Exchange-Correlation

Tutor: Edrick

Content

- Homogeneous Electron Gas (HEG)
- Exchange & Correlation Energy for HEG
- Local Density Approximation (LDA) for Real Materials
- Classification

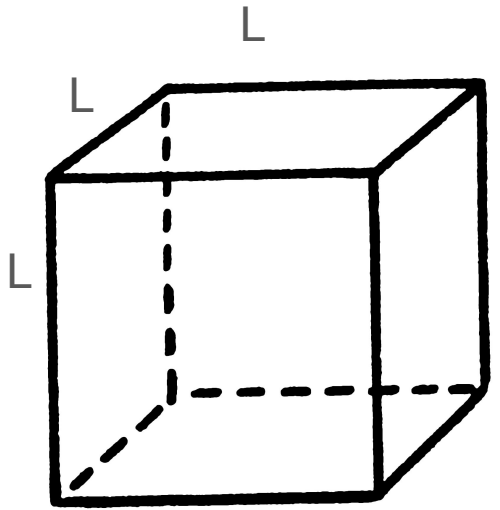
Homogeneous Electron Gas

- For each electron

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = \mathcal{E}\psi(\mathbf{r})$$

- Periodic Boundary Conditions

$$\psi(x, y, z + L) = \psi(x, y, z)$$
$$\psi(x, y + L, z) = \psi(x, y, z)$$
$$\psi(x + L, y, z) = \psi(x, y, z)$$



$V=L^3$

N electrons

$n = N/L^3$

- Solution

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}} \qquad \mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

$$k_x = \frac{2\pi n_x}{L}, \qquad k_y = \frac{2\pi n_y}{L}, \qquad k_z = \frac{2\pi n_z}{L}, \qquad n_x, n_y, n_z \text{ entiers}$$

Exchange and Correlation energy for HEG

HEG

- For this system, $E_{XC}^{HEG} = E_{X}^{HEG} + E_{C}^{HEG}$
- $E_{\mathrm{X}}^{\mathrm{HEG}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{4}{3}} V$ Dirac, 1930
- In 1980, Ceperley & Alder computed numerically the correlation E_{C}^{HEG}
- In 1981, Perdew & Zunger parametrized $E_C(n)$

Hohenberg-Kohn theorem, 1964
Kohn-Sham formulation, 1965

LDA for Real Materials

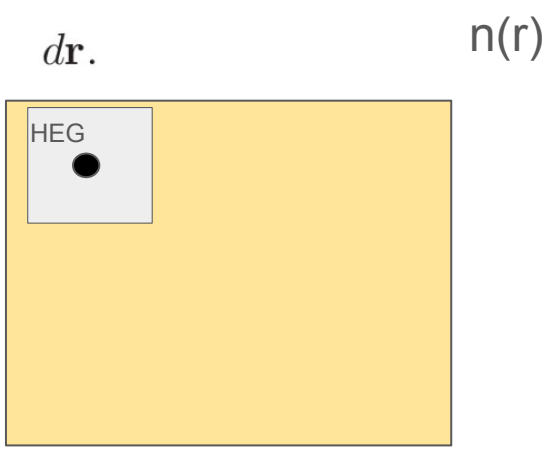
- Assuming that n(r) is known…

- Locally, we approximate the material as a HEG

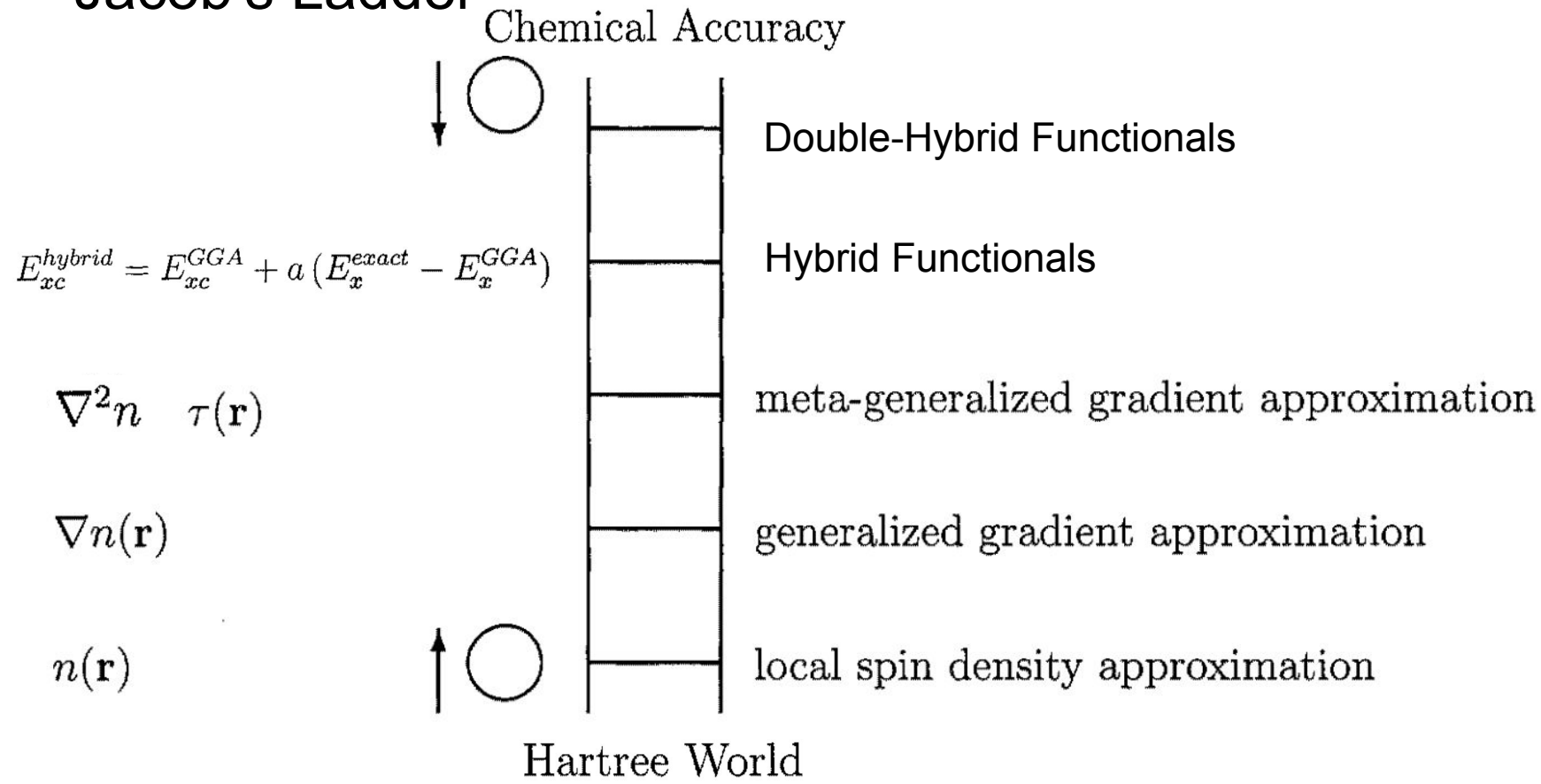
$$E_{xc} = \int_V \frac{E_{xc}^{\mathrm{HEG}}[n(\mathbf{r})]}{V}\, d\mathbf{r}.$$

- The exchange contribution is

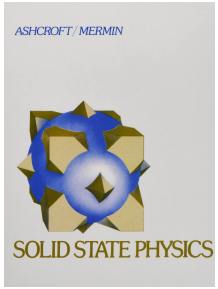
$$E_x = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int_V n^{4/3}(\mathbf{r}) d\mathbf{r}.$$



Jacob's Ladder



References

- Homogeneous Electron Gas: 

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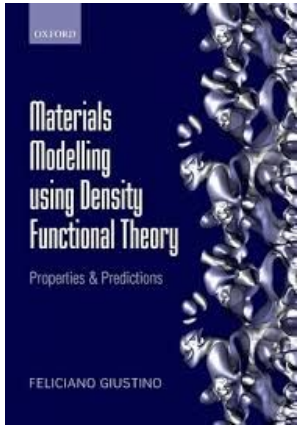
- Local Density Approximation: 

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- Jacob's Ladder

Which functional should I choose?

Dmitrij Rappoport, Nathan R. M. Crawford, Filipp Furche, and Kieron Burke

Jacob's Ladder of Density Functional Approximations for the Exchange-Correlation Energy

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Thank you for your attention!