



**Short Course on
Density Functional Theory and Applications
II. Kohn-Sham Procedure**

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Trivial Example of DFT [H.L. Neal, Amer. J. Phys. 72, 605 (2004)]

Consider a single particle in a one-dimensional potential $V(x)$ with stated boundary conditions

$$\left[-\frac{1}{2} \frac{d^2}{dx^2} + v(x) \right] \phi_j(x) = \varepsilon_j \phi_j(x), \quad j = 0, 1, 2, \dots$$

$$n_0(x) = |\phi_0(x)|^2 \quad \leftarrow \text{the ground state density}$$

For real-valued ϕ

$$\phi_0(x) = n_0^{1/2}(x)$$

$$\Rightarrow \varepsilon_0 = \int dx n_0^{1/2}(x) \left(-\frac{1}{2} \frac{d^2}{dx^2} \right) n_0^{1/2}(x) + \int dx n_0(x) v(x)$$

Define a functional

$$T_w[n] = \int dx n^{1/2}(x) \left(-\frac{1}{2} \frac{d^2}{dx^2} \right) n^{1/2}(x) = \frac{1}{8} \int dx \frac{1}{n(x)} \left(\frac{dn(x)}{dx} \right)^2$$

Then

$$\varepsilon[n] = T_w[n] + \int dx n(x) V(x) \geq \varepsilon_0$$

$$\delta \left\{ \varepsilon[n] - \lambda \left(\int dx n(x) - N_e \right) \right\} = 0 \Rightarrow \frac{\delta \varepsilon[n]}{\delta n} = \lambda$$

$$n = n_0 \Leftrightarrow \lambda = \varepsilon_0$$

which leads to

$$\frac{\delta \varepsilon[n]}{\delta n} = \frac{\delta T_w[n]}{\delta n} + V(x)$$

$$\frac{\delta T_w[n]}{\delta n} = \frac{1}{8} \left\{ 2n^{-1} \frac{d^2 n}{dx^2} - n^{-2} \left(\frac{dn}{dx} \right)^2 \right\}$$

$$\Rightarrow \left[-\frac{1}{2} \frac{d^2}{dx^2} + v(x) + \frac{1}{4} \left(\frac{d \ln n}{dx} \right)^2 \right] n = 2\lambda n$$

Remarks: (i) The density equation is more complicated than the original S.E. This is a bit troubling since DFT is supposed to simplify matters. (ii) T_w is, in fact, the von Weizsäcker KE.

DFT Variation Principle and Euler Equation

Recall HK-II

$$E_{v_{ext}}[n] = F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) \geq E_0$$

$$E_{v_{ext}}[n_0] = E_0 = \min_{n(\bar{r})} E_{v_{ext}}[n] \quad \forall \text{ physically acceptable } n(\mathbf{r})$$

$$\int d\mathbf{r} n(\mathbf{r}) = N_e$$

Do the variation with a Lagrange multiplier for fixed particle number

$$\delta \left\{ F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) - \mu \left(\int d\mathbf{r} n(\mathbf{r}) - N_e \right) \right\} = 0$$

$$\Rightarrow \frac{\delta F}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r}) = \mu$$

Existence Theorems and Proceeding Constructively

- The **big challenge**: HK-II says that $F[n]$ exists but **does not** give a form that can be used to do the variational problem just displayed.
- But we do know how to form $F[n]$ explicitly for a system of non-interacting fermions **with the same density**, as follows:

$$F[n] := \min_{\Phi \mapsto n} \langle \Phi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Phi \rangle \equiv \langle \Phi_{min;n} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Phi_{min;n} \rangle$$

$$\hat{\mathcal{V}}_{ee} = 0 \Rightarrow T_S[n] := F_{non-interacting}[n] = \min_{\Phi \mapsto n} \langle \Phi | \hat{\mathcal{T}} | \Phi \rangle \equiv \langle \Phi_{min;n} | \hat{\mathcal{T}} | \Phi_{min;n} \rangle$$

Non-interacting fermions means $\Phi_{min;n}(1, \dots, N_e) = \frac{1}{\sqrt{N_e!}} \det |\varphi_1 \dots \varphi_{N_e}|$
 $\Phi_{min;n}$ is a Slater determinant.

The Slater determinant 1- and 2-RDMs are $\gamma_{SD}(x|x') = \sum_{j=1}^{N_e} \varphi_j^*(x') \varphi_j(x)$

$$\Gamma_{SD}^{(2)}(x_1 x_2 | x'_1 x'_2) = \frac{1}{2} \det \begin{pmatrix} \gamma_{SD}(x_1 | x'_1) & \gamma_{SD}(x_1 | x'_2) \\ \gamma_{SD}(x_2 | x'_1) & \gamma_{SD}(x_2 | x'_2) \end{pmatrix}$$

So the KS kinetic energy is $T_s[n] \equiv T_s[\{\varphi[n]\}] = -\frac{1}{2} \sum_{j=1}^{N_e} \int d\mathbf{r} \varphi_j^*(x) \nabla^2 \varphi_j(x)$

How is this useful?

Existence Theorems and Proceeding Constructively (cont'd.)

By definition, the non-interacting (independent particle) system must have an energy

$$E_s[n] \equiv T_s \left[\{ \varphi[n] \} \right] + \int d\mathbf{r} n(\mathbf{r}) v_{eff}(\mathbf{r})$$

Again, do the variation with a Lagrange multiplier for fixed particle number

$$\delta \left\{ T_s[n] + \int d\mathbf{r} n(\mathbf{r}) v_{eff}(\mathbf{r}) - \mu \left(\int d\mathbf{r} n(\mathbf{r}) - N_e \right) \right\} = 0$$
$$\Rightarrow \frac{\delta T_s}{\delta n(\mathbf{r})} + v_{eff}(\mathbf{r}) = \mu$$

We chose the Lagrange multiplier to be the same as in the original system by setting the zero of the potential v_{eff} (adding a constant).

**So we have mapped the problem into that of constructing v_{eff} .
How can that be done?**

Remark: v -representability of the ground-state density n_0 has been reintroduced as an assumption.

Kohn-Sham Construction

Use the definition of the universal functional and rearrange by adding and subtracting the KS KE and by isolating the classical (or Hartree) Coulomb energy:

$$\begin{aligned} E_{v_{ext}}[n] &= F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) = \langle \psi_{min;n} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi_{min;n} \rangle + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) \\ &= T[n] + \frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) \Gamma_{min;n}^{(2)}(x_1 x_2 | x'_1 x'_2) \Big|_{\substack{x'_1=x_1 \\ x'_2=x_2}} + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) \\ &= T_s[n] + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_1) n(\mathbf{r}_2) \\ &\quad + \frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) \left(\Gamma_{min;n}^{(2)}(x_1 x_2 | x'_1 x'_2) \Big|_{\substack{x'_1=x_1 \\ x'_2=x_2}} - n(\mathbf{r}_1) n(\mathbf{r}_2) \right) + T[n] - T_s[n] \\ &\quad + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) \end{aligned}$$

The expression in **blue** defines the exchange-correlation energy in DFT:

$$E_{v_{ext}}[n] = T_s[n] + E_{ee}[n] + E_{xc}[n] + E_{ext}[n]$$

Euler Equations Again

What we have done is

$$E_{v_{ext}}[n] := F[n] + E_{ext}[n] = T_S[n] + E_{ee}[n] + E_{xc}[n] + E_{ext}[n]$$

$$F[n] = T_S[n] + E_{ee}[n] + E_{xc}[n]$$

Thus, the variation principle and Euler equation for the physical system become

$$\delta \left\{ F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) - \mu \left(\int d\mathbf{r} n(\mathbf{r}) - N_e \right) \right\} = 0$$

$$\Rightarrow \frac{\delta T_S}{\delta n(\mathbf{r})} + v_{ee}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r}) = \mu$$

Comparison with the Euler Equation for the KS system $\frac{\delta T_s}{\delta n(\mathbf{r})} + v_{eff}(\mathbf{r}) = \mu$

shows that $v_{eff}(\mathbf{r}) = v_{ee}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r})$

New task: construct E_{xc}

Exchange and Correlation Subtleties in DFT

$$E_{xc}[n] = \frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) \left(\Gamma_{min;n}^{(2)}(x_1 x_2 | x'_1 x'_2) \Big|_{\substack{x'_1=x_1 \\ x'_2=x_2}} - n(\mathbf{r}_1)n(\mathbf{r}_2) \right) + T[n] - T_s[n]$$
$$E_{xc}[n] = E_x[n] + E_c[n]$$

The exchange energy in DFT is **defined** with respect to the KS determinant, **NOT** the Hartree-Fock determinant:

$$E_x[n] = \langle \Phi_{min;n} | \hat{\mathcal{V}}_{ee} | \Phi_{min;n} \rangle - \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_1)n(\mathbf{r}_2)$$
$$= -\frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) \gamma_{KS;n}(x_1 | x_2) \gamma_{KS;n}(x_2 | x_1)$$

Thus “exact exchange” in DFT is not “Hartree-Fock exchange” despite common usage to the contrary.

It follows from the second line of the preceding equation that $E_x[n] \leq 0$

Exchange and Correlation Subtleties in DFT (continued)

The DFT and conventional correlation energies differ subtly but significantly also

$$\begin{aligned} E_c[n] &= \langle \psi_{min;n} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi_{min;n} \rangle - \langle \Phi_{min;n} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Phi_{min;n} \rangle \\ &\equiv \frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) \left\{ \Gamma_{min;n}^{(2)}(x_1 x_2 | x'_1 x'_2) \Big|_{\substack{x'_1=x_1 \\ x'_2=x_2}} \right. \\ &\quad \left. - n(\mathbf{r}_1)n(\mathbf{r}_2) + \gamma_{KS;n}(x_1 | x_2) \gamma_{KS;n}(x_2 | x_1) \right\} + T[n] - T_s[n] \end{aligned}$$

$$E_c^{conventional} = E[n_0] - E_{HF}$$

From definitions of $\psi_{min;n}$ and $\Phi_{min;n}$ it follows from the first line of the first equation that

$$E_c[n] \leq 0$$

Kohn-Sham Construction – Why might it be useful?

The XC energy contains everything we do not know explicitly

$$E_{xc}[n] = \frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 g(\mathbf{r}_1, \mathbf{r}_2) \left(\Gamma_{min;n}^{(2)}(x_1 x_2 | x'_1 x'_2) \Big|_{\substack{x'_1=x_1 \\ x'_2=x_2}} - n(\mathbf{r}_1)n(\mathbf{r}_2) \right) + T[n] - T_s[n]$$

- T_s should be most of the KE, so $(T - T_s)$ should be small and positive.
- Exchange and Coulomb correlation are relatively small compared to the Hartree energy.
- The Coulombic and KE contributions to E_{xc} have offsetting signs.
- E_{xc} is known quite accurately for the homogeneous electron gas.
- Thus there is hope of writing reasonable approximations for E_{xc} . See Lecture III.

Kohn-Sham Procedure (non-spin polarized)

Assuming that we have a suitable E_{xc} (ordinarily an approximate one), the Kohn-Sham scheme to find the variational minimum is

$$E_{v_{ext}}[n] = T_S[n] + E_{ee}[n] + E_{xc}[n] + E_{ext}[n]$$

$$T_S[n] \equiv -\frac{1}{2} \sum_{j=1}^{N_e/2} n_j \int d\mathbf{r}_1 \varphi_j(\mathbf{r}) \nabla^2 \varphi_j(\mathbf{r})$$

$$E_{ee}[n] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}; \quad E_{ext} = \int d\mathbf{r} v_{ext}(\mathbf{r}) n(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{j=1}^{N_e/2} n_j |\varphi_j(\mathbf{r})|^2; \quad n_j = 2$$

Vary the density by varying the KS orbitals

$$\frac{\delta E_{v_{ext}}}{\delta n} = 0 \rightarrow \frac{\delta E_{v_{ext}}}{\delta \varphi_j^*} = 0; \quad 1 \leq j \leq N_e / 2$$

Result is the KS equation (next slide)

The Kohn-Sham Equation

The Kohn-Sham equation (non-spin-polarized for simplicity) for electrons in the field of nuclei Z_I is:

$$\left\{ -\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|} + \int d\mathbf{r}_2 \frac{n(\vec{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + v_{xc}(\mathbf{r}_1) \right\} \phi_j(\mathbf{r}_1) = \epsilon_j \phi_j(\mathbf{r}_1)$$

with the eXchange-Correlation potential given by $v_{xc}[n] = \frac{\delta E_{xc}}{\delta n}$

For comparison, here's the H-F equation

$$\left\{ -\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \int d\mathbf{r}_2 \frac{n_{HF}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\} \phi_j^{HF}(\mathbf{r}_1, \sigma_1) - \sum_{i=1}^{N_e} \delta_{m_i, m_j} \left[\int d\mathbf{r}_2 \frac{\phi_i^{HF*}(\mathbf{r}_2, \sigma_2) \phi_j^{HF}(\mathbf{r}_2, \sigma_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \phi_i^{HF}(\mathbf{r}_1, \sigma_1) = \epsilon_j^{HF} \phi_j^{HF}(\mathbf{r}_1, \sigma_1)$$
$$n_{HF}(\mathbf{r}) = \sum_{i, \sigma}^{N_e} |\phi_i^{HF}(\mathbf{r}, \sigma)|^2$$

KS Equation vs. HF Equation

- **The Kohn-Sham and Hartree-Fock equations are similar in that both**
 - **are mean-field theories**
 - **present *self-consistent field (SCF) problems* that must be solved in iterative fashion.**
- **The KS equation is formally simpler than the HF equation because the KS effective potential is *local*, in contrast to the non-local nature of the exchange term of the HF operator.**
- **Distinct from the HF formalism, the KS procedure in principle takes *electron correlation* fully into account.**
- **In practice in all but a few cases, the KS equation is used with an approximate E_{xc} , whereas the HF formalism involves no further approximation (beyond the single determinant).**
- **The meanings of the KS determinant and the KS eigenvalues differ significantly from the HF determinant and eigenvalues.**

Credit: N. Rösch



Remarks About the Kohn-Sham Procedure

- If $n(\mathbf{r})$ is non-interacting ν -representable, then ν_{xc} is a local potential $\nu_{xc}(\mathbf{r})$ and the KS orbitals are occupied in the density by the *aufbau prinzip* (from lowest KS eigenvalue upward).

$$n(\mathbf{r}) = \sum_{j=1}^{N_e} n_j |\varphi_j(\mathbf{r})|^2, \quad \varepsilon_1 \leq \varepsilon_2 \leq \varepsilon_3 \dots \leq \varepsilon_i \leq \varepsilon_{i+1} \dots$$

$n_j = 1, 2$ depending on treatment of spins

- If $n(\mathbf{r})$ is NOT non-interacting ν -representable, then in principle ν_{xc} is NON-local .

An attempt to force it to be local will result in a density that violates the *aufbau prinzip* (i.e. has “holes below the Fermi level”). In the spin-explicit case, this looks like

$$n(\mathbf{r}) = \sum_{j=1}^{N_L > N_e} n_j |\varphi_j(\mathbf{r})|^2, \quad \varepsilon_1 \leq \varepsilon_2 \leq \varepsilon_3 \dots \leq \varepsilon_i \leq \varepsilon_{i+1} \dots$$

$n_i = 1$ except $n_j = 0$ for at least one value of $j \leq N_e$

HK and KS for Non-integer Particle Number

- p -particle ensemble reduced density matrices are convex combinations of pure-state p -rdms for states ψ_i :

$$\Gamma_{ens}^{(p)}(x_1 \dots x_p | x'_1 \dots x'_p) = \sum_i w_i \Gamma_{\psi_i}^{(p)}(x_1 \dots x_p | x'_1 \dots x'_p); \quad \sum_i w_i = 1; \quad 0 \leq w_i \leq 1$$

- The definition generalizes readily to non-integer electron number. Thus for $N_e = N + \beta$, we have

$$\Gamma_{ens, \beta}^{(p)} = (1 - \beta) \Gamma_N^{(p)} + \beta \Gamma_{N+1}^{(p)}, \quad 0 \leq \beta \leq 1$$

- Such ensembles allow the introduction of generalized HK functionals and KS constructions. Proofs omitted. The key changes are

$$E_{v_{ext}}[n] = F_{ens, \beta}[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r})$$

$$F_{ens, \beta}[n] = \sum_i w_i Tr[(\hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee}) \Gamma_{i, N_i, min; n}]$$

$$Tr[\hat{A} \Gamma^p] := \int d\mathbf{Q} [\hat{A}(\mathbf{Q}) \Gamma^p(\mathbf{Q} | \mathbf{Q}')]_{\mathbf{Q}=\mathbf{Q}'}$$

$$\bar{\Gamma}^{(1)}(x_1 | x'_1) := \sum_{j=1}^{\infty} n_j \varphi_j(x_1) \varphi_j^*(x'_1); \quad 0 \leq n_j \leq 1; \quad \int d\mathbf{r} \varphi_i(\mathbf{r}) \varphi_j^*(\mathbf{r}) = \delta_{ij}; \quad \sum_{j=1}^{\infty} n_j = N_e$$

$$T_s[n] = -\frac{1}{2} \sum_{j=1}^{\infty} n_j \int d\mathbf{r} \varphi_j^*(\mathbf{r}) \nabla^2 \varphi_j(\mathbf{r})$$

Slater-Janak Theorem

▪ A recurring issue is interpretation of the KS quantities, especially the eigenvalues. This next theorem has a key role in that. The generalized (to include continuous electron number) KS equation is

$$h^{KS}(\mathbf{r})\varphi_j(\mathbf{r}) \equiv \left\{ -\left(\frac{1}{2}\right)\nabla^2 + v_{ext}(\mathbf{r}) + v_{ee}(\mathbf{r}) + v_{xc}(\mathbf{r}) \right\} \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r})$$

Theorem [J.C. Slater and J.H. Wood, Internat. J. Quantum Chem. S 4, 3 (1971); J.F. Janak, Phys. Rev. B 18, 7165 (1978)]:

$$\frac{\partial E_{v_{ext}}}{\partial n_j} = \varepsilon_j$$

Proof:

$$E_{v_{ext}} = \sum_{j=1}^{\infty} n_j \left\{ t_j + \int d1 |\varphi_j(1)|^2 \left[\frac{1}{2} v_{ee}[n] + v_{ext} \right] \right\} + E_{xc}$$

$$\frac{\partial E_{xc}}{\partial n_\ell} = \int d\mathbf{r} \frac{\partial E_{xc}}{\partial n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial n_\ell}$$

Typical functional derivative chain rule

$$\frac{\partial E_{v_{ext}}}{\partial n_\ell} = t_\ell + \int d1 |\varphi_\ell(1)|^2 [v_{ee} + v_{ext} + v_{xc}]$$

$$+ \sum_{j=1}^{\infty} n_j \left\{ \frac{\partial t_j}{\partial n_\ell} + \int d1 \frac{\partial |\varphi_j(1)|^2}{\partial n_\ell} [v_{ee} + v_{ext} + v_{xc}] \right\}$$

This line zero by variational stability

$$\frac{\partial E_{v_{ext}}}{\partial n_\ell} = t_\ell + \int d1 |\varphi_\ell(1)|^2 [v_{ee} + v_{ext} + v_{xc}]$$

$$t_\ell = \varepsilon_\ell - \int d1 |\varphi_\ell(1)|^2 [v_{ee} + v_{xc} + v_{ext}] \Rightarrow \frac{\partial E_{v_{ext}}}{\partial n_\ell} = \varepsilon_\ell$$

Interpretation of T_s

- For a one-electron system or a two-electron singlet (closed shell), the KS kinetic energy is the exact system KE.

$$T_s [n] \equiv T[n] = -\frac{1}{2} \int d\mathbf{r} \varphi_0(\mathbf{r}) \nabla^2 \varphi_0(\mathbf{r})$$

$$n_0(\mathbf{r}) = (\varphi_0(\mathbf{r}))^2 \Rightarrow \varphi_0(\mathbf{r}) = n_0^{1/2}(\mathbf{r})$$

$$T_s [n] \equiv T[n] = \frac{1}{8} \int d\mathbf{r} \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} := T_w[n] \equiv \int d\mathbf{r} \tau^w(n, \nabla n)$$

Remarks: (a) T_w is the von Weizsäcker KE. (b) Unsurprisingly, the KE contribution to E_{xc} is zero in these systems. (c) The KE contribution to E_{xc} is a result of either a non-singlet (2 electrons) or more than 2 electrons.

Densities other than Singlets – Spin-Polarization

▪ Although there are some subtleties, the introduction of spin-polarization is straightforward procedurally. Detailed proofs omitted.

Recall from Lecture 1 that for an arbitrary normalized state ψ the spin densities and total density are

$$n_{\psi}(\mathbf{r}\sigma) = \gamma_{\psi}(\mathbf{r}\sigma | \mathbf{r}\sigma)$$

$$n_{\psi}(\mathbf{r}) = n_{\psi}(\mathbf{r}\alpha) + n_{\psi}(\mathbf{r}\beta) := n_{\alpha}(\mathbf{r}) + n_{\beta}(\mathbf{r})$$

For general particle number, extend the HK and KS constructions to be:

$$E_{v_{ext}}[n] = T_S[n] + E_{ee}[n] + E_{xc}[n_{\alpha}, n_{\beta}] + E_{ext}[n]$$

$$T_S[n] \equiv -\frac{1}{2} \sum_{j,\sigma} n_{j,\sigma} \int d\mathbf{r}_1 \varphi_{j,\sigma}(\mathbf{r}) \nabla^2 \varphi_{j,\sigma}(\mathbf{r})$$

$$E_{ee}[n] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}; \quad E_{ext} = \int d\mathbf{r} v_{ext}(\mathbf{r})n(\mathbf{r})$$

$$n_{\sigma}(\mathbf{r}) = \sum_{j=1}^{N_{\sigma}} n_{j\sigma} |\varphi_{j\sigma}(\mathbf{r})|^2$$

Densities other than Singlets – Spin-Polarization

N_σ depends on target spin. For example, $N_\uparrow = N_\downarrow + 2$ gives a triplet

To get the KS equations, do the variation as before but w/r to the *spin densities and spin orbitals*

$$\frac{\delta E_{v_{ext}}}{\delta n_\sigma} = 0 \rightarrow \frac{\delta E_{v_{ext}}}{\delta \varphi_{j\sigma}^*} = 0; \quad 1 \leq j \leq N_\sigma$$

$$h_\sigma^{KS} \varphi_{i,\sigma} \equiv \left\{ -\nabla^2 + v_{ext}(\mathbf{r}) + v_{ee}(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) \right\} \varphi_{i,\sigma} = \varepsilon_{i,\sigma} \varphi_{i,\sigma}$$

$$v_{xc,\sigma}[n] = \frac{\delta E_{xc}}{\delta n_\sigma}$$