FYS4480/9480, lecture
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Kohn-Sham equations

Kohn-Sham kinetic energy

$$\langle T_s \rangle = T_s[n] =$$

$$\sum_{i=1}^{N} \int d\vec{r}\, \varphi_i^*(\vec{r}) \left(-\frac{\nabla_i^2}{2} \right) \varphi_i(\vec{r})$$

$$= \sum_{i=1}^{N} \int d\vec{r}\, |\nabla_i \varphi_i(\vec{r})|^2$$

$$\Phi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \cdots & \varphi_1(x_N) \\ \vdots & & \vdots \\ \varphi_N(x_1) & & \varphi_N(x_N) \end{vmatrix}$$

Hartree-term

$$E_{Hartree}[n] = \frac{1}{2}\int d\vec{r}\int d\vec{r}\,'\,\frac{n(\vec{r})\,n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

Kohn-sham functional

$$E_{KS}[n] = T_s[n] + \overbrace{\int d\vec{r}\, V_{ext}(\vec{r})\, n(\vec{r})}^{E_{Ext}}$$

$$+ E_{Hartree}[n] + E_{xc}[n]$$

$$(+ E_{II})$$

The Kohn-Sham Variational equations:

$$\frac{\delta E_{KS}}{\delta \psi_i^*(\vec{r})} = \frac{\delta T_S}{\delta \psi_i^*}$$

$$+ \left[\frac{\delta E_{ext}}{\delta n} + \frac{\delta E_{Hartree}}{\delta n} + \frac{\delta E_{xc}}{\delta n} \right]$$

$$\times \frac{\delta n}{\delta \psi_i^*} = 0$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

$$\frac{\delta n}{\delta \psi_i^*} = \psi_i(\vec{r})$$

$$n(\vec{r}) = \frac{1}{n} \sum_{i=1}^{N} |\psi_i(\vec{r})|^2$$

$$\frac{\delta T_s}{\delta \psi_i^*} = -\frac{1}{2}\nabla^2 \psi_i(\vec{r})$$

$$\left(\hat{H}_{KS} - \varepsilon_i\right)\psi_i(\vec{r}) = 0$$

$$\hat{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}(\vec{r})$$

$$V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + \underbrace{\frac{\delta E_{Hartree}}{\delta n}}_{V_{Hartree}} + \underbrace{\frac{\delta E_{xc}}{\delta n}}_{V_{xc}(\vec{r})}$$

$$V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}(\vec{r})$$

$$+ \underbrace{V_{xc}(\vec{r})}$$

assume

function of $n(\vec{r})$ only,

local density approx

See for example the

electron gas results

$$E_{xc} \sim n^{4/3}$$

$(\rho(\vec{r}_1, \vec{r}_2))$

FCI, $\underbrace{\text{HF, DFT}}_{\text{mean field}}$, MBPT

FCI

a state $|\Psi_i\rangle$ (exact)
can be written in terms of
a basis (SD) $|\Phi_i\rangle$

Example $|\Psi_0\rangle$

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{ai} C_i^a |\Phi_i^a\rangle$$
$$+ \sum_{\substack{ab \\ ij}} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \ldots \quad \text{NpNh}$$

E_0 follows from $\hat{H}|\Psi_0\rangle$
$= E_0|\Psi_0\rangle$

$$E_0 = \langle\Phi_0|\hat{H}|\Phi_0\rangle + \Delta E_0$$

$$\Delta E_0 = \sum_{ia} c_i^a \underbrace{\langle\Phi_0|H-E_0|\Phi_i^a\rangle}_{\langle a|f|i\rangle}$$

$$+ \sum_{\substack{ab \\ ij}} c_{ij}^{ab} \underbrace{\langle\Phi_0|H-E_0|\Phi_{ij}^{ab}\rangle}_{\langle ab|v|ij\rangle_{AS}}$$

$$= \sum_{ai} c_i^a \underbrace{\langle a|f|i\rangle}_{=0 \text{ if HF}} + \sum_{\substack{ab\\ij}} c_{ij}^{ab} \langle ab|v|ij\rangle_{AS}$$

MBPT to second order in H_I

$$c_i^a = \frac{\langle i|f|a\rangle}{\varepsilon_i - \varepsilon_a} \qquad c_{ij}^{ab} = \frac{\langle ij|v|ab\rangle_{AS}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

(Keep in mind that we have higher-order terms)

Simple example before formal derivation.

$$\mathcal{H}_0 = \sum_{p=1}^{2} \varepsilon_p a_p^\dagger a_p$$

$$\mathcal{H}_I = g \sum_{pq} a_p^\dagger a_q$$

$$\varepsilon_1 < \varepsilon_2$$

ONB $|1\rangle$ and $|2\rangle$

$$\langle 1|2\rangle = 0 \quad (\langle i|j\rangle = \delta_{ij})$$

$$\mathbb{1} = |1\rangle\langle 1| + |2\rangle\langle 2|$$

$$\mathcal{H}_0 |i\rangle = \varepsilon_i |i\rangle$$

$$\hat{P} = |1\rangle\langle 1| \quad \wedge \quad \hat{Q} = |2\rangle\langle 2|$$

$$\hat{P}^2 = \hat{P} \quad \wedge \quad \hat{Q}^2 = \hat{Q} \;, \quad [\hat{P}, \hat{Q}] = 0$$

$$|1\rangle = a_1^\dagger |0\rangle \qquad |2\rangle = a_2^\dagger |0\rangle$$

$$\langle 1|\mathcal{H}_0|1\rangle = \varepsilon_1 \quad \wedge \quad \langle 2|\mathcal{H}_0|2\rangle = \varepsilon_2$$

$$\langle p|\mathcal{H}_I|q\rangle = g \quad \Rightarrow$$

$$\Big(g \langle 1| \sum_{pq} a_p^\dagger a_q |2\rangle = \sum_{pq} \langle 0| a_1 a_p^\dagger a_q a_2^\dagger |0\rangle \times g \, \delta_{p1} \delta_{q2}$$

$$H = \begin{bmatrix} \varepsilon_1 + g & g \\ g & \varepsilon_2 + g \end{bmatrix}$$

$$\det(H - \lambda) = 0$$

$$\lambda_{1,2} = \frac{\varepsilon_1 + \varepsilon_2}{2} + g \pm \sqrt{\frac{(\varepsilon_1 - \varepsilon_2)^2}{4} + g^2}$$

$$(\varepsilon_1 - \varepsilon_2)\sqrt{1 + \frac{4g^2}{(\varepsilon_1 - \varepsilon_2)^2}}$$

$$x = \left(\frac{2g}{\varepsilon_1 - \varepsilon_2}\right)^2 \ll 1 \qquad \sqrt{1+x} = 1 + \frac{x}{2} - \frac{x^2}{8} + \frac{x^3}{16} + \ldots$$

$$\Rightarrow \varepsilon_1 + g - \frac{g^2}{\varepsilon_1 - \varepsilon_2} + \frac{g^4}{(\varepsilon_1 - \varepsilon_2)^3} + \cdots$$

$$H_0 |1\rangle = \varepsilon_1 |1\rangle$$

non-interacting (unperturbed) energy

MBPT to first order in the interaction

MBPT(2) : 2nd order

MBPT(3) : zero no 3rd order

MBPT(4) : 4th order

⋮

Formal MBPT

FCI ; $|\Psi_c\rangle = d|\Phi_c\rangle + \sum_{PH} c_H^P |\Phi_H^P\rangle$

1p1h

2p2h

⋮

npnh

intermediate normalization

$\langle \Phi_c | \Phi_c \rangle = 1$

$\langle \Psi_c | \Phi_c \rangle = 1$

$$|\Psi_c\rangle = |\Phi_c\rangle + \sum_{m=1}^{D(\infty)} C_m |\Phi_m\rangle$$

$$\hat{H}_0 |\Phi_0\rangle = E_0 |\Phi_0\rangle$$ ansatz

$$\hat{H} |\Psi_0\rangle = E_0 |\Psi_0\rangle$$ Exact GS

$$\hat{H} = \hat{H}_0 + \hat{H}_I$$

$$\langle \Phi_0 | \hat{H} | \Psi_0 \rangle = E_0 =$$

$$\underbrace{\langle \Phi_0 | H | \Phi_0 \rangle}_{E_0^{Ref}} + \underbrace{\sum_{m=1}^{D} c_m \langle \Phi_0 | H | \Phi_m \rangle}_{\sum_{PH} c_H^P \langle \Phi_0 | H | \Phi_H^P \rangle}$$

$$\Rightarrow \quad E_0 - E_0^{Ref} = \sum_m C_m \langle \Phi_0 | H | \Phi_m \rangle$$

$$= \Delta E_0 \quad (\text{From FCI})$$

$$\langle \Phi_0 | \hat{H}_0 + \hat{H}_I | \Psi_0 \rangle =$$

$$\left(\langle \Phi_0 | \hat{H}_0 | \Psi_0 \rangle = \langle \Psi_0 | H_0 | \Phi_0 \rangle^* = \mathcal{E}_0 \right)$$

$$= \mathcal{E}_0 + \langle \Phi_0 | \hat{H}_1 | \Psi_0 \rangle$$

$$E_0 - \mathcal{E}_0 = \langle \Phi_0 | \hat{H}_I | \Psi_0 \rangle$$

$$\Delta E_0 (\text{MBPT})$$

$$E_0 - \varepsilon_0 = \langle \Phi_0 | H_I | \Phi_0 \rangle$$

1st-order in H_I

$$+ \sum_m c_m \langle \Phi_0 | H_1 | \Phi_m \rangle$$

$$E_0^{Ref} = \langle \Phi_0 | H | \Phi_0 \rangle =$$

$$\langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | H_I | \Phi_0 \rangle$$

Define:

$$\hat{P} = | \Phi_0 \rangle \langle \Phi_0 | \qquad \hat{P}^2 = \hat{P}$$

$$\hat{Q} = \sum_{m=1} | \Phi_m \rangle \langle \Phi_m | , \quad \hat{Q}^2 = \hat{Q}$$

$$[\hat{P}, \hat{Q}] = 0$$

$$|\Psi_0\rangle = (\hat{P} + \hat{Q})|\Psi_0\rangle \quad \Big| \quad (\omega - \hat{H})^{-1}$$

$$\left(\hat{P} + \hat{Q} = \underline{\mathbb{1}}\right)$$

$$= |\Phi_0\rangle + \hat{Q}|\Psi_0\rangle$$

$$(\hat{H}_0 + H_I)|\Psi_0\rangle = E_0|\Psi_0\rangle$$

introduce $\omega|\Psi_0\rangle$

$$(\omega - \hat{H}_0)|\Psi_0\rangle = (\omega - E_0 + H_I)|\Psi_0\rangle$$

$(\omega - \hat{H}_0)^{-1}$ exists

(Resolvent)

$$[\hat{P}, \hat{H}_0] = [\hat{Q}, \hat{H}_0]$$

$$H_0 |\Phi_m\rangle = \varepsilon_m |\Phi_m\rangle$$

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0| \; ; \; \hat{Q} = \sum_{m=1}^{D} |\Phi_m\rangle\langle\Phi_m|$$

$$(\omega - \hat{H}_0)^{-1} = \frac{1}{\omega - \hat{H}_0}$$

$$\hat{Q}\frac{1}{\omega - \hat{H}_0} = \hat{Q}\frac{1}{\omega - \hat{H}_0}\hat{Q}$$

$$= \frac{\hat{Q}}{\omega - \hat{H}_0}$$

$$\hat{Q}|\Psi_c\rangle = \frac{\hat{Q}}{\omega - H_0}(\omega - E_0 + H_I)|\Psi_c\rangle$$

$$|\Psi_c\rangle = |\Phi_c\rangle + \frac{\hat{Q}}{\omega - H_0}(\omega - E_0 + H_I) \times |\Psi_c\rangle$$

Solve iteratively

start with $|\Phi_0\rangle$ on the right hand side.

$$|\Psi_0^{(1)}\rangle = |\Phi_c\rangle + \frac{\hat{Q}}{\omega - H_0}(\omega - E_0 + H_I)|\Phi_0\rangle$$

$$|\Psi_0\rangle = \sum_{n=0}^{\infty} \left\{ \frac{\hat{P}}{\omega - \mathcal{H}_0} (\omega - E_0 + \mathcal{H}_I) \right\}^n$$

known

$$\times |\Phi_0\rangle$$

known

known

E_0 is unknown

(i) Brillouin-Wigner MBPT

$$\omega = E_0$$

(ii) Rayleigh-Schrödinger pert theory

$$\omega = \varepsilon_0$$

$$H_0 |\Phi_0\rangle = \varepsilon_0 |\Phi_0\rangle$$

$$\langle \Phi_0 | \mathcal{H}_1 | \Psi_0 \rangle = \Delta E_0 (\text{MBPT})$$

$$= \sum_{n=0}^{\infty} \langle \Phi_0 | \hat{\mathcal{H}}_1 \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E_0 + H_I) \right\}^n$$

$$\times | \Phi_0 \rangle$$

(i) BW pert theory

$$\omega = E_0$$

$$\Delta E_0 = \sum_{n=0}^{\infty} \langle \Phi_0 | \mathcal{H}_1 \left\{ \frac{\hat{Q}}{E_0 - H_0} \cancel{\mathcal{H}_I} \right\}^n | \Phi_0 \rangle$$

$$= \langle \Phi_c | H_I | \Phi_0 \rangle \qquad (1\text{st order})$$

$$+ \langle \Phi_c | H_I \frac{\hat{Q}}{E_c - H_0} H_I | \Phi_0 \rangle \quad (2\text{nd})$$

$$+ \langle \Phi_c | H_I \frac{\hat{Q}}{E_0 - H_0} H_I \frac{\hat{Q}}{E_0 - H_0} H_1 | \Phi_0 \rangle$$

$$(3\text{rd})$$

$$+ \quad - - - -$$

E_c - dependence, unwanted

$\Rightarrow$ Rayleigh - Schrödinger