Density Functional Theory - Kohn-Sham Equations

Lecture 29

CHM 652 / PHY 626
Electronic Structure of Materials

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Lecture Plan

- Ensemble DFT
- Kohn-Sham Approach to DFT

Ensemble DFT

The density-based variational principle as well as the existence of a universal functional can be extended to "ensemble" densities, i.e. those derived from mixed states.

Finite-temperature Canonical-ensemble Theory

Density Matrix

$$\hat{\Gamma}_N = \sum_i p_{Ni} \left|\Psi_i^N\right\rangle \left\langle\Psi_i^N\right|$$

$$p_{Ni} \geq 0$$

$$\sum_i p_{Ni} = 1$$

State weights

$$A_0 = A[\hat{\Gamma}_N^0]$$

$$= \min_{n(\mathbf{r})} \left\{ F[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \right\}$$

$$F[n] = \min_{\hat{\Gamma}_N \to n(\mathbf{r})} \mathrm{Tr} \left\{ \hat{\Gamma}_N \left(\hat{T} + \hat{W} + \frac{1}{\beta} \ln \hat{\Gamma}_N \right) \right\}$$

1. $n_0(\mathbf{r})$ => $\hat{\Gamma}_N^0$ uniquely and, hence, all equilibrium properties.
2. There holds a free-energy variational principle into which enters the universal functional.

Ensemble DFT

The density-based variational principle as well as the existence of a universal functional can be extended to "ensemble" densities, i.e. those derived from mixed states.

Finite-temperature Grand-Canonical-ensemble Theory

Density matrix

$$\hat{\Gamma} = \sum_N \sum_i p_{Ni} \left|\Psi_i^N\right\rangle \left\langle\Psi_i^N\right|$$

$$p_{Ni} \geq 0$$

$$\sum_N \sum_i p_{Ni} = 1$$

State weights

$$\Omega_0 = \Omega[\hat{\Gamma}^0]$$

$$= \min_{n(\mathbf{r})} \left\{ F[n] + \int d^3 r n(\mathbf{r})(v(\mathbf{r}) - \mu) \right\}$$

$$F[n] = \min_{\hat{\Gamma} \to n(\mathbf{r})} \mathrm{Tr} \left\{ \Gamma \left(\hat{T} + \hat{W} + \frac{1}{\beta} \ln \hat{\Gamma} \right) \right\}$$

1. n$_0$(**r**) => $\hat{\Gamma}^0$ uniquely and, hence, all equilibrium properties.
2. There holds a free-energy variational principle into which enters the universal functional.

Kohn-Sham Approach to DFT

It can be shown that *N*-representable densities can be written in terms of smooth, continuous and quadratically integrable orthonormal orbitals.

$$n(\mathbf{r}) = \int d\sigma \sum_i f_i |\psi_i(x)|^2$$

$$0 \le f_i \le 1$$

So, in principle, we can approximate a large part of the kinetic energy of an interacting system by the kinetic energy constructed out of these orbitals.

$$T_s[n] = \sum_i f_i \left\langle \psi_i \middle| -\frac{\nabla^2}{2} \middle| \psi_i \right\rangle$$

This idea was used by Kohn and Sham to devise a way to solve for the ground-state density.

Kohn-Sham Approach to DFT

Hohenberg-Kohn theorem applies to both interacting and non-interacting systems. So we ask what external potential $v_s(\mathbf{r})$ when acting on a non-interacting system would yield the same ground-state density as an interacting system under an external potential $v(\mathbf{r})$?

Non-interacting system

As we have seen before, for such a system the eigenstates are given by Slater determinants formed from 1-electron spin-orbitals $\{\psi_j(\mathbf{r},\sigma)\}$such that

$$\left(-\frac{\nabla^2}{2}+v_s(\mathbf{r})\right)\psi_j(x)=\epsilon_j\psi_j(x) \quad x=(\mathbf{r},\sigma)$$

$$n(\mathbf{r})=\int d\sigma\sum_{j=1}^{N}\psi^*(x)\psi(x)$$

$$T_s=\sum_{j=1}^{N}\left\langle\psi_j\left|-\frac{\nabla^2}{2}\right|\psi_j\right\rangle$$

From HK Theorems, we have

$$v_s\equiv v_s[n](\mathbf{r})$$

Therefore,

$$\psi_j\equiv\psi_j[n]$$

And

$$\boxed{T_s\equiv T_s[n]}$$

Kohn-Sham Approach to DFT

Interacting system

We break up the total energy as follows, for some orthonormal 1-electron orbitals $\{\psi_j(\mathbf{r},\sigma)\}$

$$E[n] = T_s[n] + J[n] + E_{xc}[n] + \int d^3r n(\mathbf{r})v(\mathbf{r})$$

Non-interacting K.E. $$T_s[n] = \sum_{i=1}^{N} \left\langle \psi_j \middle| -\frac{\nabla^2}{2} \middle| \psi_j \right\rangle$$

$$\boxed{n(\mathbf{r}) = \int d\sigma \sum_{j=1}^{N} \psi^*(x)\psi(x)}$$

Hartree energy $$J[n] = \frac{1}{2}\int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Here, $$E_{xc}[n] = (T[n] - T_s[n]) + (W[n] - J[n])$$

Exchange-correlation energy

Exact K.E.

Exact Interaction energy.

Kohn-Sham Approach to DFT

Interacting system

Since the density is now *represented* by the 1-electron spin-orbitals, we can write Euler-Lagrange equations in terms of the latter subject to the orthonormality constraint.

$$\frac{\delta E[n]}{\delta \psi_i(x)^*} = \sum_{j=1}^{N} \mu_{ij} \psi_j(x)$$

i=1,N

Lagrange multipliers

$$\left(-\frac{\nabla^2}{2} + v_{eff}(\mathbf{r})\right)\psi_i(x) = \sum_{j=1}^{N} \mu_{ij}\psi_j(x)$$

$$n(\mathbf{r}) = \int d\sigma \sum_{j=1}^{N} \psi^*(x)\psi(x)$$

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[n](\mathbf{r})$$

Local potential

Kohn-Sham Approach to DFT

Interacting system

The potentials in the previous expression are derived as functional derivatives of the corresponding energies. For instance,

$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

It is straightforward to show that the 1-electron equations can be converted to canonical eigenvalue equations by a suitable unitary trasnformation of the orbitals. This yields the **Kohn-Sham equations**.

$$\left(-\frac{\nabla^2}{2} + v_{eff}[n](\mathbf{r})\right)\psi_i(x) = \epsilon_i \psi_i(x)$$

$$n(\mathbf{r}) = \int d\sigma \sum_{j=1}^{N} \psi^*(x)\psi(x)$$

Kohn-Sham Approach to DFT

Interacting system

Comparing the non-interacting and interacting cases we realise we have basically introduced an auxiliary non-interacting system to solve our interacting electron problem such that both yield the same ground state density.

In particular, at the ground-state density we have

$$v_s(\mathbf{r}) = v_{eff}[n_0](\mathbf{r})$$

$v_s(\boldsymbol{r})$ is called the Kohn-Sham potential. It is the answer to the question we asked.