Density Functional Theory: Many Body? Single Particle?

Notation: $\hat{H} = \hat{H}_0 + \hat{V}$; $\hat{H}_0 = \hat{T} + \hat{\mathcal{U}}$, $\hat{V} \equiv \int v(r)\,\hat{n}(r)\,d^3r$

3N coordinates

Hohenberg-Kohn Thrm. $\hat{V} = \hat{V}[n]$, $\hat{V}$ is a functional of g.s. density $n(\underline{r})$.

Reductio ad absurdum.

Suppose for two systems w/ same # of particles,

The two differential equations are different $\Rightarrow \Psi' \neq \Psi$.

$\Longleftarrow$ $v'(r) \neq v(r) + \text{const.}$, but that $n'(r) = n(r)$ [we suppose]

Then $\hat{H}|\Psi) = (\hat{H}_0 + \hat{V})|\Psi) = \mathcal{E}|\Psi)$

and $\hat{H}'|\Psi') = (\hat{H}_0 + \hat{V}')|\Psi') = \mathcal{E}'|\Psi')$ and $|\Psi') \neq |\Psi)$.

Then

$$\mathcal{E} = (\Psi|\hat{H}|\Psi) < (\Psi'|\hat{H}|\Psi') = (\Psi'|\hat{H}_0 + \hat{V}' + (\hat{V} - \hat{V}')|\Psi')$$

$$= \mathcal{E}' + (\Psi'|\hat{V} - \hat{V}'|\Psi') = \mathcal{E}' + \int [v(r) - v'(r)]\,n(r).$$

Exchange primed $\Leftrightarrow$ unprimed

$$\mathcal{E}' \quad < \quad \mathcal{E} + \int [v'(r) - v(r)]\,n(r).$$ Adding,

$$\mathcal{E}' + \mathcal{E} < \mathcal{E}' + \mathcal{E}$$ $\therefore$ Contradiction, $\Rightarrow n'(r) \neq n(r)$

So — two different potentials cannot give the same g.s. density.

I.e. given $n(r) \Longrightarrow$ some particular $v(r)$,

$\Longrightarrow$ or v is a functional of n: $V = V[n]$

Of course, also n is a fn'al of v, so $v \Longleftrightarrow n$ is 1-to-1.

In principle, any property of the system is a fn'al of n! Each is its own functional.

In particular, the total energy of the system:

$$\mathcal{E} \equiv (\Psi_{g.s.}|H|\Psi_{g.s.}) = \underset{\uparrow\text{kinetic}}{T[n]} + \underset{\uparrow\text{potential}}{\mathcal{U}[n]} + \underset{\nwarrow\text{interaction w/ ext. potential.}}{V[n]} = \mathcal{E}[n] \quad \text{g.s. energy.}$$

$\Longrightarrow$ Also, the density that minimizes $\mathcal{E}[n]$ for a fixed number of electrons is the g.s. density:

Hohenberg-Kohn Thrm. #2

$$\left.\frac{\delta}{\delta n(r)}\Big[\mathcal{E}[n] - \mu N[n]\Big]\right|_{n_{g.s.}} = 0 \;\Rightarrow\; \frac{\delta \mathcal{E}[n]}{\delta n(r)} = \mu = \text{constant.}$$

$$\frac{\delta T}{\delta n(r)} + \frac{\delta \mathcal{U}}{\delta n(r)} + v(r) - \mu = 0$$

Kohn-Sham procedure: separate $\mathcal{E}[n]$ in different way: $v_c(r) \equiv \frac{e^2}{|\underset{\sim}{r}|}$

$$\mathcal{E}[n] = T_0[n] + \mathcal{U}_H[n] + \int v n + E_{xc}[n] \;;\; \mathcal{U}_H[n] = \frac{1}{2}\iint n(r)\, v_c(r-r')\, n(r')$$

= "Hartree energy"

$T_0[n]$ = K.E. of non-interacting system with density n, i.e. with $n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2$, $T_0[n] \doteqdot \sum_{i=1}^{N} \int \phi_i^* \left(-\frac{\hbar^2\nabla^2}{2m}\right)\phi_i \, d^3r$

Now,

minimize $\mathcal{E}[n]$ w.r.t. orbitals ~~$\frac{\delta}{\delta n} \to \sum_{i=1}^{N} \frac{\delta}{\delta \phi_i^*}$~~

using, where necessary, $\frac{\delta}{\delta\phi_i^*} = \frac{\delta n}{\delta\phi_i^*}\frac{\delta}{\delta n} = \phi_i \frac{\delta}{\delta n}$ (if ϕ_i is occupied).

Constraining to normalized orbitals:

$$\frac{\delta}{\delta\phi_i^*(r)}\left[\mathcal{E}[n] - \sum_{j=1}^{N} \varepsilon_j \left(\int |\phi_j|^2 - 1\right)\right] = 0$$

$$-\frac{\hbar^2\nabla^2}{2m}\phi_i + \underset{\overset{\uparrow}{v_h(r;n)}}{v_h(r)}\phi_i + v(r)\phi_i + \underset{\overset{\uparrow}{v_{xc}(r;n)}}{\frac{\delta E_{xc}}{\delta n(r)}}\phi_i = \varepsilon_i \phi_i$$

If the resulting density is the same as the density, then the fu'al is minimized $\Rightarrow n_{gs}$ and $\mathcal{E}_{gs}$.

Thus the problem is reduced to a self-consistent field problem.

$$\left\{-\nabla^2 + v_{eff}(r,n)\right\}\phi_i = \varepsilon_i \phi_i \implies n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 \qquad \text{SCF.}$$

! BUT —

this looks like a system of non-interacting particles in an effective potential.

BUT —

it's really a many-body theory for $\mathcal{E}_{g.s.}$ and $n_{g.s.}$

$\varepsilon_i \to \varepsilon_{\underset{\sim}{k}n}$ is the band structure. Come back to this later.

THE EXCHANGE-CORRELATION ENERGY FUNCTIONAL

"Adiabatic Connection"; Coupling Constant Integration

Introduce λ in $v_{c,\lambda} = \lambda \frac{e^2}{|\underset{\sim}{r}-\underset{\sim}{r}'|}$, scaling of Coulomb repulsion.

In DFT, functionals depend only n and e^2, $\hbar$, m.
with λ, DFT holds again but functionals depend on λ.
Thus, for a given n, there exists an external potential v_λ that gives n as the ground state density.

Then —
let $n(r)$ be the g.s. density corresponding to $\lambda = 1$,
i.e. to $v = v_{\lambda=1} = v_1$ and full coulomb repulsion.

Denote
$$H_\lambda = T + V_\lambda + \lambda \mathcal{U}, \quad V_\lambda \equiv \int v_\lambda(r)\hat{n}(r)\, d^3r.$$

where at each λ, v_λ is that potential which gives n,
i.e. $n(r)$ is *fixed* as λ varies between 0 and 1. !

Also,
$$H_\lambda \Phi_\lambda = \mathcal{E}_\lambda \Phi_\lambda$$

Hellman-Feynman theorem gives $\frac{d\mathcal{E}_\lambda}{d\lambda} = \left(\Phi_\lambda \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \Phi_\lambda\right)$

and $\frac{\partial H_\lambda}{\partial \lambda} = \frac{\partial v_\lambda}{\partial \lambda} + v_c$. $\left\{\text{Better notation: } \frac{\partial H}{\partial \lambda} = \frac{\partial V_\lambda}{\partial \lambda} + \mathcal{U}\right\}$

Also,
$$\int_0^1 \frac{\partial \mathcal{E}_\lambda}{\partial \lambda} d\lambda = \mathcal{E}_1 - \mathcal{E}_0 .$$

$\lambda = 0$: $\mathcal{E}_0 = T[n] + \int v_0 n = T_s[n] + \int v_0 n$; non-interacting system.

$T_s[n] \equiv T_0[n]$ (sorry; both notations are used for the same functional)

$$\lambda=1: \mathcal{E}_1 = T_s[n] + \int v_1 n + \mathcal{U}_H[n] + E_{xc}[n]$$

Then

$$\mathcal{E}_1 - \mathcal{E}_0 = \int v_1 n - \int v_0 n + \mathcal{U}_H[n] + E_{xc}[n].$$

Now, other term is

$$\int_0^1 \frac{\partial \mathcal{E}_\lambda}{\partial \lambda} d\lambda = \int_0^1 d\lambda \left\{ \left(\psi_\lambda \left| \frac{\partial v_\lambda}{\partial \lambda} + v_c \right| \psi_\lambda \right) \right\}$$

$$= \int_0^1 d\lambda \left\{ \int \frac{dv_\lambda}{d\lambda} n(r) d^3r + \left(\Psi_\lambda \left| \frac{1}{2} \iint \hat{n}(r) v_c(r-r') \hat{n}(r') \right| \Psi_\lambda \right) \right.$$

$$= \int [v_1(r) - v_0(r)] n(r) d^3r$$

$$+ \frac{1}{2} \int_0^1 d\lambda \iint v_c(r-r') \underbrace{\left(\Psi_\lambda \left| \hat{n}(r) \hat{n}(r') \right| \Psi_\lambda \right)}_{\equiv\, n(r) n(r') g_\lambda(r,r')}$$

$\leftarrow$ def'n of pair correlation function

g(r,r') is pair correlation fn.

Putting everything together with $E_{xc}[n]$ on left side,

$$E_{xc}[n] = \frac{1}{2} \iint v_c(r-r') n(r) n(r') \underbrace{\int_0^1 d\lambda\, g_\lambda(r,r')}_{\overline{g}(r,r')} - \mathcal{U}_H[n]$$

$\leftarrow$ coupling-constant-averaged pair correlation function.

$$= e^2 \frac{1}{2} \int d^3r \underbrace{\int d^3r'\, n(r) \frac{[\overline{g}(r,r') - 1]}{|r-r'|} n(r')}$$

$$\equiv \int d^3r\, n(r)\, \epsilon_{xc}(r;n), \quad \{\overline{g} = \overline{g}(r,r';n)\}$$

LDA: $\epsilon_{xc}(r;n) \longrightarrow \epsilon^h_{xc}(n(r))$. Simple!

Surprisingly good!

Meaning of eigenvalues ε_i, etc.

KS eqn: $\{-\nabla^2 + v + v_h + v_{xc}\}\phi_i = \varepsilon_i \phi_i$

Corresponding Green's function $G^{DFT}(r,r';\varepsilon) = \sum_i \frac{\phi_i(r)\phi_i^*(r')}{\varepsilon - \varepsilon_i + i\delta}$.

Then

$$-\frac{1}{\pi}\mathrm{Im}\int^{\varepsilon_F} G(r,r';\varepsilon)\,d\varepsilon\Big|_{r'=r} = -\frac{1}{\pi}\mathrm{Im}\Big\{-i\pi\sum_i\int^{\varepsilon_F}\delta(\varepsilon-\varepsilon_i)|\phi_i(r)|^2 d\varepsilon$$

or

$$\boxed{-\frac{1}{\pi}\mathrm{Im}\int^{\varepsilon_F} G^{DFT}(r,r;\varepsilon)\,d\varepsilon = \sum_{\varepsilon_i<\varepsilon_F}|\phi_i(r)|^2 = n(r).}$$

From many-body theory, the exact single particle Green's fn satifies

$$\boxed{-\frac{1}{\pi}\mathrm{Im}\int^{\varepsilon_F} G(r,r;\varepsilon)\,d\varepsilon = n(r)}$$ almost from its definition

Thus G^{DFT} "contains a great deal" of G!

Equations the Green's functions satisfy: (complex energy z)

Full. $\{-z - \nabla_r^2 + v(r) + v_h(r)\}G(r,r';z) + \int dr''\,\Sigma(r,r'';z)G(r'',r';z) = \delta(r-r')$

DFT $\{-z - \nabla_r^2 + v(r) + v_h(r)\}G^{DFT}(r,r';z) + v_{xc}(r)\,G^{DFT}(r,r';z) = \delta(r-r')$

self energy

Thus: v_{xc} can be viewed as a local ($r'=r$), real, static approx. to $\Sigma(r,r';z)$.

ε_i are approximations to the single particle excitations,

a "good" mean field approximation to excitation energies.

N.B. both $\Sigma(r,r';z)$ and v_{xc} give rise to the same density.

DFT & the Many Body Problem

The Hamiltonian can be written

$$\hat{\mathcal{H}} = \hat{T} + \hat{V} + \hat{\mathcal{U}} \equiv \hat{T} + \hat{V} + \hat{V}_{hxc} + (\hat{\mathcal{U}} - \hat{V}_{hxc}) = \mathcal{H}_0 + \Delta\hat{V}$$

where, of course, $\hat{V}_{hxc}$ could be anything. However, if we choose

$$\hat{V}_{hxc} = \int [v_h(r) + v_{xc}(r)]\,\hat{n}(r) = \sum_{i=1}^{N} [v_h(r_i) + v_{xc}(r_i)], \text{ where } v_h = \frac{\delta \mathcal{U}_h}{\delta n(r)}$$

then

$$\hat{\mathcal{H}}_0 = \sum_{i=1}^{N} \left[-\frac{\hbar^2 \nabla_i^2}{2m} + v(r_i) + v_h(r_i) + v_{xc}(r_i) \right] \leftarrow \text{Kohn-Sham Hamiltonian for each particle}$$

$$= \sum_{i=1}^{N} h(r_i), \text{ where } h\phi_i = \varepsilon_i \phi_i .$$

Now,

$\Delta\hat{V} = \hat{\mathcal{U}} - \hat{V}_{hxc}$ is the full, bare, long-range Coulomb repulsion between pairs, minus a one-body potential $v_h + v_{xc}$.

$\Delta\hat{V}$ does not change the charge density from $\mathcal{H}_0$, !

but it gives a big change in the energy: $\langle \Psi_0 | \mathcal{H}_0 | \Psi_0 \rangle = \sum_{i=1}^{N} \varepsilon_i$, while $\mathcal{E} = \langle \Psi | \mathcal{H} | \Psi \rangle$ is much different.

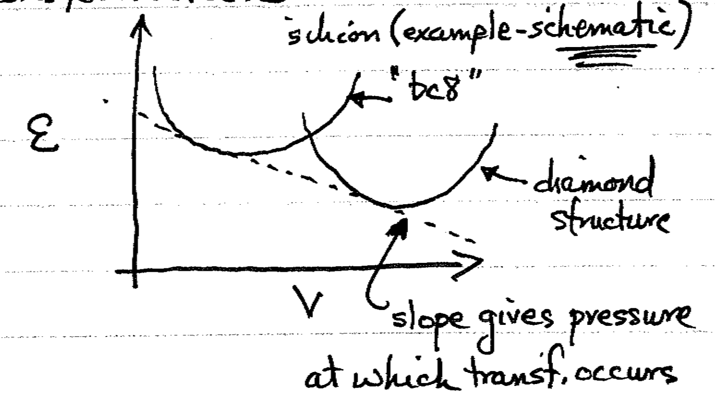
Density Functional Theory: Progression / Generalization

- Non-relativistic, non-magnetic: $\mathcal{E}[n]$, $n(r)$
- Non-relativistic, magnetic: $\mathcal{E}[n_{\alpha\beta}]$, $\frac{1}{2}n(r)\,\underset{\approx}{1} + \overset{m(\underset{\sim}{r})}{m}\cdot\underset{\underset{\text{Pauli matrices}}{\approx}}{\sigma}$
- Relativistic, magnetic: $\mathcal{E}[j_\mu]$, 4-current $j_{\mu\sigma}(\underset{\sim}{r})$
- Non-relativistic, $\underset{\sim}{B}$ field: $\mathcal{E}[j_\mu]$, charge density, current density
- t-dependent $v_{ext}(r,t)$: $\mathcal{E}[n(t'), t'<t]$
- Superconducting state: $\mathcal{E}[n,\Delta]$, charge density, pair density
- DFT for excited states (orthogonal to g.s.)
- DFT for other properties: momentum distrib. fn.
  Compton profile.
- DFT for ferroelectrics (density-polarization functional theory)
- Temperature-dependent (finite T) DFT
- Density functional theory for the Hubbard model (!)
  or practically any other model, exists.

Properties Calculated Using Density Functional Theory

$\mathcal{E}(\{\underset{\sim}{R}_i\})$, $\{\underset{\sim}{R}_i\}$ = atom positions in solid (or molecule); "relaxation of structure"

- ground state structure: bcc, fcc, hcp, Pnma, etc. etc.
  (but with many independent coordinates there are many local minima)
- pressure: $P = -\frac{\partial\mathcal{E}}{\partial V}$ (V = volume)
- pressure-driven structural transformations
- phonons: $\frac{\partial^2\mathcal{E}}{\partial \underset{\sim}{R}_i \partial \underset{\sim}{R}_j}$
- elastic constants
- defect energies



$\mathcal{E}(\{\underset{\sim}{R}_i^0\})$: ground state density
electric field gradients
ionization potential / work function
? Fermi surfaces? No, not exactly, but usually very good!

Magnetic properties from Spin Density Functional Theory
- magnetic order of ground state; magnetic impurities
- hyperfine fields at nuclei
- exchange coupling

Electric polarization

Forces on atom ⟹ ab initio molecular dynamics ("Car-Parrinello")

Effects of constraints "constrained density functional theory"
- example: energy vs. f electron occupation number in ions/atoms

? Excitation energies? beginning to, from t-dep. DFT, for finite systems.