Comparison between Hartree-Fock and Kohn-Sham Theory

both methods deal with problem of N interacting electrons described by Hamiltonian

$$\hat{H} = \underbrace{\sum_i -\frac{\nabla_i^2}{2} + V(\vec{r}_i)}_{\hat{H}_1} + \underbrace{\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\hat{H}_2} =: \sum_i \hat{h}(i) + \frac{1}{2}\sum \hat{w}(i,j)$$

with $\hat{h}(i) = -\frac{\nabla_i^2}{2} + V(\vec{r}_i)$; $\hat{w}(i,j) = \frac{1}{|\vec{r}_i - \vec{r}_j|}$

Idea of Hartree-Fock method:

Use variational principle to find an upper bound for true g.s. energy by minimizing the expectation value $\langle\Phi|\hat{H}|\Phi\rangle$ with respect to a Slater-Determinant Φ of (ortho-)normalized single-particle orbitals $\varphi_n(\vec{x})$ $\vec{x} = (\vec{r}, \underset{\text{spin}}{\sigma})$, i.e., find that Slater determinant which gives lowest

$$E_{HF} = \langle\Phi|\hat{H}|\Phi\rangle$$

$$\Phi(\vec{x}_1, \dots \vec{x}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \varphi_{n_1}(\vec{x}_{P_1})\varphi_{n_2}(\vec{x}_{P_2}) \dots \varphi_{n_N}(\vec{x}_{P_N})$$

Def: Antisymmetrization operator: $\hat{A} = \frac{1}{N!}\sum_P (-1)^P \underset{\text{permutation operator}}{\hat{P}}$

$$\Phi(\vec{x}_1, \dots \vec{x}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \hat{P}\, \varphi_{n_1}(\vec{x}_1)\varphi_{n_2}(\vec{x}_2) \dots \varphi_{n_N}(\vec{x}_N)$$

$$= \sqrt{N!}\,\hat{A}\,\Phi_H(\vec{x}_1 \dots \vec{x}_N)$$

where $\Phi_H(\vec{x}_1, \dots \vec{x}_N) = \varphi_{n_1}(\vec{x}_1) \dots \varphi_{n_N}(\vec{x}_N)$

$(-1)^P = \begin{cases} +1 & \text{if } P \text{ even} \\ -1 & \text{if } P \text{ odd} \end{cases}$ permutation of $(1, 2, \dots N)$

if $\hat{P}_1$ is operator of arbitrary permutation: $\leadsto \hat{P}_1\hat{A} = (-1)^{P_1}\hat{A}$

$$\hookrightarrow \hat{A}^2 = \frac{1}{N!}\sum_{P_1} (-1)^{P_1}\hat{P}_1\hat{A} = \frac{1}{N!}\sum_{P_1}\hat{A} = \hat{A}$$

note further: $[\hat{H}_1, \hat{A}] = 0 \; , \; [\hat{H}_2, \hat{A}] = 0 \; \rightarrow [\hat{H}, \hat{A}] = 0$

$$\Rightarrow \langle \Phi | \hat{H}_1 | \Phi \rangle = N! \, \langle \Phi_H | \hat{A} \hat{H}_1 \hat{A} | \Phi_H \rangle$$

$$= N! \, \langle \Phi_H | \hat{H}_1 \underbrace{\hat{A}^2}_{\hat{A}} | \Phi_H \rangle$$

$$= \sum_{i=1}^{N} \sum_{P} (-1)^P \underbrace{\langle \Phi_H | \hat{h}(i) \hat{P} | \Phi_H \rangle}_{\text{only non-vanishing for } \hat{P} = \mathbb{1}}$$

$$= \sum_{i=1}^{N} \langle \Phi_H | \hat{h}(i) | \Phi_H \rangle = \sum_{i=1}^{N} \int d\vec{x} \; \varphi^*_{n_i}(\vec{x}) \; \hat{h}(i) \; \varphi_{n_i}(\vec{x})$$

$$\left[\int d\vec{x} = \int d^3 r \sum_{\sigma = \uparrow, \downarrow} \right]$$

$$\langle \Phi | \hat{H}_2 | \Phi \rangle = N! \, \langle \Phi_H | \hat{A} \hat{H}_2 \hat{A} | \Phi_H \rangle = N! \, \langle \Phi_H | \hat{H}_2 \hat{A} | \Phi_H \rangle$$

$$= \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \sum_{P} (-1)^P \underbrace{\langle \Phi_H | \hat{w}(i,j) \hat{P} | \Phi_H \rangle}_{\text{only non vanishing for } \hat{P} = \mathbb{1} \text{ or } \hat{P} = \hat{P}_{ij}}$$

$$= \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \langle \Phi_H | \hat{w}(i,j) \, (\mathbb{1} - \hat{P}_{ij}) \, | \Phi_H \rangle$$

$$= \frac{1}{2} \sum_{\substack{i,j \\ \cancel{i \neq j}}} \int d\vec{x} \int d\vec{x}' \, \frac{|\varphi_{n_i}(\vec{x})|^2 \, |\varphi_{n_j}(\vec{x}')|^2}{|\vec{r} - \vec{r}'|}$$

$$- \frac{1}{2} \sum_{\substack{i,j \\ \cancel{i \neq j}}} \int d\vec{x} \int d\vec{x}' \, \frac{\varphi^*_{n_i}(\vec{x}) \varphi_{n_j}(\vec{x}) \; \varphi^*_{n_j}(\vec{x}') \varphi_{n_i}(\vec{x}')}{|\vec{r} - \vec{r}'|}$$

for spin-orbitals: $\varphi_{n_i}(\vec{x}) = \varphi_{k_i s_i}(\vec{r}) \, \delta_{s_i \sigma}$ $\qquad N = N_\uparrow + N_\downarrow = \sum_\sigma N_\sigma$

$$E[\{\varphi_{k_i\sigma}\}] = E_{HF} = \langle \Phi | \hat{H} | \Phi \rangle = \sum_{\sigma = \uparrow,\downarrow} \sum_{k_i = 1}^{N_\sigma} \int d^3 r \; \varphi^*_{k_i \sigma}(\vec{r}) \left(-\frac{\nabla^2}{2} + v(\vec{r}) \right) \varphi_{k_i \sigma}(\vec{r})$$

$$+ \frac{1}{2} \sum_{\sigma\sigma'} \sum_{k_i}^{N_\sigma} \sum_{k_j}^{N_{\sigma'}} \int d^3 r \int d^3 r' \; \frac{|\varphi_{k_i \sigma}(\vec{r})|^2 \, |\varphi_{k_j \sigma'}(\vec{r}')|^2}{|\vec{r} - \vec{r}'|}$$

$$- \frac{1}{2} \sum_{\sigma} \sum^{N_\sigma} \sum^{N_{\sigma'}} \int d^3 r \int d^3 r' \; \frac{\varphi^*_{k_i \sigma}(\vec{r}) \varphi_{k_j \sigma}(\vec{r}) \varphi^*_{k_j \sigma}(\vec{r}') \varphi_{k_i \sigma}(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

→ reformulate minimization problem:
find those single particle orbitals $\varphi_{k\sigma}(\vec{r})$ for which $E[\{\varphi_{k\sigma}\}]$ is minimal under the constraint that the $\varphi_{k\sigma}$ are normalized (included through Lagrange multipliers)

$$\frac{\delta}{\delta \varphi^*_{j\sigma}(\vec{r})} \left[E[\{\varphi_{k\sigma}\}] - \sum_{\sigma'} \sum_{k=1}^{N_{\sigma'}} \varepsilon_{k\sigma'} \left(\int d^3r' |\varphi_{k\sigma'}(\vec{r}')|^2 - 1 \right) \right] = 0$$

result of this variation: HF equations

$$\boxed{\begin{aligned} &\left(-\frac{\nabla^2}{2} + v(\vec{r})\right)\varphi_{k\sigma}(\vec{r}) + \overbrace{\int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}}^{v_H(\vec{r})} \varphi_{k\sigma}(\vec{r}) \\ &\qquad - \int d^3r' \frac{\rho_\sigma(\vec{r}\,\vec{r}')}{|\vec{r}-\vec{r}'|} \varphi_{k\sigma}(\vec{r}') = \varepsilon_{k\sigma} \varphi_{k\sigma}(\vec{r}) \end{aligned}}$$

where
$$\rho_\sigma(\vec{r}\,\vec{r}') = \sum_{k=1}^{N_\sigma} \varphi^*_{k\sigma}(\vec{r}')\, \varphi_{k\sigma}(\vec{r})$$
$$n(\vec{r}) = \sum_\sigma \rho_\sigma(\vec{r},\vec{r}) = \sum_\sigma \sum_{k=1}^{N_\sigma} |\varphi_{k\sigma}(\vec{r})|^2$$

remarks: – self-consistent equations

– "exchange" potential $-\int d^3r' \frac{\rho_\sigma(\vec{r}\,\vec{r}')}{|\vec{r}-\vec{r}'|} \, \_\_ \underline{\varphi_{k\sigma}(\vec{r}')} \, \_\_$ is non-local operator (~~$\varphi_{k\sigma}$ depends on~~ for fixed $\vec{r}$ its action on $\varphi_{k\sigma}$ depends on $\varphi_{k\sigma}$ at <u>all</u> $\vec{r}'$)

$$E_{HF} = \sum_\sigma \sum_{k=1}^{N_\sigma} \int d^3r\, \varphi^*_{k\sigma}(\vec{r}) \left(-\frac{\nabla^2}{2}\right) \varphi_{k\sigma}(\vec{r}) + \int d^3r\, v(\vec{r})\, n(\vec{r})$$
$$+ \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r}-\vec{r}'|} - \frac{1}{2} \sum_\sigma \int d^3r \int d^3r' \frac{|\rho_\sigma(\vec{r}\,\vec{r}')|^2}{|\vec{r}-\vec{r}'|}$$

Comparison HF - KS

Hartree - Fock	Kohn - Sham
1) approximate wavefunction by Slater determinant; write energy as functional of sp orbitals $E[\{\varphi_{k\sigma}\}]$	1) write gs energy as functional of gs density; formally exact if exact $E_{xc}[n_\uparrow n_\downarrow]$ is used
2) minimize energy fct wrt orbitals (≙ find Slater determinant for which $\langle\Phi\|\hat{H}\|\Phi\rangle$ is minimal)	2) minimize energy wrt density (HK variational principle)
3) effective single particle equation (HF eq)	3) effective SP equation (KS equation)
$\left(-\frac{\nabla^2}{2}+v(r)+v_H(r)\right)\varphi_{k\sigma}(r) - \int d^3r' \frac{\rho_\sigma(r,r')}{\|\vec{r}-\vec{r}'\|}\varphi_{k\sigma}(\vec{r}') = \varepsilon_{k\sigma}\varphi_{k\sigma}(\vec{r})$	$\left(-\frac{\nabla^2}{2}+v(r)+v_H(r)+v_{xc\sigma}(r)\right)\varphi_{k\sigma}(\vec{r}) = \varepsilon_{k\sigma}\varphi_{k\sigma}(\vec{r})$ $v_{xc\sigma}(\vec{r}) = \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\vec{r})}$
4) non-local exchange potential	4) KS potential is local and multiplicative