Mean field approach; Introduction to DFT

Computational Physics

28. február 2002

DFT, density functional theory

Systems with inhomogeneous electron density

P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964):

The mean total energy per electron is a functional of the density:

$$E[n] = \int V_{\rm conf}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + G[n] \quad (*)$$

$$G[n] \equiv T_s[n] + E_{xc}[n]$$

W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965): $E_{xc} = E_x + E_c$,
but E_x and E_c are in general not functionals of n individually.

If n($\mathbf{r}$) is slowly varying, then

$$E_{xc}[n] = \int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))d\mathbf{r}$$

$\epsilon_{xc}(n)$ is the mean exchange and correlation energy per electron in a homogeneous system

$\uparrow$

LDA, Local Density Approximation, (gradient corrections can be added . . .)

LDA

Kohn and Sham found that the variational condition $\int \delta n(\mathbf{r}) d\mathbf{r} = 0$ on (*) gives a Schrödinger-type "LDA-equation of motion":

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + [\varphi(\mathbf{r}) + V_{xc}(n(\mathbf{r}))]\right\}\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

$$\varphi(\mathbf{r}) = V_{\text{conf}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2, \qquad T = 0 \text{ formalism}$$

$$V_{xc}(n) = d(n\epsilon_{xc}(n))/dn$$

The total energy of an electron is:

$$E = \sum_{i=1}^{N} \epsilon_i \quad - \quad \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$+ \quad \int n(\mathbf{r})[\epsilon_{xc}(n(\mathbf{r})) - V_{xc}(n(\mathbf{r}))] d\mathbf{r}$$

Later we see how $\epsilon_{xc}(n)$ is derived

Only E and n have a meaning

Similar complexity as in the Hartree Approximation

Simpler than HFA or exact diagonalization ...

Spin polarization

U. Barth and L. Hedin, J. Phys. C **5**, 1629 (1972):

When spins can be polarized we have to use $n_\downarrow$ and $n_\uparrow$ instead of n, (LSDA):

$$E_{xc}^{LSDA}[n_\uparrow, n_\downarrow] = \int d\mathbf{r}\, n(\mathbf{r})\epsilon_{xc}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})]$$

Magnetic field

Is still being researched, M. I. Lubin et al, Phys. Rev. B **56**, 10373 (1997)

Instead of a density n comes a filling factor ν and polarization ζ:

$$V_{xc,\sigma}(r, B) = \frac{\partial}{\partial n_\sigma}(n\epsilon_{xc}[n_\uparrow, n_\downarrow, B])|_{n_\sigma = n_\sigma(r)}$$

Change of variables: $n_\uparrow$ and $n_\downarrow \rightarrow \nu$ and ζ

$$\nu_\sigma = 2\pi l_B^2 n_\sigma, \quad l_B = \sqrt{\left(\frac{\hbar c}{eB}\right)} \quad \text{magnetic length}$$

$$\nu = \nu_\uparrow + \nu_\downarrow$$

$$\zeta = (\nu_\uparrow - \nu_\downarrow)/(\nu_\uparrow + \nu_\downarrow)$$

$$V_{xc,\uparrow} = \frac{\partial}{\partial \nu}(\nu \epsilon_{xc}) + (1-\zeta)\frac{\partial}{\partial \zeta}\epsilon_{xc}$$

$$V_{xc,\downarrow} = \frac{\partial}{\partial \nu}(\nu \epsilon_{xc}) - (1+\zeta)\frac{\partial}{\partial \zeta}\epsilon_{xc}$$

$$\zeta = (n^\uparrow - n^\downarrow)/n$$

Example: 2DEG in a magnetic field

Recipe for ϵ_{xc}:

B. Tanatar and M. Ceperley, Phys. Rev. B **39**, 5005 (1989)

Monte Carlo for $B = 0$, $1 < r_s < 100$, $\zeta = 0$ and $\zeta = 1$

Analytical methods for $B \to \infty$

Interpolation for the magnetic field:

$$\epsilon_{xc}^{B}(\nu, \zeta) = \epsilon_{xc}^{\infty}(\nu) e^{-f(\nu)} + \epsilon_{xc}^{0}(\nu, \zeta)(1 - e^{-f(\nu)})$$

$$f(\nu) = \frac{3}{2}\nu + 7\nu^4$$

$$\epsilon_{xc}^{\infty}(\nu) = -0,782\sqrt{\nu}\left(\frac{e^2}{kl}\right)$$

Interpolation for spin polarization:

$$\epsilon^0_{xc}(\nu,\zeta) = \epsilon_{xc}(\nu,0) + f^i(\zeta)\left\{\epsilon_{xc}(\nu,1) - \epsilon_{xc}(\nu,0)\right\}$$

$$f^i(\zeta) = \frac{(1+\zeta)^{3/2} + (1-\zeta)^{3/2} - 2}{2^{3/2} - 2}$$

Division into exchange and correlation:

$$\epsilon_{xc}(\nu,\zeta) = \epsilon_x(\nu,\zeta) + \epsilon_c(\nu,\zeta)$$

$$\epsilon_x(\nu,0) = -\frac{4}{3\pi}\sqrt{\nu}\left(\frac{e^2}{kl}\right)$$

$$\epsilon_x(\nu,1) = -\frac{4}{3\pi}\sqrt{2\nu}\left(\frac{e^2}{kl}\right)$$

With interpolation for correlation:

$$\epsilon_c(\nu, \zeta) = a_0 \frac{1 + a_1 x}{1 + a_1 x + a_2 x^2 + a_3 x^3} E^*_{Ryd}$$

with:

	liquid $\zeta = 0$	polarized liquid $\zeta = 1$
a_0	-0.3568	-0.0515
a_1	1.1300	340.5813
a_2	0.9052	75.2293
a_3	0.4165	37.0170

$$x = \sqrt{r_s} = (2/\nu)^{1/4} \left(l/a^*_B\right)^{1/2}$$

Finally the “potentials”, V_{xc}, are assembled:

$$V_{xc{\uparrow \atop \downarrow}} = \frac{\partial}{\partial \nu}(\nu \epsilon^B_{xc}) \pm (1 \mp \zeta) \frac{\partial}{\partial \nu} \epsilon^B_{xc}$$

$$\nu \rightarrow 2\pi l^2 (n^{\uparrow}(\mathbf{r}) + n^{\downarrow}(\mathbf{r})) \quad \text{and} \quad \zeta \rightarrow \frac{n^{\uparrow}(\mathbf{r}) - n^{\downarrow}(\mathbf{r})}{n^{\uparrow}(\mathbf{r}) + n^{\downarrow}(\mathbf{r})}$$

CSDFT

G. Vignale and M. Rasolt, Phys. Rev. B **37**, 10685 (1988):

In a magnetic field E_{xc} is also a functional of the diamagnetic part of the current density

$$\mathbf{j}_{p\sigma}(\mathbf{r}) = -\frac{i\hbar}{2m}\left\{\psi_\sigma^\dagger(\mathbf{r})\nabla\psi_\sigma(\mathbf{r}) - \left[\nabla\psi_\sigma^\dagger(\mathbf{r})\right]\psi_\sigma(\mathbf{r})\right\}$$

So we have to add the vector potential:

$$\frac{e}{c}\mathbf{A}_{xc\sigma} = \frac{\delta E_{xc}[n_\sigma, \mathbf{j}_{p\sigma}]}{\delta \mathbf{j}_{p\sigma}}$$

Often a small correction, but necessary due to conservation laws

Time-dependent DFT

Development

- E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984)
- G. Vignale and W. Kohn, Phys. Rev. Lett. **77**, 2037 (1996)

Application

- L. L. Serra, M. Barranco, A. Emperador, M. Pi, and E. Lipparini, Phys. Rev. B 59, 15290 (1999)
- C. A. Ullrich and G. Vignale, Phys. Rev. B 61, 2729-2736 (2000)
- K. Capelle, G. Vignale, and B. L. Györffy, Phys. Rev. Lett. 87, 206403 (2001)
- Z. Qian and G. Vignale Phys. Rev. Lett. 88, 056404 (2002)

EM absorption, plasmons ...

DFT, what now?

- 1995 there are more articles in INSPEC with the keyword DFT than the keyword Hartree-Fock
- More accuracy, shorter computational time. larger systems
- Good results for atoms - molecules - mesoscopic systems - crystals
- The parameterization of E_{xc} is difficult
- Unsolved problems with E_{xc} in a magnetic field

  K. Capelle and G. Vignale Phys. Rev. Lett. 86, 5546-5549 (2001)
- DFT is in full development and application!

  W. Kohn, Nobel Lecture: Electronic structure of matter-wave functions and density functionals, Rev. Mod. Phys. 71, 1253-1266 (1999).

  M. Seidl, J. P. Perdew, and S. Kurth, Density functionals for the strong limit, Phys. Rev. A 62, 012502 (2000).