

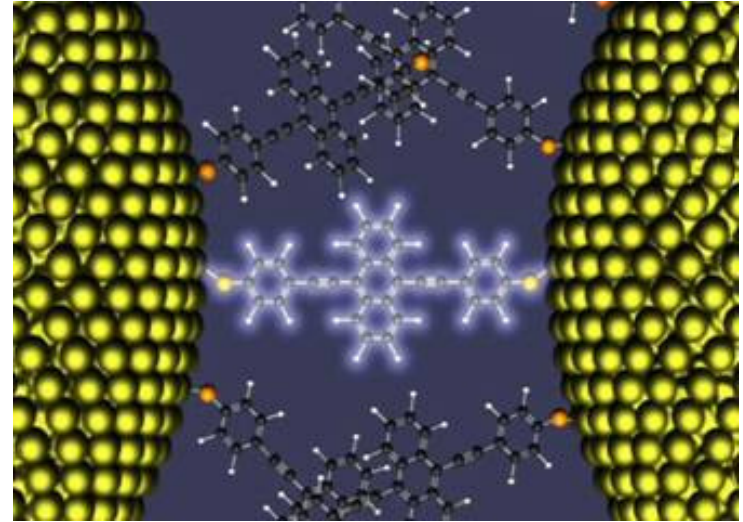
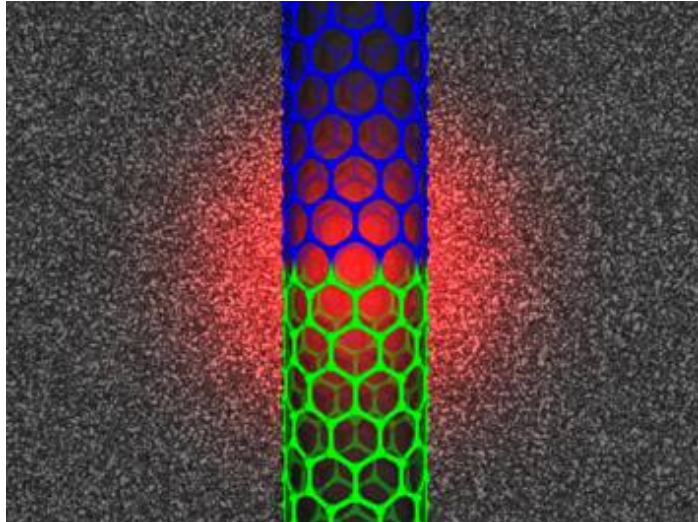
# Density functional method: the theory of materials

*O. Pankratov*

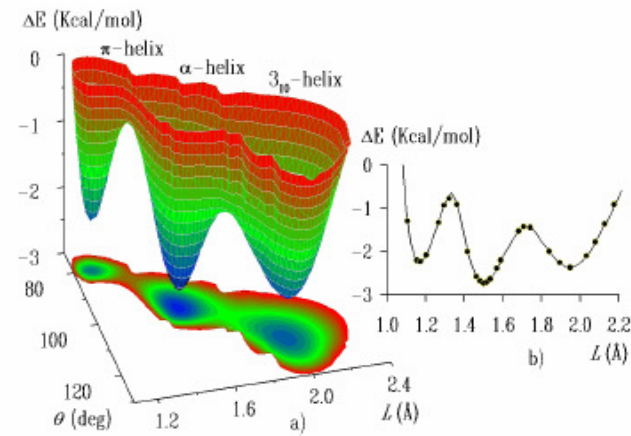
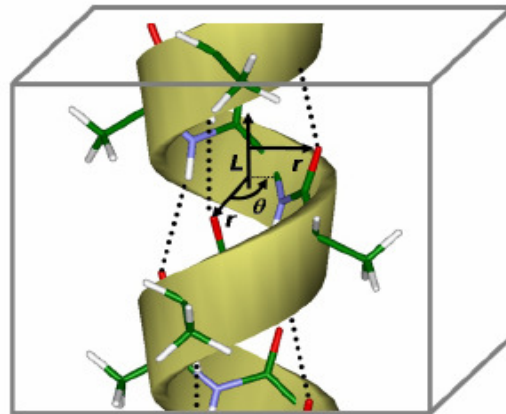
*University of Erlangen-Nürnberg*



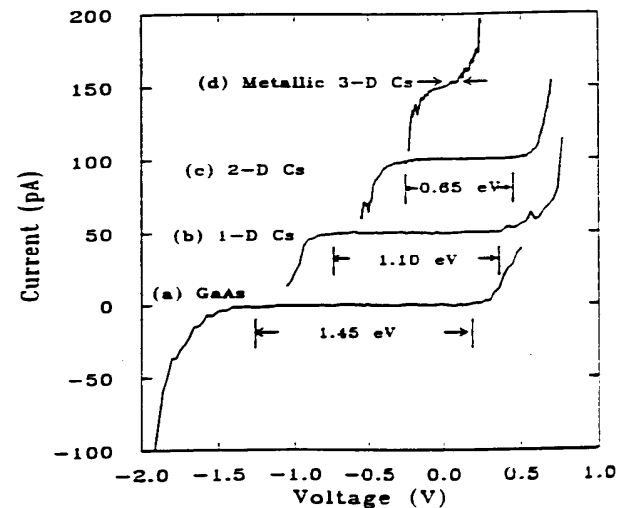
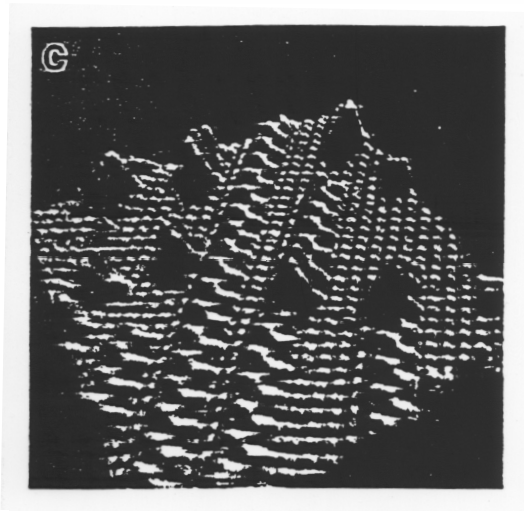
# Molecular devices



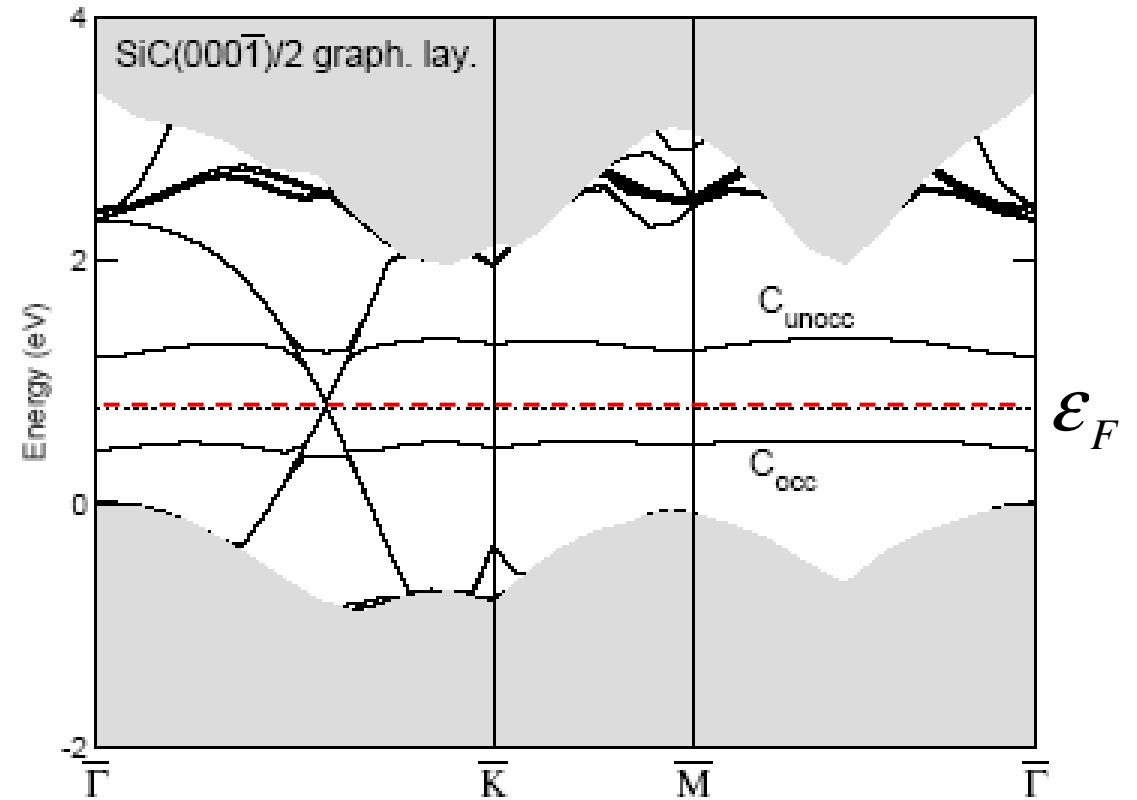
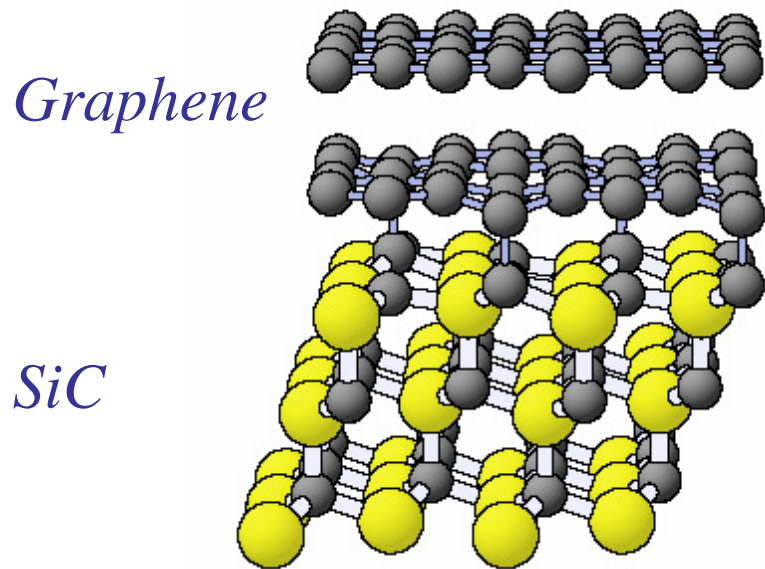
# Complex molecules: protein structure



# Complex surfaces: Cs chains on GaAs (110)



# Theory-aided design of new materials



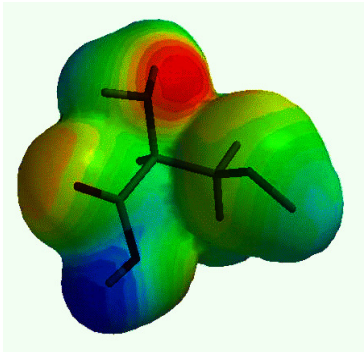
# The outline

- Density Functional Theory: fundamentals
- Implementation: Kohn-Sham method and approximations
- DFT extensions: time-dependent theory and excited states

# Density Functional Theory



*The 1998 Nobel Prize in quantum chemistry  
to Walter Kohn and John A. Pople*



DFT returns an intuitive picture: Density "clouds"  $n(\mathbf{r})$

$$n(\mathbf{r}) = N \int d\mathbf{r}_2 \dots d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)|^2$$

# Hohenberg-Kohn Theorems

$$\left[ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{i,\gamma} \frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_\gamma|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{r}_1, \dots) = E \Psi(\mathbf{r}_1, \dots)$$

Any observable is a functional of density

$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \Rightarrow n(\mathbf{r})$ . For ground state  $n(\mathbf{r}) \Rightarrow \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  and  $n(\mathbf{r}) \Rightarrow v(\mathbf{r})$

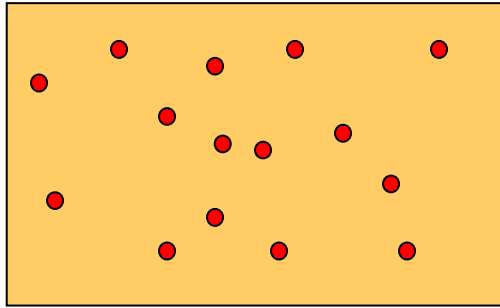
Minimum principle and energy functional

$$E_{v_{ext}}[n] = \langle \Psi[n] | \hat{T} + \hat{W} + V_{ext} | \Psi[n] \rangle \quad \text{and} \quad E_0 \leq E_{v_{ext}}[n]$$

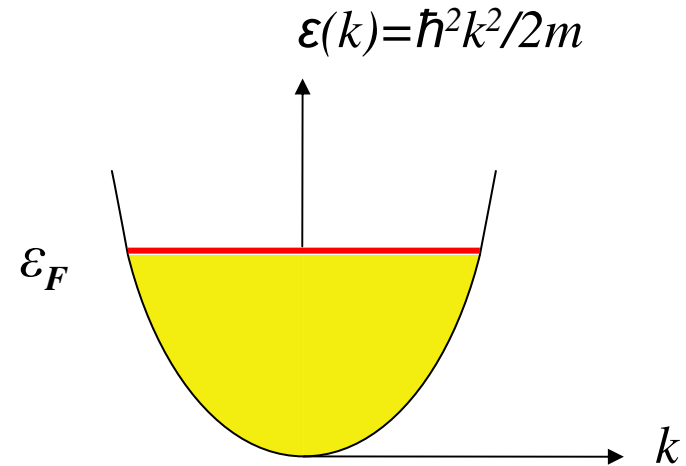
Universal functional

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle$$

# Homogeneous electron gas



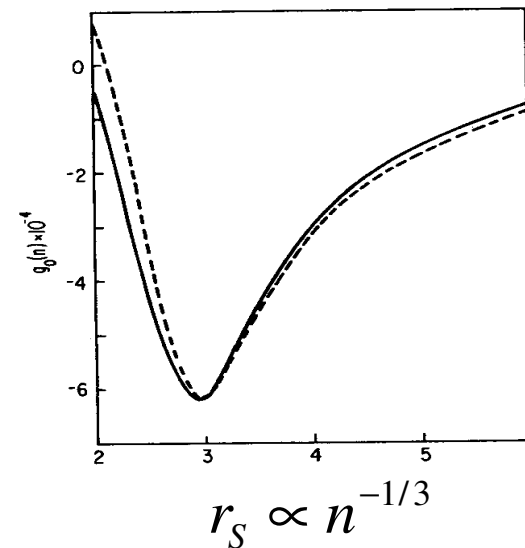
Density  $n=N/V=const$



Fermi energy  $\epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$

Kinetic energy  $T = \frac{3}{5} \epsilon_F N$

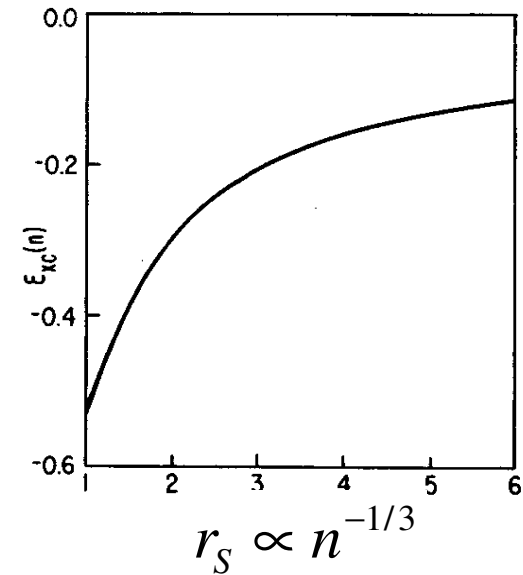
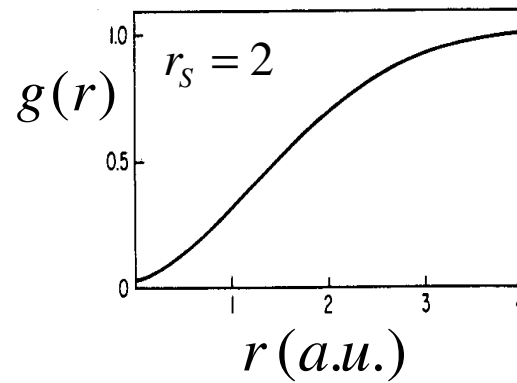
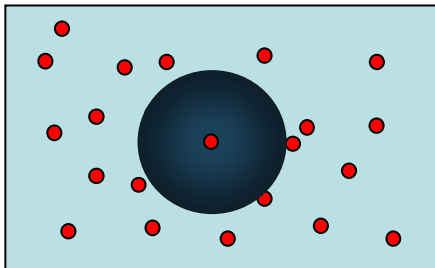
Total energy  $E(n) = T(n) + W(n)$





# Coulomb energy of a homogeneous electron gas

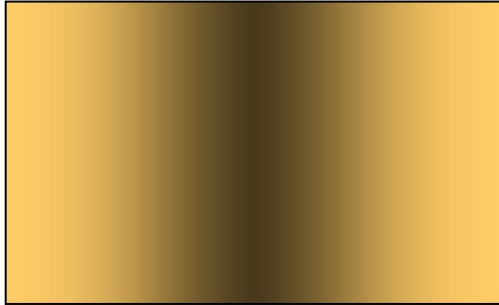
*Exchange-correlation hole*



*Exchange-correlation energy*

$$E_{xc} = \frac{e^2}{2} N \int \frac{n_{xc}(\mathbf{r})}{r} d\mathbf{r} < 0$$

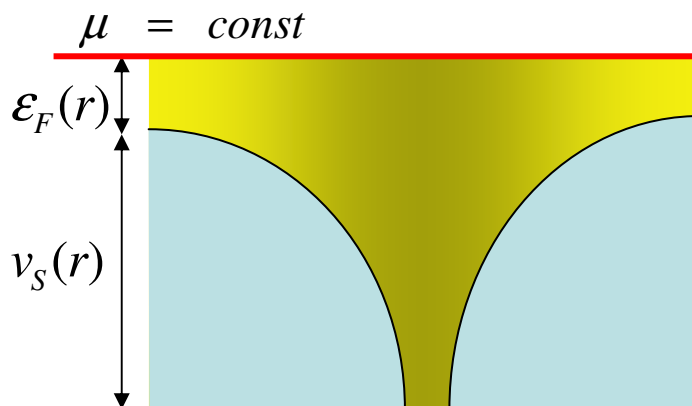
# Thomas-Fermi method



$$T = \int d\mathbf{r} \frac{3}{5} \varepsilon_F(\mathbf{r}) n(\mathbf{r})$$

$$E_{xc} = \int d\mathbf{r} \varepsilon_{xc}(n(\mathbf{r}))$$

$$E[n(\mathbf{r})] = \int d\mathbf{r} \frac{3}{5} \varepsilon_F(\mathbf{r}) n(\mathbf{r}) + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int d\mathbf{r} v_{ext}(\mathbf{r})n(\mathbf{r})$$



$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \varepsilon_F(\mathbf{r}) + \{v_H(\mathbf{r}) + v_{ext}(\mathbf{r})\} = \mu$$

$$\varepsilon_F(\mathbf{r}) + v_S(\mathbf{r}) = \mu$$

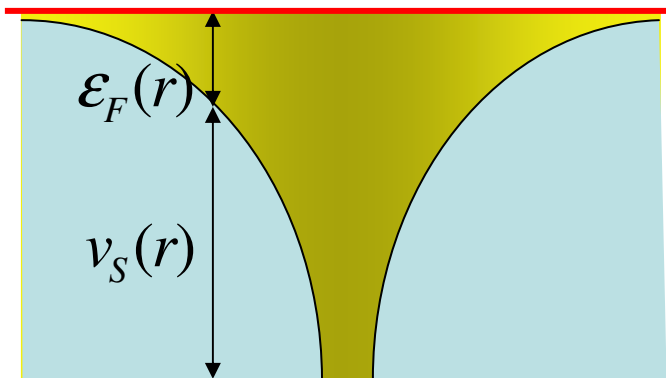
# Thomas-Fermi equation

$$\mathcal{E}_F(n(\mathbf{r})) + v_H(\mathbf{r}) + v_{ext}(\mathbf{r}) = \mu$$

$$\Delta \mathcal{E}_F(\mathbf{r}) = 4\pi e^2 [n(\mathbf{r}) + n_{ext}(\mathbf{r})]$$

$$\mathcal{E}_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

Atom :  $\mu = 0$



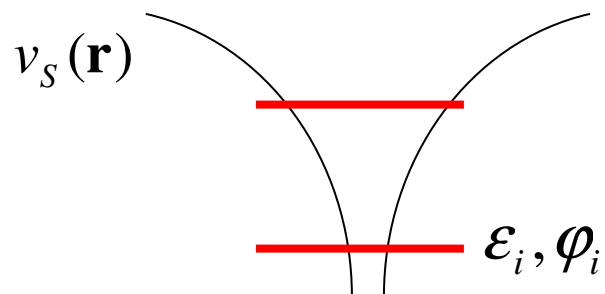
*Thomas-Fermi screening*

$$n(x) = n_0 \exp(-x / L_{TF})$$

$$\left( \frac{1}{L_{TF}} \right)^2 = \frac{6\pi e^2 n}{\mathcal{E}_F}$$

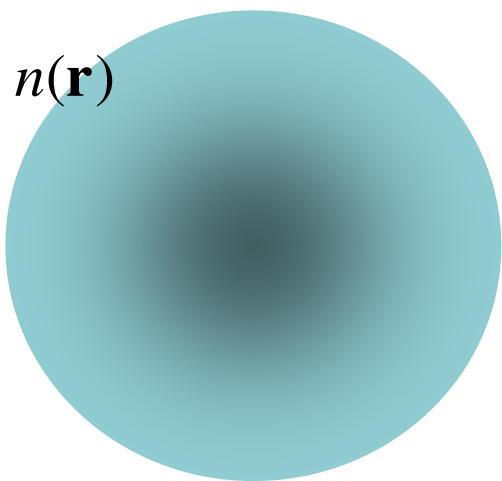
- No energy quantization
- No sharp size of atoms
- No molecules (e.g.  $H_2$ )

# Kohn-Sham method: non-interacting particles



$$\left[ \frac{-\hbar^2 \nabla^2}{2m} + v_S(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad , i = 1 \div N$$

Energy functional for density  $n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2$



$$E_S[n] = T_S[n] + \int d\mathbf{r} v_S(\mathbf{r}) n(\mathbf{r}) \quad \text{where} \quad T_S[n] = \sum_{i=1}^N \langle \varphi_i | \frac{-\hbar^2 \nabla^2}{2m} | \varphi_i \rangle$$

# Kohn-Sham functional for interacting particles

$$E[n] = \langle \Psi | \hat{T} + \hat{W} + V_{ext} | \Psi \rangle = T_S[n] + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int d\mathbf{r} v_{ext}(\mathbf{r})n(\mathbf{r}) + E_{xc}[n]$$

*Exchange-correlation energy*  $E_{xc}[n] = T + W - T_S - E_H = \int d\mathbf{r} \varepsilon_{xc}(\mathbf{r})$

*Kohn-Sham equation*  $\left[ \frac{-\hbar^2 \nabla^2}{2m} + v_S(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad i = 1 \div N, \quad n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2$

$$\begin{aligned} \delta T_S[n] &= \delta \sum_{i=1}^N \langle \varphi_i | \frac{-\hbar^2 \nabla^2}{2m} | \varphi_i \rangle = \delta \left\{ \sum_{i=1}^N \varepsilon_i - \int d\mathbf{r} v_S(\mathbf{r})n(\mathbf{r}) \right\} = \\ &= \sum_{i=1}^N \langle \varphi_i | \delta v_S(\mathbf{r}) | \varphi_i \rangle - \delta \int d\mathbf{r} v_S(\mathbf{r})n(\mathbf{r}) = - \int d\mathbf{r} v_S(\mathbf{r})\delta n(\mathbf{r}) \end{aligned}$$

*Hence*  $\frac{\delta T_S}{\delta n(\mathbf{r})} = -v_S(\mathbf{r})$

# Kohn-Sham potential

The ground state: 
$$\frac{\delta}{\delta n(\mathbf{r})} \{E[n] - \mu \int d\mathbf{r} n(\mathbf{r})\} = 0$$

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta}{\delta n(\mathbf{r})} \{T_S + E_H + E_{ext} + E_{xc}\} = \mu$$

*xc-potential*

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = -v_S(\mathbf{r}) + v_H(\mathbf{r}) + v_{ext}(\mathbf{r}) + v_{xc}(\mathbf{r}) = \mu = const$$

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

*Kohn-Sham potential* 
$$v_S(\mathbf{r}) = v_H(\mathbf{r}) + v_{ext}(\mathbf{r}) + v_{xc}(\mathbf{r})$$

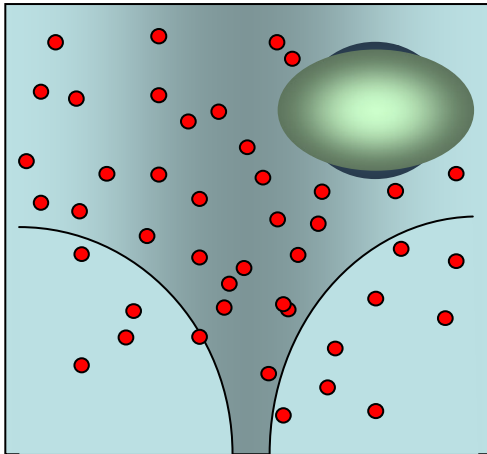
*is a functional of density:* 
$$v_S^{[n]}(\mathbf{r})$$

# Local Density Approximation (LDA)

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int d\mathbf{r} \varepsilon_{xc}^h(n(\mathbf{r}))$$

$$\varepsilon_{xc}^h = -\frac{0.458}{r_s} n + \varepsilon_c(n)$$

*Correlations are assumed the same as in a homogeneous electron gas*

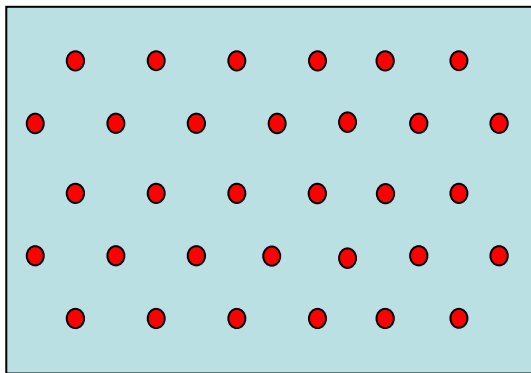


*xc-hole  $n_{xc}(\mathbf{r})$  is assumed spherical*

$$E_{xc}^{LDA} = \frac{e^2}{2} \iint \frac{n(\mathbf{r}) n_{xc}^h(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

# LDA may give wrong ground state: Wigner crystal

$$\frac{\text{Coulomb interaction energy}}{\text{kinetic energy}} : \frac{e^2 / d}{\varepsilon_F} \approx \frac{e^2 n^{1/3}}{\hbar^2 n^{2/3} / m} \approx \frac{me^2}{\hbar^2 n^{1/3}} \approx \frac{d}{a_B} = r_s$$



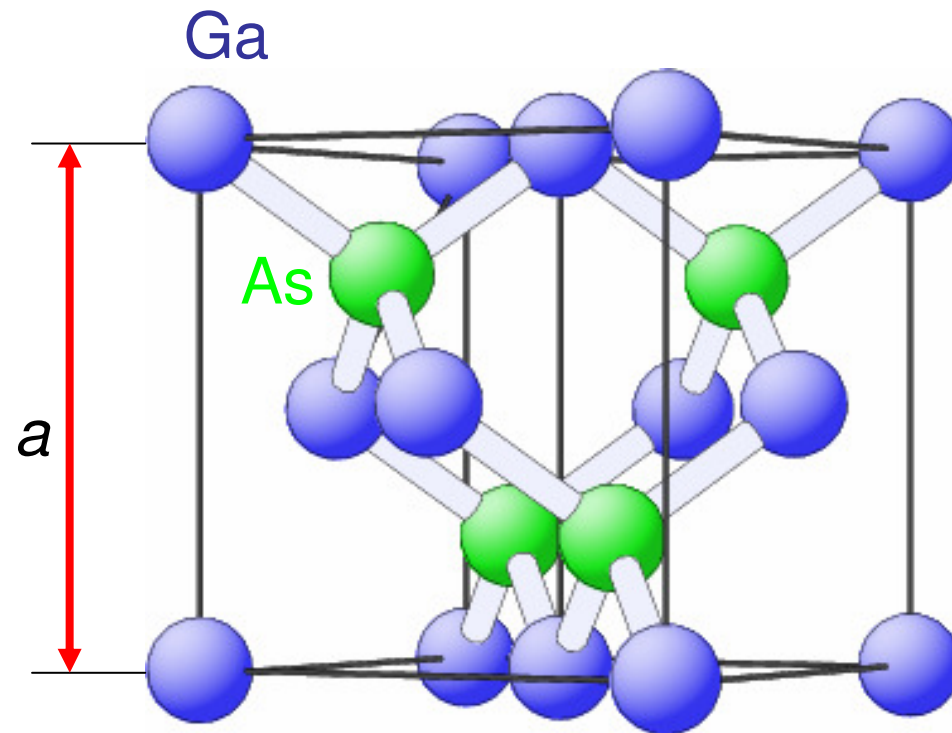
## Wigner crystal

- 3D:  $r_s \sim 67$
- 2D:  $r_s \sim 37$
- 1D:  $r_s \sim 1-5$



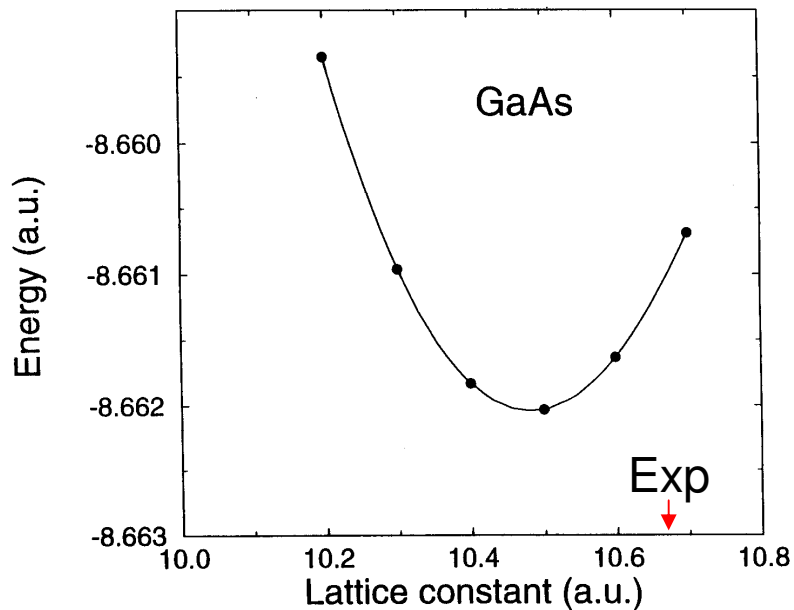
# Calculation of a crystal structure

## Lattice constant of GaAs



# Total energy of ions and electrons

$$E_{total}[\mathbf{R}_i, n(\mathbf{r})] = E_{ions}(\mathbf{R}_i) + E_{electrons}[n(\mathbf{r})]$$



Ground state

$$\min E_{total}[\mathbf{R}_i, n(\mathbf{r})] \Rightarrow \mathbf{R}_i^{(0)}, n_0(\mathbf{r})$$

Forces on ions

$$\mathbf{F}_{\mathbf{R}_i} = -\nabla_{\mathbf{R}_i} E_{total}[\mathbf{R}_i, n(\mathbf{r})]$$

Ab-initio molecular dynamics

# Electron energy levels

$$\left[ \frac{-\hbar^2 \nabla^2}{2m} + v_S(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad \textit{Kohn-Sham levels } \varepsilon_i; \quad n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2$$

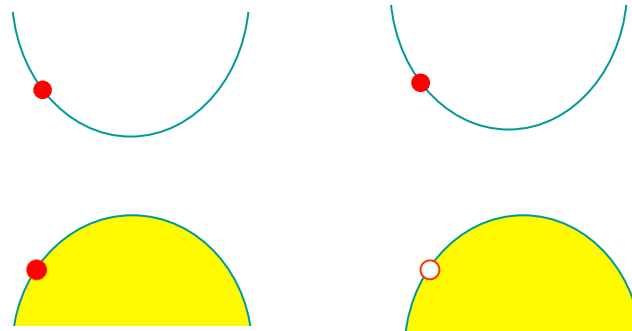
$$E = T_S + \frac{1}{2} \int v_H(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} v_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{xc}[n]$$

$$T_S = \sum_{i=1}^N \langle \varphi_i | \frac{-\hbar^2 \nabla^2}{2m} | \varphi_i \rangle = \sum_{i=1}^N \varepsilon_i - \int d\mathbf{r} v_S(\mathbf{r}) n(\mathbf{r}) = \sum_{i=1}^N \varepsilon_i - \int d\mathbf{r} \{v_H(\mathbf{r}) + v_{ext}(\mathbf{r}) + v_{xc}(\mathbf{r})\} n(\mathbf{r})$$

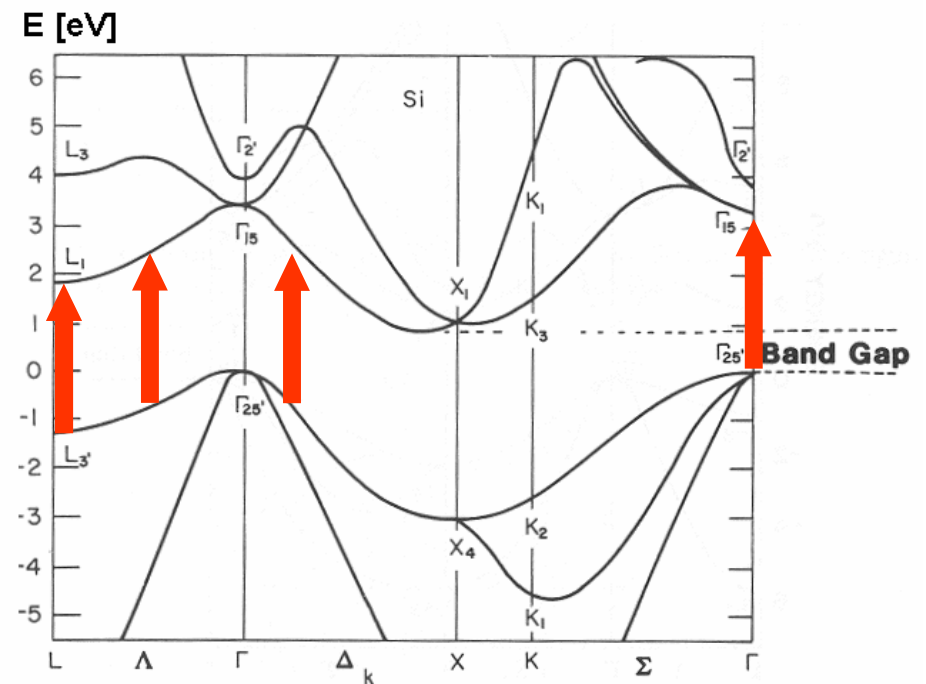
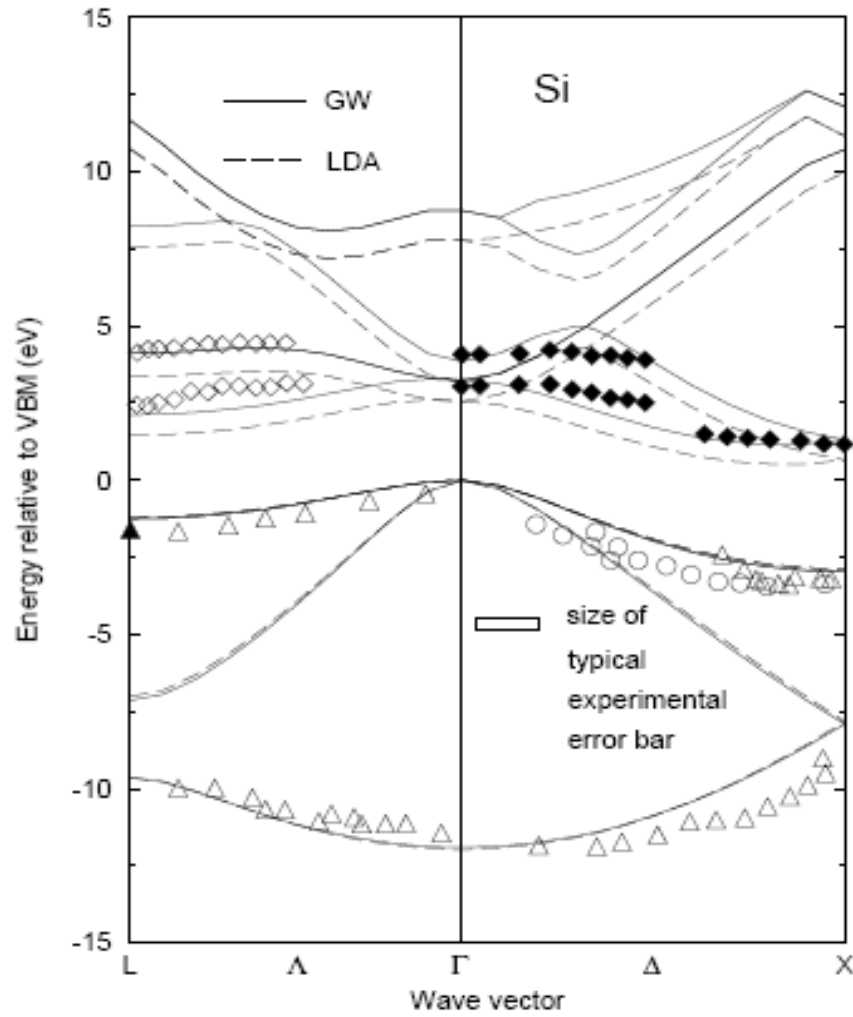
$$E = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int v_H(\mathbf{r}) d\mathbf{r} + \int d\mathbf{r} [\varepsilon_{xc}(\mathbf{r}) - v_{xc}(\mathbf{r}) n(\mathbf{r})]$$

$\varepsilon_N$  is the one-particle excitation energy if  $\Delta E = E(N) - E(N-1) \approx \varepsilon_N$

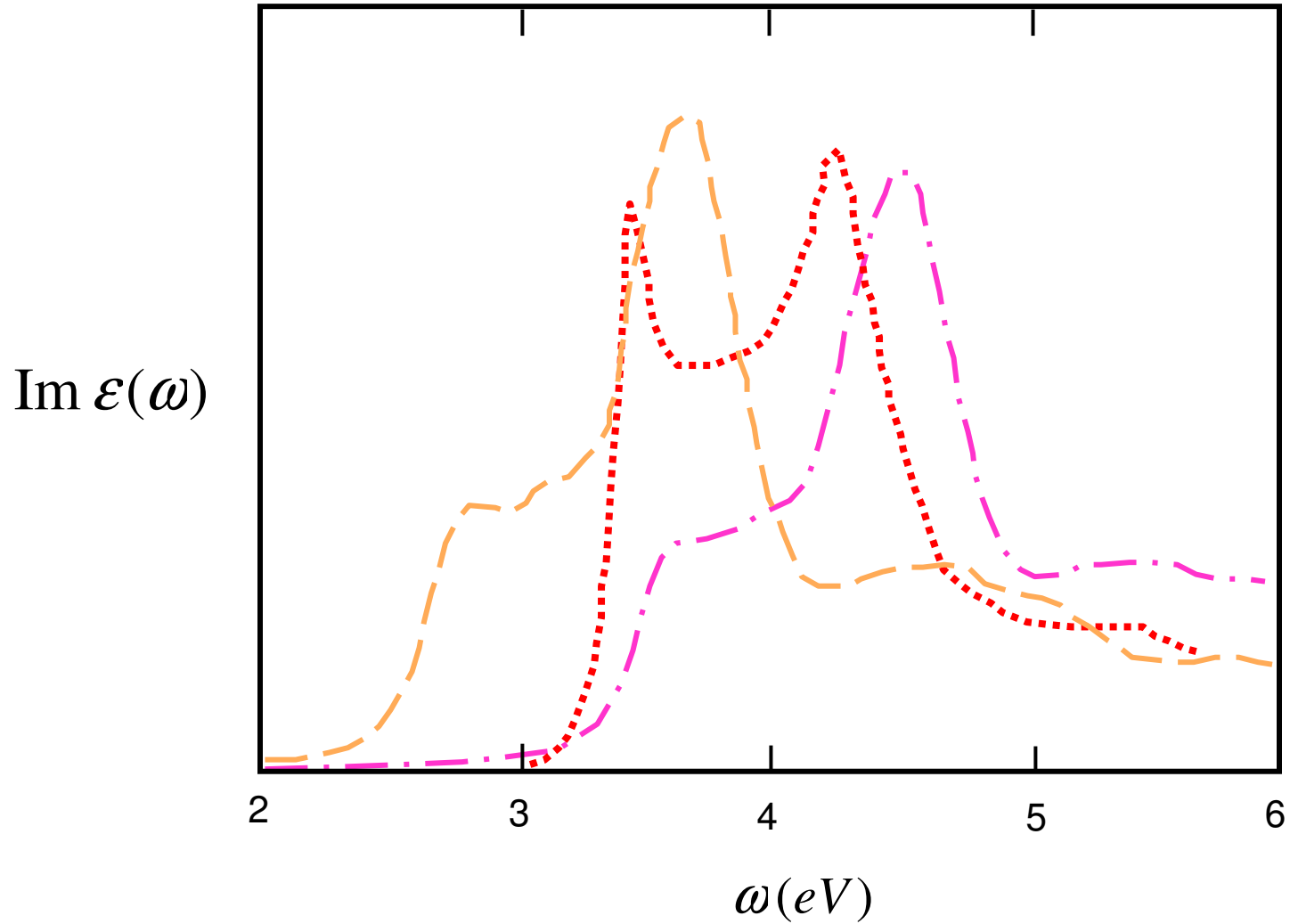
However the  $xc$  potential  $v_{xc}(\mathbf{r})$  may change with electron number: LDA may give the wrong band gap



# Kohn Sham and the “true” band structure: Si



# Light absorption spectrum: Si



# Time dependent density functional theory

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H}(t) \Psi \quad \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t) \Leftarrow n(\mathbf{r}, t)$$

*Time-dependent Kohn-Sham equations*

$$n(\mathbf{r}, t) = \sum_{i=1}^N |\varphi_i(\mathbf{r}, t)|^2 \quad i\hbar \frac{\partial}{\partial t} \varphi_i(\mathbf{r}, t) = \left[ \frac{-\hbar^2 \nabla^2}{2m} + v_S(\mathbf{r}) \right] \varphi_i(\mathbf{r}, t)$$

*Adiabatic time-dependent xc-potential*

$$v_{xc}(\mathbf{r}, t) = \frac{\delta E_{xc}([n], t)}{\delta n(\mathbf{r}, t)} \quad E_{xc}^{ALDA}([n], t) = \int d\mathbf{r} \varepsilon_{xc}^h(n(\mathbf{r}, t))$$

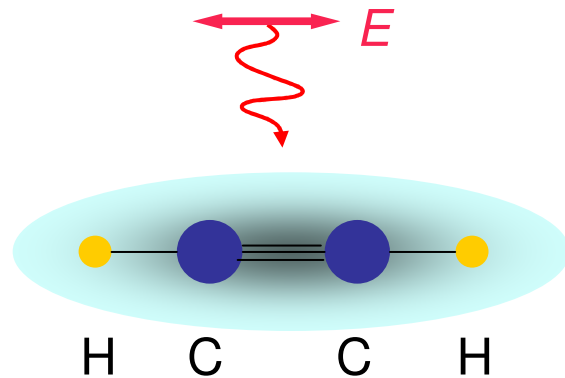
# Time dependent processes on electron's time scale

The time scale:  $\frac{\hbar}{Ry} \approx \frac{6.6 \cdot 10^{-16} \text{ eV} \cdot \text{s}}{13.6 \text{ eV}} \approx 0.5 \cdot 10^{-16} \text{ s}$

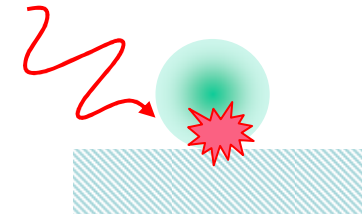
Femto:  $1 \text{ fs} = 10^{-15} \text{ s}$

Atto:  $1 \text{ as} = 10^{-18} \text{ s}$

Laser excitation of a molecule



Laser-stimulated desorption



*Probability to find same-spin electron close to reference electron*

$$D_{\sigma}(\mathbf{r}, t) = \sum_i |\nabla \varphi_{i,\sigma}(\mathbf{r}, t)|^2 - \frac{1}{4} \frac{|\nabla n_{\sigma}(\mathbf{r}, t)|^2}{n_{\sigma}(\mathbf{r}, t)} - \frac{j_{\sigma}^2(\mathbf{r}, t)}{n_{\sigma}(\mathbf{r}, t)}$$

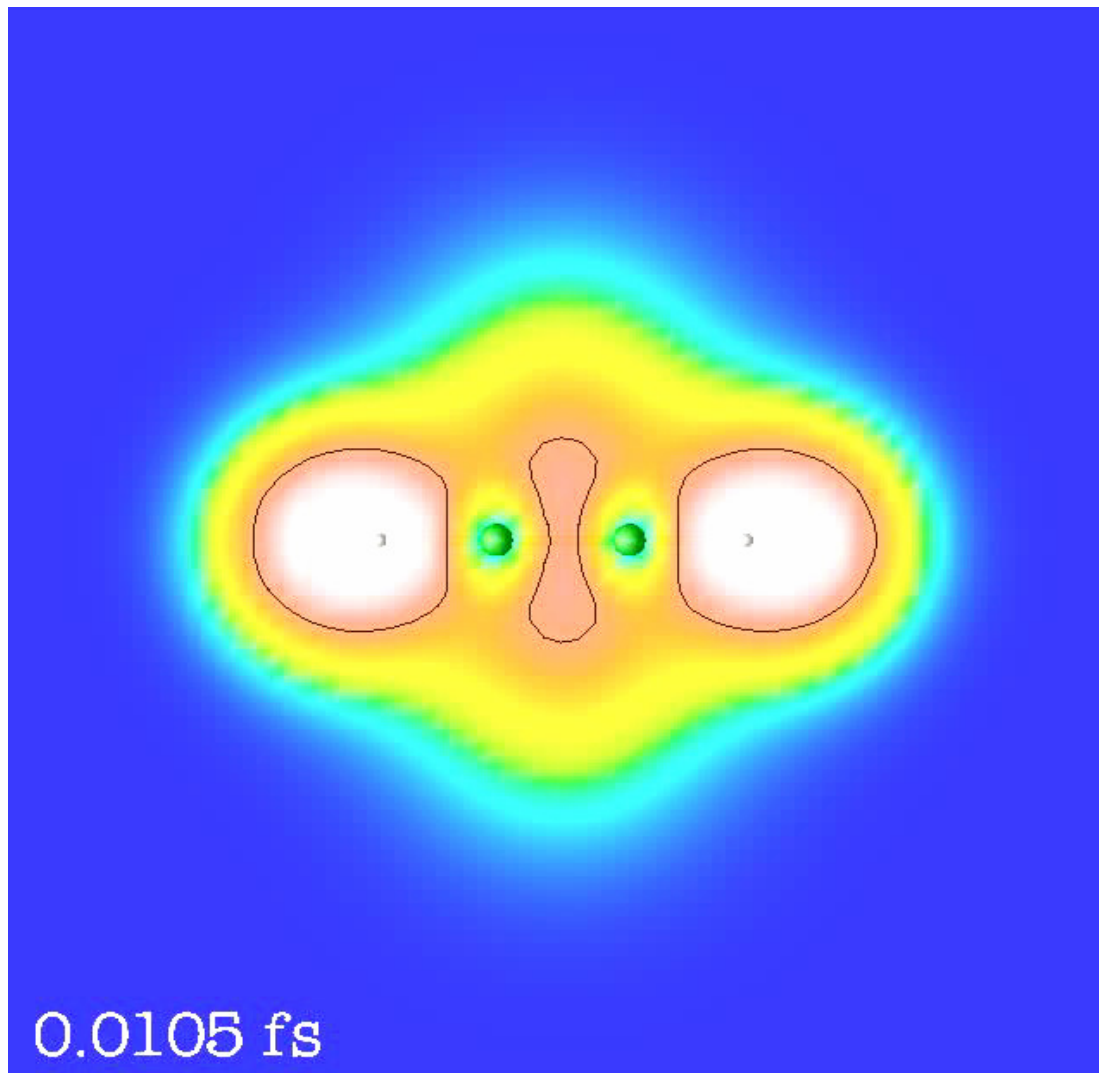
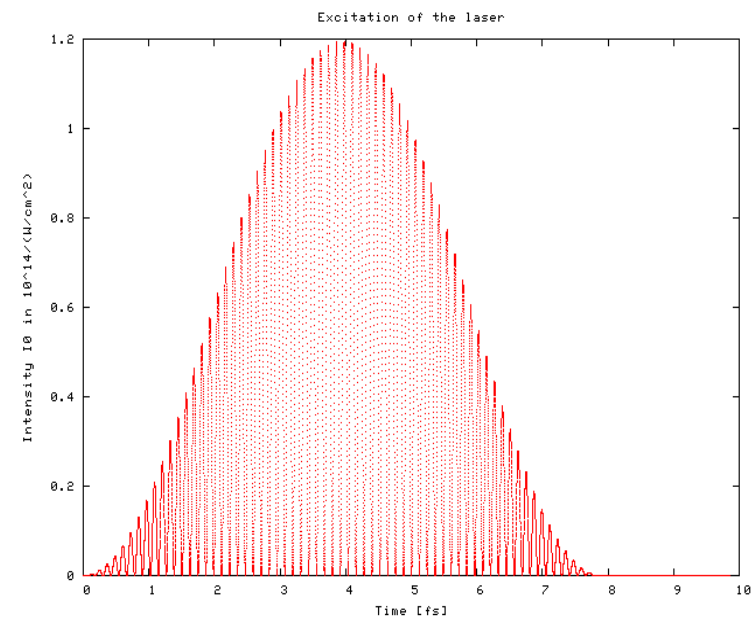
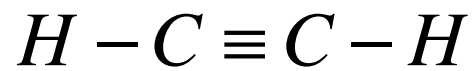
*Electron localization function*

$$f_{ELF}(\mathbf{r}) = \{1 + D_{\sigma}^2(\mathbf{r}, t) / D_{\text{hom},\sigma}^2(\mathbf{r}, t)\}$$



# Laser excitation of acetylen (*Gross et al*)

$$\hbar\omega = 17 \text{ eV}; \quad I_{\text{max}} = 10^{14} \text{ W} \cdot \text{cm}^{-2}; \quad \Delta T = 8 \text{ fs}$$



# Summary

- DFT allows calculations for about 200 atoms
- Atomic structure, molecular dynamics
- Excited states can be calculated
- Time-dependent theory: quantum dynamics on femto/atto-second timescale
- Strong electron correlations, superconductivity, etc
- Quantum transport (e.g. through molecules)

*Prediction of materials (complex molecules, solids, surfaces, nanostructures...) and their properties*