

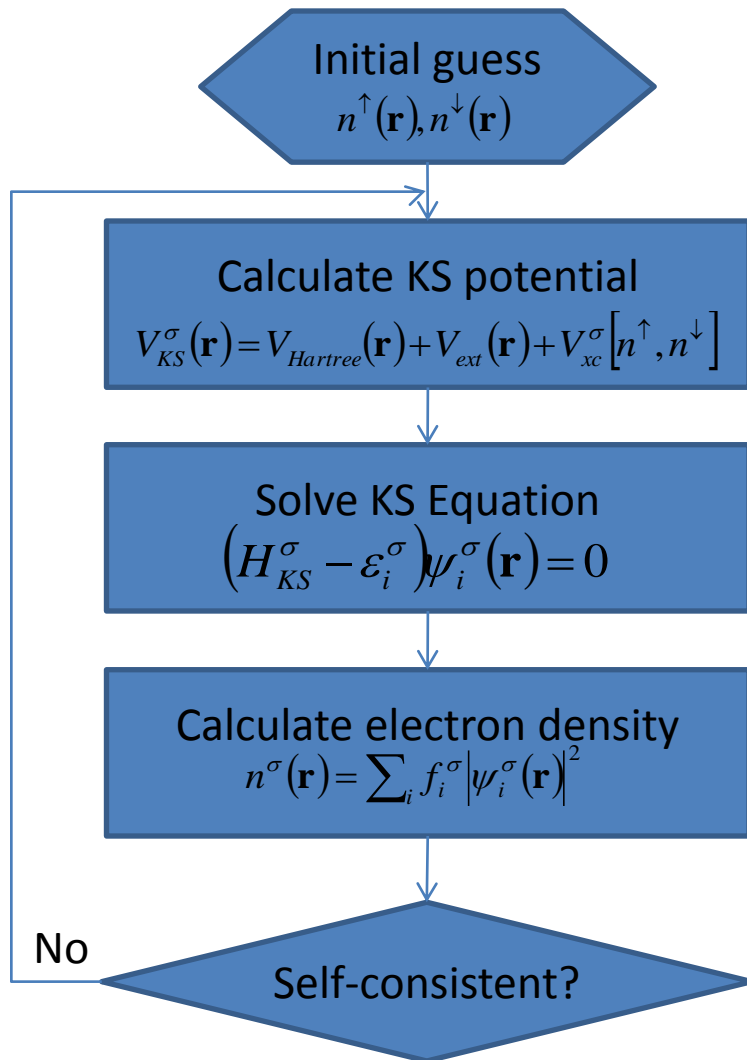


Chapter 5: Solving Kohn-Sham Equation

1. Flow chart
2. Preparation
3. Functional
4. K-space
5. Examples



Self-consistent KS equation



Total energy functional

$$E_{KS}[n] = T_s[n] + E_{Hartree}[n] + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{nuclei} + E_{xc}[n]$$

$$E_{xc}[n] = F_{HK}[n] - (T_s[n] + E_{Hartree}[n])$$

$$\epsilon_i^\sigma = \langle \psi_i^\sigma | H_{KS}^\sigma | \psi_i^\sigma \rangle$$

$$E_s = \sum_{\sigma} \sum_{i=1}^{N^\sigma} \epsilon_i^\sigma$$

Non-interacting system

KS

$$E_{KS}[V^{in}] = E_s[V^{in}] - \underbrace{\sum_{\sigma} \int d^3r V^{\sigma, in}(\mathbf{r})n^{out}(\mathbf{r}, \sigma)}_{T_s} + E_{pot}[n^{out}]$$

Explicit

$$E_{HWF}[n^{in}] = E_s[V_{n^{in}}] - \sum_{\sigma} \int d^3r V_{n^{in}}^{\sigma}(\mathbf{r})n^{in}(\mathbf{r}, \sigma) + E_{pot}[n^{in}]$$

Generalized

$$E[V^{in}, n^{in}] = E_s[V^{in}] - \sum_{\sigma} \int d^3r V^{\sigma, in}(\mathbf{r})n^{in}(\mathbf{r}, \sigma) + E_{pot}[n^{in}]$$



Mixing scheme

Density function

$$n(\mathbf{r}) = \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = N \frac{\int d^3 r_2 \dots d^3 r_N \sum_{\sigma_1} |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)|^2}{\int d^3 r_1 d^3 r_2 \dots d^3 r_N |\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)|^2}$$

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$$

Linear mixing

$$n_{i+1}^{in} = \alpha n_i^{out} + (1 - \alpha) n_i^{in} = n_i^{in} + \alpha (n_i^{out} - n_i^{in})$$

$$\delta n^{out} [n^{in}] = n^{out} - n_{KS} = (\tilde{\chi} + 1) (n^{in} - n_{KS})$$

$$(\tilde{\chi} + 1) = \frac{\delta n^{out}}{\delta n^{in}} = \frac{\delta n^{out}}{\delta V^{in}} \frac{\delta V^{in}}{\delta n^{in}}$$

$$n_{i+1}^{in} (best) = n_{KS}$$



$$n_{KS} = n^{in} + \tilde{\chi}^{-1} (n^{in} - n^{out})$$

Response function

$$\tilde{\chi}(\mathbf{r}, \mathbf{r}') = \sum_m \chi_m f_m(\mathbf{r}) f_m(\mathbf{r}')$$

Numerical mixing

$$n_{i+1}^{in} = n_i^{in} - J_i^{-1} (n_i^{out} - n_i^{in})$$

Broyden method



LDA

Functional for exchange and correlation

$$E_{KS}[n] = T_s[n] + E_{Hartree}[n] + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{nuclei} + E_{xc}[n]$$

$$E_{xc}[n] = F_{HK}[n] - (T_s[n] + E_{Hartree}[n]) = ?$$

Local (spin) density approximation

$$E_{xc}^{LSDA}[n] = \int d^3r n(\mathbf{r}) \varepsilon_{xc}^{hom}[n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})]$$

$$= \int d^3r n(\mathbf{r}) \left\{ \varepsilon_x^{hom}[n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})] + \varepsilon_c^{hom}[n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})] \right\}$$

Fractional spin polarization

$$\zeta(\mathbf{r}) = \frac{n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r})}{n(\mathbf{r})}$$

Exchange and correlation potentials of homogeneous gas

$$n^\uparrow(\mathbf{r}) = n^\downarrow(\mathbf{r}) = n(\mathbf{r})/2$$

Total density

$$T_0^\sigma = \frac{\hbar^2}{2m_e} \frac{4\pi \int_0^{k_F^\sigma} dk k^4}{4\pi \int_0^{k_F^\sigma} dk k^2} = \frac{3}{5} E_{F0}^\sigma$$

$$\frac{4\pi}{3} (k_F^\sigma)^3 = \frac{(2\pi)^3}{\Omega} N_e^\sigma \Rightarrow k_F^\sigma = (6\pi^2 n^\sigma)^{1/3}$$

Unpolarized systems, LDA

$$E_{F0}^\sigma = \frac{\hbar^2}{2m_e} (k_F^\sigma)^2 = \frac{1}{2} (k_F^\sigma)^2$$

Unpolarized systems

$$k_F^\sigma = (3\pi^2 n)^{1/3} = \left(\frac{9}{4}\pi\right)^{1/3} / r_s$$

The potential:
$$\delta E_{xc}^{LSDA}[n] = \sum_\sigma \int d^3r \left[\varepsilon_{xc}^{hom} + n \frac{\partial \varepsilon_{xc}^{hom}}{\partial n^\sigma} \right]_{\mathbf{r}, \sigma} \delta n(\mathbf{r}, \sigma) \Rightarrow V_{xc}^\sigma(\mathbf{r}) = \left[\varepsilon_{xc}^{hom} + n \frac{\partial \varepsilon_{xc}^{hom}}{\partial n^\sigma} \right]_{\mathbf{r}, \sigma}$$



Exchange energy

Exchange operator

$$K_j(\mathbf{r})\phi_i(\mathbf{r}) = \left[\int \phi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_i(\mathbf{r}') d\mathbf{r}' \right] \phi_j(\mathbf{r})$$

$$\hat{V}_x^{i,\sigma}(\mathbf{r}) = - \sum_j \int \phi_j^{\sigma*}(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_i^\sigma(\mathbf{r}') d\mathbf{r}' \frac{\phi_j^\sigma(\mathbf{r})}{\phi_i^\sigma(\mathbf{r})}$$

Exchange energy for homogeneous gas

$$\varepsilon_x^{\sigma, \text{hom}} = E_x^\sigma / N^\sigma = \frac{1}{2} \frac{k_F^\sigma}{\pi} f(x) \quad \langle f(x) \rangle = -3/2 \quad \longrightarrow \quad -\frac{3k_F^\sigma}{4\pi} = -\frac{3}{4} \left(\frac{6}{\pi} n^\sigma \right)^{1/3}$$

$$f(x) = - \left(1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right| \right), \quad x = k/k_F$$

$$n^\uparrow(\mathbf{r}) = n^\downarrow(\mathbf{r}) = n(\mathbf{r})/2$$

Unpolarized systems, LDA

$$\varepsilon_x^{\text{hom}} = -\frac{3}{4\pi} \left(\frac{9}{4} \pi \right)^{1/3} / r_s$$

Exchange hole

Joint probability

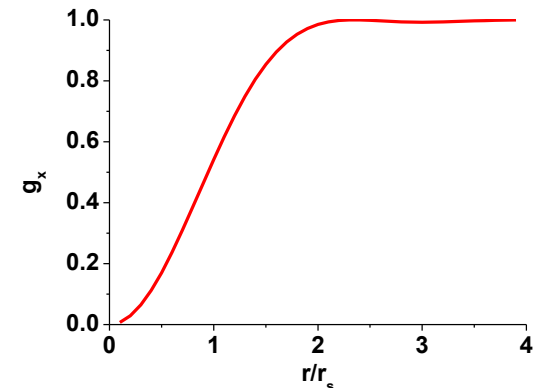
$$n(\mathbf{r}, \sigma; \mathbf{r}', \sigma') = \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\sigma - \sigma_i) \delta(\mathbf{r}' - \mathbf{r}_j) \delta(\sigma' - \sigma_j) \right\rangle$$

Pair distribution function

$$g(\mathbf{r}, \sigma; \mathbf{r}', \sigma') = \frac{n(\mathbf{r}, \sigma; \mathbf{r}', \sigma')}{n(\mathbf{r}, \sigma)n(\mathbf{r}', \sigma')} = 1 + \frac{\Delta n(\mathbf{r}, \sigma; \mathbf{r}', \sigma')}{n(\mathbf{r}, \sigma)n(\mathbf{r}', \sigma')}$$

HG

$$g_x(\mathbf{r}, \sigma; \mathbf{r}', \sigma') = \delta_{\sigma_1, \sigma_2} g_x^{\sigma_1, \sigma_2}(|\mathbf{r}|) = 1 - \left[3 \frac{\sin(y) - y \cos(y)}{y^3} \right]^2$$





Correlation energy

Thomas Fermi screening

$$\frac{1}{k^2} \rightarrow \frac{1}{k^2 + k_{TF}^2} \quad \text{Exponentially decay screening}$$

$$k_{TF} = r_s^{1/2} \left(\frac{16}{3\pi^2} \right)^{1/3} \quad k_F = \left(\frac{12}{\pi} \right)^{1/3} r_s^{-1/2} \quad \text{Unpolarized systems}$$

Correlation energy for homogeneous gas

Wigner (1934)

Low density limit: electrostatic energy

High density limit:

$$\varepsilon_c = -\frac{0.44}{r_s + 0.78} \text{ (a.u.)} \quad \text{Per electron}$$

Gellmann and Breuckner (1957)

Unpolarized systems $n^\uparrow(\mathbf{r}) = n^\downarrow(\mathbf{r}) = n(\mathbf{r})/2$

High density limit: $r_s \rightarrow 0$

$$\varepsilon_c(r_s) \rightarrow 0.311 \ln(r_s) - 0.048 + r_s [A \ln(r_s) + C] + \dots$$

Low density limit:

$$\varepsilon_c(r_s) \rightarrow \frac{a_1}{r_s} + \frac{a_2}{r_s^{3/2}} + \frac{a_3}{r_s^2} \dots$$

Other methods:

Quantum Monte Carlo (most accurate)

Random phase approximation (RPA)

GW

GGA

Generalized gradient approximation

$$E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int d^3r n(\mathbf{r}) \varepsilon_{xc} [n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r}), |\nabla n^\uparrow(\mathbf{r})|, |\nabla n^\downarrow(\mathbf{r})|]$$

$$\equiv \int d^3r n(\mathbf{r}) \varepsilon_{xc}^{\text{hom}}(n) F_{xc} [n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r}), |\nabla n^\uparrow(\mathbf{r})|, |\nabla n^\downarrow(\mathbf{r})|]$$

The potential:

$$\delta E_{xc}^{GGA}[n] = \sum_{\sigma} \int d^3r \left[\varepsilon_{xc}^{\text{hom}} + n \frac{\partial \varepsilon_{xc}^{\text{hom}}}{\partial n^{\sigma}} + n \frac{\partial \varepsilon_{xc}^{\text{hom}}}{\partial \nabla n^{\sigma}} \nabla \right]_{\mathbf{r}, \sigma} \delta n(\mathbf{r}, \sigma)$$

Integration by part

$$V_{xc}^{\sigma}(\mathbf{r}) = \left[\varepsilon_{xc}^{\text{hom}} + n \frac{\partial \varepsilon_{xc}^{\text{hom}}}{\partial n^{\sigma}} - \nabla \left(n \frac{\partial \varepsilon_{xc}^{\text{hom}}}{\partial \nabla n^{\sigma}} \right) \right]_{\mathbf{r}, \sigma}$$

Numerical difficulties

By wave function

$$\langle \psi_j | \hat{V}_{xc} | \psi_i \rangle = \int [\tilde{V}_{xc} \psi_j^* \psi_i + \psi_j^* \mathbf{V}_{xc} \cdot \nabla \psi_i + (\mathbf{V}_{xc} \cdot \nabla \psi_j^*) \psi_i]$$

$$\tilde{V}_{xc} = \varepsilon_{xc}^{\text{hom}} + n \frac{\partial \varepsilon_{xc}^{\text{hom}}}{\partial n^{\sigma}}; \mathbf{V}_{xc} = n \frac{\partial \varepsilon_{xc}^{\text{hom}}}{\partial \nabla n^{\sigma}}$$

Vector operator, costly

Density gradient

$$V_{xc}^{\sigma}(\mathbf{r}_m) = \left[\varepsilon_{xc}^{\text{hom}} + n \frac{\partial \varepsilon_{xc}^{\text{hom}}}{\partial n^{\sigma}} \right]_{\mathbf{r}_m, \sigma} + \sum_{m'} \left[n \frac{\partial \varepsilon_{xc}^{\text{hom}}}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \right]_{\mathbf{r}_{m'}, \sigma} \mathbf{C}_{m'-m}$$

$$\nabla n(\mathbf{r}_m) = \sum_{m'} \mathbf{C}_{m-m'} n(\mathbf{r}_{m'})$$

$$\frac{\delta \nabla n(\mathbf{r}_m)}{\delta n(\mathbf{r}_{m'})} \rightarrow \frac{\partial \nabla n(\mathbf{r}_m)}{\partial n(\mathbf{r}_{m'})} = \mathbf{C}_{m-m'}$$

Hybrid functionals

Orbital dependent Hartree-Fock + explicit density functional

Half-half:

$$E_{xc} = \int_0^1 E_{xc}^\lambda d\lambda \rightarrow \frac{1}{2} (E_x^{HF} + E_{xc}^{DFA})$$

LDA or GGA

B3LYP:

$$E_{xc} = E_{xc}^{LDA} + a_0 (E_x^{HF} - E_x^{DFA}) + a_x E_x^{Becke} + a_c E_c + (1-c) E_c^{VWN}$$

PBE:

$$E_{xc} = E_{xc}^{LDA} + \frac{1}{4} (E_x^{HF} - E_{xc}^{DFA})$$

LYP correlation

PBE0:

$$E_{xc}^{PBE0} = \frac{1}{4} E_x^{HF} + \frac{3}{4} E_x^{PBE} + E_c^{PBE}$$

non-empirical

HSE03:

$$E_{xc}^{HSE03} = \frac{1}{4} E_x^{HF,SR}(\mu) + \frac{3}{4} E_x^{PBE,SR}(\mu) + E_x^{PBE,LR}(\mu) + E_c^{PBE}$$

Semi-empirical

J. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. 105, 9982 (1996).

J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).

Materials Computation and Simulation



Hybrid functionals

Exchange energies ($-E_x$ in hartree) for some spherically symmetric atoms.^a

	E_x^{exact}	E_x^{LSD}	E_x^{PBE}	E_x^{RPBE}	E_x^{BLYP}	E_x^{HCTH}	E_x^{PKZB}	E_x^{VS98}	E_x^{FT98}
H	0.3125	0.2680	0.3059	0.3112	0.3098	0.3055	0.3081	0.3148	0.3120
He	1.0258	0.8840	1.0136	1.0313	1.0255	1.0063	1.0202	1.0399	1.0302
Li	1.7807	1.5379	1.7572	1.7876	1.7753	1.7454	1.7682	1.7893	1.7852
Be	2.6658	2.3124	2.6358	2.6801	2.6578	2.6114	2.6482	2.6579	2.6707
N	6.6044	5.9008	6.5521	6.6252	6.5961	6.5145	6.5255	6.5968	6.6045
Ne	12.1050	11.0335	12.0667	12.1593	12.1378	12.0114	11.9514	12.1404	12.1260
Na	14.0131	12.7859	13.9506	14.0528	14.0304	13.9009	13.8115	14.0374	14.0177
Mg	15.9884	14.6117	15.9147	16.0260	16.0005	15.8596	15.7448	15.9967	15.9862
P	22.6341	20.7931	22.5028	22.6369	22.6221	22.5016	22.2475	22.6365	22.6089
Ar	30.1747	27.8632	29.9961	30.1494	30.1535	30.0751	29.6437	30.1918	30.1429
Kr	93.8330	88.6245	93.4257	93.6645	93.8721	95.1802	92.2949	94.8248	93.8407
Xe	179.0635	170.5660	178.2450	178.5649	179.0427	183.2130	176.2574	181.6907	179.0636
mare (in %)		9.8	0.8	0.3	0.2	1.4	1.3	0.5	0.1

^aAll functionals were evaluated with self-consistent exchange-only OEP orbitals and densities [47]. Exact values, E_x^{exact} , were obtained by evaluating Eq. (11) with these orbitals. The “mare” is the mean absolute value of the relative error.

S. Kurth, J. P. Perdew, P. Blaha, Molecular and solid-state tests of density functional approximations: LSD, GGAs, and meta-GGAs, Int. J. Quan Chem, 1999, 75, 889.



Hybrid functionals

Correlation energies ($-E_c$ in hartree) for some spherically symmetric atoms.^a

	E_c^{exact}	E_c^{LSD}	E_c^{PBE}	E_c^{BLYP}	E_c^{HCTH}	E_c^{PKZB}	E_c^{KCIS}	E_c^{VS98}	E_c^{FT98}
H	0.0000	0.0222	0.0060	0.0000	0.0132	0.0000	0.0000	0.0000	0.0000
He	0.0420	0.1125	0.0420	0.0438	0.0753	0.0473	0.0408	0.0399	0.0464
Li	0.0455	0.1508	0.0514	0.0534	0.0961	0.0544	0.0498	0.0626	0.0555
Be	0.0950	0.2240	0.0856	0.0945	0.1505	0.0936	0.0861	0.1251	0.0916
N	0.1858	0.4268	0.1799	0.1919	0.2772	0.1841	0.1805	0.2342	0.1912
Ne	0.3929	0.7428	0.3513	0.3835	0.5046	0.3635	0.3667	0.4344	0.3661
Na	0.3988	0.8010	0.3715	0.4083	0.5370	0.3821	0.3905	0.4671	0.3909
Mg	0.4424	0.8874	0.4110	0.4594	0.6080	0.4252	0.4364	0.5384	0.4411
P	0.5446	1.1127	0.5265	0.5664	0.7457	0.5377	0.5551	0.6897	0.5513
Ar	0.7314	1.4242	0.7067	0.7508	0.9533	0.7229	0.7457	0.9117	0.7277
Kr		3.2693	1.7672	1.7486	2.0788	1.7849	1.8875	1.9554	1.8037
Xe		5.1773	2.9184	2.7440	3.1789	2.9364	3.1269	3.0873	2.9468
mare (in %)		128.3	6.4	4.5	51.8	5.8	4.3	22.3	5.5

^aAll functionals were evaluated with self-consistent exchange-only OEP orbitals and densities [47]. Exact correlation energies are taken from Ref. [25]. The “mare” excludes H, Kr, and Xe.

S. Kurth, J. P. Perdew, P. Blaha, Molecular and solid-state tests of density functional approximations: LSD, GGAs, and meta-GGAs, Int. J. Quan Chem, 1999, 75, 889.