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Some additional notes/comments on Skyrme calculations...

- We introduced the "spin exchange" operator $P^0 = \frac{1}{2}(1 + \vec{\sigma}^{(1)} \cdot \vec{\sigma}^{(2)})$
- If we build a product wave function out of a space, spin, and isospin part, then

$$\langle r_1 s_1 t_1, r_2 s_2 t_2 | 12 \rangle = \langle r_1, r_2 | \chi(s_1, s_2) \rangle \langle t_1, t_2 |$$

can have. Four combinations of symmetry under exchange of the space and spin parts (and then the isospin component is determined by requiring the total wave function to be antisymmetric) to be consistent with the Pauli principle:

Ψ	χ	ξ
even	singlet	+ (even)
even	triplet	- (odd)
odd	singlet	- (odd)
odd	triplet	+ (even)

So $P^0 \langle r_1, r_2 | \chi(s_1, s_2) \rangle \langle t_1, t_2 | = \langle r_1, r_2 | \chi(s_2, s_1) \rangle \langle t_1, t_2 |$

The total spin $\vec{S} = \frac{1}{2}(\vec{\sigma}^{(1)} + \vec{\sigma}^{(2)})$ so

$$P^0 = \frac{1}{2}(1 + 2(\vec{S}^2 - \frac{3}{4}) - S^{(1)2}) = S(S+1) - 1 = \begin{cases} 1 & \text{for triplet} \\ -1 & \text{for singlet} \end{cases}$$

[check: $\frac{1}{2}(1 + 2S(S+1) - 2 \cdot \frac{1}{2} \cdot \frac{3}{2} - 2 \cdot \frac{1}{2} \cdot \frac{3}{2}) = S(S+1) - 1 \checkmark$]

which makes sense, since the triplet state is symmetric, so exchanging spins leaves it unchanged, while the singlet state is antisymmetric, so exchanging spins picks up a minus sign.

We similarly define the isospin exchange operator: $P^0 = \frac{1}{2}(1 + \vec{\tau}^{(1)} \cdot \vec{\tau}^{(2)})$

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Let's examine the mysterious term proportional to W_0 , which we claim is a spin-orbit force:

$$V_{ls}(1,2) = iW_0 (\vec{\sigma}^{(1)} + \vec{\sigma}^{(2)}) \cdot \vec{K}' \times \delta(\vec{r}_1 - \vec{r}_2) \vec{K}$$

with $\vec{K} \equiv \frac{1}{2}(\vec{p}_1 - \vec{p}_2)$ acting to the right and \vec{K}' acting to the left on wave functions (we've flipped the primed and unprimed momenta from (3.2) to be consistent with the literature — it's irrelevant which we choose!).

So start with what we might expect for a finite range spin-orbit force:

$$V_{ls}(1,2) = (\vec{\sigma}_1 + \vec{\sigma}_2) \cdot (\vec{r}_1 - \vec{r}_2) \times (\vec{k}_1 - \vec{k}_2) \tilde{V}(r_{12})$$

where $\vec{L} = \hat{r} \times \hat{p}$ is formed from the relative coordinate and relative momentum. $\tilde{V}(r_{12}) \equiv \tilde{V}(|\vec{r}_1 - \vec{r}_2|)$ is a central potential.

Look at this in momentum space, since we want to do a short-distance expansion, which is a Taylor expansion in momentum.

$$\Rightarrow \langle \vec{k}_1' \vec{k}_2' | V_{ls} | \vec{k}_1 \vec{k}_2 \rangle = \frac{1}{V^2} \int d^3r_1 d^3r_2 e^{-i\vec{k}_1'\vec{r}_1 - i\vec{k}_2'\vec{r}_2} e^{i\vec{k}_1\vec{r}_1 + i\vec{k}_2\vec{r}_2} (\vec{\sigma}_1 + \vec{\sigma}_2) \cdot (\vec{r}_1 - \vec{r}_2) \times (\vec{k}_1 - \vec{k}_2) \tilde{V}(r_{12})$$

where \vec{k}_1, \vec{k}_2 are just vectors now. We define $\vec{k} = \frac{1}{2}(\vec{k}_1 - \vec{k}_2)$, $\vec{k}' = \frac{1}{2}(\vec{k}_1' - \vec{k}_2')$.

Switch variables to $\vec{r} = \vec{r}_1 - \vec{r}_2$ and $\vec{r}' = \vec{r}_2$:

$$\begin{aligned} \langle \vec{k}_1' \vec{k}_2' | V_{ls} | \vec{k}_1 \vec{k}_2 \rangle &= \frac{1}{V} \int d^3r' e^{-i(\vec{k}_1' + \vec{k}_2 - \vec{k}_1)\vec{r}'} \left(\frac{1}{V} \int d^3r (\vec{\sigma}_1 + \vec{\sigma}_2) \cdot \vec{r} \tilde{V}(r) e^{i\vec{k}\vec{r}} \right) \times 2\vec{k} \\ &= \delta_{\vec{k}_1'\vec{k}_2', \vec{k}_1\vec{k}_2} \frac{1}{V} (\vec{\sigma}_1 + \vec{\sigma}_2) \cdot \left(\int d^3r \vec{r} \tilde{V}(r) \right) e^{i\vec{k}\vec{r}} \times 2\vec{k} \end{aligned}$$

since momentum conservation means $\vec{k}_1' - \vec{k}_1 = \frac{1}{2}((\vec{k}_1' + \vec{k}_2) + (\vec{k}_2 - \vec{k}_1)) = \vec{k} - \vec{k}$

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So all we need is (with $\vec{q} = \vec{k}_1 - \vec{k}_2$):

$$\begin{aligned} \int d^3r e^{i\vec{q}\cdot\vec{r}} \vec{r} V(r) &= \frac{4\pi}{i} \vec{q} \int d^3r e^{i\vec{q}\cdot\vec{r}} V(r) \\ \text{plane wave} &= \frac{4\pi}{i} \vec{q} \int d^3r \sum_{l=0}^{\infty} (2l+1) i^l j_l(qr) P_l(\cos\theta_{qr}) V(r) \\ \text{series} &= \frac{4\pi}{i} \vec{q} \int_0^{\infty} dr r^2 j_0(qr) V(r) \end{aligned}$$

$$\begin{aligned} \text{But } \vec{\nabla}_q j_0(qr) &= \hat{q} \frac{d}{dq} j_0(qr) = \hat{q} \frac{d}{dq} \left(\frac{\sin qr}{qr} \right) \\ &= \hat{q} \left[\frac{\cos qr}{q} - \frac{\sin qr}{q^2 r} \right] = \frac{\hat{q}}{q^2} \left(\cos qr - \frac{\sin qr}{qr} \right) \end{aligned}$$

So we find that

$$\langle \vec{k}_1, \vec{k}_2 | V_{LS} | \vec{k}_1, \vec{k}_2 \rangle = -\delta_{\vec{k}_1+\vec{k}_2, \vec{k}_1+\vec{k}_2} (\vec{\sigma}_1 \otimes \vec{\sigma}_2) \cdot (\vec{k}_1 \times \vec{k}_2) W(|\vec{k}_1 - \vec{k}_2|)$$

$$\text{where } W(q) = \frac{8\pi}{q^2} \int_0^{\infty} dr r^2 V(r) \left(\cos qr - \frac{\sin qr}{qr} \right) \quad [\text{and } \vec{k}_1 \times \vec{k}_2 = 0]$$

• Now if $V(r)$ is short-ranged, $W(q)$ has an expansion in powers of q , starting with a constant W_0 .

• Transforming this back to coordinate space, a constant in q becomes a delta function $\delta(\vec{k}_1 - \vec{k}_2)$ and we have the expression we started with in (18).

• So, in summary, $V_{LS}(1,2)$ is the short-ranged potential limit of an ordinary spin-orbit force.

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The Hartree-Fock equations follow in the Green's function formalism from the Dyson's equation for G^{HF} :

Try iterating it!

This is an integral equation for G^{HF} (using four-vector notation: $x \equiv (\vec{x}, t)$):

$$G^{\text{HF}}(x, x') = G^0(x, x') + \int d^4x_1 d^4x_2 G^0(x, x_1) \Sigma_{\text{HF}}^*(x_1, x_2) G^{\text{HF}}(x_2, x')$$

with the proper self-energy Σ_{HF}^* given by:

$$\Sigma_{\text{HF}}^*(x_1, x_2) = -i\delta(t_1 - t_2) \left[\delta(\vec{x}_1 - \vec{x}_2) \int d^3x_3 G^{\text{HF}}(\vec{x}_2, t_2, \vec{x}_3, t_2^+) V(\vec{x}_1 - \vec{x}_3) - V(\vec{x}_1 - \vec{x}_2) G^{\text{HF}}(\vec{x}_2, t_2, \vec{x}_2, t_2^+) \right]$$

(note the t_2^+ and t_2^+)

← assume $H_0 = -\frac{\nabla^2}{2m} + U(x)$ and $H_0 \psi_j^0(\vec{x}) = \epsilon_j^0 \psi_j^0(\vec{x})$

Recall that G^0 has the form (with $\psi_j^0(\vec{x})$ a complete set of states, such as plane waves)

$$iG^0(\vec{x}t, \vec{x}'t') = \sum_j \psi_j^0(\vec{x}) \psi_j^0(\vec{x}')^* e^{-i\epsilon_j^0(t-t')} \left[\theta(t-t') \theta(\epsilon_j^0 - \epsilon_F) - \theta(t'-t) \theta(\epsilon_F - \epsilon_j^0) \right]$$

Since Σ_{HF} is independent of frequency when transformed (since $\propto \delta(t-t')$), we expect G^{HF} to have the same form as G^0 , introducing $\{\psi_j(\vec{x})\}$:

$$iG^{\text{HF}}(\vec{x}t, \vec{x}'t') = \sum_j \psi_j(\vec{x}) \psi_j(\vec{x}')^* e^{-i\epsilon_j(t-t')} \left[\theta(t-t') \theta(\epsilon_j - \epsilon_F) - \theta(t'-t) \theta(\epsilon_F - \epsilon_j) \right]$$

Substituting into the Σ_{HF} expression, we get (with $\Sigma_{\text{HF}}^*(x, x') = \sum_{\text{HF}} \psi_j(x) \psi_j(x')^* \delta(t-t')$)

$$\begin{aligned} \Sigma_{\text{HF}}^*(\vec{x}_1, \vec{x}_2) &= \left\{ \delta(\vec{x}_1 - \vec{x}_2) \int d^3x_3 V(\vec{x}_1 - \vec{x}_3) \sum_j |\psi_j(\vec{x}_3)|^2 \right\} - V(\vec{x}_1 - \vec{x}_2) \sum_j \psi_j^*(\vec{x}_2) \psi_j(\vec{x}_2) \\ &= \delta(\vec{x}_1 - \vec{x}_2) \rho_H(\vec{x}_2) + \rho_{\text{ex}}(\vec{x}_2, \vec{x}_2') \end{aligned}$$

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We get an equation for $\psi_*(\vec{x})$ by using the differential equation that G^0 satisfies:

$$\left(i \frac{\partial}{\partial t} - H_0 \right) G^0(\vec{x}, \vec{x}', t) = \delta(\vec{x} - \vec{x}') \delta(t - t')$$

and then substituting the expansion of G^{HF} and using the orthonormality of the $\{\psi_j(\vec{x})\}$ to project out the simple Hartree-Fock equation written down on (33):

$$\left[-\frac{\nabla^2}{2m} + U(\vec{x}_1) \right] \psi_j(\vec{x}_1) + \int d^3x_2 \sum_{\text{HF}}^* (\vec{x}_1, \vec{x}_2) \psi_j(\vec{x}_2) = \epsilon_j \psi_j(\vec{x}_1)$$

• details left for the reader!

• So \sum^* acts as a static, Hermitian, but non-local potential.

• Since it is independent of j , the usual proof of orthogonality goes through, which justifies our use of it a posteriori.

• The fact that our ansatz for G^{HF} satisfies the equations justifies it.

• We can take $U(\vec{x}) \equiv 0$ or else keep it as a static (spin-independent) potential (like the Coulomb potential of a nucleus).

• See Fetter and Walecka Chapter 4 for further discussion.

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A few comments on (34) and (35)...

- The evaluation of E_0 is straightforward because we have delta function interactions, but some of the terms are a bit tedious.
- With the restriction to $N=Z$, time-reversal invariant nuclei, we don't get a contribution from $t_0 x_0 p^0 \delta(\vec{r}_1 - \vec{r}_0)$. Do you see why?
- Do you see why we get $\frac{3}{8} t_0 p^2$? (Remember there will be a direct and an exchange piece. What is g ?)
- For spherical symmetry, we expect the spin-orbit term to be proportional to $\frac{d\rho}{dr}$, because it is the only direction that can be crossed into the nucleus's momentum to get an angular momentum.
 - The spin-orbit term is surface-peaked, because in the uniform part of the nucleus, there is only one direction singled out (by the nucleus's velocity).
- The paper "Towards a Hartree-Fock mass formula" gives results of a fit to 1719 nuclei (!) of "10 parameter Skyrme force + 4 parameter δ function pairing force.
 - note the motivation from stellar nucleosynthesis
 - The Skyrme force has 4 extra parameters: x_1, x_2, x_3 that come with P_0 terms, and χ , which is a fractional power of the density that replaces the three body term (which yields ρ^3 in the energy density, so the new functional has $\rho^{2+\chi}$). $\chi=1/3$ here.
 - note how Coulomb is included (equation (3b)).
 - The 4 parameters of the pairing are four strengths for neutrons and protons, and even and odd numbers of nucleons. Note the rationale after Eq. (10).

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Density Functional Theory (DFT)

- When all is said and done, the Skyrme Hartree-Fock approach is less about parametrizing an interaction between nucleons than parametrizing the energy functional.
 - The idea of having A orbitals that satisfy local Schrödinger equations and which give the density in the form $\rho(\vec{x}) = \sum_i |\psi_i(\vec{x})|^2$ would seem to be restricted to Hartree-Fock.
 - For example, including a the beachball diagram, even with the simple Hartree-Fock propagator G^{HF} would be a nonlocal, time (or, rather energy) dependent ~~mass~~.
- We claim, however, that we can consider the Skyrme approach to be a reasonable approximation to Kohn-Sham density functional theory, which can (in principle!) reproduce the exact ground state energy and density with the same simple orbitals and iteration procedure.
- We'll first do an overview of DFT based on the very nice American Journal of Physics article by Aravamudan and Makov.
 - You have a copy to read on your own.
 - We'll cover some important sections but not everything.
- Then we'll see how to carry out DFT in the effective action formalism for an effective field theory \Rightarrow DFT/EFT!
- Figure 2 in Aravamudan and Makov (A+M) illustrates the growth of DFT applications (calibrated by reference to Hartree-Fock in INSPEC database of journal articles)
 - Has leveled off at about 2000/year (comparable to total number of nuclear theory papers per year!)

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• To what problems is DFT applied?

- 99.9% application is to inhomogeneous electron gas

• Coulomb interaction between fermions (electrons)

• A static external potential $V(\vec{r})$

• Coulomb potential from nuclei fixed in space

⇒ Born-Oppenheimer approximation (time scale for nuclear movement \gg electron time scale)

• So, basically, the problem is to find the energy and density distribution of the electron cloud around a collection of fixed charges.

• applied to atoms, molecules, crystals, surfaces

• Usual approach (historical) to DFT is not transparent

⇒ AT&S use thermodynamics analogy

• Where we're heading: Hohenberg-Kohn theorems say there exists (existence, not how to find it!) an energy functional

$$E_V[n] = F_{HK}[n] + \int d^3x V(\vec{r}) n(\vec{r})$$

• all dependence on external $V(\vec{r})$ is in simple 2nd term

• $F_{HK}[n]$ is universal \Rightarrow same function if you are calculating on H_2 molecule or DNA! (!)

• $E_V[n]$ is minimized for the exact ground state density $n(\vec{r})$.

• Contains everything (beachballs, rings, ladders...)

• Kohn and Sham said we can find the density $n(\vec{r})$ by solving the problem of single-particle independent orbitals self-consistently:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\vec{r}) \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

where $n(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2$ and $V_{\text{eff}} = V_{\text{eff}}[n, \vec{r}]$ from $F_{HK}[n]$.

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• It turns out that one can make a very simple approximation to $E_{\text{KS}}[n]$, the local density approximation, that works amazingly well.

• Much effort has gone into going beyond LDA.

• Some quotes from the literature:

• A Chemist's Guide to DFT (Koch & Holthausen, 2000)

"To many, the success of DFT appeared somewhat miraculous, and maybe even unjust and unjustified. Unjust in view of the easy achievement of accuracy that was so hard to come by in the wave function based methods. And unjustified it appeared to those who doubted the soundness of the theoretical foundations. There has been misunderstanding concerning the status of the one-determinantal approach of Kohn and Sham, which superficially appeared to preclude the incorporation of correlation effects."

• Density Functional Theory (ASP, Argaman + Makov, 2000)

"It is important to stress that all practical applications of DFT rest on essentially uncontrolled approximations, such as the LDA..."

• "Meta-Generalized Gradient Approximation" (Perdew et al., 1999)

"Some say that 'there is no systematic way to construct density functional approximations.' But there are more or less systematic ways, and the approach taken... here is one of the former."

• The goal of the DFT/EFT program is to provide the systematic construction (and justification) of Kohn-Sham functionals for nuclear (and perhaps Coulomb) systems.

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Ok, let's follow Argaman and Makov's Thermodynamics analogy.

• Start with the grand potential ($\beta \equiv \frac{1}{T}$)

$$\Omega(\mu, T, V) = -\frac{1}{\beta} \ln Z$$

with

$$Z = \text{Tr} e^{-\beta(\hat{H} - \mu\hat{N})}$$

[cf. ArM eqs. (1)-(3)]

• After calculating Ω and a function of μ , we find

$$N \sim \langle \hat{N} \rangle = -\frac{\partial \Omega}{\partial \mu}$$

which gives us $N(\mu)$.

• We can invert to find $\mu(N)$ because Ω is convex
 $\Rightarrow N$ is monotonically increasing function of μ .

• Find the Helmholtz free energy $F(N, T, V)$ from a Legendre transformation:

$$F(N, T, V) = \Omega(\mu(N), T, V) + \mu(N)N$$

• Here $\mu(N)$ is not independent.

• But we can create a function $\Omega_\mu(N, T, V)$ that has the same content but μ independent:

$$\Omega_\mu(N, T, V) \equiv F(N, T, V) - \mu N$$

and minimizing Ω_μ wrt. N : $\frac{\partial \Omega_\mu}{\partial N} = 0 = \frac{\partial F}{\partial N} - \mu$ gives the original $\Omega(\mu(N), T, V) = \Omega_{\mu_{\min}}(N, T, V)$.

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- This is analogous to the energy functional.
 - μ plays the role of the external potential $v(\vec{r})$
 - $\Omega_\mu(N)$ is like $E[N]$
 - $F(N) \rightarrow F_{HK}[N]$ is universal (no appearance of μ in the function).
 - All of the μ dependence in Ω_μ from the $-\mu N$ term $\Rightarrow \int v(\vec{x}) n(\vec{x}) d^3x$ term
 - Only when the function Ω_μ (functional $E[N]$) is minimized do we build in that $N=N(\mu)$ ($n(\vec{x})=n(\mu, \vec{x})$)

- In fact, we can generalize μ to simply depend on position \Rightarrow add the potential $v(\vec{x})$ to \hat{H}

$$\Rightarrow \Omega(\mu, T, [v(\vec{x})]) = -\frac{1}{\beta} \ln \left\{ \text{Tr} e^{-\beta \left(\int d^3x \hat{n}(\vec{x}) (v(\vec{x}) - \mu) \right)} \right\}$$

where we've used the density operator $\hat{n}(\vec{x}) = \hat{\psi}^\dagger(\vec{x}) \hat{\psi}(\vec{x})$ in a somewhat schematic notation.

- We could introduce a potential $v'(\vec{x}) \equiv v(\vec{x}) - \mu$ or else just measure energies wrt μ , so that $\mu=0$.

- We see that $v(\vec{x})$ is just like a source term we add to a path integral (what we usually call $J(\vec{x})$), so we know that $\langle \hat{n}(\vec{x}) \rangle$ follows from a functional derivative:

$$n(\vec{x}) = \langle \hat{n}(\vec{x}) \rangle = \frac{\delta \Omega}{\delta v(\vec{x})} \quad \left[\text{cf. } N = -\frac{\delta \Omega}{\delta \mu} \right]$$

so we can Legendre transform $\Omega[v(\vec{x})]$:

$$F_{HK}[n(\vec{x})] = \Omega[v(\vec{x})] - \int d^3x n(\vec{x}) v(\vec{x})$$

which should look familiar (effective action!).

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The density functional we're looking for is the generalization of the Ω_{HK} functional; now with $n(\vec{r})$ and $v(\vec{r})$ independent:

$$\Omega_{\nu}[n(\vec{r})] \equiv E_{HK}[n(\vec{r})] + \int d^3x n(\vec{r}) V(\vec{r})$$

which yields

$$\frac{\delta E_{HK}}{\delta n(\vec{r})} = -V(\vec{r})$$

universal \rightarrow no dependence on $v(\vec{r})$

when minimized wrt $n(\vec{r})$ at fixed $v(\vec{r})$ (which is the physical problem of interest).

• And when this holds, we get the desired grand potential (from which we get the energy at zero temperature).

• So we have as an almost immediate consequence of Legendre transformations and thermodynamic convexity a demonstration that we can find a density functional $E_{\nu}[n(\vec{r})]$.

• How do we calculate it?

• For an inhomogeneous electron gas, usually decompose E_{HK} :

$$E_{HK}[n(\vec{r})] = E_{ni}[n(\vec{r})] + E_{es}[n(\vec{r})] + E_{xc}[n(\vec{r})]$$

where

$$E_{ni}[n(\vec{r})] = E_{HK}[n(\vec{r})] \big|_{v(\vec{r})=0}$$

"non-interacting"

$$E_{es}[n(\vec{r})] = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

electrostatic
(Hartree) energy

$$E_{xc}[n(\vec{r})] \Rightarrow \text{everything else!}$$

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- One approach is to construct E_{HK} as an explicit functional of $n(\vec{x})$. Thomas and Fermi did this first:

$$E_{TF}[n(\vec{x})] = \int d^3x \frac{3}{5} \frac{1}{2m} [3\pi^2 n(\vec{x})]^{2/3} n(\vec{x})$$

which uses $n = \frac{k_F^3}{3\pi^2}$ for $g=2$ in a uniform system and $E_0 = \frac{3}{5} (k_F^2/2m)$ in such a system \Rightarrow assume each small volume d^3x at \vec{x} has this energy density

$\Rightarrow n \rightarrow n(\vec{x})$ "local density approximation"

• This approximation to E_{TF} works at sufficiently high density, but not very well for molecules

\Rightarrow LDA is not a good approximation to the kinetic energy.

- Kohn and Sham say: Find $V_{eff}(\vec{r})$ such that solving

$$\left(-\frac{1}{2m} \nabla^2 + V_{eff}(\vec{r}) \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

for N states yields $n(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2$ then

$$E_{KS}[n(\vec{x})] = \sum_{i=1}^N \langle \psi_i | \hat{t}_i | \psi_i \rangle = \sum_{i=1}^N \epsilon_i - \int d^3r n(\vec{r}) V_{eff}(\vec{r})$$

What is V_{eff} ? Take $\frac{\delta E_{HK}}{\delta n(\vec{x})}$ of the E_{HK} decomposition:

at the minimum $\frac{\delta E_{HK}}{\delta n(\vec{x})} = -V(\vec{x}) = -V_{eff}(\vec{x}) - e\psi(\vec{x}) + V_{xc}(\vec{x})$

where we used $\frac{\delta E_{TF}}{\delta n(\vec{x})} = -V_{eff}(\vec{x})$ and defined

$$\psi(\vec{x}) = - \int d^3x' \frac{n(\vec{x}')}{|\vec{x} - \vec{x}'|} \quad \text{and} \quad V_{xc}(\vec{x}) = \frac{\delta E_{xc}}{\delta n(\vec{x})}$$

\uparrow
Hartree potential

\uparrow
exchange-correlation potential

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Rearranging to solve for V_{eff} :

$$V_{\text{eff}}(\vec{r}) = V(\vec{r}) - e\phi(\vec{r}) + V_{\text{xc}}(\vec{r})$$

• $V(\vec{r})$ is known• $\phi(\vec{r})$ is a simple functional of $n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$

\Rightarrow an approximation to $E_{\text{xc}}[n(\vec{r})]$ yields $V_{\text{xc}}(\vec{r})$ and we can solve the Kohn-Sham problem iteratively until self-consistent:

$$V_{\text{eff}}(\vec{r}) \rightarrow \{\psi_i\} \rightarrow n(\vec{r}) \rightarrow V_{\text{eff}}(\vec{r}) \text{ and so on.}$$

It turns out that an LDA for E_{xc} is a good starting point (unlike for E_{ci}):

$$E_{\text{xc}}[n(\vec{r})] \doteq \int d^3x E_{\text{xc}}(n_0) \Big|_{n_0=n(\vec{r})} n(\vec{r})$$

where $E_{\text{xc}}(n)$ is the energy density in a uniform electron gas of density n .

\Rightarrow find $E_{\text{xc}}(n)$ numerically (Green's function Monte Carlo) and parametrize, e.g.

$$E_{\text{xc}}(n) = -0.458/r_s - 0.0666 G\left(\frac{r_s}{11.4}\right) \text{ hartrees,}$$

where $r_s \propto \frac{1}{k_F}$ and $G(x) = \frac{1}{2} \left((1+x^3) \log(1+\frac{1}{x}) - x^3 + \frac{x}{2} - \frac{1}{3} \right)$

• See Figure 3 for the plot. Then $V_{\text{xc}}(\vec{r}) = \frac{d(nE_{\text{xc}}(n))}{dn} \Big|_{n=n(\vec{r})}$ and

$$E_0 = \sum_{i=1}^N \epsilon_i - E_{\text{es}}[n(\vec{r})] + \int d^3x n(\vec{r}) (E_{\text{xc}}(n(\vec{r})) - V_{\text{xc}}(n(\vec{r})))$$

check out Figure 4!