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

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

For real-valued $\phi$

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

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

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

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

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

$$n = n_0 \iff \lambda = \varepsilon_0$$

which leads to

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

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

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

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

\[ \int d\mathbf{r} \, n(\mathbf{r}) = N_e \]

Do the variation with a Lagrange multiplier for fixed particle number

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

\[ \Rightarrow \frac{\delta F}{\delta n(\mathbf{r})} + v_{\text{ext}} (\mathbf{r}) = \mu \]
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:

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

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

Non-interacting fermions means $\Phi_{min;n}$ is a Slater determinant.

The Slater determinant 1- and 2-RDMs are

\[
\gamma_{SD}(x | x') = \sum_{j=1}^{N_e} \varphi_j^*(x') \varphi(x)
\]

\[
\Gamma_{SD}^{(2)}(x_1x_2 | x'_1x'_2) = \frac{1}{2} \det \begin{pmatrix}
\gamma_{SD}(x_1 | x'_1) & \gamma_{SD}(x_1 | x'_2) \\
\gamma_{SD}(x_2 | x'_1) & \gamma_{SD}(x_2 | x'_2)
\end{pmatrix}
\]

So the KS kinetic energy is

\[
T_s[n] \equiv T_s \left[ \{ \varphi[n] \} \right] = -\frac{1}{2} \sum_{j=1}^{N_e} \int d\mathbf{r} \, \varphi_j^*(x) \nabla^2 \varphi_j(x)
\]

How is this useful?
Existence Theorems and Proceeding Constructively (cont’d.)

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

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

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

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

\[ \Rightarrow \frac{\delta T_s}{\delta n(\mathbf{r})} + v_{\text{eff}}(\mathbf{r}) = \mu \]

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

So we have mapped the problem into that of constructing \( v_{\text{eff}} \).

How can that be done?

Remark: \( \nu \)-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:

\[
E_{v_{\text{ext}}} [n] = F [n] + \int d\mathbf{r} \, n(\mathbf{r}) \, v_{\text{ext}} (\mathbf{r}) = \langle \psi_{\text{min}; n} | \hat{T} + \hat{V}_{ee} | \psi_{\text{min}; n} \rangle + \int d\mathbf{r} \, n(\mathbf{r}) \, v_{\text{ext}} (\mathbf{r})
\]

\[
= T[n] + \frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 \, g(\mathbf{r}_1, \mathbf{r}_2) \, \Gamma^{(2)}_{\text{min}; n} \left( x_1 x_2 \, | \, x'_1 x'_2 \right)_{x'_1 = x_1; x'_2 = x_2} + \int d\mathbf{r} \, n(\mathbf{r}) \, v_{\text{ext}} (\mathbf{r})
\]

\[
= T_s[n] + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \, g(\mathbf{r}_1, \mathbf{r}_2) \, n(\mathbf{r}_1) n(\mathbf{r}_2)
\]

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

\[
+ \int d\mathbf{r} \, n(\mathbf{r}) \, v_{\text{ext}} (\mathbf{r})
\]

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

\[
E_{v_{\text{ext}}} [n] = T_s[n] + E_{ee} [n] + E_{xc} [n] + E_{ext} [n]
\]
**Euler Equations Again**

What we have done is

\[
E_{\text{ext}}[n] := F[n] + E_{\text{ext}}[n] = T_S[n] + E_{ee}[n] + E_{xc}[n] + E_{\text{ext}}[n]
\]

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

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

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

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

Comparison with the Euler Equation for the KS system

\[
\frac{\delta T_S}{\delta n(\mathbf{r})} + v_{\text{eff}}(\mathbf{r}) = \mu
\]

shows that

\[
v_{\text{eff}}(\mathbf{r}) = v_{ee}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r})
\]

New task: construct \( E_{xc} \)
Exchange and Correlation Subtleties in DFT

\[ E_{xc}[n] = \frac{1}{2} \sum_{\sigma} \int dr_1 dr_2 g(r_1, r_2) \left( \Gamma_{\min;n}^{(2)} \left( x_1 x_2 \mid x'_1 x'_2 \right) \right|_{x'_1 = x_1, x'_2 = x_2} - n(r_1) n(r_2) \right) + T[n] - T_s[n] \]

\[ E_{xc}[n] = E_x[n] + E_c[n] \]

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

\[ E_x[n] = \langle \Phi_{\min;n} | \hat{\gamma}_{\text{ee}} | \Phi_{\min;n} \rangle - \frac{1}{2} \int dr_1 dr_2 g(r_1, r_2) n(r_1) n(r_2) \]

\[ = -\frac{1}{2} \sum_{\sigma} \int dr_1 dr_2 g(r_1, r_2) \gamma_{KS;n} \left( x_1 \mid x_2 \right) \gamma_{KS;n} \left( x_2 \mid x_1 \right) \]

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

\[
E_c [n] = \langle \psi_{\text{min};n} | \hat{T} + \hat{V}_{ee} | \psi_{\text{min};n} \rangle - \langle \Phi_{\text{min};n} | \hat{T} + \hat{V}_{ee} | \Phi_{\text{min};n} \rangle
\]

\[= \frac{1}{2} \sum \int dr_1 dr_2 g(r_1, r_2) \left\{ \Gamma_{\text{min};n}^{(2)} (x_1, x_2 | x'_1, x'_2) \right|_{x_1 = x_1, x_2 = x_2} - n(r_1) n(r_2) + \gamma_{KS;n} (x_1 | x_2) \gamma_{KS;n} (x_2 | x_1) \right\} + T[n] - T_s[n]
\]

\[
E_{c,\text{conventional}} = E[n_0] - E_{HF}
\]

From definitions of \( \psi_{\text{min};n} \) and \( \Phi_{\text{min};n} \) 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

\[
E_{xc} [n] = \frac{1}{2} \sum_{\sigma} \int dr_1 dr_2 g(r_1, r_2) \left( \Gamma^{(2)}_{\text{min};n} \left( x_{1} x_{2} \mid x_{1}' x_{2}' \right) \bigg|_{x_{1}'=x_{1}; x_{2}'=x_{2}} - n(r_{1})n(r_{2}) \right) + T[n] - T_{s}[n]
\]

- \( T_{s} \) 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

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

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

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

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

Vary the density by varying the KS orbitals

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

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:

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

with the eXchange-Correlation potential given by

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

For comparison, here's the H-F equation

$$\left\{-\frac{\hbar^2}{2m} \nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} + \int d\mathbf{r}_2 \frac{n_{HF}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\} \phi_{jI}^{HF}(\mathbf{r}_1, \sigma_1)$$

$$-\sum_{i=1}^{N_e} \delta_{m_i,m_j} \left[ \int d\mathbf{r}_2 \frac{\phi_i^{HF*}(\mathbf{r}_2, \sigma_2) \phi_j^{HF}(\mathbf{r}_2, \sigma_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \phi_{jI}^{HF}(\mathbf{r}_1, \sigma_1) = \varepsilon_{jI}^{HF} \phi_{jI}^{HF}(\mathbf{r}, \sigma_1)$$

$$n_{HF}(\mathbf{r}) = \sum_{i,\sigma} \left| \phi_{iI}^{HF}(\mathbf{r}, \sigma) \right|^2$$
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 \( n(r) \) is non-interacting \( \nu \)-representable, then \( \nu_{xc} \) is a local potential \( \nu_{xc}(r) \) and the KS orbitals are occupied in the density by the \textit{aufbau prizip} (from lowest KS eigenvalue upward).

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

\( n_j = 1, 2 \) depending on treatment of spins

- If \( n(r) \) is NOT non-interacting \( \nu \)-representable, then in principle \( \nu_{xc} \) is NON-local.

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

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

\( n_i = 1 \) 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 $\psi_i$:

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

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

$$\Gamma^{(p)}_{\text{ens}, \beta} = (1 - \beta) \Gamma^{(p)}_N + \beta \Gamma^{(p)}_{N+1}, \quad 0 \leq \beta \leq 1$$

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

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

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

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

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

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

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


\[
\frac{\partial E^{\text{ext}}}{\partial n_j} = \varepsilon_j
\]

Proof:

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

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

Typical functional derivative chain rule

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

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

This line zero by variational stability

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

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

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

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

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

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 $\psi$ the spin densities and total density are

$$n_\psi (r \sigma) = \gamma_\psi (r \sigma | r \sigma)$$

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

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

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

$$T_S [n] \equiv -\frac{1}{2} \sum_{j,\sigma} n_{j,\sigma} \int dr_1 \varphi_{j,\sigma} (r) \nabla^2 \varphi_{j,\sigma} (r)$$

$$E_{ee} [n] = \frac{1}{2} \int dr_1 dr_2 \frac{n(r_1) n(r_2)}{|r_1 - r_2|}; \quad E_{\text{ext}} = \int dr v_{\text{ext}} (r) n (r)$$

$$n_\sigma (r) = \sum_{j=1}^{N_\sigma} n_{j\sigma} \left| \varphi_{j,\sigma} (r) \right|^2$$
Densities other than Singlets – Spin-Polarization

\( N_\sigma \) depends on target spin. For example, \( N_{\uparrow\uparrow} = N_{\downarrow\downarrow} + 2 \) gives a triplet

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

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

\[
h^{KS}_\sigma \varphi_{i,\sigma} \equiv \left\{ -\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{ee}(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) \right\} \varphi_{i,\sigma} = \varepsilon_{i,\sigma} \varphi_{i,\sigma}
\]

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