Center for Molecular Modeling

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Computational Materials Physics

method of Kohn & Sham

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http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

method of Kohn & Sham

" The exact ground state density of a N-electron system is

$$\rho(\vec{r}) = \sum_{i=1}^{N} \varphi_i^*(\vec{r})\varphi_i(\vec{r})$$

where the single-particle wave functions φ_i are the N lowest-energy solutions of the Kohn-Sham equations :

$$\hat{H}_{KS}\varphi_i = \varepsilon_i\varphi_i$$

with

$$\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{ext} + \hat{V}_{xc} = -\frac{\hbar^2}{2m}\vec{\nabla}_i^2 + \frac{e^2}{4\pi\varepsilon_0}\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,' + \hat{V}_{ext} + \hat{V}_{xc}$$

and

$$\hat{V}_{xc} = \frac{\delta V_{xc}[\rho]}{\delta\rho} \quad ."$$

The Kohn-Sham equations are an exact transformation of the original problem (coupled differential equations) in single-particle equations (uncoupled)

Schrödinger

$$H = -\sum_i \frac{\nabla^2}{m_i}$$

• electrons with kinetic energy

$$-\sum_{i,j}\frac{(eZ_i)\ e}{|\vec{R}_i - \vec{r}_j|}$$

• subject to Coulomb potential of nuclei

$$+\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

• Coulomb-interacting with other electrons

Kohn-Sham

$$H = -\sum_i \frac{\nabla^2}{m_i}$$

• quasi-particles with kinetic energy

$$-\sum_{i,j}\frac{(eZ_i)\ e}{|\vec{R}_i - \vec{r}_j|}$$

• subject to Coulomb potential of nuclei

$+ V_H$

• interacting with the average, static distribution of all other quasi-particles

$+ V_{xc}$

• subject to the effect of a mysterious 'exchange-correlation' potential

Much easier maths, but you have to know V_{xc}