}.$$

This provides a way of carrying out efficient numerical simulations that do not suffer from the difficulty that $\rho \simeq 0$ in some areas. (CJGC '07).

The TFW theory is well understood, and Catto, Le Bris, Lions '01 computed the thermodynamic limit, extending Lieb & Simon's work '77 on TF. This allows the study of, for example, elastic properties of solids. (see CJGC, Lu & E '07) in the context of Cauchy-Born elasticity.

Although other forms of the kinetic energy have appeared in the literature, it is very hard to quantify how accurate these are.

Note that the functionals discussed here, (TF and TFW) are convex. When Dirac exchange

is added, $-C\int \rho^{4/3}$, the functional lose convexity, ~~and~~ ~~not~~ in which case the theory is not as well understood in the context of solids (infinite systems).

Both TF and TFW fall within what is usually called Orbital-free DFT.

In 1965, Kohn and Sham proposed an approach to approximate the functional $F_{HK}[\rho]$ and solve the ground state problem.

Consider the subset of A_N:

$$\tilde{A}_N = \left\{ \rho \geq 0 \;\middle|\; \rho \text{ comes from a ground state slater determinant} \right\}.$$

This means that $\rho \in \tilde{A}_N$, iff $\exists$ v potential and $\phi_1 \cdots \phi_N$ ~~ground states of~~ corresponding to the smallest e-values of

$$(-\Delta + v)\phi = \lambda\phi$$

s.t. $\rho = \sum_{j=1}^{N} |\phi_j|^2$.

As with A_N, this class is unknown. Given $\rho \in \tilde{A}_N$, Kohn-Sham define the kinetic energy of ~~interacting~~ non-interacting

electrons as

$$T[\rho] = \inf \left\{ \langle \psi_\rho | -\tfrac{1}{2}\sum \Delta_{x_i} | \psi_\rho \rangle : \right.$$

ψ_ρ is a Slater determinant, and it generates density ρ $\Big\}$

From our discussion of Hartree-Fock, we see that

$$T[\rho] = \inf_{\phi_1 \dots \phi_N} \left\{ \tfrac{1}{2}\sum_i \int |\nabla \phi_i|^2 \;\middle|\; (\phi_i, \phi_j) = \delta_{ij} \right.$$
$$\left. \phi_j \in H^1(\mathbb{R}^3), \text{ and } \rho = \sum_{j=1}^{N} |\phi_j|^2 \right\}.$$

Then, we can write

$$F_{HK}[\rho] = T[\rho] + \tfrac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|} + E_{xc}[\rho]$$

where E_{xc} is the exchange and correlation energy; note that this equation simply defines E_{xc}

Kohn-Sham then compute

$$E^0(v) = \inf \left\{ \tfrac{1}{2}\sum_j \int |\nabla \phi_j|^2 + \tfrac{1}{2}\iint \frac{\rho(x)\rho(y)}{|x-y|} + E_{xc}(\rho) \right.$$
$$\left. + \int \rho v \;\middle|\; \rho = \Sigma |\phi_i|^2, \; (\phi_i, \phi_j) = \delta_{ij}, \; \phi_j \in H^1 \right\}.$$

This leads to the self-consistent equations

$$\left(-\frac{1}{2}\Delta + V_{eff}(\rho)\right)\phi_i = \varepsilon_i \phi_i \qquad i = 1 \dots N$$

$$\rho = \sum_{j=1}^{N} |\phi_j|^2 \,, \qquad V_{eff} = \rho * \frac{1}{|x|} + V + \frac{\delta E_{xc}}{\delta \rho}$$

and the self-consistent ~~eqn~~ iteration:

Given ρ^0 initial approximation, for $k \geq 0$ define $V_{eff}[\rho^{(k)}]$, diagonalize

$$\left(-\frac{1}{2}\Delta + V_{eff}(\rho^{(k)})\right)\phi_i^{(k+1)} = \varepsilon_i^{(k+1)} \phi_i^{(k+1)}$$

Define $\rho^{(k+1)} = \sum_i |\phi_i^{(k+1)}|^2$ (or similar)

and repeat until the density converges.

There is a long literature of numerical methods for this problem. One of the main interests is to develop so called linear scaling methods (Goedecker '99, CJGC, ~~Kuan~~, Lu, Xuan, E '09). These methods rely on localization properties of the solution to the ~~Kohn-Sham equations~~ Schrödinger equation.

~~The Kohn-Sham~~ The theory has been extended to time-dependent DFT by Runge and Gross '84, but it is not as well understood from

a mathematical point of view.

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